# THE STRUCTURE AND DYNAMIC MECHANICAL PROPERTIES OF SOME PLASTICISED STYRENE-VINYLPYRIDINIUM IODIDE IONOMERS

by

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D WALMANN Shortened Thesis Title:

# Structure and Properties of Styrene-Vinylpyridinium Iodide Ionomers

# Abstract

The effects of plasticisation on the phase behaviour in random and ABA triblock styrene-N-alkyl-4-vinylpyridinium iodide ionomers were studied using small angle X-ray scattering and dynamic mechanical techniques. It was found that the internal plasticisation of a random ionomer by quaternisation with n-iodoalkanes does not result in phase separation. The glass transition temperatures of such materials can be predicted on the basis of the vinylpyridine content and the iodoalkane chain length. Plasticisation of the random ionomers with nonpolar additives, either internally, *via* alkylation of the phenyl ring with 1-decene, or externally, by the addition of diethylbenzene, results in the phase separation of the material into a multiplet-containing phase and clusters. In the internally plasticised ionomers, the multiplet phase predominated at low levels of alkylation, and the cluster phase predominated when more than 20 mole % of the styrene had been alkylated. The cluster phase was always dominant in the externally plasticised ionomers. ABA triblocks of styrene (B) and vinylpyridine (A) are phase separated even in the nonionic state. Quaternisation of the end blocks yielded ionomers whose domains exhibited different morphologies depending on the midblock, end block and quaternising chain lengths, even though they had the same sample history. It was found that the styrene matrix $T_g$ in the quaternised materials was depressed relative to a comparable styrene homopolymer, this reduction was attributed to inefficient packing of the styrene chains around the vinylpyridinium domains. Plasticisation of the ABA ionomers with diethylbenzene reduced the glass transition temperature of the styrene matrix, but did not affect the ionic phase. Plasticisation of the ionic regions with glycerol resulted in the depression of the vinylpyridinium $T_g$, but did not appear to affect the nonpolar matrix.

# Résumé

Les effets de la plastification sur le comportement de phase d'ionomères statistiques et triséquencés (ABA) du styrène et d'iodure de N-alkyl-vinyl-4-pyridinium ont été étudiés à l'aide de la diffraction de rayons-X aux petits angles et des propriétés méchaniques dynamiques Il a été démontré que la plastification interne d'un ionomère statistique par quaternisation avec des iodures de n-alcane n'entraine aucune séparation de phase La température de transition vitreuse de ces ionomères peut être prédite d'après le contenu en vinylpyridine et la longueur de la chaîne de l'iodure d'alcane. D'autre part, la plastification d'ionomères statistiques avec des additifs non-polaires a été réalisée de façon interne, par l'alkylation du groupement phényle avec du 1-décène, et externe, par l'addition de diéthylbenzene Ce type de plastification conduit à une séparation en deux types de phases; l'une contenant une faible concentration d'ions, la phase des multiplets, et l'autre une forte concentration d'ions, la phase des amas (clusters) Pour les ionomères à plastification interne, la phase des multiplets prédominait lorsque la proportion de groupements phényles alkylés est faible, alors que la phase des amas prédominait à des niveaux d'alkylation supérieures à 20 %. La phase des amas était toujours dominante pour les ionomères à plastification externe Les copolymères triséquencés de type ABA composés du polystyrène (B) et de la poly(vinyl-4-pyridine) (A) présentent des phases séparées même à l'état non-ionique. La quaternisation des séquences terminales produit des ionomères dont les domaines présentent des morphologies différentes, bien que tous les échantillons aient été préparés selon les même conditions Ces morphologies dépendent de la longueur des séquences centrale et terminales ainsi que de la longueur de la chaîne utilisée pour la quaternisation Il fut observé que la température de transition vitreuse de la matrice styrènique de l'ionomère quaternisé était inférieure en comparaison avec du polystyrène pure, cet abaissement fut attribué à l'empilement inefficace des chaînes de polystyrène autour des domaines polyvinylpyridiniums La plastification des ionomères de type ABA avec du diéthylbenzene diminua la température de transition vitreuse de la matrice styrènique sans affecter celui de la phase ionique La plastification des domaines ioniques avec du glycérol abaisse [illegible]érature de transition vitreuse de la polyvinylpyridinium sans affecter la matrice non-polaire

# Foreword

In accordance with guideline 7 of the "Guidelines Concerning Thesis Preparation" (Faculty of Graduate Studies and Research, McGill University), the following text is cited:

> "The candidate has the option, subject to the approval of the Department, of including as part of the thesis the text, or duplicated published text, of an original paper, or papers. In this case the thesis must still conform to all other requirements explained in Guidelines Concerning Thesis Preparation. Additional material (procedural and design data as well as descriptions of equipment) must be provided in sufficient detail (e.g. in appendices) to allow a clear and precise judgement to be made of the importance and originality of the research reported. The thesis should be more than a mere collection of manuscripts published or to be published. *It must include a general abstract, a full introduction and literature review and a final overall conclusion.* Connecting texts which provide logical bridges between different manuscripts are usually desirable in the interests of cohesion.
>
> It is acceptable for theses to include as chapters authentic copies of papers already published, provided these are duplicated clearly on regulation thesis stationery and bound as an integral part of the thesis. Photographs or other materials which do not duplicate well must be included in their original form *In such instances, connecting texts are mandatory and supplementary explanatory material is almost always necessary.*
>
> The inclusion of manuscripts co-authored by the candidate and others is acceptable but the candidate is required to make the explicit statement on who contributed to such work and to what extent, and supervisors must attest to the accuracy of the claims, e.g. before the Oral Committee. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make the responsibilities of the authors perfectly clear. Candidates following this option must inform the Department before it submits the thesis for review."

This dissertation is written in the form of seven papers, two of which constitute the introduction of the thesis. The remaining five papers each comprise one chapter, with general conclusions contained in the eighth chapter.

Following normal procedure, all the papers have been or will be submitted shortly for publication in scientific journals, with the research director, Dr. Adi Eisenberg, as co-author. Nevertheless, all of the work has been done by the author of this thesis, excepting the normal supervision and advice given by a research director. The paper that is Chapter 3 of this thesis was published with Dr. S. Gauthier as a second co-author, recognizing the advice and direction that she contributed. Chapters 4 and 5 have been submitted with Dr C E Williams as the second co-author, because of her help and advice regarding the small angle X-ray scattering experiments and interpretation of the results

The papers have been submitted as follows:

Chapter 1: Multicomponent Polymer Systems, eds. I. Miles and S. Rostami (accepted).

Chapter 2 Contemporary Topics in Polymer Science, 6, ed. W. Culbertson (accepted)

Chapter 3: Polymer Engineering and Science, 26, 1451 (1986).

Chapter 4. not yet submitted.

Chapter 5: Journal of Polymer Science, Polymer Physics Edition.

Chapter 6: Journal of Polymer Science, Polymer Letters Edition.

Chapter 7: not yet submitted.

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# Preface

The aim of the work described in this thesis was the exploration of the effects of plasticisation on styrene-vinylpyridinium ionomers. A number of previous studies have investigated the effects of plasticisation in anionic ionomers; however, until now, no systematic investigation of the plasticisation of cationic materials has been reported This particular study became of interest when it was shown that upon plasticisation, these ionomers may become phase separated.

Styrene-vinylpyridinium ionomers having both random and ABA triblock architectures were investigated using dynamic mechanical and small angle X-ray scattering techniques. Different families of plasticisers were used. Some were "internal", and could be incorporated into the polymer chain, while others were "external", and were free to plasticise certain areas of the ionomers.

As outlined in the Foreword, the introduction to this thesis is made up of two papers, both of which have been submitted for publication. The first chapter of the introduction is a general review of the phase behavior encountered in ionomeric materials, thus some sections, for example those on halatotelechelic polymers and on blends of ionomers, deal with topics not directly covered in the dissertation. The second chapter of the introduction consists of a review describing the methods, such as plasticisation, which can be used to modify the phase behavior of ionomers.

Because of the range of materials used in this work, the experimental part of the thesis is divided logically into two parts. One section deals with the effects of plasticisation on random styrene-vinylpyridinium ionomers, and the other is concerned with a parallel study on the triblock materials.

Chapters 3 and 4 explore the plasticisation of random styrene vinylpyridinium ionomers. The first of these two chapters describes the internal plasticisation of the ionic units in the copolymers *via* quaternisation with n-iodoalkanes, and the effect of this plasticisation on the dynamic mechanical properties of the materials. In Chapter 4, the plasticisation of random styrene N-methyl-vinylpyridinium iodide ionomers *via* internal and external methods is described, together with the effects of such plasticisation on the dynamic mechanical properties. Chapter 4 is rounded out by a study on the effects of all three types of plasticisation on the morphologies of such materials.

Chapters 5, 6 and 7 are all papers which deal with the effects of internal and external plasticisation on the morphology and dynamic mechanical behavior of styrene (B)-co-4-vinylpyridinium (A) ABA triblock ionomers. Chapter 5 is concerned with a morphological study of ABA styrene-N-alkyl-vinylpyridinium iodides. The unexpected depression of the styrene matrix glass transition temperature in such materials is the subject of Chapter 6. Finally, Chapter 7 describes the dynamic mechanical behavior of the plasticized styrene vinylpyridinium blocks in general.

This thesis concludes in Chapter 8 with a general discussion and suggestions for future work.

Appendix A is a reprint of Chapter 3. Appendix B is a preprint of an article which has been accepted for publication in Journal of Polymer Science, Polymer Letters Edition It is not included in the thesis proper, because although the ionomers described in the report were synthesised by the candidate, the experimental measurements were made elsewhere. Appendix C is a short study related to the work done for this thesis but was not included in the main text, because the thesis is submitted in paper format

Finally, Appendix D contains the supporting data. This includes the data for the torsion pendulum, the DMTA and the SAXS studies.

# Chapter 1

# Phase Behaviour in Ionomers

## 1.1 Introduction

Ionomers are synthetic polymers containing small amounts of an ionic comonomer[1]. Due to the inclusion of this material and the resultant phase separation, ionomers generally exhibit behaviour not observed in nonionic systems. Many aspects of ionomers, ranging from their syntheses to their physical properties in the bulk and in solution are currently under investigation. It is, however, their unique phase behaviour in the solid state which generates much of the interest, both academically and because of their industrial potential. Consequently, considerable effort has been devoted to the elucidation of the reasons for phase separation in these materials. The results of these studies are well-documented and appear in numerous books[2,3], symposia[4,5,6,7,8] and review articles[9,10,11,12,13].

Now, over twenty years since ionomers were first found to have practical application, many uses are being explored for these materials. Ionomers are important in the packaging film industry[1]. They are also being used as semipermeable membranes[14], in the oil drilling industry[15], in triboelectrification processes[16,17] and for medicinal purposes[18], to name just a few areas of current research Other fields in which ionomers are being employed may be found in two recent review articles[15,19].

Phase separation is common in polymeric materials, particularly when two different polymers are present in the form of blends or block copolymers. In ionomers, phase separation occurs on several different scales and some of these phase separated aggregates are unique.

At the smallest scale of aggregation, only the ionic portions are involved. Typically, in media of low dielectric constant, ions are known to associate into ion pairs, which are likely to further aggregate into ionic quartets, sextets and even octets[20]. In random ionomers, these entities are called multiplets[21]. The ion-ion interaction is typically of the order of 400 kJ/mol. The interaction between two ion pairs is *ca* 100 kJ/mol[22]; in further aggregation, the forces are reduced to considerably less than 100 kJ/mol[21], but are still powerful. Larger aggregates are also believed to be present in many ionomers; these are called clusters[21]. Clusters contain, in addition to the ion pairs, a significant proportion of the chain material from the backbone of the polymer.

The existence of multiplets and clusters is a direct consequence of the presence of the ionic groups. In comparison with the size of the polymer molecule, these groups are very small. The size of the aggregate is also small with respect to that of the rest of the chain; multiplets have been estimated to be about 5-10 Å in diameter[23], while clusters are thought to be of the order of 20-50 Å in diameter[10,12]. Multiplets are believed to behave as crosslinks in ionomers, which raise the glass transition temperature of the materials[12]. Clusters exhibit more complex behaviour and experimental evidence suggests that they possess a $T_g$ of their own[9,10].

As a rule, the presence of crystalline domains in ionomers is reduced or even eliminated by comparison to similar nonionic polymers[24,25]. This behaviour is qualitatively no different from the effects on crystallinity of copolymerisation with nonionic species. Consequently, crystallinity in ionomers will not be discussed further in this chapter.

In the case of block ionomers, one or more of the blocks is ionic. As in other, nonionic, block copolymers, the morphologies of the phase separated regions depend heavily on the relative amounts of the two components, while the sizes depend on the absolute molecular weight of the segments. However, because of the strong driving forces for phase separation, even very short ionic segments can phase separate. Using small angle X-ray scattering[26], the sizes of the domains have been estimated. For samples containing ionic block lengths of 10 - 50 units, sizes of the ionic regions range from *ca.* 50 Å to 300 Å.

Ionic interactions represent a particularly useful method of controlling phase separation in blends. Several different types of ionomer blends can be distinguished. The simplest is a blend of an ionomer with nonionic material of the same backbone. The behaviour governing these materials is qualitatively no different from the interaction of copolymers with homopolymers, in that above a minimum concentration of ions, phase separation is to be expected. Another type of behaviour is encountered when ionic interactions are used to enhance miscibility. Starting with an immiscible polymer pair, the compatibility can be enhanced if the cation is attached to one chain and the anion to the other. Depending on the nature of the polymer backbone and the ion concentration, the materials can range from highly phase separated to completely homogeneous, even at relatively low ion contents[27,28].

Thus, phase separation in ionomers can be considerably more complex than in nonionic systems and this complexity leads to materials which may contain one or more of the above-mentioned phase separated aggregates

Many factors are involved in the various types of phase separation phenomena described above. These factors can be conveniently separated in terms of the architectural and molecular characteristics of each ionomer. By the latter is meant the nature of the chemical moieties present so that when the composition of the ionomers is changed, for instance when styrene-co-styrene sodium sulfonate is used instead of styrene-co-sodium methacrylate, a molecular factor is altered. A change in the architectural factors of the ionomer implies that the ions have a different organisation with respect to the chain, as is to be found when random and block ionomers of styrene-co-sodium methacrylate are compared.

The effects of various types of molecular factors that can influence the phase behaviour observed in ionomers will now be discussed briefly.

The concentration of the ionic groups is one of the molecular parameters which affects the aggregation process. Consequently, a change in the number of ionic groups present in the nonionic matrix has a dramatic impact on the physical properties of the material as a whole[29].

Another factor which affects the driving force for aggregation is the dielectric constant of the matrix. In many synthetic polymers, such as polyethylene or polystyrene, the dielectric constant of the material is very low. Other polymers, for example poly(ethyl acrylate), have much higher dielectric constants, and thus interact more strongly with the ion pairs. Thus the former materials show behaviour associated with large scale aggregation (clusters) at lower ion concentrations than the latter[23,30].

The type of ionic groups present in the ionomer also influences the phase separation observed. In general, the larger the ion pair, the poorer the phase separation. This is due to weakened ionic interactions, as is evident when one compares random ionomers. For example, the dynamic mechanical behaviour of styrene-co-N-methyl-4-vinylpyridinium iodide, regardless of ion concentration, resembles that of a single phase material[31]. By contrast, styrene-co-sodium methacrylate, above a certain threshold ion concentration, exhibits behaviour associated with clustered materials[23].

The final factor to be considered here is the magnitude of kT relative to the glass transition temperature of the matrix and the strength of the ionic interactions. It is known that, as a general trend, those ionomer matrices with lower glass transition temperatures are more likely to exhibit evidence of clustering than those with higher $T_g$'s. The reduction is the glass transition temperature may be achieved through the use of a different monomer[32], or it may be the result of plasticisation of the matrix by a nonpolar diluent[33,34].

The placement of the ion attached to the polymer backbone has a pronounced effect on the type of aggregation observed in the material. The ions can be arranged in a number of different configurations. In the case of ionomers, most studies have been devoted to those polymers in which the ions are distributed randomly along the backbone; the are the subject of most of the examples listed above[30,31,32,33,34,35,36,37,38]. However, there are other architectures possible for ionomers and a brief description of these follows.

Modifications have been made to some ionomers, for example styrene[39] and perfluorinated polyethylene[40] matrices, so that the ions are removed from the backbones by short, flexible chains. Thus, clusters are more readily formed, but they are expected to have different morphologies. Furthermore, the longer the side chain, the more difficult it is for the ions to immobilise the polymer backbone[39,41].

Ionomers have been made in which the ions are not distributed randomly along the chain. One example is the family of ionenes. Here, the ionic groups are distributed very uniformly along the backbone, leading to interesting morphologies[42,43]. Alternatively, the ions may be placed all together on the chain, resulting in ionomers with blocky structures. The ionic blocks can vary widely, from single ions on the chain tips, as found in linear telechelics[44,45,46,47] and their branched counterparts, stars[48], to segments many thousands of units long[49,50]. These block ionomers can be of two or three segments, AB and ABA blocks respectively, or in many sections along the chain, as in segmented polyurethanes[51].

In this chapter, the phase behaviour observed in ionomers is discussed for the different kinds of phase separation that are seen. The first section deals with ionomers which show no evidence of aggregation other than that which can be explained by the formation of multiplets; for the sake of convenience, these are called "homogeneous" ionomers. This is followed by a section on the larger aggregates known as clusters and the random ionomers which exhibit behaviour which is consistent with their presence. The final sections deal with the other kinds of aggregation that are observed in polymers, specifically those encountered in blocks and blends.

## 1.2 "Homogeneous" Ionomers

In order to be considered truly homogeneous, materials must not exhibit any differences in their local composition between one area and another; thus molecular solutions are homogeneous because there is no discernible domain formation. Few, if any, ionomers could be expected to be homogeneous in this sense, because the driving force for the formation of multiplets is large[21]. However, multiplets are so small as to be undetectable by the majority of morphological techniques. Their existence can be inferred from an increase in the glass transition temperature, an increase in the modulus characteristic of crosslinking and an increase in the melt viscosity; most multiplets are too small, except under special conditions, to be observed by small angle X-ray scattering or electron microscopy techniques. For the purposes of this discussion, homogeneous ionomers will be considered as those which, because of the absence of phenomena associated with larger aggregates, are believed to contain only multiplets.

Within the above framework, a number of ionomers are homogeneous, for example styrene-co-N-methyl-4-vinylpyridinium iodide copolymers[31]. The striking resemblance of the shape of the modulus - temperature curve for one such ionomer and polystyrene is seen in Fig. 1.1. The SAXS profile of the copolymer is shown in Fig. 1.2. The lack of a peak in the profile is indicative of the absence of scattering domains in the material. Several other ionomer systems have also been found to be homogeneous, notably ethyl acrylate-co-N-methyl-4-vinylpyridinium iodide[52] and styrene-co-4-

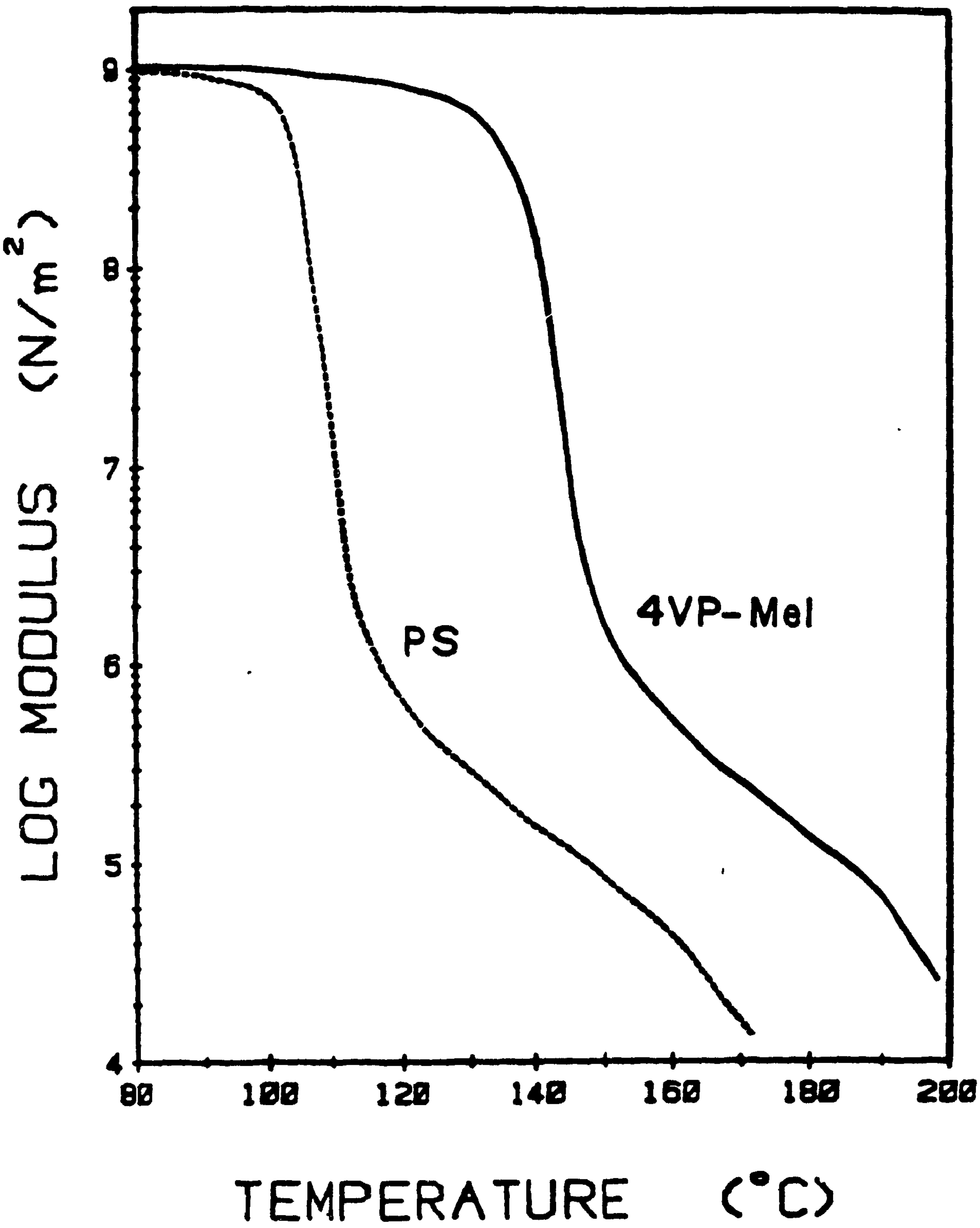

Fig. 1.1: A comparison of the storage modulus-temperature curves of a styrene homopolymer and a random styrene-co-N-methyl-4-vinylpyridinium iodide ionomer (9.7 mole % ions); from ref. 31.

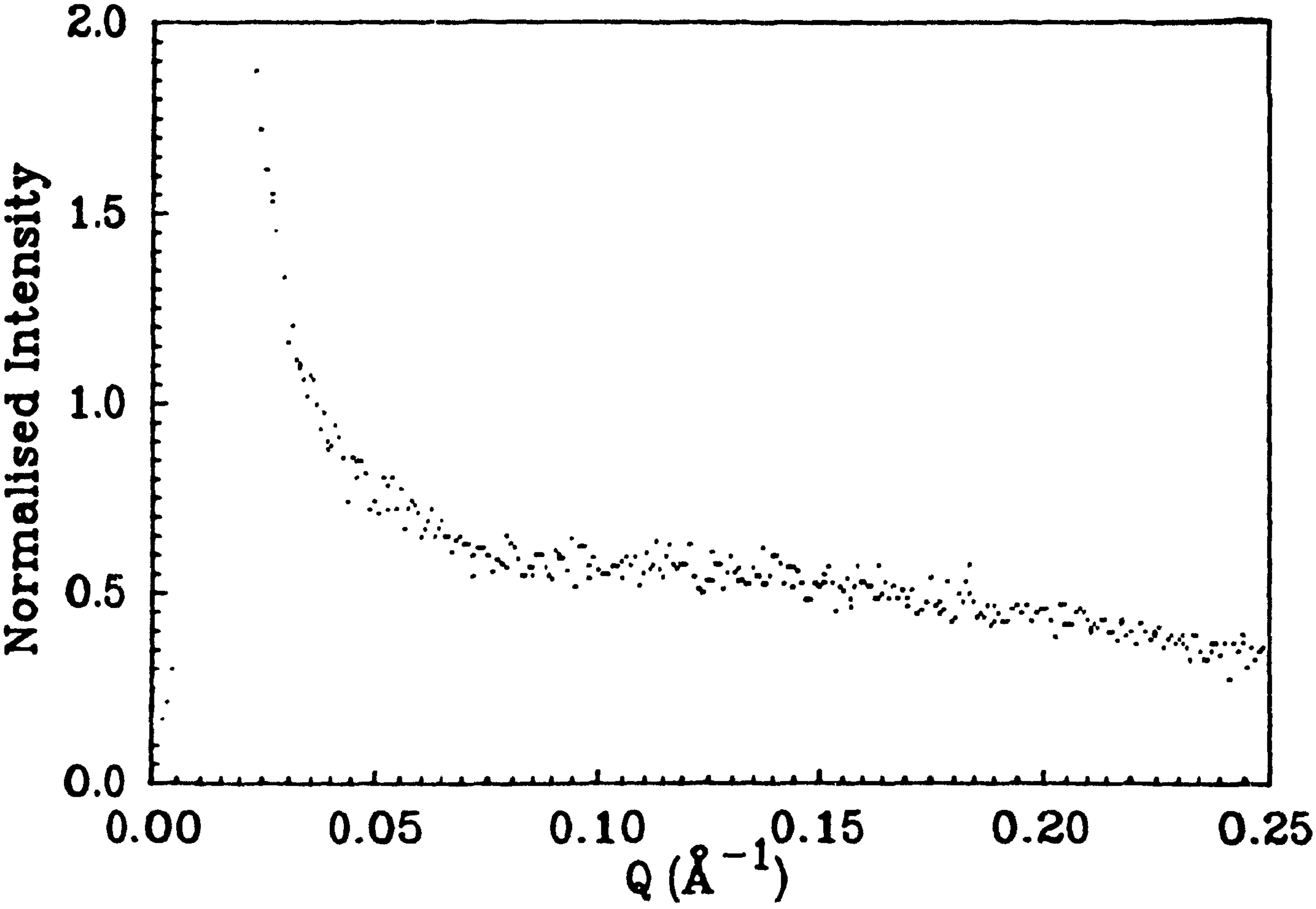

Fig. 1.2: The small angle x-ray scattering profile for a homogeneous ionomer, styrene-co-N-methyl-4-vinylpyridinium iodide.

sodium hydroxymethyl styrene[53]. In all these systems, the ionic groups are rather large or they are removed from the benzene ring by a short spacer. Both of these factors tend to make clustering less important[31,39].

Elastomers are yet another class of random ionomers which are homogeneous, at least at low ion concentrations. They were the first ionomeric materials to be studied extensively, because of interest in the improvements to the solvent resistance in the then-current elastomers[54]. While the field of ionomers grew rapidly to include materials of elevated $T_g$ and model ionomers, interest in the materials with lower glass transition temperatures flagged. However, when it was shown that the aggregation of sulfonate groups was stronger than for carboxylates[55], new academic interest developed in elastomeric ionomers[56].

Within the last decade, there has been a proliferation of new elastomeric ionomers, in particular with EPDM or pentenamer backbones[36,37]. Segmented polyurethane backbones are also currently the subject of much interest[51,57]. Results from these new studies have been mixed. Not surprisingly, in some of these materials, the phase behaviour observed was that which was expected for clustered ionomers, as is described in the following section. However, in a number of instances, the materials appeared not to have altered their physical properties significantly and resembled homogeneous materials, or the acid precursor, as is seen in Fig. 1.3. Two factors may contribute to this apparent homogeneity. The concentration of the ionic groups in ionic elastomers is generally low. Furthermore, the size of the ionic group is often large.

Another group of homogeneous ionomers are the halatotelechelic polymers. Halatotelechelic polymers are considered to contain only multiplets. The case of the telechelics is somewhat more complicated, however, in that a range of multiplet sizes have been postulated for different materials. Telechelic polymers include branched, or

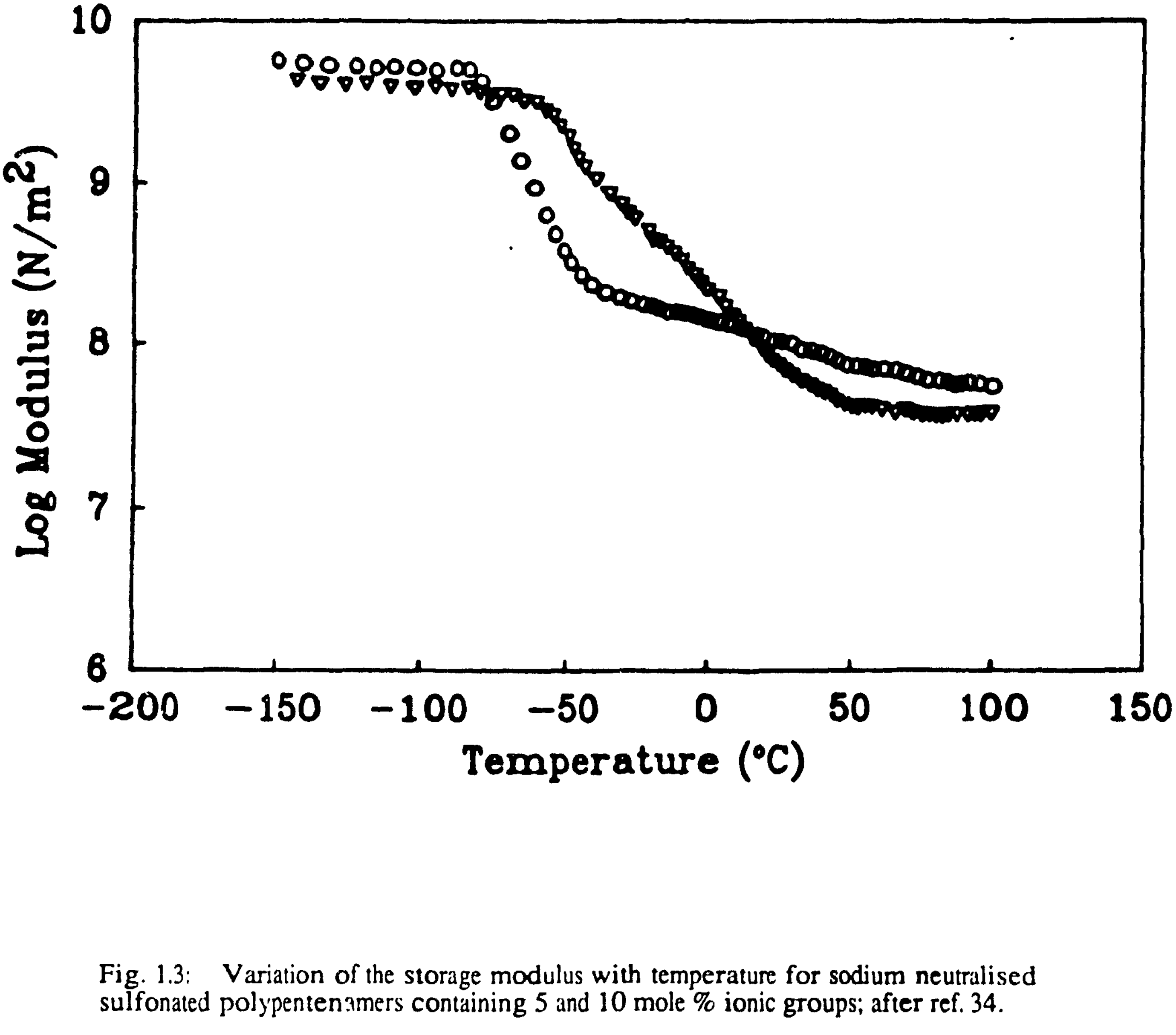

Fig. 1.3: Variation of the storage modulus with temperature for sodium neutralised sulfonated polypentenamers containing 5 and 10 mole % ionic groups; after ref. 34.

"star", architectures[48,58,59], in addition to linear, single or double-tipped, species[46,47,60,61,62].

A number of studies have examined the phase separation in telechelic ionomers. It has been shown that the backbone composition, molecular weight of the polymer (which affects the ion concentration as well as the chain length) and the counter ion all have significant effects on the complexity of the behaviour observed[59,61,63].

Results of small angle X-ray scattering experiments on the linear telechelics have clearly shown the presence of aggregates in materials of low molecular weight ($M_n$)[46] and results from extended X-ray absorption fine structure, EXAFS, experiments indicate the domains possess a regular structure[64]. The most recent conclusions from SAXS are that these linear samples contain large multiplets with a radius of 6 - 9 Å[65]. Thus, linear telechelics represent a borderline case of homogeneous ionomers. Because of the terminal ion placement, large numbers of ion pairs can aggregate, thus increasing the size of the phase separated domains. However, the chain material is not incorporated into the aggregates, so that these materials contain only multiplets.

Stars, on the other hand, form only very small aggregates. Only the samples of the very lowest molecular weight show any evidence of even a shoulder in the SAXS profile, and the indications here are that the multiplets consist only of two ion pairs[59]. The proposed structure of stars is shown in Fig. 1.4.

## 1.3 Clustered Ionomers

The majority of ionomers show behaviour in many different experiments that is much more complex than that found in the so-called "homogeneous" ionomer systems. It has been argued that these differences are due to new phase separation mechanisms and that these ionomers are clustered, the clusters being much larger than the multiplets[21]. Thus, while a consensus has not yet emerged regarding the exact nature

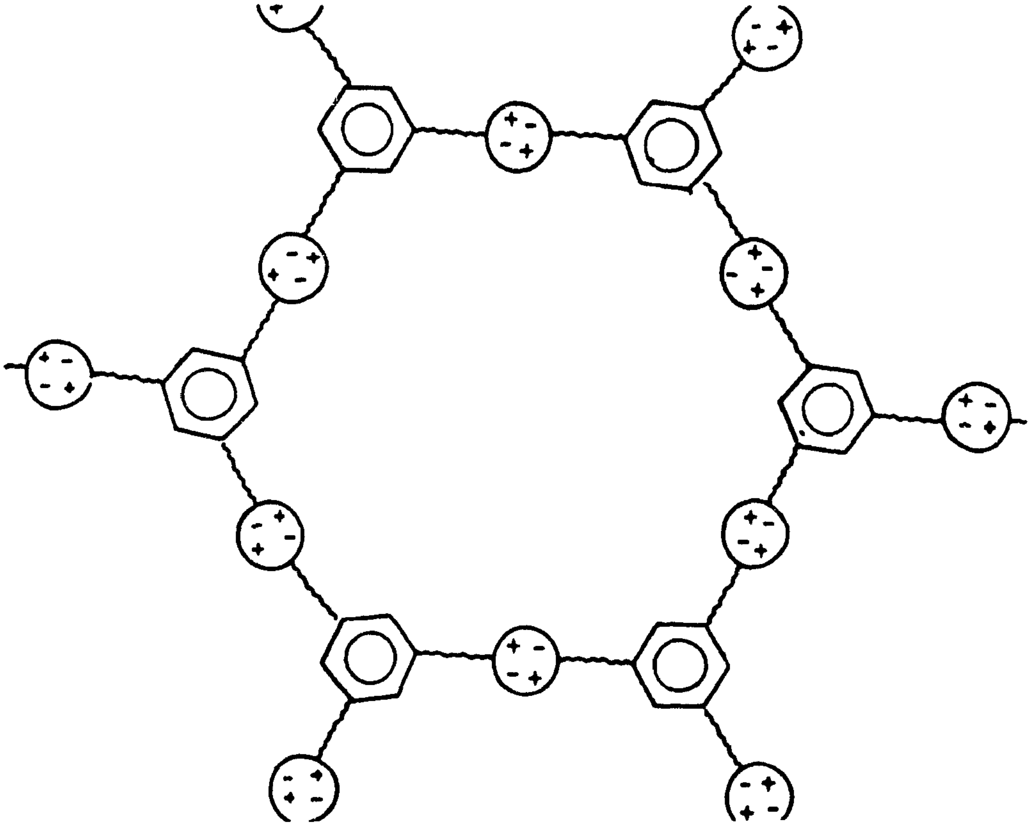

Fig. 1.4: Model of aggregation in star telechelics; after ref. 58.

of the clusters, there is a significant body of data from which the effects of clustering on ionomer systems can be assessed.

Perhaps the most compelling evidence for the phase separation into clustered regions has been found through dynamic mechanical studies, notably loss tangent maxima. Nonionic polymers and homogeneous ionomers display very similar modulus - temperature profiles. This indicates that the sizes of the inhomogeneities in such materials are smaller than those which give rise to mechanical responses consistent with a separate phase.

Ionomers which are clustered commonly display two glass transition temperatures in dynamic mechanical experiments. These are due to the matrix and the cluster $T_g$'s. The relative sizes of the two peaks have been seen to change with variations in the ion content as shown in Fig. 1.5. In general, with increasing ion content, the matrix $T_g$ is shifted to higher temperatures, typically of the order of 3 °C/mole percent of ionic groups[23,31,66,67,68].

The second glass transition temperature is found at much higher temperatures and its dependance on molecular parameters is much more complex. Two factors which influence this $T_g$ are the ion concentration and the type of ions involved. With an increase in the concentration of the ions the second glass transition temperature maximum grows rapidly at the expense of the lower one and also moves to higher temperatures[29] Initially, identification of the second peak as a glass transition temperature was not universally accepted. However, the high activation energy of this peak and the accompanying drop in the storage modulus are most readily explained by such an interpretation Other dynamic methods which have been used to explore the phase behaviour in ionomers have included dielectric studies[69,70,71,72,73]. The results from these studies support the conclusions drawn from the mechanical

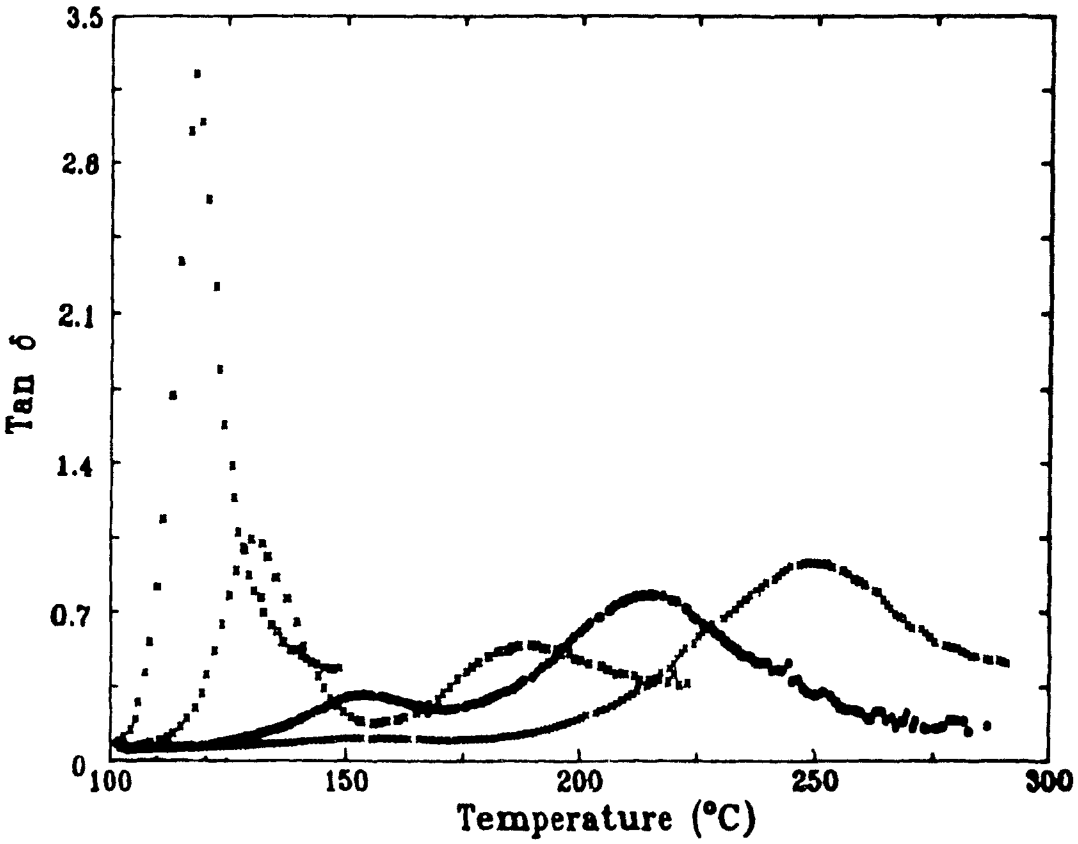

Fig. 1.5: Variation in the loss tangent with temperature for styrene-co-sodium methacrylate containing from 0 tc 14 mole % ionic groups.

experiments.

Static techniques have also been used to confirm the presence of clusters in ionomers. Unlike the dynamic mechanical experiments discussed above, these probe only the morphology of the materials.

One experimental method which has proved particularly fruitful is small angle X-ray scattering, or SAXS. SAXS and its counterpart, SANS (small angle neutron scattering), rely on differences, either in the electron density or the neutron scattering cross-section, between the various regions. Results from SAXS and SANS indicate that, in general, the majority of ionomers show a peak associated with the presence of phase separated domains[74,75,76,77]. A typical SAXS profile from a clustered ionomer is shown in Fig. 1.6. The position of the peak can be related to the size of the domains and it has been seen to vary with the ion content of the material and its sample history[78]. In general, however, most models suggest that the typical dimensions associated with the scattering centres in random ionomers are about 30 Å in diameter.

A wide range of spectroscopic techniques have also been employed in the exploration of phase separation in ionomers. The field of solid state NMR spectroscopy is beginning to be explored for ionomers[79,80], although the focus of most such interest to date has been with ionomeric blends[81,82,83,84,85]. Infrared and Raman spectroscopy have also been utilised in the examination of phase separation in ionomers[86,87,88,89,90]. Unfortunately, however, interpretations of the results from the systems studied have been subject to controversy and these two techniques have not yielded unequivocal evidence for clusters in ionomers. Mössbauer spectroscopy has been applied to solid ionomers as well[91,92]. The results here indicate that there exists more than one phase in the ion-containing samples.

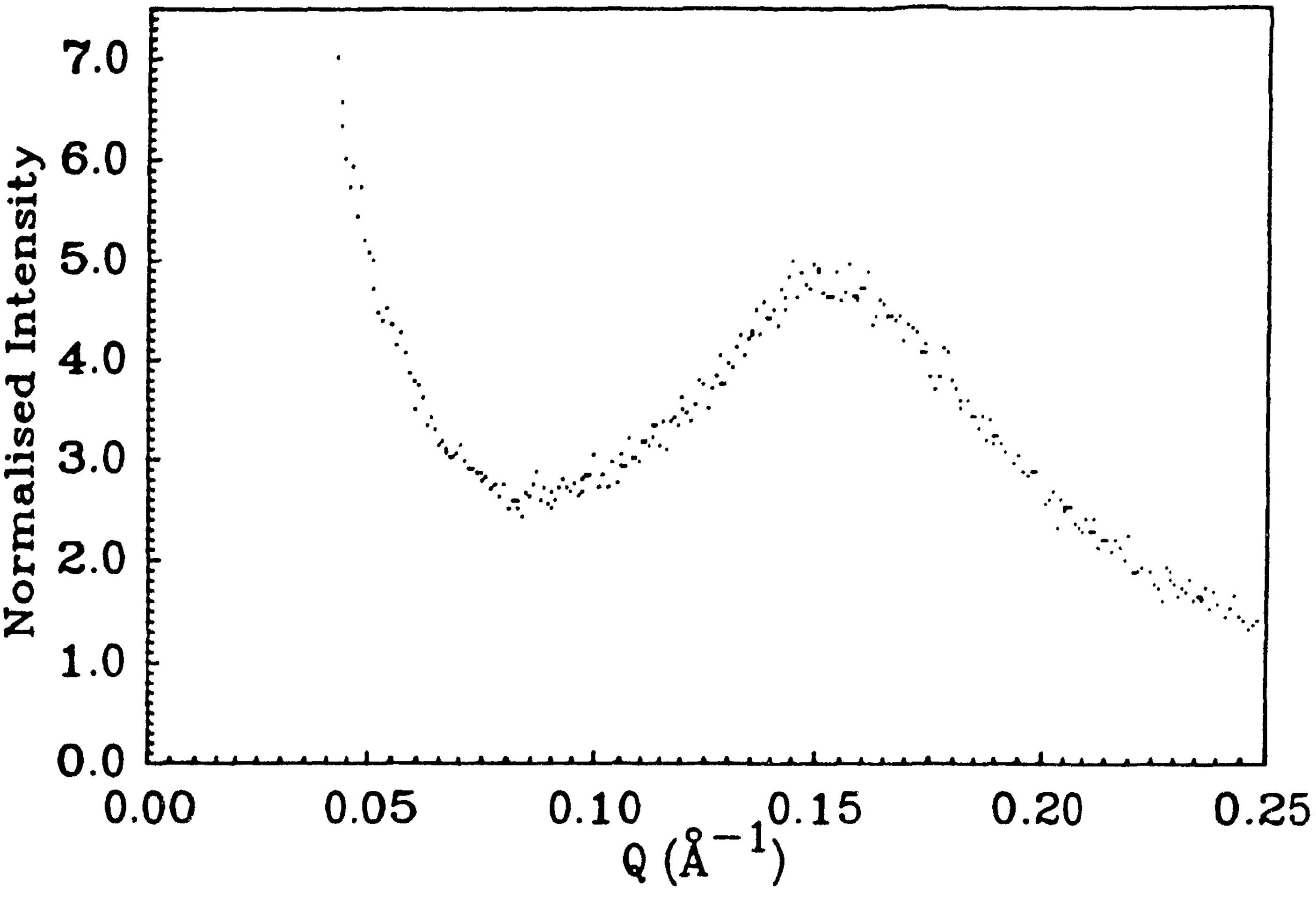

Fig. 1.6: Small angle X-ray scattering profile for a clustered ionomer, containing styrene-co-styrene-p-cesium sulfonate (8 mole % ions).

Fluorescence spectroscopy experiments have yielded results of considerable interest and much information is available through these techniques. For example, the quenching of the fluorescence from a probe attached to the ionic moieties in an ionomer has led to the conclusion that ionic aggregates are present in such systems[93]. Other experiments have exploited the fact that the polarity of the local environment of some probes affects their emission spectra. Thus, these probes have been localised in either the matrix or the ionic domains, and then utilised in studies which confirm the existence of chain material in the ionic regions and studies which have examined the effects of water on the ionomer morphology[94,95].

The above experiments have dealt with the characterisation of clusters. A number of very recent studies have gone beyond this exploration and have focussed on the manipulation of clusters through modification of the polymer backbone alone or *via* the addition of diluents of different polarities.

Plasticisation is a common industrial technique for the modification of many polymers. Plasticisers are used extensively to change the glass transition temperatures of polymers for both their moulding stages and for permanent end uses[96]. In the case of ionomers, because of the difference between the dielectric constants in the clustered regions and the matrix, diluents with different polarities affect the properties of the material very differently.

A number of studies have been performed to explore the effects of plasticisation with diluents of high polarity, such as water and glycerol[33,97]. It has been shown that the addition of small amounts of such plasticisers readily obliterates the dynamic mechanical features associated with the clustered aggregates without affecting the glass transition temperature of the matrix significantly. It seems, therefore, that these diluents are incorporated almost exclusively into the clusters.

Other experiments were devoted to the plasticisation of ionomers through the addition of plasticisers of polarity comparable to that of the matrix, such as diethylbenzene or styrene oligomers in styrene-based systems[33,34,98,99] and dimethyl malonate in ethyl acrylate systems[32]. In these cases, it was shown that small amounts of the diluent can actually enhance the phase separation ascribed to clustering. At high levels of loading, however, the features associated with clustering are no longer observed.

One of the disadvantages in the use of plasticisers is their volatility. For long term use, loss of the diluent cannot be tolerated. Thus, a number of studies have been concerned with the permanent incorporation of plasticiser into the ionomer. One method of achieving this plasticisation is *via* alkylation of the matrix monomer[34]. The results of these studies indicate that the overall effect of such nonpolar plasticisers is independant of whether they are affixed to the polymer chains or not However, much higher alkylation levels are required to obtain the same degree of plasticisation *via* alkylation than by the addition of diluent.

Plasticisers may also be incorporated into the ionic domains through the neutralisation of the comonomer with appropriate diluents Dynamic mechanical studies of different systems show that the rigidity and size of the attached plasticiser influences the glass transition temperatures of the materials[100,101,102]. This implies that, unlike the case of external plasticisers, some of the diluent resides in the matrix. However, attached and free plasticisers show similar effects on the phase behaviour of otherwise clustered ionomers and appear to disrupt such aggregation.

One series of studies has yielded unexpected results on the effects of adding small molecules to polymers. Ionomers containing nitro groups were prepared through the plasticisation of styrene-co-sodium methacrylate with nitrobenzene and, independantly, by the nitration of the benzene rings[103]. Nitro groups are highly polar, yet the dynamic mechanical results that were obtained indicated that the ionomer was behaving as though a nonpolar plasticiser had been added to the material. This behaviour was explained in terms of the three dimensional solubility parameters. Most materials with a high polarity have a large component of the solubility parameter due to hydrogen bonding, $\delta h$; however, nitrobenzene is an exception. Those plasticisers with a high $\delta h$ do disrupt the clusters.

Phase separation in ionomers has also been the subject of theoretical interest. The existence of two different kinds of aggregate morphologies in ionomers, i.e. multiplets and clusters, was first proposed in 1970[21]. It was suggested, on the basis of thermodynamic considerations, that clusters, which contain both ionic and nonionic material in close proximity, should be stable.

Since then, a number of theories have been published dealing with the formation of aggregates such as clusters. These have been the subject of a recent review[13]. The majority of theories incorporate the presence of clusters in ionomers, however, not every subsequent publication has found it necessary to invoke clustering as a process in order to explain the experimental results.

## 1.4 Block Ionomers

Phase separation in block ionomers is well established[104,105,106,107]. The segregation of the different components of the blocks results from the immiscibility of different polymers, which is due to entropic factors.

The same phenomena are observed in the phase behaviour encountered in block ionomers. However, the driving force for phase separation is even greater in ionic materials, since ionic and nonionic blocks should be particularly incompatible.

The phase separated regions in blocks are quite different from those previously described for random ionomers and resemble more those in regular block copolymers. The domains are much larger than multiplets or clusters and contain mostly or solely the ionic component. Because of their ionic nature and the presumed absence of nonionic chain material, they have been termed "supermultiplets"[26]. As in the case of block copolymers in general, there is likely to be an interfacial area between the ionic aggregates and the surrounding matrix, although in the case of the ionomers, this would be expected to be smaller than for the nonionic systems.

Several studies have been devoted to ABA block ionomers, where the A blocks represent the ionic portion of the molecule[26,49,50]. Since ionomers have been defined as possessing a low ion content, the majority of these studies have been concerned with short end block systems.

A number of review have been published dealing with phase separation in block copolymers in general as well as with the specific mechanical properties of these materials. Only very few studies have been concerned with the dynamic mechanical properties of block ionomers[47,108]. It would be expected that, as is observed for the nonionic materials, block ionomers would show phase separation in the form of two separate glass transitions Regrettably, in the system studied, styrene-co-N-methyl-4-vinylpyridinium iodide, dequaternisation of the pyridinium moieties occurred before the expected high $T_g$ of the ionic end blocks could be observed[50]. Further experiments, using polymers quaternised with higher iodoalkanes or with plasticised ionic domains, are currently underway[109].

Confirmation of the phase separation in block ionomers has been obtained directly through SAXS studies. Because small angle X-ray scattering requires electron density differences, most commonly through the presence of atoms or ions of high atomic number, ionomers have an advantage over nonionic systems in that the heavier counter ions are directly discernible through SAXS

Results from studies using SAXS and SANS techniques on the same block ionomers mentioned above, as well as on polymers with anionic end blocks[108], show that these materials are clearly phase separated over the range studied, i.e. 200 - 1000 styrene midblock units and 10 - 50 N-methyl-4-vinylpyridinium iodide units in each end block[26]. Based on the data, it was concluded that the ionic domains are spherical. Furthermore, the number of chains emanating from each supermultiplet is much higher than expected from nonionic systems.

Ionomers of AB architecture have also been prepared and are now under study. It is expected that these materials would likewise be phase separated. In dynamic mechanical experiments, AB ionomers are expected to exhibit viscous flow at high temperatures, and not the crosslinked behaviour seen in the triblock ionomers. To date, most of the interest in these materials has focussed not on their mechanical properties, but rather on their behaviour in solution[110,111]. Thus, the AB block ionomers will not be discussed further.

### 1.5 Blends with Ionomers

Polymer-polymer mixtures, or blends, are commonly incompatible. However, if anions are attached to one of the polymers and cations to the other, obviously the miscibility between the two chains is enhanced. It was shown recently[27] that in a system consisting of sulfonated polystyrene and ethyl acrylate-co-4-vinylpyridine copolymers, one phase behaviour was observed at a functional group concentration as low as 4 mole percent In the absence of functional groups, the two polymers were immiscible, while at concentrations between 0 and 4 mole percent, an increasing degree of miscibility was observed. The miscibility enhancement was due to ionic interactions resulting from proton transfer from the sulfonic acid to the pyridine groups. Thus, by this technique, the phase behaviour of a very wide range of blends can be controlled all the way from complete phase separation to complete miscibility as is shown in Fig. 1.6.

Even highly dissimilar materials can be rendered miscible by this method. For example, it was shown recently that sulfonated poly(tetrafluoroethylene), Nafion®, and ethyl acrylate-co-4-vinylpyridine exhibit considerable miscibility enhancement, in that they show many characteristics of one phase systems[28].

Ion-dipole interactions are also useful in enhancing polymer-polymer miscibility. Thus, while styrene is not miscible with poly(ethylene oxide) or poly(propylene oxide), a styrene ionomer containing 5 - 10 mole percent lithium methacrylate shows considerable miscibility with these polar homopolymers[112]. The cloud point behaviour in these systems is typical of blends subject to specific interactions.

It is worth noting that blends of ionomers with commercially important crystalline polymers have been discussed extensively in the patent literature[113]. For example, Surlyn® ionomers have been used in mixtures with polycarbonates and nylons to yield materials with considerably modified properties. In these systems, the ionomer is the minor component and the effect is primarily to modify the crystalline behaviour of the major components.

## 1.6 Conclusions

Ionomers of different architectures exhibit many different kinds of phase behaviour, on their own or as blends The ions can aggregate to give small multiplets and larger clusters, or in the case of block ionomers, very large supermultiplets. In some cases a gradation of behaviour can be observed. For example, in the case of styrene-co-N-methyl-4-vinylpyridinium iodide, we have a system containing only multiplets. The addition of a nonpolar plasticiser allows the material to cluster, so that evidence of both types of aggregation is seen On the other hand, styrene-co-sodium methacrylate is highly clustered. However, the addition of a polar interacting

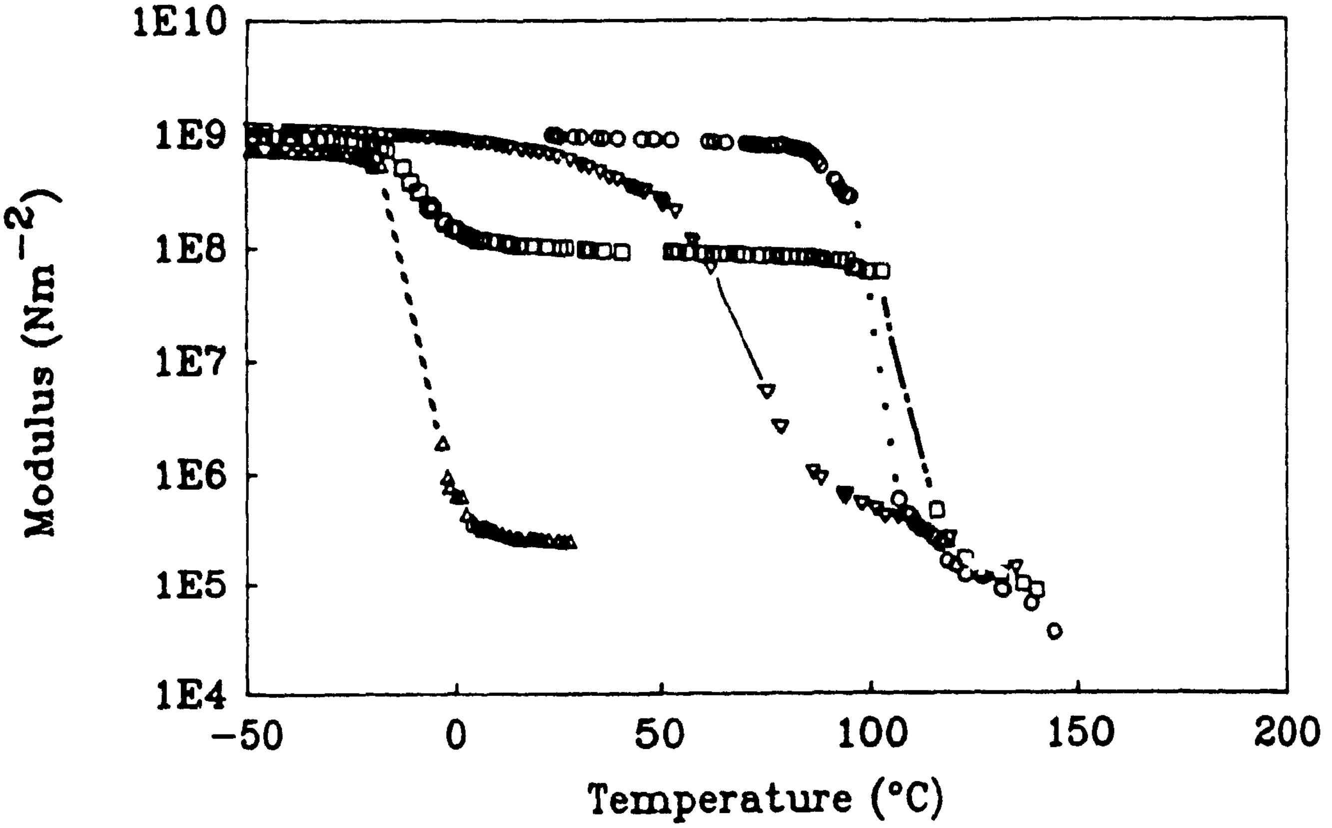

Fig. 1.7: Variation in the storage modulus with temperature for four materials: poly(ethyl acrylate), △, polystyrene, ` , a 50/50 blend of these homopolymers, □, and a 50/50 blend of styrene-co-styrene-p-sulfonic acid (6 mole % acid) and ethyl acrylate-co-4-vinylpyridine (EA-0.06VP), ▽.

plasticiser, such as glycerine, can eliminate the rheological effects due to clusters. The architectures of many ionomers affect their phase behaviour. Thus, copolymers which do not show phase separation with random architectures do so when the ionic groups are organised into blocks. Because of the strong driving force for phase separation, even segments of 10 units phase separate. Finally, ionic interactions provide a powerful method for the control of miscibility in polymer blends. Depending on the functional group content, one can obtain a range of materials which, starting from heterogeneous homopolymer blends, may exhibit increasing degrees of miscibility up to total compatibility.

## 1.7 Acknowledgements

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## 1.8 References

(1) R. W. Rees and D. J. Vaughan, ACS, Polym. Prepr., **6**, 287 (1965).

(2) L. Holliday, Ionic Polymers, Wiley, New York (1975).

(3) A. Eisenberg and M. King, Ion-Containing Polymers, Academic Press, New York (1977).

(4) Ion-Containing Polymers, ed. A. Eisenberg, J. Polym. Sci., Polym. Symp., **45**, John Wiley and Sons, New York (1974).

(5) Ions in Polymers, ed. A. Eisenberg, ACS Symp. Ser., **187**, American Chemical Society, Washington (1980).

(6) Perfluorinated Ionomer Membranes, eds. A. Eisenberg and H. L. Yeager, ACS Symp. Ser., **180**, American Chemical Society, Washington (1982).

(7) Coulombic Interactions in Macromolecular Systems, eds. F. Bailey and A. Eisenberg, ACS Symp. Ser., **302**, American Chemical Society, Washington (1986).

(8) Structure and Properties of Ionomers, eds. M. Pineri and A. Eisenberg, NATO ASI Series, **C198**, D. Reidel Publ. Co., Dordrecht (1987).

(9) C. G. Bazuin and A. Eisenberg, Ind. Eng. Chem. Prod. Res. Dev., **20**, 271 (1981).

(10) W. J. MacKnight and T. R. Earnest, J. Polym. Sci., Macromol. Rev., **16**, 41 (1981).

(11) J. J. Fitzgerald and R. A. Weiss, J. Macromol. Sci., Rev. Macromol. Chem. Phys., **C28**, 99 (1988).

(12) M. R. Tant and G. L. Wilkes, ibid., **28**, 1 (1988).

(13) K. A. Mauritz, ibid., **C28**, 65 (1988).

(14) H. L. Yeager, ref. 6, 41.

(15) R. D. Lundberg, ref. 8, 429.

(16) D. E. Bugner and J. H. Anderson, ACS Polym Prepr., **29**, 463 (1988).

(17) A. Diaz, D. Fenzel-Alexander, D. C. Miller, D. Wollmann and A. Eisenberg, manuscript submitted to 63rd Symposium on Colloid and Surface Science.

(18) S.-D. Clas, ACS Polym. Prepr., **29**, 438 (1988).

(19) J. S. Tan, ref. 8, 439.

(20) L. D. Pettit and S. Bruckenstein, J. Am. Chem. Soc., **88**, 4783 (1966).

(21) A. Eisenberg, Macromolecules, **3**, 147 (1970).

(22) Ref. 3, 19-20.

(23) A. Eisenberg and M. Navratil, Macromolecules, **6**, 604 (1973).

(24) R. Longworth, in ref. 2, Ch. 2.

(25) W. J. MacKnight, W. P. Taggart and L. McKenna, J. Polym. Sci., Polym. Symp., **46**, 83 (1974).

(26) J.-P. Gouin, C. E. Williams and A. Eisenberg, submitted to

Macromolecules.

(27) P. Smith and A. Eisenberg, J Polym. Sci., Polym. Lett. Ed., **21**, 223 (1983).

(28) A. Natansohn, R. Murali and A. Eisenberg, Makromol. Chem., Makromol Symp., **16**, 175 (1988).

(29) B. Hird and A. Eisenberg, manuscript submitted to J. Polym. Sci, Polym. Phys. Ed..

(30) A. Eisenberg, H. Matsuura and T. Tsutsui, J. Polym. Sci., Polym. Phys. Ed., **18**, 479 (1980).

(31) S. Gauthier, D. Duchesne and A. Eisenberg, Macromolecules, **20**, 753 (1987).

(32) D. Duchesne and A. Eisenberg, manuscript in preparation.

(33) C. G. Bazuin and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **24**, 1137 (1986).

(34) M. Gauthier and A. Eisenberg, manuscript submitted to Macromolecules.

(35) C. Azuma and W. J. MacKnight, J. Polym. Sci., Polym. Chem. Ed., **15**, 547 (1978).

(36) D. Rahrig and W. J. MacKnight, ref. 5, 77.

(37) D. Rahrig and W. J. MacKnight, ref. 5, 91.

(38) H. S. Makowski, R. D. Lundberg, L. Westerman and J. Bock, ACS Polym. Prepr., **19**, 292 (1978).

(39) M. Gauthier and A. Eisenberg, submitted to Macromolecules.

(40) D. J. Connolly and W. F. Gresham, U.S. Patent 3282875 (1966).

(41) R. B. Moore and C. R. Martin, submitted to Macromolecules.

(42) A. Rembaum, W. Baumgartner and A. Eisenberg, J. Polym Sci., Part B, **6**, 159 (1968).

(43) D. Feng, L. N. Venkateshwaran, G. L. Wilkes, B. Lee and J. E. McGrath, ACS Polym. Prepr., **29**, 134 (1988).

(44) R. Jérôme and G. Broze, Rubber Chem. Technol., **58**, 223 (1985).

(45) M. R. Tant, J. H. Song, G. L. Wilkes and J. P. Kennedy, ACS Polym. Prepr., **27**, 351 (1986).

(46) C. E. Williams, T. P. Russell, R. Jérôme and J. Horrion, Macromolecules, **19**, 2877 (1986).

(47) G. Vlaic, C. E. Williams, R. Jérôme, M. R. Tant and G. L. Wilkes, Polymer, **29**, 173 (1988).

(48) M. Hara, A. Eisenberg, R. F. Storey and J. P. Kennedy, ref. 7, 176.

(49) R. D. Allen, T. L. Huang, D. K. Mohanty, S. S. Huang, H. D. Qin and J. E. McGrath, ACS Polym. Prepr., **24**, 41 (1983).

(50) S. Gauthier and A. Eisenberg, Macromolecules, **20**, 760 (1987).

(51) T. A. Speckhard, K. K. S. Hwang and S. L. Cooper, Polym. Mat. Sci. Eng., **50**, 24 (1984).

(52) D. Duchesne, Ph. D. Thesis, McGill University (1985).

(53) S.-D. Clas, Ph. D. Thesis, McGill University (1985).

(54) H. P. Brown, Rubber Chem. Technol., **35**, 1347 (1957).

(55) R. D. Lundberg and H. S. Makowski, ref. 5, 21.

(56) W. J. MacKnight and R. D. Lundberg, Rubber Chem. Technol., **57**, 652 (1984).

(57) S. L. Hsu, H. X. Xiao, H. H. Szmant and K. C. Frisch, J. Appl. Polym. Sci., **29**, 2467 (1984).

(58) S. Bagrodia, Y. Mohajer, G. L. Wilkes, R. F. Storey and J. P. Kennedy, Polym. Bull., **8**, 281 (1982).

(59) S. Bagrodia, M. R. Tant, G. L. Wilkes and J. P. Kennedy, Polymer,**28**, 2207 (1987).

(60) Y. Mohajer, D. Tyagi, G. L. Wilkes, R. F. Storey and J. P. Kennedy, Polym. Bull., **8**, 47 (1982).

(61) G. Broze, R. Jérôme, P. Teyssié and C. Marco, J. Polym. Sci., Polym. Phys Ed., **21**, 2205 (1983).

(62) G. Broze, R. Jérôme, P. Teyssié and C. Marco, Macromolecules, **18**, 1376 (1985).

(63) J. Horrion, R. Jérôme, P. Teyssié, C. Marco and C. E. Williams, Polymer, **39**, 1203 (1988).

(64) G. Vlaic, C. E. Williams and R. Jérôme, Polymer, **28**, 1566 (1987).

(65) C. E. Williams, paper presented at the ACS Biennial Conference, Nov. 1988.

(66) M. Rigdahl and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **19**, 1641 (1981).

(67) N. Brockman and A. Eisenberg, ibid., **23**, 1145 (1985).

(68) S.-D. Clas and A. Eisenberg, Ibid., **24**, 2767 (1986).

(69) I. M. Hodge and A. Eisenberg, Macromolecules, **11**, 283 (1978).

(70) P. J. Phillips and W. J. MacKnight, J. Polym. Sci., Part A2, **8**, 727 (1970).

(71) S. Yano, K. Tadano, T. Sugiara and E. Hirasawa, ref. 8, 481.

(72) G. Boiteux, Ibid., 227.

(73) A. Belfkira, M. Camps, J. P. Monthéard and G. Boiteux, Eur. Polum. J., **23**, 979 (1987).

(74) T. R. Earnest, J. S. Higgins and W. J. MacKnight, Macromolecules, **15**, 1390 (1982).

(75) J. S. Higgins, D. L. Handlin, W. J. MacKnight, T. R. Earnest and W. C. Forsman, ACS Polym. Prepr., **25**, 300 (1984).

(76) W. J. MacKnight, W. P. Taggart and R. S. Stein, J. Polym. Sci., Polym. Symp., **45**, 113 (1974).

(77) M. Pineri, R. Duplessix, S. Gauthier and A. Eisenberg, ref. 5, 283.

(78) R. A. Weiss and J. J. Fitzgerald, ref. 8, 361.

(79) N. G. Boyle, V. J. McBrierty and A. Eisenberg, Macromolecules, **16**, 80 (1983).

(80) V. J. McBrierty, G. Smyth and D. C. Douglass, ref. 8, 149.

(81) A. Natanschn, M. Rutkowska and A. Eisenberg, Polymer, **28**, 885 (1987).

(82) A. Natansohn, M. Rutkowska and A. Eisenberg, J. Polym. Mater., **4**, 9 (1987).

(83) A. Natansohn and A. Eisenberg, Macromolecules, **20**, 323 (1987).

(84) L. Belfiore and R. J. Shah, ACS Polym. Mat. Sci. Eng., **54**, 490 (1986).

(85) L. Belfiore and A. A. Patwardhan, ACS Polym. Mat. Sci. Eng., **54**, 638 (1986).

(86) W. Y. Hsu, Macromolecules, **16**, 745 (1983).

(87) D. G. Peiffer, B. L. Hager, R. A. Weiss, P. K. Agarwal and R. D. Lundberg, J. Polym Sci., Polym. Phys. Ed., **23**, 1869 (1985).

(88) B. A. Borozoski, M. M. Coleman and P. C. Painter, Macromolecules, **17**, 230 (1984).

(89) V. D. Mattera and W. M. Risen, J. Polym. Sci., Polym Phys. Ed., **22**, 67 (1984).

(90) A. Neppel, I. S. Butler and A. Eisenberg, Macromolecules, **12**, 948 (1979).

(91) M. Pineri, ref. 7, 159.

(92) B. Rodmacq, J. M. D. Coey and M. Pineri, ref. 6, 171.

(93) E. Banks, Y. Okamoto and Y. Ueba, J. Appl. Polym. Sci., **25**, 359 (1980).

(94) M. N. Szentirmay, N. E. Prieto and C. R. Martin, J. Phys. Chem., **89**, 3017 (1985).

(95) M. N. Szentirmay, N. E. Prieto and C. R. Martin, Talanta, **32**, 745 (1985).

(96) J. R. Darby and J. K. Sears, in Encyclopedia of Polymer Science and Technology, eds. H. F. Mark and N. G. Gaylord, **10**, Interscience Publishers, New York (1969).

(97) M. Navratil and A. Eisenberg, Macromolecules, **7**, 84 (1974).

(98) C. G. Bazuin and S. Villeneuve, ACS Polym. Mat. Sci. Eng., **58**, 1069 (1988).

(99) D. Wollmann, C. E. Williams and A. Eisenberg, mansucript in preparation.

(100) R. A. Weiss, P. K. Agarwal and R. D. Lundberg, J. Appl. Polym. Sci., **29**, 755 (1984).

(101) P. Smith and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **26**, 569 (1988).

(102) D. Wollmann, S. Gauthier and A. Eisenberg, Polym. Eng. Sci., **26**, 1451 (1986).

(103) M. Gauthier and A. Eisenberg, manuscript submitted to Macromolecules.

(104) G. M. Estes, S. L. Cooper and A. V. Tobolsky, J. Macromol. Sci., Rev. Macromol. Chem., **C4**, 313 (1970).

(105) B. R. M. Gallot, Adv. Polym. Sci., **29**, 85 (1978).

(106) D. J. Meier, NATO ASI Series, **E89**, 173 (1985).

(107) S. Krause and M. Iskandar, ACS Symp. Ser., **176**, 205 (1979).

(108) C. D. DePorter, L. N. Venkateshwaran, G. A. York, G. L. Wilkes and J. E. McGrath, ACS Polym. Prepr., **30**, 201 (1989).

(109) D. Wollmann and A. Eisenberg, manuscript in preparation.

(110) J. Selb and Y. Gallot, Makromol. Chem., **181**, 2605 (1980).

(111) F. C. Schwab and I. J. Hellwell, Ind. Eng. Chem. Prod. Res. Dev., **27**, 1306 (1984).

(112) M. Hara and A. Eisenberg, Polym. Eng. Sci., **27**, 1306 (1984).

(113) See for example, J. Nakabashi, R. Nakai and T. Hamada, JP 62/68851 A2 [87/68851] and P. E. Glover, Eur. Pat. 267742 A2, among many others.

# Chapter 2

## Control of Ionomer Properties via Aggregate Modification

### 2.1 Abstract

The presence of small ions attached to polymers of low dielectric constant results in the phase separation commonly observed in ionomers. This leads to the formation of multiplets and clusters. However, when the ions are large, or both cations and anions are polymeric, aggregation may become impossible. Following a review of aggregation in ionomers, the factors, both geometric and electrostatic, which affect ion aggregation in the random materials and, thus, the properties of the materials, are discussed. Likewise, the effect of various parameters on phase separation in block ionomers is also presented.

Plasticisation is of special interest in this context, since it can influence the phase behaviour. It is possible to modify the level of aggregation in a material selectively in both directions. Thus, in plasticised systems, the ionic phase can be severely disrupted by diluents of high dielectric constant. By contrast, in homogeneous systems verging on phase separation, the latter can be induced by the addition of a plasticiser of low dielectric constant. This makes it possible to modify at will the physical properties of the ionomers.

### 2.2 Introduction

The incorporation of small amounts of ions into synthetic polymers can have major effects on the properties of the resulting systems. Such materials have been termed "ionomers"[1], and have been produced and studied for over twenty years[2,3]. An illustrative example of these effects can be found in a comparison of the mechanical behaviour of polystyrene and poly(styrene-co-sodium methacrylate) at elevated temperatures[4,5]. Even when the comonomer constitutes only some ten mole percent of the polymer, the effect of the ions is very apparent. Thus, at 140 °C, polystyrene is a syrup, while the ionomer has a modulus of nearly $10^9$ N/m$^2$ and remains a glassy solid. In part, this is due to an increase in the glass transition temperature, which has been raised some 30 °C with respect to the $T_g$ of pure polystyrene. However, when one compares the temperatures for the two materials at which they exhibit a modulus of $10^7$ N/m$^2$, a much greater difference is seen. This level is attained in polystyrene at about 120 °C, but in the ionomer only around 200 °C. Thus, the shape of the modulus - temperature curve is profoundly affected by the inclusion of ionic groups as shown in Fig. 2.1.

This is just one of many examples of the influence which ions exert on the physical properties of polymers. Other areas where this is manifested are, as mentioned before, the glass transition temperatures, as well as the melt viscosities of the materials[6] and the diffusion of small molecules through them[7]. Evidently, the incorporation of even minor amounts of ions can have major consequences, as has recently been reviewed in detail[8].

It is not surprising that these effects make ionomers of increasing interest and, ultimately, utility in industrial applications. The original commercial ionomers, such as Surlyn®, were exciting because of their enhanced toughness and clarity, making them very useful for packaging. Since then, ionomers have founds niches in industry for use as ion-selective membranes[9], as in Nafion® or Flemion®, and as additives to drilling fluids[10], sulfonated polystyrene being an example, to mention just two applications. Ionomers are also employed for more specialised uses, such as floor waxes and golf balls. The potential for new applications is equally diverse, with studies ranging from medicinal, for the absorption of bile acids[11], to triboelectrification[12], for utilisation in photocopying machines. Many other uses can be found in two recently published review articles[10,13].

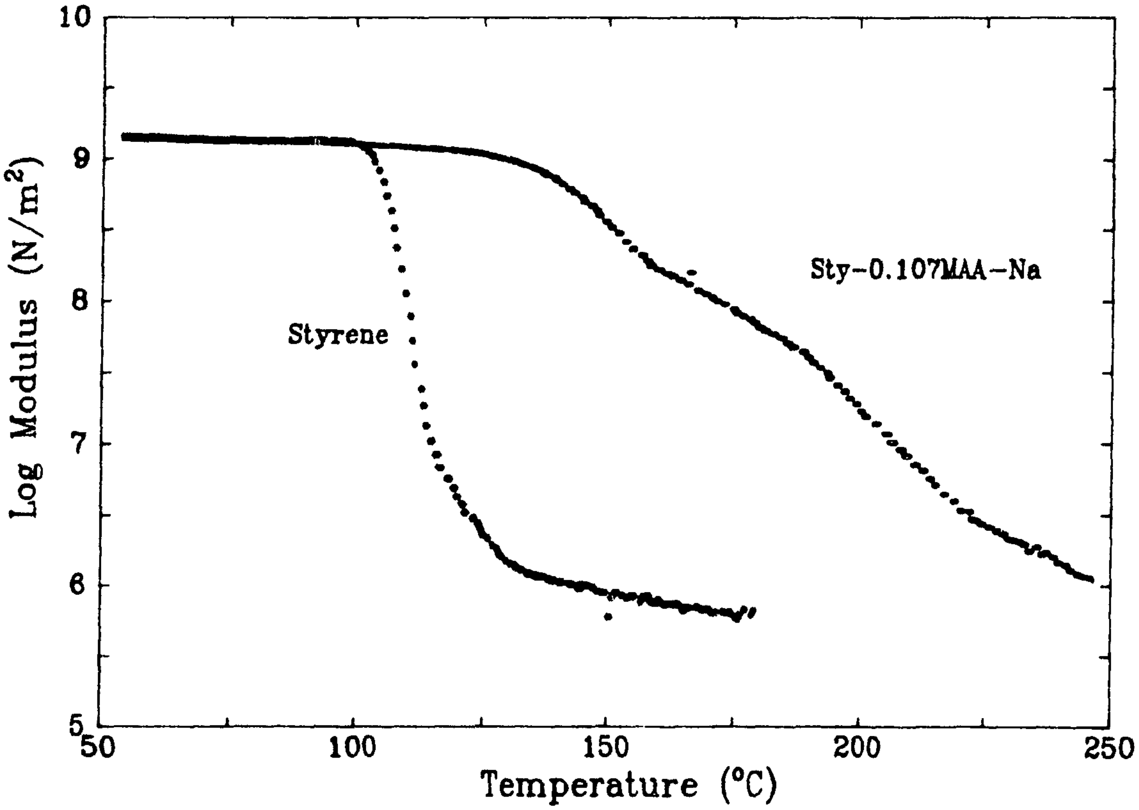

Fig. 2.1: Storage modulus for polystyrene and a styrene-co-sodium methacrylate ionomer (10 mole % ions), from ref. 5.

This paper is divided into two sections. The first contains a very brief review of the materials which have been explored to date together with a discussion of how features of ionomer structure and morphology affect the observed behaviour. The second part describes how major modifications in this phase behaviour can be brought about through relatively minor changes to the polymer.

## 2.3 A Brief Review of Ionomers

Ionomers are typically synthetic polymers which contain relatively low amounts, generally less than 15 mole percent, of ionic groups which are attached to the chains. The neutralisation of carboxylic acid containing elastomers by Brown in 1957[2] represents possibly the earliest such material reported. The word "ionomer" was not coined until the mid 1960's, however, when it was used by DuPont[1], to describe their novel product, Surlyn®. Since then, the field has grown substantially. The majority of ionomers consist of a main monomer, such as ethylene, butadiene or styrene, with a comonomer of some neutralised acid or ionised base such as sodium acrylate or N-methyl-4-vinylpyridinium iodide. Many other systems have been reported, however, such as sulfonated perfluoroethylene, known as Nafion®, a variety of ion-containing polypentenamers[14], and the ionenes[15], to mention just a few examples.

Many different parameters determine the actual physical properties of an ionomer. A large number of these result from the composition of the sample and are discussed next. Others are due to its sample history and follow later

It can be understood from the preceding paragraphs that very different ionomers can be obtained by changing the monomer under study, for example using isoprene instead of styrene, or changing the ionic groups, e g by replacing a sulfonate group with a carboxylate one All these chemistry related changes and their effects on morphology will be discussed in a subsequent section In this section the focus will be on the changes which can be achieved by keeping the ionic group and the backbone the same while varying the other parameters.

In this context, the concentration of the ionic groups is an obvious variable, as is the molecular weight. One of the less immediately obvious parameters is the architecture of the ionomer. Thus, in addition to the original ionomers, in which the ionic groups were randomly placed on the chain, polymers with ionic end groups have been prepared, with the number of end units varying from one, as in the telechelics[16], to many thousands, as exemplified by the block ionomers[17]. The ions have been put on the ends of chains of varying architecture, the extreme being star-shaped telechelics[18], and combs of varying spacer length attached to the main backbone[19]. These geometric structures are depicted in Fig. 2.2.

Sample history also greatly influences the physical properties displayed by the sample. For example, the concentration of the solution from which an ionomer was freeze-dried has been shown to alter the mechanical properties of the same ionomer[20]. the presence of water or other diluents can exert a profound influence on the material[21,22,23]. The material can be affected by the temperature at which it was annealed, etc.

Despite all their differences in structure and composition, ionomers share certain physical traits which set them apart from their nonionic precursors. The underlying reasons for all these changes are logically the presence in ionomer of ionic groups and their association.

### 2.4 A Review of Aggregation

If they are soluble at all, in media of low dielectric constant, ionic systems of low molecular weight are known to exist in an associated form, such as ion pairs; aggregation of these pairs leads to higher ordering, such as quartets, sextets and octets. This same behaviour occurs in ionomers, so that the ions are organised into sites of

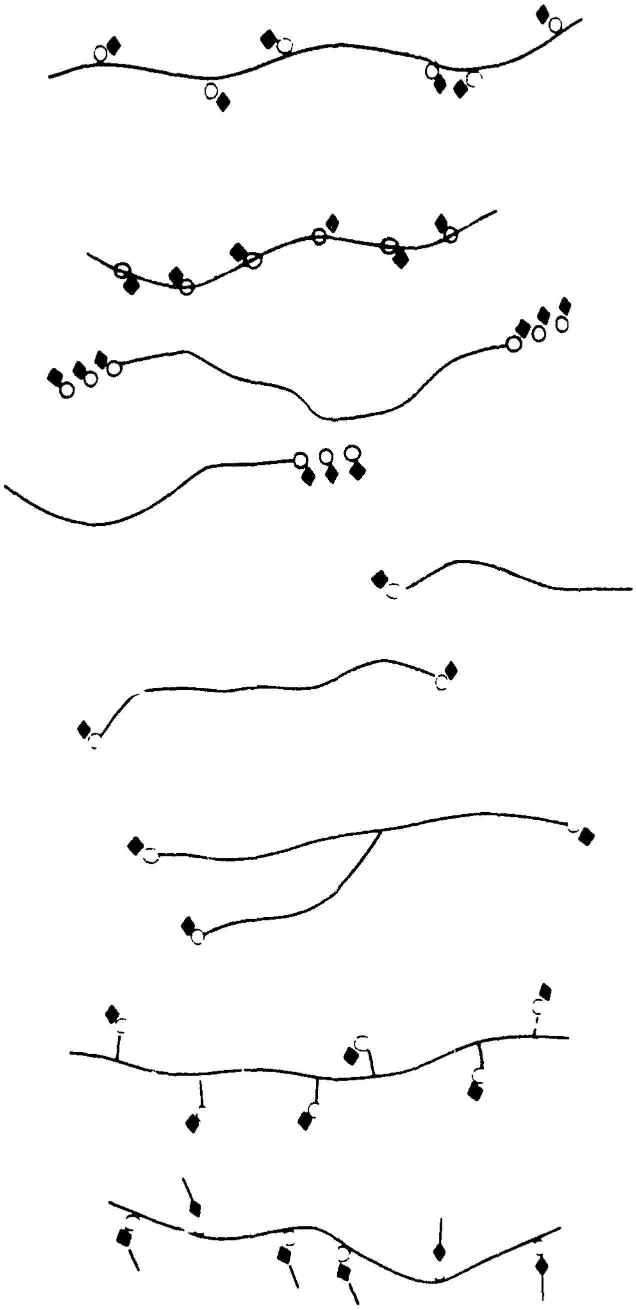

Fig. 2.2: Possible ionomer architectures. Top to bottom: random, ionene, ABA block, AB block, single- and double-tipped telechelics, star telechelic, comb and inverted comb.

varying sizes with proportionately higher local ion concentration than that present on the average in the material. This is shown schematically in Fig. 2.3.

It was proposed[24] from theoretical considerations that two types of aggregate should exist in ionomers. These have been called multiplets and clusters. Since the appearance of this theory, other treatments of ion aggregation in ionomers have been published, further refining the concepts overall and, in some cases, applying them to particular ionomers. For a review of these theories and an accompanying critique, the reader is referred to a recent publication[25]. However, it is widely accepted that the types of aggregates first described nearly twenty years ago do, indeed, exist.

The first, multiplets, are aggregates of a few ion pairs. They are relatively small in size and do not contain any nonionic material, thus they are centres of very high polarity. Multiplets are believed to be partly responsible for the increases observed in the glass transition temperatures with respect to the nonionic precursor.

Much larger aggregates can also be found in ionomers. These clusters, in addition to the ionic species, also contain a significant proportion of chain material. They are more polar than the matrix and may also represent regions of higher overall glass transition than their surroundings. In many ionomers, two glass transition temperatures are observed in dynamic mechanical studies. Under some circumstances, clusters disrupt the time-temperature superposition observed in thermorheologically simple homopolymers and ionomers containing multiplets alone[4]. Evidence for clustering is also found in SAXS studies, from which the sizes of the phase separated regions have been estimated to be in the vicinity of 20 - 100 Å[26,27,28]. Raman studies suggest that at very low ion concentrations, the aggregates formed seem to be exclusively multiplets, while at higher concentrations, evidence for clusters is also observed[29]. For a given ionomer family, the actual threshold at which cluster dominated rheological behaviour is observed appears dependent on the experimental technique used. However, when

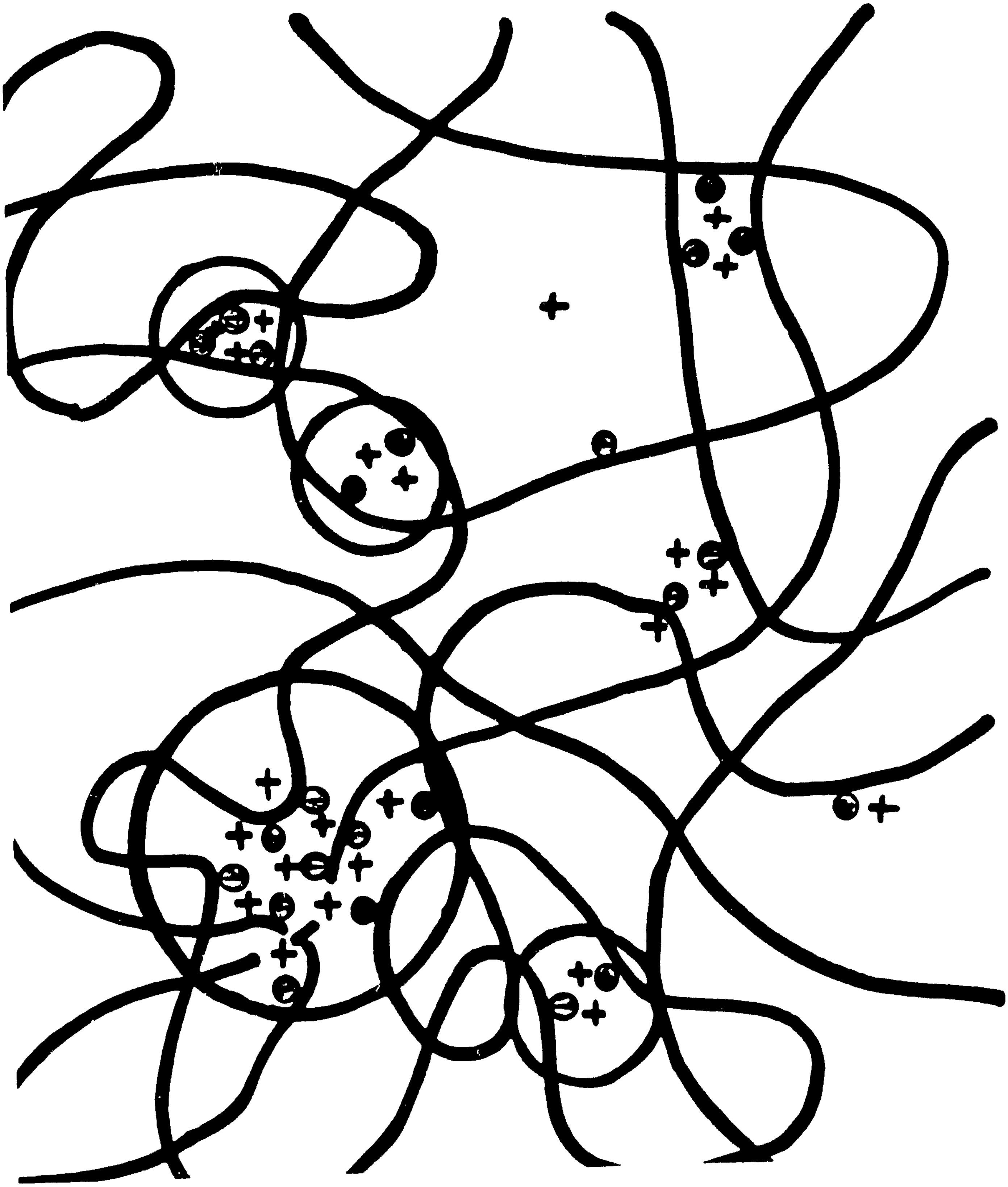

Fig. 2.3· Different ionic aggregates within a random ionomer matrix Small circles containing few ion pairs and little chain material represent multiplets. The larger circle containing many ion pairs and a substantial amount of chain material represents a cluster.

the same method is used on samples of different composition, it is clear that the concentration at which clustering is first manifested depends on a number of factors, both geometric and electrostatic.

The actual structures of multiplets and clusters have not been resolved. Indeed their existence, while largely acknowledged, has not been unquestioned. A review of the proposed structures in phase separated ionomers was published some years ago[30].

Since a cluster is not simply an overgrown multiplet, but possesses different characteristics, caused by the inclusion of chain material, it is apparent, that other, weaker forces are involved in its formation. In devising a scheme for cluster formation, most models have relied heavily on X-ray scattering data, because it yields information on the size or spacings of the scattering centres.

An early model for clusters suggested that they contained the original "core" of a very large multiplet and its surrounding hydrocarbon chain to which were attracted other, smaller multiplets, growing to a maximum diameter of 10 - 20 Å[31].

Alternatively, it has been suggested that clusters are much larger structures, with a diameter of some 100 Å, in which were to be found multiplets spaced some 20 Å apart[32].

A third model was suggested by Marx *et al.* in 1973[33]. Based on their analyses of X-ray scattering data, they concluded that there was no evidence for clustering and they could explain all their results through the existence of multiplets alone.

The arguments in favour of moderate sized clusters have grown. More recently, Dreyfus has proposed a model for aggregation to multiplets and clusters using electrostatic principles[34].

Recently, a new aggregate has been described. This is the so-called supermultiplet[35]. Like the original multiplet, it contains only ionic material. The ionomers which form these supermultiplets have a different architecture than the previously mentioned materials. In these cases, the ionic groups are located in blocks on the chain, in particular on the ends of the polymer chains. Thus, the supermultiplets are envisaged to contain exclusively a number of these very polar chain ends, quite analogous to the phase separation observed in nonionic block copolymers. SAXS studies involving ABA triblock copolymers such as styrene (B) and N-alkyl-4-vinylpyridinium iodide (A) have been performed recently. All the conclusions need not be presented here, except that it appears that the sizes of the supermultiplets are up to ten times larger than those of the clusters and are very sensitive to block length and sample history[35,36,37].

Since, clearly aggregation is an important part of ionomer morphology, many studies have been undertaken to determine whether specific materials are clustered and if so what fraction of the ionic groups are incorporated These can be divided into two basic approaches, dynamic and static, although some techniques overlap.

Static methods depend on disparities between the clusters and the matrix such as electron density differences, as in SAXS[35,38], EXAFS[39] or electron microscopy[40], or differences in neutron scattering cross-section, as utilised in SANS[41]. A variety of more common spectroscopic techniques have also been employed. These include NMR[42], infrared[43,44], Raman[29], fluorescence[45], electron spin resonance[46] and Mössbauer[21] spectroscopies.

As mentioned above, dynamic mechanical studies reveal two $T_g$'s in clustered systems This suggests that clusters have minimum dimensions of 50 - 100 Å, otherwise they would not have their own glass transition temperature. Dielectric methods give the same type of information[47]

The result of so many studies has made it possible to outline the parameters which have been observed to play a role in the phase behaviour in ionomers without reference to the imprecise and disputed nature of the phase separated regions themselves.

## 2.5 Factors Influencing Phase Separation in Ionomers

The following section will briefly discuss some of the molecular parameters which affect the phase separation observed in many random ionomer systems. The term molecular parameters is used to describe those factors which are changed in the substitution of one monomer for another, thus altering the actual monomer under consideration.

The size of the ion pair has been seen to affect the phase separation behaviour of ionomers. Two general cases can be envisioned. In the first, the ion pair itself is large. Then the attraction between the ions is reduced due to charge delocalisation resulting from resonance effects or decreased charge density, as is the case with many of the ionomers containing N-methyl-4-vinylpyridinium iodide units[48]. Alternatively, the formation of the ion pair can be accompanied by the incorporation of a very large amount of nonionic material. This situation is to be found when two ionomers are blended[49]. In both of these cases, such systems do not exhibit the sort of behaviour which has indicated phase separation in other ionomers.

Studies involving materials in which the dielectric constant of the matrix is relatively high have shown that these ionomers are less likely to exhibit phase separated behaviour, presumably as a result of the improved solvating power of the matrix for the ion pairs[50] Consequently, higher concentrations of ions are necessary for the appearance of changes in behaviour associated with clustering.

There also seems to be a correlation with the strength of the electrostatic interactions between the multiplets and the glass transition temperature of the matrix. This has been studied in some systems of methyl methacrylate, ethyl acrylate and butyl acrylate, with N-methyl-4-vinylpyridinium iodide constituting the ionic moiety[51].

When the glass transition temperature of the ionomer has been sufficiently reduced, a second peak in the loss tangent is observed, indicating that phase separation into clustered regions has become significant.

With the variety of ionomer systems studied, their different behaviour can be explained as the result of a number of different molecular factors The architecture of the materials, described earlier, similarly affects the ease of phase separation.

## 2.6 Modification of Clusters

It has also proven possible to modify the aggregation in a particular material through the application of certain techniques, such as plasticisation and post-polymerisation reactions These methods differ from those in the previous section by degree, for now the ionomer is considered to be only modified by these changes and not substantially altered.

Because of the dramatic changes in the properties of ionomers which are clustered as opposed to those which are not, it is clearly of great interest to be able to induce or prevent this type of aggregation at will The modification of the state of aggregation of ionomers has been explored in considerable detail It is now apparent that it is possible to enhance or disrupt the phase behaviour characteristic of clustered ionomers without too much difficulty in a wide range of systems

In some cases, it might be desirable to increase the amount of clustered material in an ionomer, for example, as a means to improve the modulus or strength of a material Different approaches may be used, with the method of choice depending on the requirements of the situation

A small change in the composition of the ionomer can be achieved with the substitution of a smaller counter ion for the original By increasing the charge density of the ionic moieties, it would be possible to promote clustering in the material, as in the case of neutralisation of styrene-co-methacrylic acid with lithium instead of rubidium[52]. Evidently, the neutralisation of such an ionomer with a counter ion of higher valence would also lead to greater aggregation, although in these instances, there is the additional complication of crosslinking through the necessity of charge neutrality.

Reducing the glass transition temperature plays an important role in increasing the amount of clustering in a given material. Recently, a number of studies dealing with the plasticisation of different ionomers using a variety of methods have been undertaken. Internal plasticisation has been achieved through the addition of nonpolar alkyl chains to styrene backbones[53,54]. Small molecule diluents, such as diethylbenzene and dimethyl malonate, with a polarity and structure similar to the matrix, have been added to the ionomer samples as external plasticisers[21,53,54]. Styrene oligomers have also been used as diluents in the plasticisation of styrene-based ionomers[55]. It has been shown that when small amounts of the matrix-compatible plasticisers are added to the material, either internally or externally, clustering may be greatly enhanced. Evidence of this is shown in Fig. 2.4.

At other times, the disruption of clusters in a material may be advantageous. While one approach might be to try the reverse of the strategies outlined above, there are some other, more subtle methods.

A very small amount of a polar plasticiser, such as glycerine or water, has been shown to effectively obliterate the clusters in materials, as judged from their dynamic mechanical behaviour[22]. The choice of plasticiser in this situation is critical, as recent studies have shown, where a diluent of high dielectric constant, nitrobenzene, was used in the plasticisation of styrene-co-sodium methacrylate[56]. In this case, the effect of the addition of this plasticiser was comparable to using a nonpolar diluent such as diethylbenzene. It would seem that in addition to being polar, such a plasticiser must

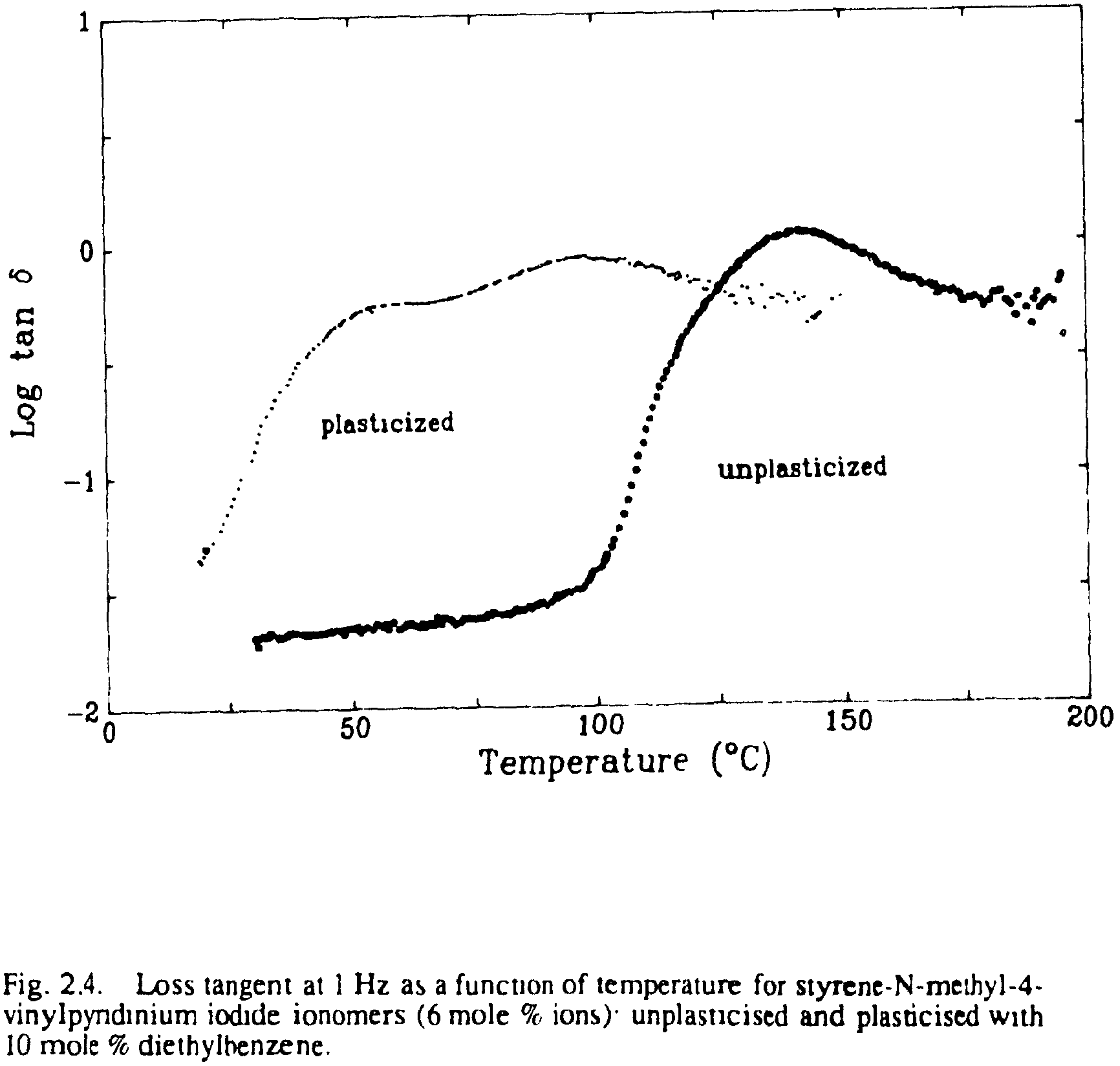

Fig. 2.4. Loss tangent at 1 Hz as a function of temperature for styrene-N-methyl-4-vinylpyridinium iodide ionomers (6 mole % ions): unplasticised and plasticised with 10 mole % diethylbenzene.

also be capable of strong interactions such as hydrogen bonding.

A large amount of nonpolar plasticiser will achieve the same result. Above a certain level of plasticisation, the enhancement of clusters is replaced by essentially a complete disruption of the aggregates[53,54]. Effectively, the chains become too bulky for aggregates to form efficiently. Here again, the inclusion of nitro groups in the polymer produces very different results. In the nitration of styrene-co-sodium methacrylate, the matrix $T_g$ increased with increasing levels of nitration, similar to the increase seen with increasing ion content, however, the glass transition temperature of the clusters did not change[56].

## 2.7 Supermultiplets

Block ionomers have not been studied as extensively as their random counterparts. This is largely due to the greater difficulty posed in their polymerisation and handling, but interest is growing in the phase behaviour of this group of materials.

In general, most block copolymers, ionic or not, are known to be predominantly phase separated Typically, the size, morphology and nature of the continuous phase depend on the relative proportions of the comonomers and the sample history[57].

It was, therefore, expected that block ionomers would also exhibit phase separation, even in the cases of those monomer pairs which do not cluster as random ionomers Because of the very small lengths of the ionic end blocks involved and their anticipated much higher glass transition temperature, results from dynamic mechanical studies involving ABA styrene-co-N-methyl-4-vinylpyridinium iodide resembled those obtained for the styrene homopolymer[17]. SAXS measurements on closely related materials show very strong phase separation of the end blocks from the styrene matrix[35].

A related finding of these studies has been that because phase separation takes place even for very short end blocks, the number of chains issuing from the supermultiplets is much greater than for nonionic systems. It would appear that the ionic interactions are responsible for the strong driving force leading to this phase separation.

## 2.8 Conclusions

Many ionomer systems have been studied to date, in order to gain insight concerning the nature of the phase separation which is, in some ways, the most perplexing and most critical aspect of their morphology. It is, in general, agreed that the aggregation which is observed in random ionomers yields two sizes of phase separated regions, multiplets and clusters. The phase behaviour of block ionomers is more akin to their nonionic counterparts. Without arguing over the precise nature of the aggregates in random ionomers, the results of many studies have shown that manipulation of clustered areas can be achieved through relatively simple techniques. This makes it possible to tailor an ionomer for specific applications.

## 2.9 References

(1) R. W. Rees and D. J. Vaughan, ACS Polym. Prepr., **6**, 287 (1965).

(2) H. P. Brown, Rubber Chem. Technol., **30**, 1347 (1957).

(3) W. E. Fitzgerald and L. E. Nielsen, Proc. Roy. Soc. (London), **A282**, 137 (1964).

(4) A. Eisenberg and M. Navratil, Macromolecules, **6**, 604 (1973).

(5) B. Hird and A. Eisenberg, submitted to J. Polym. Sci., Polym. Phys. Ed..

(6) E. Shohamy and A. Eisenberg, J.Polym. Sci., Polym. Symp., **45**, 139 (1974).

(7) H. L. Yeager, in Perfluorinated Ionomer Membranes, ACS Symposium Series, **180**, eds. A. Eisenberg and H. L. Yeager, American Chemical Society, Washington, 41 (1982).

(8) M. R. Tant and G. L. Wilkes, J. Macromol. Sci., Rev. Macromol. Chem. Phys., **C28**, 1 (1988).

(9) H. L. Yeager, in Perfluorinated Ionomer Membranes, ACS Symposium Series, **180**, eds. A. Eisenberg and H. L. Yeager, American Chemical Society, Washington, 25 (1982).

(10) R. D. Lundberg, in Structure and Properties of Ionomers, NATO ASI Series, **C198**, eds. M. Pineri and A. Eisenberg, D. Reidel Publishing Co., Dordrecht, 429 (1987).

(11) S. D. Clas, ACS Polym. Prepr., **29**, 438 (1988).

(12) D. E. Bugner and J. H. Anderson, ibid., **29**, 463 (1988).

(13) J. S. Tan, in Structure and Properties of Ionomers, NATO ASI Series, **C198**, eds. M. Pineri and A. Eisenberg, D. Reidel Publishing Co., Dordrecht, 439 (1987).

(14) D. Rahrig and W. J. MacKnight, Adv. Chem. Ser., **187**, 77 (1979).

(15) A. Eisenberg, H. Matsuura and T. Yokoyama, Polym. J., **2**, 117 (1971).

(16) C. E. Williams, T. P. Russell, R. Jérôme and J.Horrion, Macromolecules, **19**, 2877 (1987).

(17) S. Gauthier and A. Eisenberg, Macromolecules, **20**, 760 (1987).

(18) S. Bagrodia, M. R. Tant, G. L. Wilkes and J. P. Kennedy, Polymer, **28**, 2207 (1987).

(19) M. Gauthier and A. Eisenberg, submitted to Macromolecules.

(20) R. D. Lundberg and R. R. Phillips, J. Polym. Sci., Polym. Lett. Ed., **22**, 377 (1984).

(21) M. Pineri, in Coulombic Interactions in Macromolecular Systems, eds. A. Eisenberg and F. E. Bailey, ACS Symposium Series, **302**, American Chemical Society, Washington, 159 (1986).

(22) C. G. Bazuin and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **24**, 1137 (1986).

(23) J. J. Fitzgerald, D. Kim and R. A. Weiss, J. Polym. Sci., Polym. Lett. Ed., **24**, 263 (1986).

(24) A. Eisenberg, Macromolecules, **3**, 147 (1970).

(25) K. A. Mauritz, J. Macromol. Sci., Rev. Macromol. Chem. Phys., **C28**, 65 (1988).

(26) T. D. Gierke, J. Electrochem. Soc., **124**, 319 (1977).

(27) W. J. MacKnight, ACS Polym. Prepr., **21**, 76 (1980).

(28) J. Horrion, R. Jérôme, P. Teyssié, C. Marco and C. E. Williams, Polymer, **29**, 1203 (1988).

(29) A. Neppel, I. S. Butler and A. Eisenberg, Macromolecules, **12**, 948 (1979).

(30) W. J. MacKnight and T. R. Earnest, Macromol. Rev., **16**, 41 (1981).

(31) W. J. MacKnight, W. P. Taggart and R. S. Stein, J. Polym. Sci., Polym. Symp., **45**, 113 (1974).

(32) R. Longworth and D. J. Vaughan, ACS Polym. Prepr., **9**, 525 (1968).

(33) C. L. Marx, D. F. Caulfield and S. L. Cooper, Macromolecules, **6**, 344 (1973).

(34) B. Dreyfus, Macromolecules, **18**, 284 (1985).

(35) J.-P. Gouin, C. E. Williams and A. Eisenberg, submitted to Macromolecules.

(36) J.-P. Gouin, C. E. Williams and A. Eisenberg, manuscript in preparation.

(37) D. Wollmann, C. E. Williams and A. Eisenberg, submitted to J. Polym. Sci., Polym. Lett. Ed.

(38) G. Vlaic, C. E. Williams, R. Jérôme, M. R. Tant and G. L. Wilkes, Polymer, **29**, 173 (1988).

(39) Y. S. Ding, R. A. Register, M. R. Nagarajan, H. K. Pan and S. L. Cooper, J. Polym. Sci., Polym. Phys. Ed., **26**, 289 (1988).

(40) D. L. Handlin, W. J. Macknight and E. L. Thomas, Macromolecules, **14**, 795 (1981).

(41) S. Kumar and M. Pineri, J. Polym. Sci., Polym. Phys. Ed., **24**, 1767 (1986).

(42) A. Natansohn and A. Eisenberg, Macromolecules, **20**, 323 (1987).

(43) B. A. Borozoski, M. C. Coleman and P. C. Painter, ibid., **17**, 230 (1984).

(44) D. G. Peiffer, B. L. Hager, R. A. Weiss, P. K. Agarwal and R. D. Lundberg, J. Polym. Sci., Polym. Phys. Ed., **23**, 1869 (1985).

(45) M. N. Szentirmay, N. E. Prieto and C. R. Martin, J. Phys. Chem., **89**, 3017 (1985).

(46) R. A. Weiss and J. J. Fitzgerald, in Structure and Properties of Ionomers, NATO ASI Series, eds. M. Pineri and A. Eisenberg, **C198**, D. Reidel Publishing Co., Dordrecht, 361 (1987).

(47) I. M. Hodge and A. Eisenberg, Macromolecules, **11**, 283 (1978).

(48) S. Gauthier, D. Duschesne and A. Eisenberg, Macromlecules, **20**, 753 (1987).

(49) A. Eisenberg, P. Smith and Z.-L. Zhou, Polym. Eng. Sci., **22**, 1117 (1982).

(50) A. Eisenberg, H. Matsuura and T. Tsutsui, J. Polym. Sci., Polym. Phys. Ed., **18**, 479 (1980).

(51) D. Duchesne and A. Eisenberg, in preparation.

(52) A. Simmons, M. Sc. Thesis, McGill University (1987).

(53) M. Gauthier and A. Eisenberg, manuscript submitted to Macromolecules.

(54) D. Wollmann, C. E. Williams and A. Eisenberg, in preparation.

(55) C. G. Bazuin and S. Villeneuve, Polym. Mat. Sci. Eng., **58**, 1069 (1988).

(56) M. Gauthier and A. Eisenberg, manuscript submitted to Macromolecules.

(57) B. R. M. Gallot, Adv. Polym. Sci., **29**, 85 (1978).

# Chapter 3

## Glass Transition Relations in Ionomeric "Comb" Polymers

### 3.1 Abstract

The glass transition temperatures ($T_g$) and dynamic mechanical properties of random copolymers of styrene-co-4-vinylpyridine quaternised with iodoalkanes are presented for vinylpyridine contents up to ten percent and pendant alkyl chains up to ten carbons in length. Two linear relationships, between ion content and glass transition temperature and between pendant alkyl chain length and the $T_g$, are observed. An equation is presented that can be used to predict the $T_g$ for such copolymers based on their ion contents and alkyl chain lengths.

### 3.2 Introduction

The properties of many industrially important polymers have been commonly modified by the use of plasticisers. A wide range of these materials are used with the intention of either making the polymer more easily processable or altering the properties of the polymer to make it more suitable for its end use. In either case, difficulties are occasionally encountered because the plasticiser separates from the polymer over a period of time. This can be due to the volatility of the low molecular weight material, or the poor thermodynamic miscibility between the plasticiser and the polymer or possibly other mechanisms. Various remedies have been sought to overcome these difficulties, including the use of polymeric plasticisers or the chemical attachment of the plasticiser to the polymer As might be expected, both of these have their specific advantages and disadvantages.

A significant problem with trying to blend two polymers is that, in general, polymers are immiscible, due to a negligible entropy of mixing. In the case of an unfavourable enthalpy of mixing, immiscibility may also be a problem for some polymer-plasticiser systems. Typically, specific interactions are necessary to overcome this problem, for example Coulombic interactions. Several types of interactions can be envisaged involving charged species, namely ion pair - ion pair, ion - ion and ion - dipole. There have been many studies[1,2,3,4,5,6,7] exploring the use of Coulombic interactions as miscibility enhancers in attempts to mix polymers with other polymers or with plasticisers of both low and high molecular weight.

The attachment of low molecular weight groups can be achieved in three different ways using Coulombic interactions. For example, a polymer containing pendant sulfonic acid groups can be mixed with an alkyl amine[6,7] Alternatively, it would be possible to mix polymeric amines with alkyl sulfonic acids[8], although a major difficulty is presented by the latter, which is a soap. The third way, which is the subject of this paper, involves the mixing of a polymeric chain containing amine or pyridine groups with alkyl halides, followed by a reaction of the two. This method yields a primary bond between the polymer and the plasticiser, accompanied by the formation of an ion pair.

A major advantage of this last method, which it shares with the first, is that the reaction and the workup are very simple. The creation of a true chemical bond is accompanied by further advantages, not shared with the first method, namely that ion hopping should not occur and that there is a greatly reduced likelihood of the plasticiser "bleeding out" of the polymer matrix under the influence of polar solvents or salt solutions. A further advantage common to both the first and the last methods is that many of the plasticising reagents are available commercially, thus a wide range of structures can be envisaged and created. The polymer is more a "comb" polymer[9,10] than a graft copolymer, since all the side chains are of equal length. The process has a further advantage in that in most graft copolymerisations, a certain amount of the material to be grafted is present as unattached homopolymer[11], which is not the case for this comb polymer.

Before such a plasticisation technique can become a generally useful method, it is advisable to be able to correlate a wide range of physical properties with the structure of the polymer-plasticiser system to be produced Perhaps the most important single parameter in plasticised polymer systems is the $T_g$. As a result, a great deal of work[12,13,14,15,16,17,18,19] has gone into the predictions of $T_g$.

It has been recognised for a number of years that for polymers of low ion content, the $T_g$ generally increases linearly with an increase in the concentration of ions[17]. It is also widely known that the presence of alkyl chains depresses the glass transition temperature[20,21,22,23] In the materials described here, both of these competing effects are expected to be present

Specifically, this study is centred around an exploration of the $T_g$ of a styrene-co-4-vinylpyridine polymer to which alkyl halides of various chain lengths are attached, thus producing ionomer "combs" The techniques involve differential scanning calorimetry and the torsion pendulum As a result of the latter technique, the dynamic mechanical properties (*ca* 1 Hz) are also explored

### 3.3 Experimental

Random copolymer of styrene-co-4-vinylpyridine containing 1 9, 4 9, 6 9 and 9 7 mole percent 4-vinylpyridine were synthesised in the bulk using free radical initiation as described by Gauthier[24] Following isolation and freeze-drying, the 4-vinylpyridine content of the materials was assessed by two methods In one, the materials were titrated in chlorobenzene with a solution of $HClO_4$ and acetic acid, using methyl violet as indicator In the other, thin films were made by compression moulding, studied by infrared, and the ratio of the peaks at either 1870 $cm^{-1}$ or 1029 $cm^{-1}$ for styrene and 1414 $cm^{-1}$ for 4-vinylpyridine was measured against a previously prepared calibration curve[24].

Straight chain iodoalkanes, i.e. 1-iodobutane, 1-iodohexane, 1-iodooctane and 1-iodododecane, were used to quaternise the styrene-4-vinylpyridine copolymers. These reagents were distilled, either under nitrogen or partial vacuum, to purify them

The quaternisation reactions of the styrene-vinylpyridine copolymers were performed in the following manner· a known quantity of the copolymer was dissolved in dry tetrahydrofuran to make a solution of 5 percent polymer by weight. A twenty-five fold molar excess of the iodoalkane was added to the flask, either by syringe or, in the case of the solid iodooctadecane, by weight. Heating was begun, and the mixture refluxed under nitrogen for 24 hours Invariably, after heating started, the solution turned golden yellow The intensity of the colour depended on the amount and the molecular weight of the iodoalkane, darker solutions were obtained as the molecular weight of the iodoalkane increased

Once the reaction was stopped, all of the polymer samples were precipitated in a ten-fold excess, by volume, of rapidly stirred mixed hexane isomers. Each sample was filtered by suction and washed with more hexanes to remove any excess iodoalkane. The yellow quaternised ionomers were then dried in vacuum at 60 °C to remove the solvent

The extent of quaternisation in each of the styrene-based samples was checked in FTIR by the disappearance of the peak at 1414 $cm^{-1}$ Samples of each ionomer were taken, and a $T_g$ obtained for each by DSC at a heating rate of 20 °C/min

Another series of samples was then moulded for use in the torsion pendulum. These moulded samples were further treated as follows Each sample was placed in a drying pistol and subjected to vacuum for 24 hours Then, for two more days, it was heated to 78 °C under vacuum, to drive off as much water as possible Finally, the sample was heated to *ca* 130 °C under nitrogen for three days to anneal it After this, the sample was run in the torsion pendulum and a $T_g$ was obtained from the tan delta maximum.

After the torsion pendulum run, a small piece of the sample was broken off and moulded to produce a film. This film was studied by FTIR to determine whether any significant loss of quaternising agent had occurred, a complication that had been observed with previous studies using iodomethane[24].

Although iodooctadecane was used as a reagent in an attempt to quaternise the styrene-4-vinylpyridine copolymers, the reaction was unsuccessful. For the higher concentrations of vinylpyridine in particular, some degradation must have occurred due to the drastic change in the infrared spectra Thus further studies on this set of samples were abandoned.

## 3.4 Results

### 3.4.1 Infrared Studies

The infrared spectra of the samples lacked the peak at 1414 $cm^{-1}$ which is due to the unquaternised pyridine ring. This indicated that within the accuracy of the measurement, all the samples were fully quaternised The infrared spectra of the samples taken after the torsion pendulum run showed a negligible dequaternisation. The worst sample still exhibited 98 % quaternisation after the torsion pendulum run, according to the ratio of the peaks at 1414 $cm^{-1}$ and 1029 $cm^{-1}$.

### 3.4.2 DSC Studies

The DSC data obtained from these studies on the styrene-4-vinylpyridine copolymers, shown in Table 3.1 for each pyridine concentration in the first row of the vinylpyridine concentration entry, clearly indicate the pattern of differing ion contents and alkyl chain lengths on the $T_g$. The values for the glass transition were confirmed by torsion pendulum and were used for the calculations that follow in the discussion

## Table 3.1:

## Styrene-N-Alkyl-4-Vinylpyridinium Iodide Ionomers: Glass Transition Temperatures (°C)

| Mole Percent Ions | Alkylating Agent | | | |
|---|---|---|---|---|
| | Iodobutane | Iodohexane | Iodooctane | Iododecane |
| 1.9 | 110.6* | 111.6 | 109.4 | 103.9 |
| | 111.3** | 110.3 | 109.4 | 108.4 |
| | -0.7 | 1.3 | 0.0 | -4.5 |
| 4.9 | 118.4 | 116.8 | 111.2 | 107.6 |
| | 118.8 | 116.6 | 113.8 | 111.4 |
| | -0.4 | 0.2 | -2.6 | -3.8 |
| 6.9 | 124.5 | 119.8 | 112.0 | 111.4 |
| | 123.8 | 120.3 | 116.8 | 113.4 |
| | 0.7 | -0.5 | -4.8 | -2.0 |
| 9.7 | 131.3 | 126.0 | 119.7 | 112.2 |
| | 130.8 | 125.9 | 121.0 | 116.2 |
| | 0.5 | 0.1 | -1.3 | -4.0 |

---

* Glass transition temperatures from TP data.

** Glass transition temperatures from DSC data.

section.

### 3.4.3 Torsion Pendulum

Examples of tan $\delta$ and log modulus results are given in Figs. 3.1 and 3.2. The curves are all very similar, therefore not all are shown. The immediate observation from these results was that no clusters were present in any of the samples, since there was no tan delta peak for $T > T_g$ This is consistent with previous work[24]. Below the glass transition, the storage modulus was typically of the order of $10^9$ N/m$^2$. The initial modulus of the sample generally decreased as the chain length of the quaternising agent increased, as in Fig 3.2 The effect of the ion content on the initial modulus shows a similar trend, although not as clearly. Above $T_g$, the modulus of the material decreased abruptly to a level lower than that observed in other ionomers. Thus it was often difficult to get much data above $T_g$ before the experimental error became too large

The results from the torsion pendulum proved to be very sensitive to the thermal history of the sample This necessitated the elaborate annealing procedure described in the experimental section

### 3.5 Discussion

It is clear from the data obtained from both the DSC and the torsion pendulum that lengthening the pendant alkyl chain lowered the glass transition temperature of the ionomer Not surprisingly, the effect is more pronounced at higher ion contents. It has been shown elsewhere[24] that in the case of styrene-4-vinylpyridine copolymers quaternised with iodomethane the $T_g$ increases linearly with increasing ion content. This, again, proved to be true for the same polymer quaternised with iodobutane iodohexane, iodooctane and iodododecane as seen in Fig 3 3 In addition, for constant ion contents, the relationship between increasing chain length and decreasing $T_g$ is

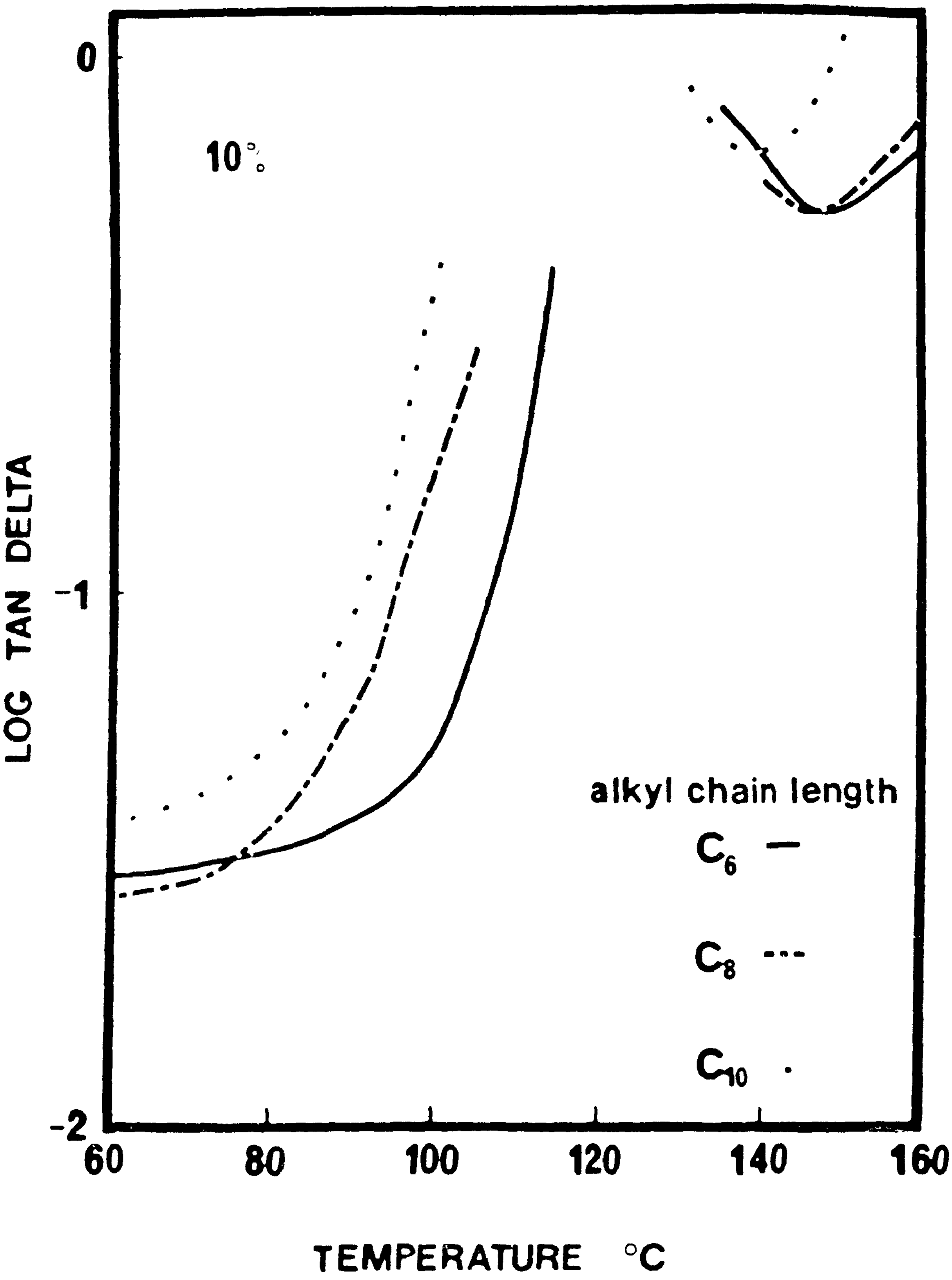

Fig. 3.1: Variation of tan delta with temperature for styrene-co-N-alkyl-4-vinylpyridinium iodide ionomers (10 mole % ions) quaternised with iodoalkanes of different lengths

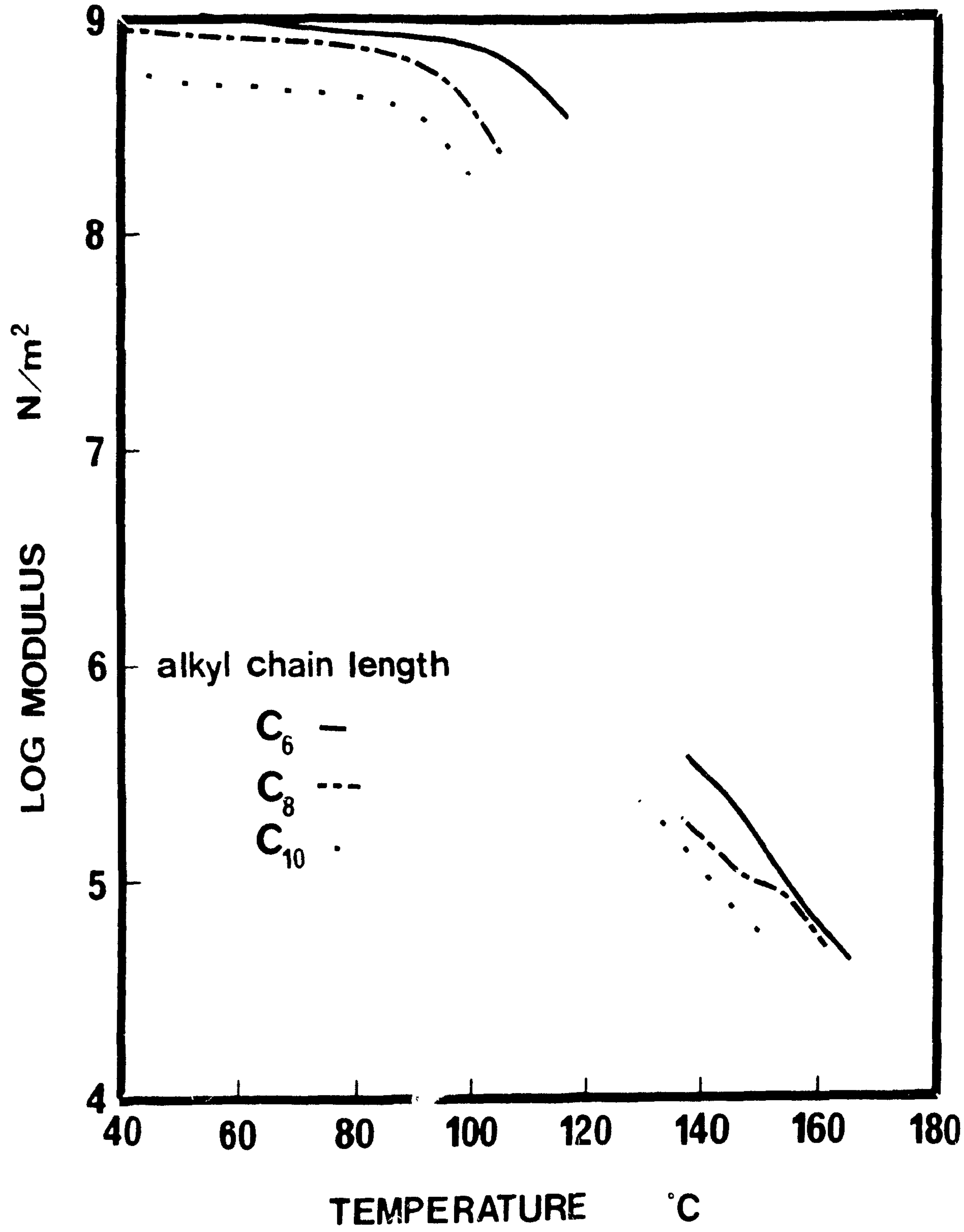

Fig. 3.2: Variation of the storage modulus with temperature for styrene-co-N-alkyl-4-vinylpyridinium iodide ionomers (10 mole % ions) quaternised with iodoalkanes of different lengths

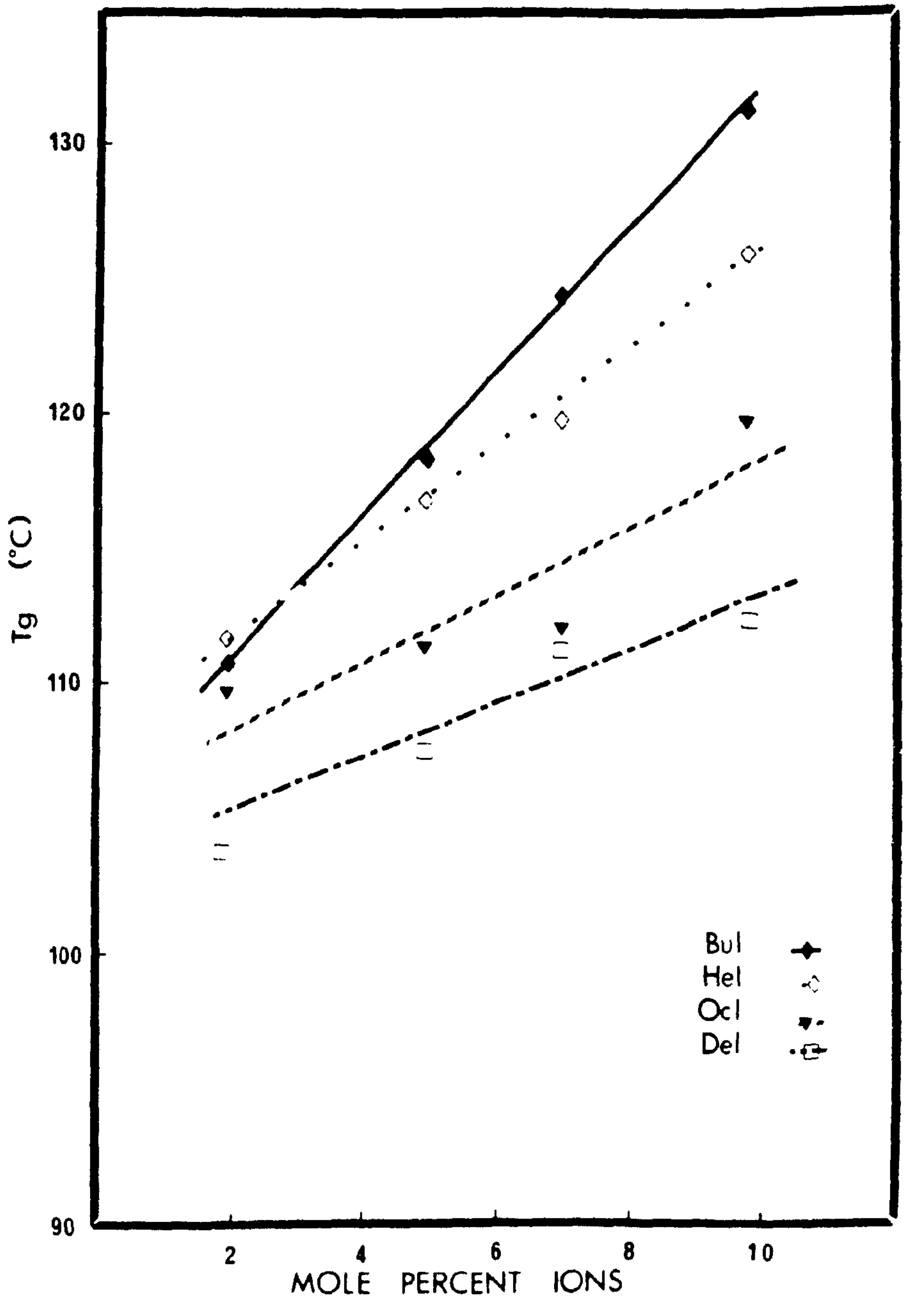

Fig. 3.3· Variation of the glass transition temperature with ion content for copolymers quaternised with different iodoalkanes.

linear, as shown in Fig. 3.4. Fig. 3.5 shows the relationship between the change in $T_g$ as a function of the vinylpyridine content, from the slopes in Fig. 3.3, and the alkyl chain length. It was found that the data could be fitted to an equation of the general form:

$$T_g = T_g{}^o + c(k_1 - k_2 n)$$

where $T_g$ is the glass transition temperature of the material and $T_g{}^o$ is the glass transition temperature of the nonionic starting material, in this case, polystyrene. The other variables in the equation are c, the concentration of the ionic groups in mole percent; $k_1$, a constant from the intercept of the plot in Fig. 3.5; $k_2$, another constant for the system, obtained from the slope in Fig. 3.5; and n, the number of carbons in the iodoalkane chain.

The slopes of the lines for the different iodoalkanes shown in Fig. 3.3 were plotted on a graph against the number of carbons in the attached chains. A similar slope that had been constructed for the iodomethane samples[24] was also used in the linear regression calculation.

The $T_g$ of the nonionic polystyrene was determined by DSC to be 106.5 °C. The value of the constant $k_1$ was determined to be 3.5 ± 0.2 degrees per mole percent ions. Represented by the slope in Fig. 3.5, $k_2$ was calculated to have the value -0.25 ± 0.02 degrees per mole percent ions per carbon atom attached. Thus, the general equation now takes the form.

$$T_g = 106.5 + c(3.5-0\ 25n)$$

The values that were obtained by the use of this equation are shown in Table 3.1 in the second row. In row three of this table are the differences between the calculated and experimental values for $T_g$. A statistical analysis shows that the average difference between these two temperatures is 1.7 °C using absolute values of the

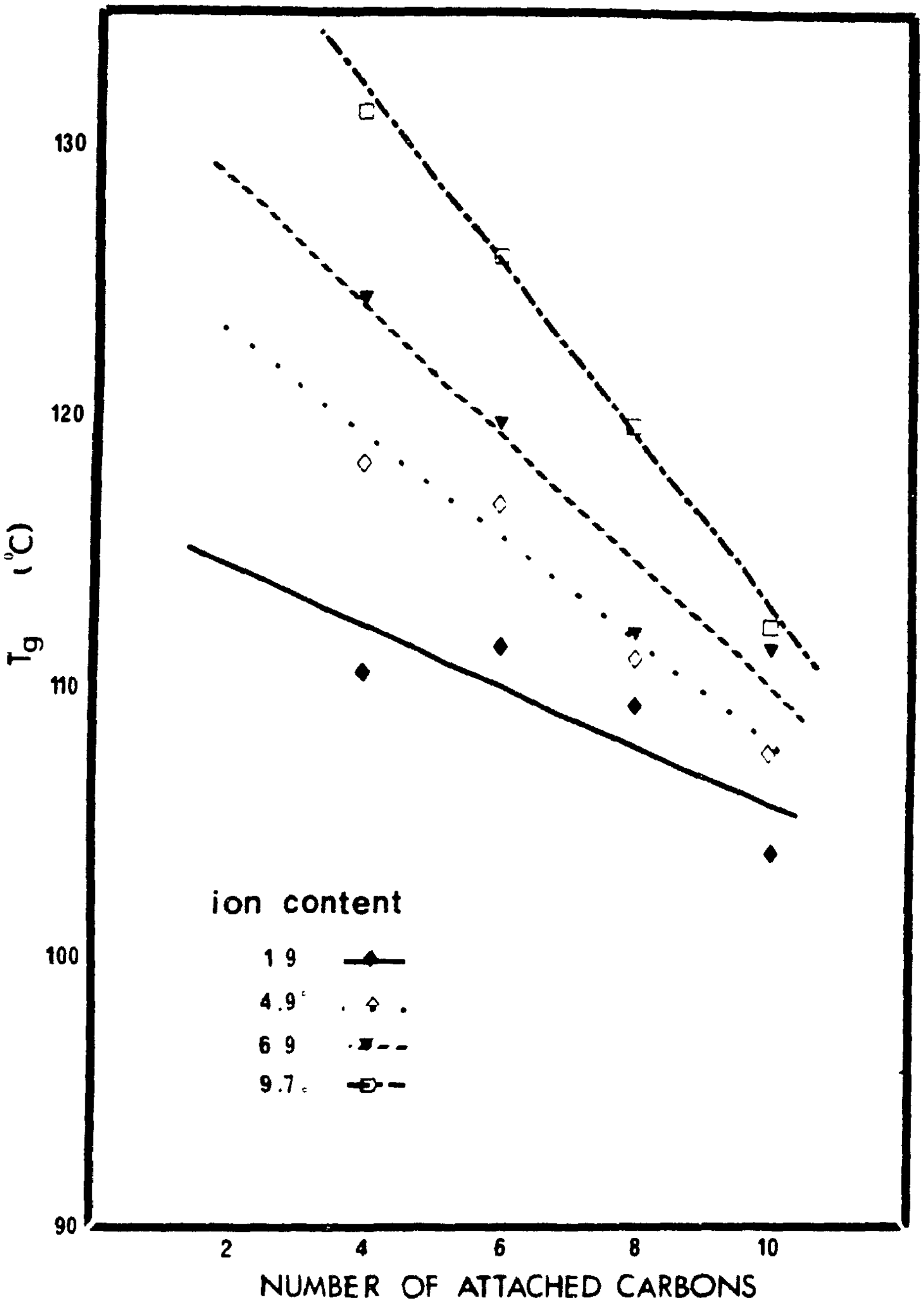

Fig. 3.4: Variation of the glass transition temperature with the length of the attached alkyl chain for copolymers of different ion contents.

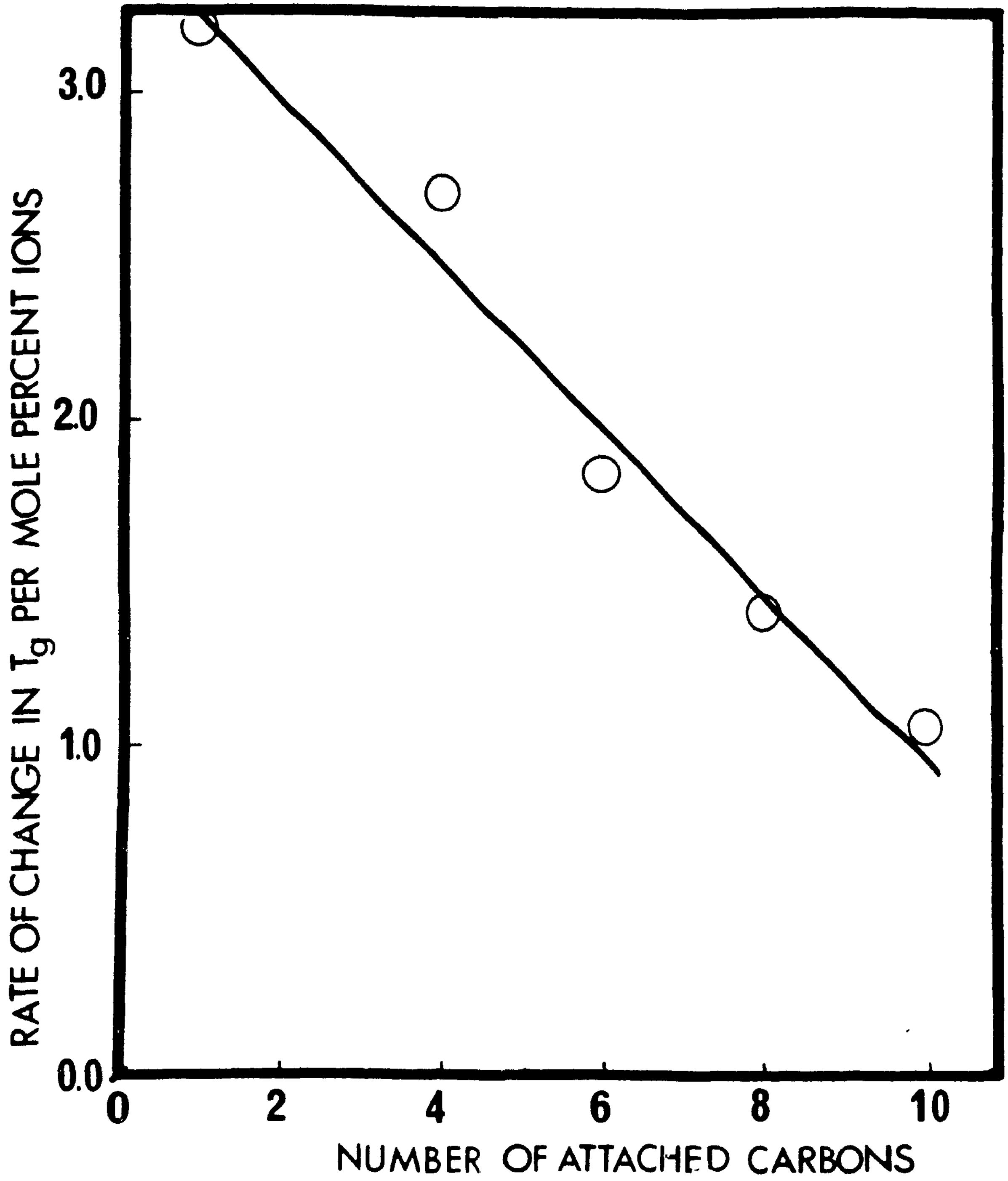

Fig. 3.5: Variation of the rate of change in the glass transition temperature for different ion contents with the length of the attached alkyl chain. Data for iodomethane from ref. 24.

difference between these two temperatures is 1.7 °C using absolute values of the differences.

As mentioned in the introduction, it has been of interest to find a means of mathematically predicting the $T_g$. Since many factors influence the glass transition temperature, a general purpose equation describing it will have many variables related to each other in complex ways. It was evident from the results obtained in this study that, over the range of ion contents encountered in the polystyrene matrix, the relationship between $T_g$ and ion content, as well as $T_g$ and attached side chain length, was linear. Yet, since this relation could not be considered general on the basis of preliminary results with other systems, the publications dealing with the prediction of $T_g$ by other equations were consulted to see if they were applicable to the materials in question here.

These other equations could not be used for the styrene-4-vinylpyridinium-iodoalkane system given the experimental data available. In particular, the absence of the $T_g$ of poly(vinylpyridinium iodoalkane) was required in these other equations. It was considered, however, that to determine these $T_g$'s were too difficult at the present time in view of the anticipated dequaternisation to warrant further study.

## 3.6 Conclusions

The glass transition temperatures and dynamic mechanical properties of random styrene-4-vinylpyridine ionomers quaternised with iodoalkanes have been presented. The behaviour of these "comb" ionomers is influenced, as expected, by the ion content and the length of the pendant alkyl chains. Within the limits of the experimental data, for example 0 to 10 mole percent vinylpyridine and 1 to 10 carbon atoms attached to the pyridine ring, it has been possible to construct an equation that correlates the $T_g$ for such a copolymer with these variables.

### 3.7 Appendix

A linear regression (programme courtesy of Mario Gauthier) was performed on each of the curves in Figs. 3.3 through 3.5. The slope and intercept for each curve are presented below, together with their standard deviation, as well as each correlation coefficient.

Figure 3.3

Iodobutane
slope: 2.68 ± 0.05 °C per mole percent vinylpyridine
intercept: 105.5 ± 0.4 °C
correlation coefficient: 1.00

Iodohexane
slope: 1.82 ± 0.07 °C per mole percent vinylpyridine
intercept: 107.9 ± 0.4 °C
correlation coefficient: 1.00

Iodooctane
slope: 1.3 ± 0.3 °C per mole percent vinylpyridine
intercept: 106 ± 2 °C
correlation coefficient: 1.00

Iododecane
slope 1.1 ± 0.2 °C per mole percent vinylpyridine
intercept: 102 ± 1 °C
correlation coefficient: 0.96

Figure 3.4

1.9 % Vinylpyridine
slope: -1.1 ± 0.4 °C per number of attached carbon atoms
intercept: 117 ± 3 °C
correlation coefficient: -0.84

4.9 % Vinylpyridine
slope: -1.9 ± 0.2 °C per number of attached carbon atoms
intercept: 127 ± 1 °C
correlation coefficient: -0.98

6.9 % Vinylpyridine
slope: -2.4 ± 0.3 °C per number of attached carbon atoms
intercept: 133 ± 2 °C
correlation coefficient: -0.96

9.7 % Vinylpyridine
slope: -3.2 ± 0.1 °C per number of attached carbon atoms
intercept: 144.6 ± 0.9 °C
correlation coefficient: -1.00

Figure 3.5

slope: -0.25 ± 0.02 (°C per mole percent vinylpyridine) per attached carbon
intercept 3.5 ± 0.2 °C per mole percent vinylpyridine
correlation coefficient: -0.98

## 3.8 Acknowledgements

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## 3.9 References

(1) A. Eisenberg, P. Smith and z.-L. Zhou, Polym. Eng. Sci., **22**, 1117 (1982).

(2) P. Smith and A. Eisenberg, J. Polym. Sci., Polym. Lett. Ed., **21**, 223 (1983).

(3) M. Rutkowska and A. Eisenberg, Macromolecules, **17**, 821 (1984).

(4) M. Hara and A. Eisenberg, Macromolecules, **17**, 1335 (1984).

(5) S.-D. Clas and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **22**, 1529 (1984).

(6) R. A. Weiss, P. K. Agarwal and R. D. Lundberg, J. Appl. Polym. Sci., **29**, 2719 (1984).

(7) P. Smith, Ph. D. Thesis, McGill University (1985).

(8) Z. I. Kuvaeva, A. V. Popov and V. S. Soldatov, Doklady Akademii Nauk BSSR, **28**, 153 (184).

(9) F. Andruzzi, C. Barone, D. Lupinacci and P. L. Magagnini, Makromol. Chem., Rapid Commun., **5**, 603 (1984).

(10) D. Lupinacci and W. T. Winter, J. Polym. Sci., Polym. Phys. Ed., **20**, 1013 (1982).

(11) Y. Minoura, T. Hanada, T. Kasabo and Y. Ueno, J. Polym. Sci., A-1, **4**, 1665 (1966).

(12) M. Gordon and J. S. Taylor, J. Appl. Chem., **2**, 495 (1952).

(13) F. Jenckel and R. Heusch, Kolloid Z., **30**, 89 (1953).

(14) T. G. Fox, Bull. Am. Phys. Soc., **1**, 123 (1956).

(15) P. R. Couchman and F. E. Karasz, Macromolecules, **11** 117 (1978).

(16) T. Czekaj and J. Kapko, Eur. Polym. J., **17**, 1227 (1981).

(17) P. R. Couchman, Macromolecules, **15**, 770 (1982).

(18) P. R. Couchman, Nature, **298**, 729 (1982).

(19) T. K. Kwei, J. Polym. Sci., Polym. Lett. Ed., **22**, 307 (1984).

(20) A. Eisenberg, H. Farb and L. Cool, J. Polym. Sci., A-2, **4**, 855 (1966).

(21) K. R. Dunham, J. Vandenberghe, J. W. H. Farber and L. E. Contois, J.Polym. Sci, **1A**, 751 (1963).

(22) J. A. Shetter, Polym. Letters, **1**, 209 (1963).

(23) W. G. Barb, J. Polym. Sci., **37**, 515 (1959).

(24) S. Gauthier, Ph. D. Thesis, McGill University (1985).

# Chapter 4

# Aggregate Modification *via* Plasticisation of Ionomers - Dynamic Mechanical and Morphological Studies

## 4.1 Abstract

Plasticisation of random styrene-N-alkyl-4-vinylpyridinium iodide ionomers was carried out using one of the following methods quaternisation of the vinylpyridine groups with n-iodoalkanes, alkylation of the styrene with 1-decene or external plasticisation with diethylbenzene The materials thus prepared were analysed using dynamic mechanical and small angle X-ray scattering techniques. It was shown that plasticisation of the styrene matrix induced clustering in these materials, while the ionomers in which the vinylpyridine groups were plasticised retained the characteristics of single phase materials The amount of material incorporated into the clusters was seen to vary depending on the mobility of the plasticiser, thus the fraction of clustered material in the externally plasticised ionomers was significantly greater than in the internally plasticised materials

## 4.2 Introduction

The incorporation of ions into nonpolar matrices commonly leads to phase separation of the materials into ion-poor and ion-rich domains and results in materials with very different properties from their nonionic, single phase precursors Styrene-co-sodium methacrylate ionomers are good examples of this phenomenon. Even at very low ion concentrations, they show behaviour significantly different from that of the parent acid copolymers in that the ionomers exhibit, for example, higher moduli at elevated temperatures and greatly increased melt viscosities[1,2,3,4,5]. All of these changes in the materials have been ascribed to the presence of phase separated ionic and nonionic domains.

In the case of random ionomers, this phase separation into ionic aggregates is believed to result in entities known as multiplets and clusters. The existence of these two types of aggregates was first suggested in 1970[6], however, there is still considerable controversy over the exact nature and structure of both multiplets and clusters[7]. As a consequence of this controversy, as well as the dramatic changes in properties resulting from ion incorporation, there is a growing body of experimental data from which the effects of this phase separation on the properties of ionomers can be assessed

It is thought that multiplets are aggregates composed of a few ion pairs With radii of the order of 5 - 10 Å, they are too small to behave as a phase distinct from the matrix Rather, they act as thermolabile crosslinks within it, thus serving to raise the glass transition temperature of the matrix[1,2,3] In most random ionomers, multiplets probably cannot be detected by small angle scattering techniques They are, however, detectable in the halatotelechelics[8,9,10,11].

Clusters, by contrast, are believed to exist as a separate phase. Clusters contain many ion pairs as well as a significant proportion of chain material and are comparatively large Consequently, clusters exhibit their own glass transition temperature and their effect on the $T_g$ of the surrounding matrix may be expected to be quite complex[1,2,12]

Both dynamic mechanical (DM) techniques and small angle X-ray scattering (SAXS)[13,14] have been used extensively to observe aggregation in ionomers In the first, the mechanical behaviour of the materials as a function of temperature is under study SAXS, on the other hand, probes the morphology of phase separated domains. These two techniques explore different aspects of materials, dynamic mechanical experiments are frequency dependent and probe the molecular motions in the various phases, while SAXS is a static technique and probes electron density differences. Thus, these two techniques are complementary, but are not necessarily sensitive to the same features of the aggregates.

In dynamic mechanical experiments, clustered ionomers are characterised by the presence of a rubbery inflection or plateau seen in the curve of storage modulus versus temperature Furthermore, it is possible to determine the glass transition temperatures of both phases from the peaks seen in plots of the loss tangent against temperature

The SAXS profile from an ionomer depicts the intensity of the radiation, I, as a function of q, which is related to the inverse of the average Bragg distance, and contains two features which are of interest At very small q, ionomers generally exhibit an intensity upturn, the meaning of which is at present unclear[15]. At slightly larger values of q, the profiles of clustered ionomers show a peak in the intensity This peak is due to the presence of domains which interact with the radiation. It is not clear in all cases whether these peaks reflect shape or structure factors[11]. However, these peaks have been used in both capacities to determine the scale of the aggregates[8,13]

On the basis of the many studies which have been directed at an understanding of the phase separation encountered in ionomers, it is clear that there are a number of factors which influence ionic aggregation[16] Only those four which are relevant to the present study will be introduced here, two pertaining to the ionic groups and the other two related to characteristics of the matrix

Unquestionably, the ionic moieties present in ionomers determine many of the properties of the material It is widely recognised that the concentration of ions markedly influences the aggregation in ionomers, with higher ion concentrations enhancing clustering, as seen in many mechanical studies[1,2,3]. The type of ion involved in the aggregation also appears to greatly affect clustering. Small ions, having a much higher charge density, enhance clustering[12], while large ion pairs may even lead to a complete disruption of the clusters[17,18].

The nature of the matrix influences the phase separation encountered in ionomers as well. Polymers which are composed of polar units are better able to solvate the ion pairs As a result, matrices which are polar are less likely to show evidence of clustered domains[19] Another aspect of the matrix which influences clustering behaviour is the glass transition temperature Experimental evidence indicates that ionomers with a lower $T_g$ are more likely to be clustered than similar materials possessing a higher glass transition temperature[20]

Thus, since a reduction in the glass transition temperature can enhance clustering, there is increasing interest in ionomers with lowered $T_g$'s. It is widely known that it is possible to decrease the glass transition temperature of a material through the introduction of plasticisers There are two basic methods of plasticisation that are of interest Plasticisers may be added to the materials as small molecule diluents or they may be chemically attached to the polymer chain via post-polymerisation reactions The former is considered an "external" plasticiser and the latter is denoted as "internal" There are certain advantages associated with each method In the case of external plasticisation, a very small amount of diluent makes a large difference in the properties of the material Furthermore, a wide range of potential plasticisers is available and the introduction of the plasticiser is often relatively simple The major disadvantage to using external plasticisation is the mobility, especially the volatility, of the plasticiser Attaching the plasticiser to the polymer chain, as in internal plasticisation, obviously removes any problem with mobility While this method of plasticisation is not as effective as the use of external plasticisers in reducing the glass transition temperature, it clearly permits a greater amount of control. However, this technique, too, has some disadvantages. Post-polymerisation reactions are associated with a number of problems, in particular the availability of reagents, possible unwanted side reactions, such as chain degradation or crosslinking, and the randomness of introduction of the new group A third method of plasticisation, monomer modification prior to polymerisation, can have its own disadvantages and will not be considered here

The other aspect of plasticisation of ionomers depends on the nature of the plasticiser Because ionomers can be phase separated into polar and nonpolar regions, diluents of different dielectric constants should tend to plasticise particular areas, i e. the matrix or the clusters Some previous studies on the plasticisation of ionomers have been concerned largely with the effects of plasticisation of the clusters using highly polar diluents[21,22,23,24,25,26], where it has been shown that this type of plasticisation eliminates the features associated with clustered materials. The introduction of plasticisers with a polarity similar to that of the matrix depresses the glass transition temperature of the matrix[27], and, at low loading levels, even favours clustering[28] Recent studies[29] have shown that the interaction between the plasticiser and the polymer are very complex; thus, plasticisation of an ionomer with plasticisers containing nitro groups, materials which are polar, but do not hydrogen bond, results in behaviour characteristic of nonpolar plasticisers

Ionomers consisting of styrene-co-N-methyl-4-vinylpyridinium iodide have been previously investigated[18] They represent one series of a small group of ionomers which do not exhibit evidence of clustering It is thought that this lack of phase separation is due to the large size of the ion pairs and the high $T_g$ of the matrix The dynamic mechanical behaviour of some styrene-co-N-alkyl-4-vinylpyridinium iodide ionomers, in which the alkyl group ranges in length from butyl (4) to decyl (10), have been previously reported and indicate that these materials also do not behave as if they were clustered[30].

The aim of the present study is to show that plasticisation, even in small amounts, can change an ionomer from an unclustered to a clustered system, accompanied by dramatic changes in mechanical properties, i.e. tan δ, and morphology, as seen in SAXS, of the material Furthermore, the differences in the effects of plasticisation *via* internal or external methods using two nonpolar plasticisers are explored. In addition, the effects of internal plasticisation using nonionic and ionic pendant groups are compared The results of this work also show that the inducement of clustering which was seen in acrylate-based vinylpyridinium ionomers[20] can be extended to styrene-based systems

The ionomers under study here are composed of styrene-co-N-methyl-4-vinylpyridinium iodide. They have been plasticised either externally or internally with nonpolar diluents, in order to reduce the glass transition temperature of the matrix and to determine if clustering is occurring with this reduction. Both dynamic mechanical and SAXS experiments were employed in these studies The SAXS data for the previously studied styrene-co-N-alkyl-4-vinylpyridinium iodide materials are also reported, and confirm that these materials do not appear to be clustered

## 4.3 Experimental

### 4.3 1 POLYMERISATION

Random copolymers of styrene and 4-vinylpyridine and a styrene homopolymer were prepared by free radical copolymerisation in the bulk as previously described[18]. The conditions of polymerisation are summarised here for convenience. Styrene (Aldrich, 98%) and 4-vinylpyridine (Aldrich, 97%) were fractionally distilled at reduced pressure (19 mm Hg and 47 °C , 16 mm Hg and 65 °C, respectively), then stored for a few hours at low temperature until needed. The initiator, benzoyl peroxide, was used as received. The quantities of monomers required, for polymer compositions ranging between 0 and 12 mole % vinylpyridine, and the desired compositional homogeneity, 30 %, were calculated. The monomers were mixed, sufficient initiator was added for a $M_n$ of 100,000 and the solution transferred to an ampoule After degassing, the ampoule was sealed and refrigerated Subsequently, the polymerisation was carried out at 60 °C for approximately 11 hours, resulting in a conversion of *ca* 30 % The polymer solution was then diluted with toluene to 5 weight %, precipitated in a 10-fold volume excess of methanol, filtered and washed with more methanol It was dried in vacuum at *ca* 60 °C to constant weight. The vinylpyridine content of the copolymers was determined both by titration of the samples in chlorobenzene solution with perchloric acid in acetic acid and from an analysis of the infrared spectra, using a previously prepared calibration curve[18].

The sequence of reactions employed following the polymerisation depended on the method of plasticisation used Materials for the internal plasticisation study were first alkylated and then quaternised. The samples for the external plasticisation study were quaternised and then plasticised The polymers that were plasticised using long n-iodalkanes were quaternised with these reagents as has been described earlier[30].

### 4.3 2 INTERNAL PLASTICISATION

The styrene-co-4-vinylpyridine copolymers were plasticised to varying extents through the alkylation of different proportions of the phenyl rings through a Friedel-Crafts reaction, similar to one reported previously[28] Before the polymers were alkylated with 1-decene (Aldrich, 96%), the reagent was purified by distillation under reduced pressure (12 mm Hg and 61 °C) and then stored at reduced temperature.

To a 3 % solution of the polymer in carbon disulfide was added a two-fold molar excess of 1-decene This was heated to refluxing and then an equimolar amount of catalyst, anhydrous aluminum trichloride (Anachemia, reagent grade), was added as a 20 % slurry in 1-nitropropane. The extent of alkylation depended on the reaction time; for lower levels of alkylation a few hours of reflux were sufficient, but the reaction was carried out for 24 hours for maximum alkylation. The alkylated polymer was recovered after precipitation into a ten-fold volume excess of methanol.

It was important to purify the polymer in order to forestall any complications from cross-linking due to remaining traces of the catalyst. A 1 % solution of the polymer in chlorobenzene was prepared and 0.01 and 0.05 % of isopropanol and distilled water, respectively, were added This mixture was refluxed for another 24 hours and then washed with distilled water. The polymer was precipitated into a 20-fold excess of methanol, filtered and dried under vacuum at 60 °C for a few days. A series of similar materials was prepared *via* the partial alkylation of the styrene homopolymer with 1-decene. The method employed was identical to that described above for the styrene-vinylpyridine copolymers.

The extent of alkylation[31] was determined from $^1$H NMR spectra obtained on a Varian XL-200. The ratios of the aromatic and aliphatic peaks were determined in relation to the amount of styrene and vinylpyridine known to be present. The pyridine group is essentially unreactive to Friedel-Crafts alkylation under the conditions used[32], thus all of the alkylation was believed to have taken place on the phenyl rings.

The alkylated samples were quaternised with iodomethane (Aldrich, 99%). This reagent was distilled under nitrogen at 41-43 °C shortly before use. The quaternisation was performed in tetrahydrofuran (THF) which had been previously dried over potassium-benzophenone complex until the purple colour persisted, and then distilled.

The samples to be quaternised were dissolved in sufficient dry THF under nitrogen to make a 5 % solution. A five-fold molar excess of iodomethane was added and the resulting light yellow solution was refluxed for 90 minutes. The polymers were recovered by precipitation into 20-fold excess volume of hexanes , then they were filtered and dried in vacuum at 60 °C to remove residual solvent.

### 4.3.3 EXTERNAL PLASTICISATION

The ionomer samples for the external plasticisation studies were first quaternised with iodomethane as described above. Subsequently, they were redissolved in benzene/methanol (90/10 v/v) and freeze-dried. The polymers were kept in vacuum at 60 °C until needed. Apart from quaternisation, the styrene homopolymer was treated in the same fashion.

Diethylbenzene ( Aldrich, 97 %, a mixture of o-, m- and p- isomers) was used as the diluent in these studies. It was purified before the plasticisation experiments by distillation under reduced pressure (10 mm Hg and 55 °C). Dry ampoules were each filled with approximately 2 mL and sealed.

For each plasticisation experiment, a sample of the freeze-dried polymer, weighing from 0,9 to 1,2 g, was used. The contents of two ampoules of diethylbenzene were added to the sample in an aluminum weighing pan lined with Teflon$^R$. To get a uniform distribution of the diluent in the sample, the following procedure was used The sample was placed in a desiccator under vacuum for one hour, then moved to a drying pistol and heated to *ca* 100 °C under nitrogen for another hour. The drying pistol was cooled to about 56 °C (boiling acetone) and placed again under vacuum The samples were removed after different lengths of time to yield different plasticiser contents. For example, a sample evacuated for about 5 hours contained approximately 10 % diethylbenzene by weight.

The actual amount of plasticiser contained within the samples was determined only for those samples used for the dynamic mechanical experiments. The polymer was weighed first after moulding, then after the experiment, and then placed in a drying pistol at approximately 100 °C under vacuum until it reached constant weight. From the initial samples, a calibration curve was prepared, and twin samples for the small angle X-ray scattering studies were prepared following it. One of these samples was used in the SAXS study and the other was dried to constant weight, so as to get a better approximation of the plasticiser content in the sample.

### 4.3.4 DYNAMIC MECHANICAL EXPERIMENTS

The samples for the dynamic mechanical experiments were compression moulded into rectangular slabs at elevated temperatures and 2 GPa pressure. The average dimensions of the moulded slabs were 12 x 35 x 2 mm. In the external plasticisation studies, as described above, the samples were weighed before the experiment. The samples were run in a dynamic mechanical thermal analyser (DMTA, Polymer Laboratories) in dual cantilever bending mode at a heating rate of 0,5 °C $min^{-1}$ in a nitrogen atmosphere. Data were obtained concurrently for five frequencies ranging from 0,3 to 30 Hz.

The dynamic mechanical experiments were stopped at temperatures not greater than 170 °C. This was used as the maximum for two reasons. There are problems with dequaternisation of the N-methyl-vinylpyridinium iodide ion pairs on prolonged exposures to temperatures above about 160 °C. Furthermore, in the case of the external plasticisation studies, the boiling point of diethylbenzene is 180-2 °C

Further analysis of the data was made possible after the run using a curve-fitting and peak-finding routine written for this laboratory by S Williams. In the cases where this program was not suitable, the glass transition temperatures were estimated by visual inspection of the peak maxima.

### 4.3.5 SMALL ANGLE X-RAY SCATTERING EXPERIMENTS

The samples for the SAXS experiments were also compression moulded, under temperatures and pressures similar to those used in the moulding of the DM samples. The samples obtained through this moulding were disks of a typical diameter 12 mm and thickness 2 mm. Because these samples were moulded several weeks before the experiments were run, they were protected from the atmosphere in the interim. The samples that were plasticised internally, either with a nonpolar group, as in the alkylated materials, or with a polar one, i.e. those samples quaternised with the n-iodoalkanes, were kept under vacuum. The samples that were plasticised with diethylbenzene were sealed in individual ampoules.

The small angle X-ray scattering experiments were run on the D-22 line at LURE. This line is characterised by moderate flux and high resolution. The energy of the beam was 8500 eV. The samples were positioned in air either 818 or 830 mm from the detector, depending on the sample holder used, and spectra were collected for 1200 s. The analysis of the data was performed using software written by O. Lyon. The spectra were corrected for sample thickness, where possible, and the blank absorbance. Not all the samples could be corrected for the thickness. For example, in the case of the highly alkylated samples, only the material of highest ion content was sufficiently below its $T_g$ to be measured. The externally plasticised samples were sealed in ampoules before it was recognised that the thickness measurement was important, and the thickness could not be determined afterwards.

### 4.4 Results

The levels of plasticisation of the different materials were determined by different techniques. $^1$H NMR spectroscopy was used to determine the extent of alkylation in the samples plasticised with 1-decene, while the amount of diethylbenzene in the externally plasticised materials was determined by weight loss; the polymers that were quaternised by n-iodoalkanes were judged to be fully quaternised when the infrared peak at 1414 $cm^{-1}$ disappeared completely. The ionomers prepared for this study, along with their relative plasticisation levels, are shown in Table 4.1.

The dynamic mechanical behaviour of the materials depended on the type and the amount of plasticisation employed, in addition to the expected dependence on ion content. For the sake of clarity, the earlier results[30] for the samples quaternised with n-iodoalkanes are first briefly recapitulated. This is followed by a description of the results observed for the alkylated and externally plasticised samples.

Quaternisation of random styrene-co-4-vinylpyridine copolymers with n-iodoalkanes can be considered a type of internal plasticisation of the polar groups by the attached alkyl chains. The styrene-co-N-alkyl-4-vinylpyridinium iodide ionomers all resemble a styrene homopolymer of comparable molecular weight in their mechanical behaviour. The principal difference is an increase in the glass transition temperature with increasing ion content. However, as the length of the attached alkyl chain increases, the effect of increasing plasticiser content offsets that of ion content. The single $T_g$ varies linearly with ion concentration and alkyl chain length over the vinylpyridine content and iodoalkane range studied. For such styrene-vinylpyridinium ionomers, it was shown that it was possible to relate the glass transition temperature to the alkyl chain length and vinylpyridine content using a simple equation. The absence of a second peak in the loss tangent versus temperature curves indicates that these materials are not clustered.

By contrast, the internal plasticisation of the nonpolar matrix in styrene-co-N-methyl-4-vinylpyridinium iodide ionomers, *via* alkylation of the phenyl groups, significantly alters the mechanical properties. When alkylated to a moderate degree, a shoulder is clearly evident on the high temperature side of the peak in the tan $\delta$ vs.

## Table 4.1:

## Relative Plasticisation Levels of Samples

### A. Internally Plasticised Samples

| Starting Material | Duration of Alkylation Reaction (min) | Extent of Alkylation (mol % styrene) |
|---|---|---|
| Polystyrene | 60 | 10 |
| | 275 | 30 |
| | 480 | 50 |
| Sty-0.0265VP(4-) | 1515 | 90 |
| Sty-0.0508VP(4-) | 1455 | 80 |
| Sty-0.0622VP(4-) | 70 | 10 |
| | 135 | 20 |
| | 335 | 30 |
| Sty-0.0791VP(4-) | 1410 | 80 |
| Sty-0.106VP(4-) | 1870 | 70 |

### B. Externally Plasticised Samples

| Starting Material | Length of Time Evacuated (min) | Diethylbenzene Content (mol % sty) |
|---|---|---|
| Polystyrene | - | 0 |
| | 300 | 7.9 |
| Sty-0.0193VP(4-) | 190 | 10.1 |
| Sty-0.0622VP(4-) | - | 0 |
| | 705 | 5.3 |
| | 315 | 7.0 |
| | 260 | 9.4 |
| | 125 | 15.2 |
| Sty-0.121VP(4-) | 190 | 3.8 |

temperature plots. The shoulder is attributed to the glass transition of a second, clustered phase, as has been done for other clustered systems. As the level of alkylation increases to above 30 mole %, the shape of this curve changes markedly and both peaks are of comparable magnitude. This is shown in Figure 4.1. In the samples with much higher levels of alkylation, it is unclear whether there is a second peak in the loss tangent because of the large scatter in the data. The storage modulus (G') curves do not have a second inflection point in any of these samples, however, the materials which are clustered have much broader transitions.

As expected, the alkylation of the styrene homopolymer to varying extents with 1-decene resulted in materials with reduced glass transition temperatures. Only one glass transition temperature was observed for all plasticiser contents, although the materials were opaque. In contrast, all of the plasticised ionomers were clear. The opacity may be due to the immiscibility of the alkane in styrene or possibly side chain crystallisation. However, since phase separation in nonionic systems was not the principal aim of this study, this observation was not followed up.

The plasticisation of the styrene-co-N-methyl-4-vinylpyridinium iodide ionomer with diethylbenzene may result also in a material with properties very different from those of the unplasticised precursor ionomer. In addition to the dependence of the phenomena on the amount of plasticiser involved, the ion content proved to be important, thus the ionomers containing very low (*ca.* 2 mole %) and very high (*ca.* 12 mole %) vinylpyridine contents did not exhibit any behaviour associated with phase separation upon plasticisation. In general, for ionomers of moderate vinylpyridine content and at the low levels of plasticisation studied, the reduction in the glass transition temperature is much more pronounced for these samples than for the internally plasticised ones. A higher temperature peak, attributed again to clusters, is also clearly observed in the loss tangent - temperature curves of the 6

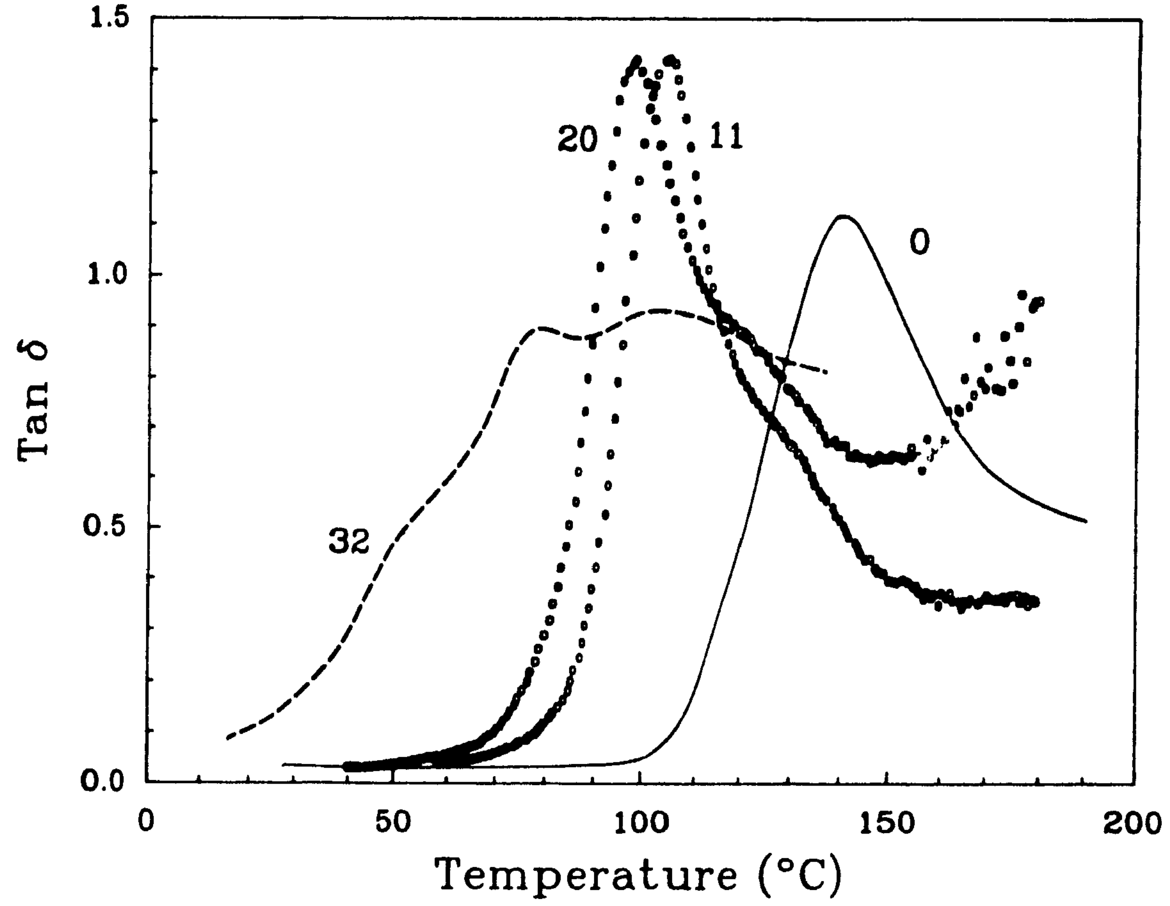

Fig. 4.1: Loss tangent as a function of temperature for internally plasticised styrene-N-methyl-4-vinylpyridinium iodide (6 mole % ions) ionomers. Numbers refer to mole % alkylation.

mole % ionomer, as shown in Figure 4.2. It is unlikely that this second peak is due to uneven plasticisation, which would result in areas of unplasticised ionomer, because the positions of both peaks depend on the amount of diethylbenzene present. Rather, the presence of two glass transitions suggests that clustering has occurred also in these ionomers, although here the higher $T_g$, that of the clusters, is predominant even at very low plasticiser contents.

The equivalent plasticisation of the styrene homopolymer with diethylbenzene also depressed the $T_g$ of the material. As in the internal plasticisation of polystyrene, no second tan $\delta$ peak is observed. However, unlike the alkylated homopolymer, the samples in these plasticisation experiments were transparent.

The results from the dynamic mechanical experiments on these ionomers are summarised in Table 4.2. The glass transition temperatures, the peak halfwidths and the activation energies calculated for the different materials are listed. A comparison of the loss tangent data for the different methods of plasticisation is shown in Figure 4.3.

The other series of experiments performed on these ionomers used small angle X-ray scattering. The results from the SAXS studies indicate that significant changes in the morphology of the ionomers accompany the reduction of the glass transition temperature. The results of the SAXS studies, i.e. the peak positions and intensities for the above mentioned samples, are also listed in Table 4.2.

The SAXS profiles of the ionomers quaternised with n-iodoalkanes did not have a peak in intensity over the observed q range and, thus, there was no evidence of aggregation in these samples. This is consistent with the dynamic mechanical results on these materials[30]. The investigation of the SAXS diffraction of the highly alkylated styrene-co-N-methyl-4-vinylpyridinium iodide ionomers yielded rather

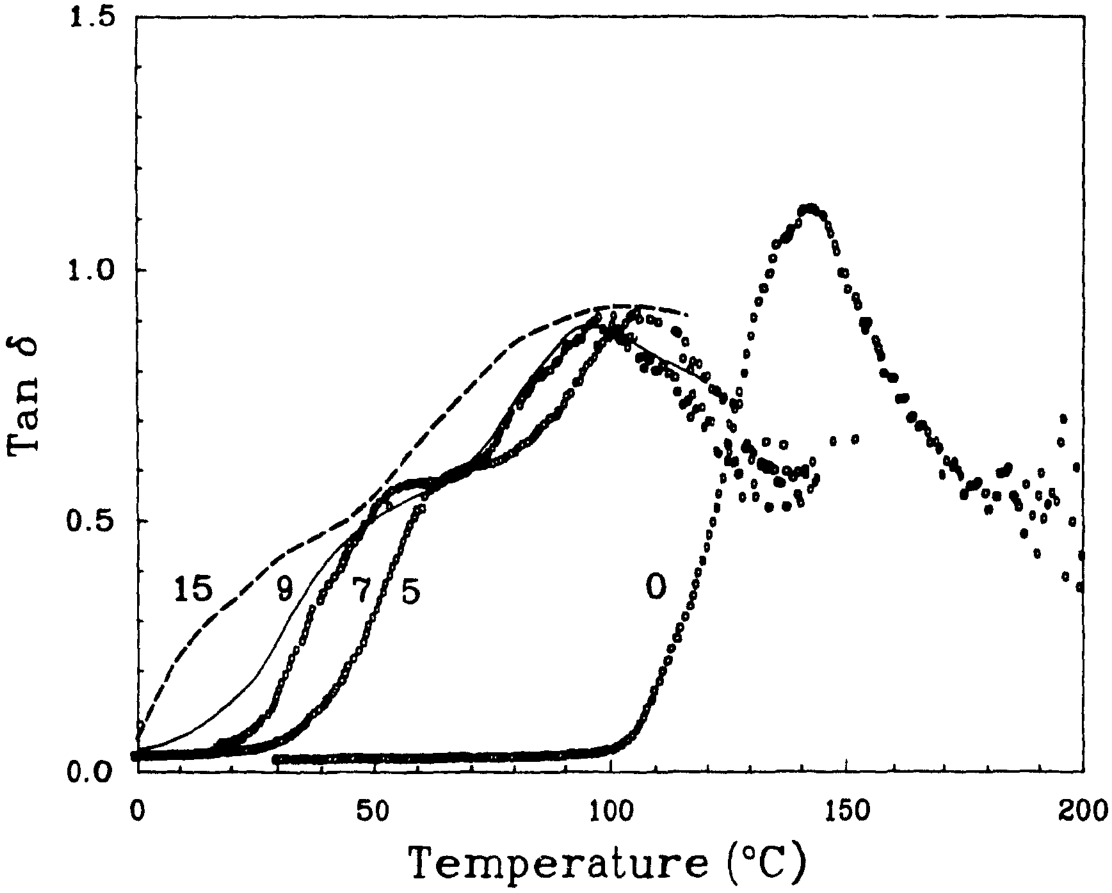

Fig. 4.2: Loss tangent at 1 Hz as a function of temperature for externally plasticised styrene-N-methyl-4-vinylpyridinium iodide (6 mole % ions) ionomers. Numbers refer to mole percent of plasticisation.

## Table 4.2: Results From Dynamic Mechanical and SAXS Experiments

### A. Internally Plasticised Samples

| Sample | Mole % plasticiser | $T_{g(low)}$ @ 1 Hz (°C) | $T_{g(high)}$ @ 1 Hz (°C) | $E_{act(low)}$ ($kJ \cdot mol^{-1}$) | $E_{act(high)}$ ($kJ \cdot mol^{-1}$) | $q_{max}$ ($Å^{-1}$) | Intensity (normalised) |
|---|---|---|---|---|---|---|---|
| Polystyrene[a,b] | 9.9 | 98.5 | - | 470 | - | - | |
| "[a,b] | 32.8 | 51.8 | - | 500 | - | - | |
| "[a,b] | 47.9 | 34 | - | 240 | - | - | |
| Sty-0.0265VP(4-)-MeI[a,c] | 91.7 | 15.5 | - | 190 | - | - | |
| Sty-0.0622VP(4-)-MeI | 11.4 | 104.4 | 128.5 | 400 | 280 | 0.181 | |
| " | 19.7 | 98.3 | 124.7 | 400 | 250 | 0.172 | |
| " | 32.3 | 53.1 | 112.4 | 390 | 310 | 0.153 | |
| Sty-0.0791VP(4-)-MeI[a] | 83.6 | 20 | - | 200 | - | 0.165 | 3e-3 |
| Sty-0.106VP(4-)-MeI[a] | 73.3 | 41 | - | 230 | - | 0.182 | 2.3e-3 |

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[a] No second peak in DM experiments.

[b] SAXS not run on sample.

[c] No peak in SAXS.

**Table 4.2** continued

## B. Externally Plasticised Samples

| Sample | Mole % plasticiser | $T_{g(low)}$ @ 1 Hz (°C) | $T_{g(high)}$ @ 1 Hz (°C) | $E_{act(low)}$ (kJ·mol$^{-1}$) | $E_{act(high)}$ (kJ·mol$^{-1}$) | $q_{max}$ (Å$^{-1}$) | Intensity (normalised) |
|---|---|---|---|---|---|---|---|
| Polystyrene[a,b] | 0 | 115.6 | - | 490 | - | | |
| "[a,b] | 7.9 | 46.3 | - | 310 | - | | |
| Sty-0.0193VP(4-)-MeI[a,b] | 10.1 | 37.5 | - | 350 | - | | |
| Sty-0.0622VP(4-)-MeI[a,c] | 0 | 140.5 | - | 580 | - | - | |
| "[d] | *2.5* | - | - | - | - | 0.129 | 5e-4 |
| "[d] | *5* | - | - | - | - | 0.133 | 3.75e-4 |
| "[b] | 5.3 | 63.7 | 105.6 | 340 | 480 | | |
| "[b] | 7.0 | 51.1 | 96 | 280 | 260 | | |
| "[b] | 9.4 | 44.6 | 98.6 | 300 | 280 | | |
| "[d] | *10* | - | - | - | - | 0.134 | 6e-4 |
| "[b] | 15.2 | 20.9 | 88.2 | 400 | 220 | | |
| "[d] | *20* | - | - | - | - | 0.130 | 4e-4 |
| Sty-0.121VP(4-)-MeI[a,b] | 3.8 | 114.4 | - | 390 | - | | |

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d SAXS sample only; DM experiments not run.

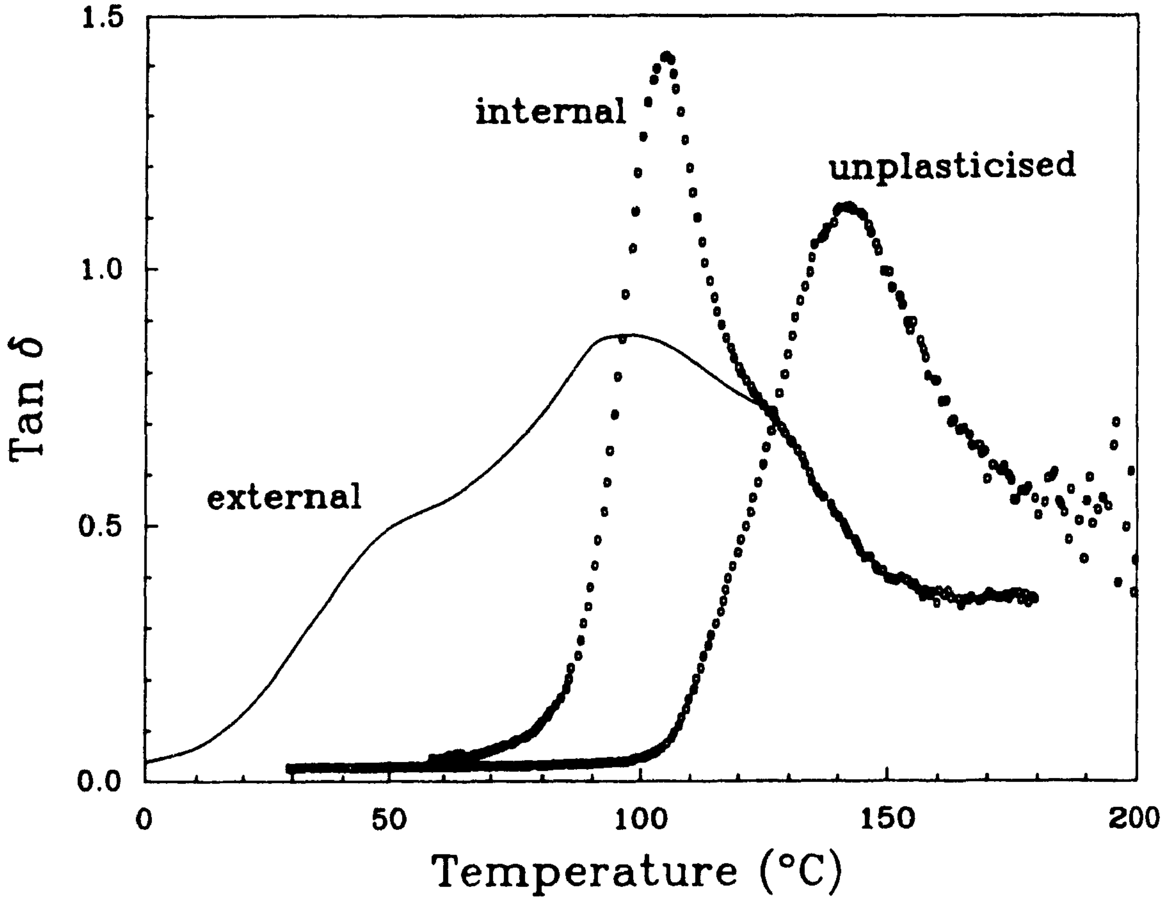

Fig. 4.3: A comparison of the loss tangent curves of styrene-co-N-methyl-4-vinylpyridinium iodide ionomers plasticised internally and externally with about 10 mole % plasticiser.

different results. While there is no conclusive evidence of phase separation in the mechanical studies because of the low modulus above the $T_g$ of the highly plasticised systems, the internally plasticised materials of higher ion contents have very distinct peaks in their SAXS profiles, demonstrating that they are phase separated. The externally plasticised samples all had peaks in their SAXS profiles. With the exception of the 10 % sample, in which the peak was a shoulder on the upturn, all the peaks were well resolved, although weaker in intensity than those found in the internally plasticised materials. The upturn at small angles, however, was present in all samples, regardless of their method of plasticisation. An example of the small angle X-ray scattering profile observed for each plasticisation scheme is shown in Figure 4.4.

## 4.5 Discussion

Previous studies have demonstrated that clustering in ionomers can be dramatically influenced by the choice of plasticiser. Thus, it is possible to "fine-tune" the properties of ionomers through selective plasticisation. For example, one way to reduce or obliterate the mechanical features associated with clustering is to reduce the strength of the ionic interactions within the cluster[21-26], for example by the addition of highly interacting plasticisers to the polar domains of the ionomers. The clusters may retain their identity, however they no longer exert an effect on the rheological properties of the material. It has also been shown that the addition of a very large amount of nonpolar plasticisers ultimately destroys much of the mechanical behaviour associated with clustering[28]. The opposite effect, the enhancement of aggregation, has been achieved through the addition of moderate amounts of nonpolar plasticisers[20,28]. Finally, there are some plasticisers which do not have very much effect on the phase separation in ionomers. In this study, the

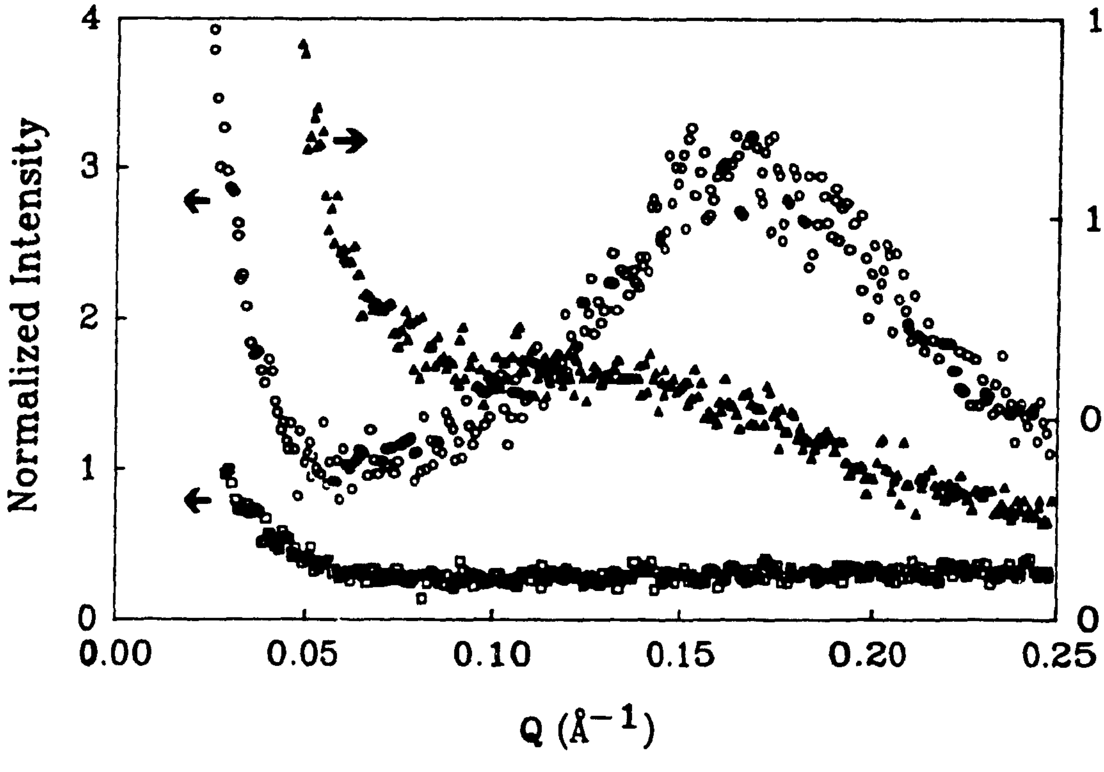

Fig. 4.4: Small angle X-ray scattering profiles of styrene-co-N-alkyl-4-vinylpyridinium iodide ionomer (*ca.* 6 mole % ions) plasticised internally and externally with about 10 mole % plasticiser. Sty[0.11p-C10]-0.0622VP-MeI, ○, Sty-0.069VP-DeI, □, and Sty-0.0622VP-MeI + Diethylbenzene, ▲.

plasticisers either induced two phase behaviour,i.e. clustering, into one-phase materials, or were ineffective, in which case the material retained the characteristics of a single phase system. The single phase materials, which for the purposes of this study are the least interesting, will be discussed first, and the final section of the discussion will deal with the two phase, or clustered, ionomers.

### 4.5.1 SINGLE PHASE IONOMERS

The quaternisation of styrene-vinylpyridine copolymers with n-iodoalkanes is an example of plasticisation which has no effect on the phase separation in these materials. Plasticisation *via* this technique enlarges the ionic group. This results in a mild depression of the $T_g$, but there is no evidence of phase separation either in dynamic mechanical or SAXS studies.

The 2 mole % styrene-N-methyl-4-vinylpyridinium iodide systems are another example of one phase materials in which no evidence for clustering has been found, even when the ionomers have been alkylated with 1-decene or plasticised with diethylbenzene. The behaviour of these materials is thus unlike that seen for *ca.* 2 mole % styrene-sodium methacrylate ionomers, in which behaviour characteristic of two phase systems has been observed using dynamic mechanical techniques[12] and Raman spectroscopy[32].

### 4.5.2 TWO PHASE IONOMERS

The addition of moderate amounts of a nonpolar plasticiser has been seen to enhance or even induce clustering in several systems[20,28]. The phenomenon of inducing clustering through plasticisation has been observed in materials of already rather low $T_g$, such as ethyl acrylate, and in the present study this observation is extended to styrene-based vinylpyridinium ionomers. A number of factors suggest that in the styrene-based systems clustering should be easier to achieve than in the acrylate systems. One such factor is the much lower dielectric constant of the styrene systems. Another is the unfavourable solubility parameter, $\chi$ (chi), between styrene and vinylpyridinium[33]. Thus the styrene-vinylpyridinium ionomers are materials that, in the unplasticised state, appear to be prevented from clustering only because of the high matrix glass transition temperature. The present experimental results indicate that styrene-vinylpyridinium ionomers would tend to cluster easily if the $T_g$ were lower. The addition of a only 5 % of diethylbenzene lowers the glass transition temperature of the matrix sufficiently to cause a large amount of the material to cluster, and yet this $T_g$ (63.7 °C) is still much higher than that of an unplasticised ethyl acrylate-vinylpyridinium ionomer of a similar ion content (*ca.* 5 °C).

Although both externally and internally plasticised styrene-N-methyl-4-vinylpyridinium iodide ionomers are phase separated, there are a number of differences in both the dynamic mechanical behaviour and the SAXS profiles between materials plasticised using the two methods of plasticisation. For convenience, the ways in which the internally and externally plasticised ionomers respond differently to the dynamic mechanical and small angle X-ray scattering experiments are summarised in Table 4.3.

An important difference between the two plasticisers lies in their structures, and which influences how they interact with the matrix. Clearly, 1-decene is much less miscible with polystyrene than is diethylbenzene. However, given that the alkyl group is attached to the styrene, and thus cannot move out, it is believed that for the two phase systems in this study, the differences in the results obtained are due to the change in mobility of the plasticiser, rather than the structure of the additive.

It is known that the mobility of a plasticiser determines its effectiveness in reducing the $T_g$. Clearly, an external plasticiser, being unattached in any way to the

# Table 4.3:

## A Comparison of the Phase Behaviour Resulting from Internal and External Plasticisation

| | Internal | External |
|---|---|---|
| Predominant $T_g$ | lower $T_g$ predominates at low plasticisation;<br>upper $T_g$ of comparable importance at plasticisation levels > 30 %; | upper $T_g$ always predominant; |
| Shift in $T_g$ | Both $T_g$'s move linearly to lower temperatures as the plasticisation levels increase; | Initially, both $T_g$'s drastically lowered as plasticiser is introduced; rate of depression slows, but always greater than internally plasticised; |
| SAXS peak position | $q_{max}$ @ *ca.* 0.18 $Å^{-1}$ | $q_{max}$ @ *ca.* 0.13 $Å^{-1}$ |
| SAXS peak maximum I | $4 \times 10^{-3}$ | $1.5 \times 10^{-3}$ |

polymer chain, introduces more free volume than can a comparable amount of attached plasticiser. Thus, materials which have been plasticised with a small molecule diluent have glass transition temperatures which are generally much lower than materials plasticised with comparable amounts of internal plasticisers. This difference in the efficiency of plasticisation is also seen in the results of this study; if approximately 10 mole % plasticiser has been incorporated internally, the $T_g$ of the matrix is reduced by about 35 °C, whereas the same amount of external plasticiser depresses the matrix glass transition temperature by *ca.* 100 °C. It is also worth noting that when two phases are present in one of these ionomers, the difference between the two $T_g$'s is also dependent on the type of plasticisation used. To continue with the previous example, the difference in the glass transition temperatures of the two phases is about 20 °C for the 10 mole % alkylated sample, but is already *ca.* 40 °C for the externally plasticised materials. These variations in behaviour may be seen in Figure 4.5*.

Another difference between the dynamic mechanical data for the internally and externally plasticised samples is seen in the relative heights of the loss tangent peaks for the separate phases. It has been suggested that the areas underneath such peaks reflect the relative amounts of material present in each phase[12,34,35]. Thus, it

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*For the ionomers quaternised by n-iodoalkanes, the values were obtained in the following steps. First, the vinylpyridine content was recalculated in terms of the styrene content alone, and the appropriate ion content chosen. The vinylpyridine content also determined the maximum plasticisation possible, based on 100% quaternisation with iodododecane. The other points are the glass transition temperatures of the same vinylpyridine content material, but with their alkyl chain length normalised to ten carbons.

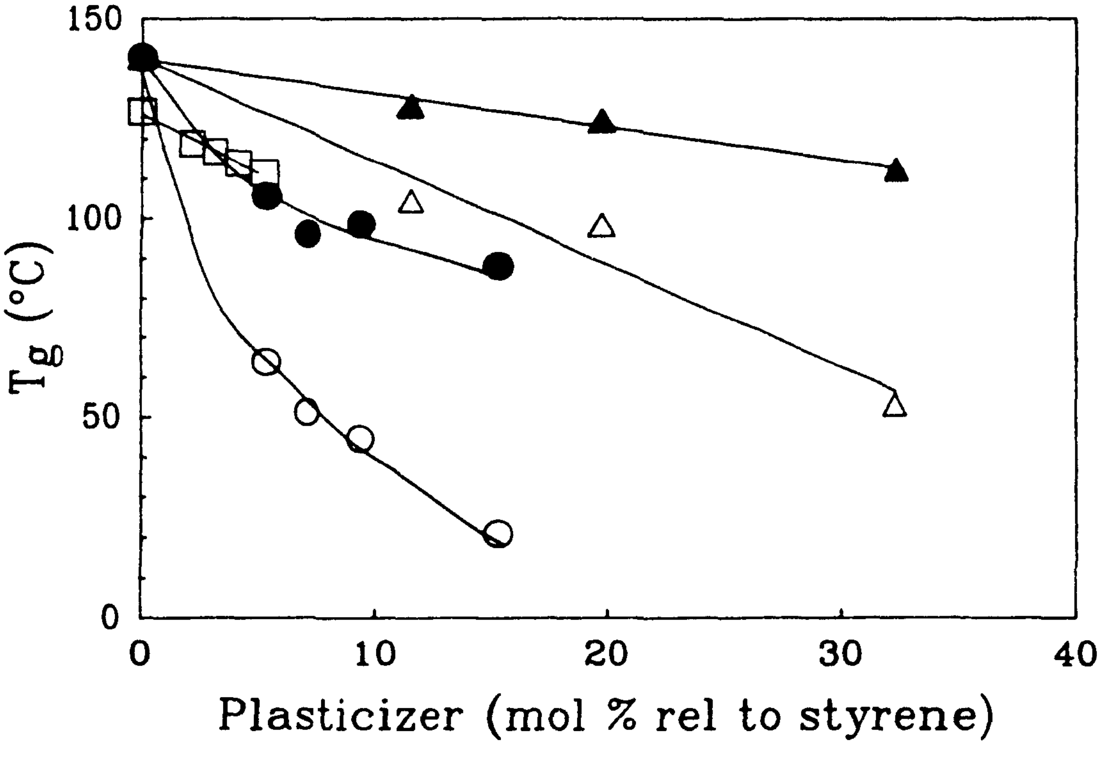

Fig. 4.5: The glass transition temperature of plasticised styrene-co-N-alkyl-4-vinylpyridinium iodide ionomers as a function of plasticiser type and content. Externally plasticised materials, ○, alkylated matrix, △, and ionomers quaternised with n-iodoalkanes, □ Coloured symbols represent upper tan δ peaks.

appears that for the internally plasticised samples, initially relatively little material is incorporated into the clustered regions at low plasticiser contents. Only when the alkylation level is much higher, i.e. *ca.* 30 %, does the amount of material in the cluster phase approach that in the multiplet-containing phase. In contrast, in the cases of the externally plasticised ionomers, the glass transition peak at higher temperatures is always substantially larger. This suggests that the phase responsible for this transition predominates in these materials.

The SAXS data show that other differences, in the positions and intensities of the peaks, exist between the internally and externally plasticised materials. Most notably, the highly alkylated materials have peaks at significantly larger q than the materials plasticised by small molecules. This implies that either the phase separated regions are much closer together in the internally plasticised ionomers, or that, in these systems, these domains are smaller. The ambiguity in this interpretation reflects the current uncertainty in understanding the small angle X-ray scattering profiles of random ionomers, because of the difficulty in attributing such SAXS peaks to structure or shape factors.

Almost as striking in the SAXS profiles is the difference in the intensities of the peaks observed in the alkylated samples compared with those of the externally plasticised ionomers. The intensities of the internally plasticised materials are some forty times the latter. This may, in part, be due to the differences in plasticiser concentrations (70-80 mole % for the alkylated materials vs. < 20 mole % for the externally plasticised ionomers), however, there is no similar increase in the maximum peak intensities in the series of externally plasticised materials with increasing diethylbenzene content. Thus, it is suggested that the differences in the mobilities of the plasticisers are responsible for the differences in peak intensities.

It is possible to explain all of the differences listed above and in Table 4.3 as a consequence of the relative plasticiser mobilities. It is expected that the alkylation of the phenyl groups in the styrene-vinylpyridine copolymers occurs randomly along the chain, and, therefore, in the solid state, the internal plasticiser should be distributed evenly throughout both phases. Because the glass transition temperatures are quite close in the internally plasticised systems, it appears that the only factor differentiating the clusters from the matrix is the presence in the former of a proportionately larger number of ions. If the peaks in small angle X-ray scattering can be attributed to the dimensions of the scattering bodies, then these peak positions of the alkylated ionomers indicate that the domains are small, and the intensities of these peaks suggest that the domains and the matrix have very different electron densities. The assumption of small domain sizes is also in agreement with the relative peak heights in the dynamic mechanical results These data are all consistent with a material which contains rather small and well organised clusters.

The situation in the externally plasticised materials is quite different because in this case, the plasticiser is free to move away from the ion-rich areas. Because of the mobility of the diethylbenzene, the matrix is expected to contain most of the plasticiser, and thus the clusters would be expected to have a $T_g$ higher than that observed for the ion-rich regions in similar internally plasticised ionomers. In fact, the glass transition temperatures of the clustered phases of the externally plasticised ionomers are lower than those of the comparable internally plasticised materials. The additional reduction in the $T_g$ can be attributed to a "soft-wall" effect which has been seen in other phase separated systems[36]. However, the differences between the glass transition temperatures of the cluster and multiplet-containing phases are still markedly larger in the externally plasticised ionomers than in the alkylated materials. These larger differences indicate that, as expected, the concentration of diethylbenzene is not uniform throughout the material as a result of the presence of ions. In externally plasticised ionomers, therefore, the clusters should be different from the matrix on the basis of both average ion content and plasticiser content. The large size of the cluster peak in the loss tangent - temperature curves suggests that these domains are predominant in these materials. Assuming again that the small angle X-ray scattering profiles are indicative of the domain size, then in the diethylbenzene containing samples these clusters are larger than the domains found in the internally plasticised ionomers. The low relative intensity of the SAXS peak and the observed depression in the glass transition temperature of the clusters relative to that of the internally plasticised materials imply that, in addition to being large, these domains are rather poorly organised.

It is clear that the externally plasticised 6 mole % styrene-vinylpyridinium ionomer is a highly clustered material. Thus, the absence of evidence for two phase behaviour in the externally plasticised 12 mole % N-methyl-4-vinylpyridinium iodide ionomer deserves special comment. The single phase behaviour suggests the following two possiblities. Either the material is truly unclustered, or it contains a single phase of high ion concentration, i.e. all clustered. In this connection, it is worth recalling that styrene-co-sodium methacrylate ionomers have been seen to become almost entirely clustered at ion contents of *ca.* 13 mole % with only a very small peak due to the low $T_g$ phase [12]; thus, it is conceivable that the same situation also exists for the plasticised styrene-co-N-methyl-4-vinylpyridinium iodide ionomers at high vinylpyridinium contents. In addition, the loss tangent peak of the cluster phase is clearly dominant already in the 6 mole % samples. Thus, although no samples were run between 6 and 12 mole % vinylpyridine concentration, which would confirm this trend to a completely clustered system, on the basis of the results in other systems, complete clustering seems most likely in the externally plasticised 12 mole % sample.

## 4.6 Conclusions

The plasticisation of styrene-N-methyl-4-vinylpyridinium iodide ionomers by the incorporation of either an internal (attached) or an external (mobile) nonpolar additive yields phase separated materials above 2 mole % ion content. At very high vinylpyridinium content, the entire material appears to be clustered. While the clustering observed in the styrene-vinylpyridinium ionomers is clearly a consequence of the reduction in the glass transition temperature of the material, the different methods of plasticisation result in different cluster sizes based on evidence from both dynamic mechanical and small angle X-ray scattering. When these ionomers have been internally plasticised with 1-decene, the material thus produced appears to contain small, well organised domains. In contrast, the introduction of diethylbenzene into these ionomers yields a material in which the clusters are relatively large and poorly organised.

## 4.7 References

(1) C. G. Bazuin and A. Eisenberg, Ind. Eng. Chem. Prod. Res. Dev., **20**, 271 (1981).

(2) W. J. MacKnight and T. R. Earnest, J. Polym. Sci., Macromol. Rev., **16**, 41 (1981).

(3) R. Longworth, Developments in Ionic Polymers, **1**, Applied Science Publishers, New York, 53 (1983).

(4) M. R. Tant and G. L Wilkes, J. Macromol. Sci. - Rev. Macromol. Chem. Phys., **C28**, 1 (1988).

(5) J.J. Fitzgerald and R. A. Weiss, J. Macromol. Sci. - Rev. Macromol. Chem. Phys., **C28**, 99 (1988).

(6) A. Eisenberg, Macromolecules, **3**, 147 (1970).

(7) K. A. Mauritz, J. Macromol. Sci. - Rev. Macromol. Chem. Phys., **C28**, 65 (1988).

(8) D. J. Yarusso and S. L. Cooper, Macromolecules, **16**, 1871 (1983).

(9) C. E. Williams, T. P. Russell, R. Jérôme and J. Horrion, Macromolecules, **19**, 2877 (1986).

(10) C. E. Williams, in Structure and Properties of Ionomers, eds. M. Pineri and A. Eisenberg, NATO ASI Series, **C198**, 163 (1987).

(11) C. E. Williams, in Contemporary Topics in Polymer Science, ed. W. Culbertson **6**, in press.

(12) B. Hird and A. Eisenberg, manuscript submitted to J. Polym. Sci., Polym. Phys. Ed..

(13) W. J. MacKnight, W. P. Taggart and R. S. Stein, J. Polym. Sci., Polym. Symp. Ed., **45**, 113 (1974).

(14) D. G. Peiffer, R. A. Weiss and R. D. Lundberg, J. Polym. Sci., Polym. Phys. Ed., **20**, 1503 (1982).

(15) B. Chu, D.-Q. Wu, W. J. MacKnight, C. Wu, J. C. Phillips, A. LeGrand, C. W. Lantman and R. D. Lundberg, Macromolecules, **21**, 523 (1988).

(16) D. Wollmann and A. Eisenberg, in Contemporary Topics in Polymer Science, ed. W. Culbertson, **6**, in press.

(17) K. Sanui and W. J. MacKnight, Br. Polym. J., **8**, 22 (1976).

(18) S. Gauthier, D. Duchesne and A. Eisenberg, Macromolecules, **20**, 753 (1987).

(19) A. Eisenberg, in Contemporary Topics in Polymer Science, **3**, 231 (1979).

(20) D. Duchesne and A. Eisenberg, manuscript in preparation; D. Duchesne, Ph. D. thesis, McGill University (1985).

(21) H. S. Makowski and R. D. Lundberg, Ions in Polymers, Advances in Chemistry Series **187**, 37 (1980).

(22) R. D. Lundberg, H. S. Makowski and L. Westerman, Ions in Polymers, Advances in Chemistry Series **187**, 67 (1980).

(23) C. G. Bazuin and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **24**, 1137 (1986).

(24) H. Matsuura and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **14**, 1201 (1976).

(25) R. A. Weiss, P. K. Agarwal and R. D. Lundberg, J. Appl. Polym. Sci., **29**, 755 (1984).

(26) P. Smith and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **26**, 569 (1988).

(27) C. G. Bazuin and S. Villeneuve, Polym. Mat. Sci. Eng., **58**, 1069 (1988).

(28) M. Gauthier and A. Eisenberg, submitted to Macromolecules.

(29) M. Gauthier and A. Eisenberg, submitted to Macromolecules.

(30) D. Wollmann, S. Gauthier and A. Eisenberg, Polym. Eng. Sci., **26**, 1451 (1986).

(31) It should be noted that in the Friedel-Crafts alkylation of aromatic rings, multiply substituted products are formed and, indeed, are favoured in heterogeneous reaction mixtures. In the alkylation procedure used in this study, the reaction mixture was homogeneous, and the monoalkylated product was favoured, although clearly some of the dialkylated material would have also been formed.

(32) J. March, Advanced Organic Chemistry, Second Edition, McGraw-Hill (1977), p. 486.

(33) A. Neppel, I. S. Butler and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **17**, 2145 (1979).

(34) A. Molnár, private communication.

(35) M. C. O. Chang, D. A. Thomas and L. H. Sperling, J. Appl. Polym. Sci., **34**, 409 (1987).

(36) M. C. O. Chang, D. A. Thomas and L. H. Sperling, J. Polym. Sci., Polym. Phys. Ed., **26**, 1627 (1988).

(37) A. T. Granger, B. Wang, S. Krause and L. J. Fetters, Multicomponent Polymer Materials, Advances in Chemistry Series, **211**, 127 (1986).

# Chapter 5

# Small Angle X-Ray Scattering in "Bottlebrush" Ionomers

## 5.1 Abstract

The dependence of the small angle X-ray scattering profiles of styrene (A)-N-alkyl-4-vinylpyridinium iodide (B) ABA triblock ionomers was studied as a function of the different block and quaternising chain lengths. Two distinct types of profiles were observed: either a broad, single peak or a narrowed peak with higher order maxima. It was possible to relate the differences in the morphologies as detected by SAXS to the changes in midblock, ionic end block or iodoalkane lengths. For example, ionomers with long midblocks were unable to rearrange to the more highly ordered morphology, while the quaternisation of the vinylpyridine end blocks with long n-iodoalkanes encouraged such reorganisation.

## 5.2 Introduction

Phase separation occurs frequently in polymeric materials. Two classes of polymers which are of great interest, because of their phase behaviour, are block copolymers and ionomers. Most block copolymers are micro-phase separated because mixing two dissimilar polymer chains is frequently an unfavourable process[1,2]. Ionomers, originally defined as random copolymers containing small amounts of an ionic comonomer[3], often phase separate because of the strong driving force for the aggregation of ions in nonpolar media.

Recently, the field of block ionomers has received increasing attention[4]. Block ionomers are hybrids of block copolymers and random ionomers. They are materials consisting of a long, nonionic polymer chain segment capped at either one end (AB) or at both ends (ABA) by a short ionic block. The AB materials are of considerable interest in solution, because of their micellar nature[4]. The ABA materials are most interesting in the solid state, where they behave as if they were cross-linked.

The dynamic mechanical properties of the ABA block copolymers have been studied for a number of systems[5,6,7]. More recently, morphological studies have examined the phase separated domains in these materials[8,9].

The results of recent small angle X-ray scattering (SAXS) experiments on an ABA block ionomer, consisting of styrene (B) and N-methyl vinylpyridinium iodide (A), yielded the following conclusions[8]. Phase separation takes place in block ionomers even with very short end block lengths. There are more chains emanating from the ionic domains than are observed from aggregates of similar size in nonionic block copolymers. Finally the sizes of the aggregates are considerably larger than the multiplets and clusters believed to be present in random ionomers.

In this publication, we wish to report a preliminary exploration of the morphologies of a related series of block ionomers, in which the same parent polymers have been quaternised with iodoalkanes ranging in length from two to ten carbons. We have called these samples "bottlebrush" ionomers because of their architecture. A single chain can be envisaged as consisting of a long, thin styrene midblock, capped at each end by a short, fuzzy end block, composed of quaternised vinylpyridinium units as depicted in Fig. 5.1.

The results from the small angle X-ray scattering indicate that, in the case of these block ionomers, even when the materials have the same sample history, major differences can be observed in the SAXS profiles of the various materials, reflecting differences in the morphologies. In this preliminary investigation, we have not attempted to give a detailed description of either morphology but, rather, to relate the presence of a given structure pattern to the molecular characteristics of the materials. These different scattering profiles are not observed in the ionomers quaternised with

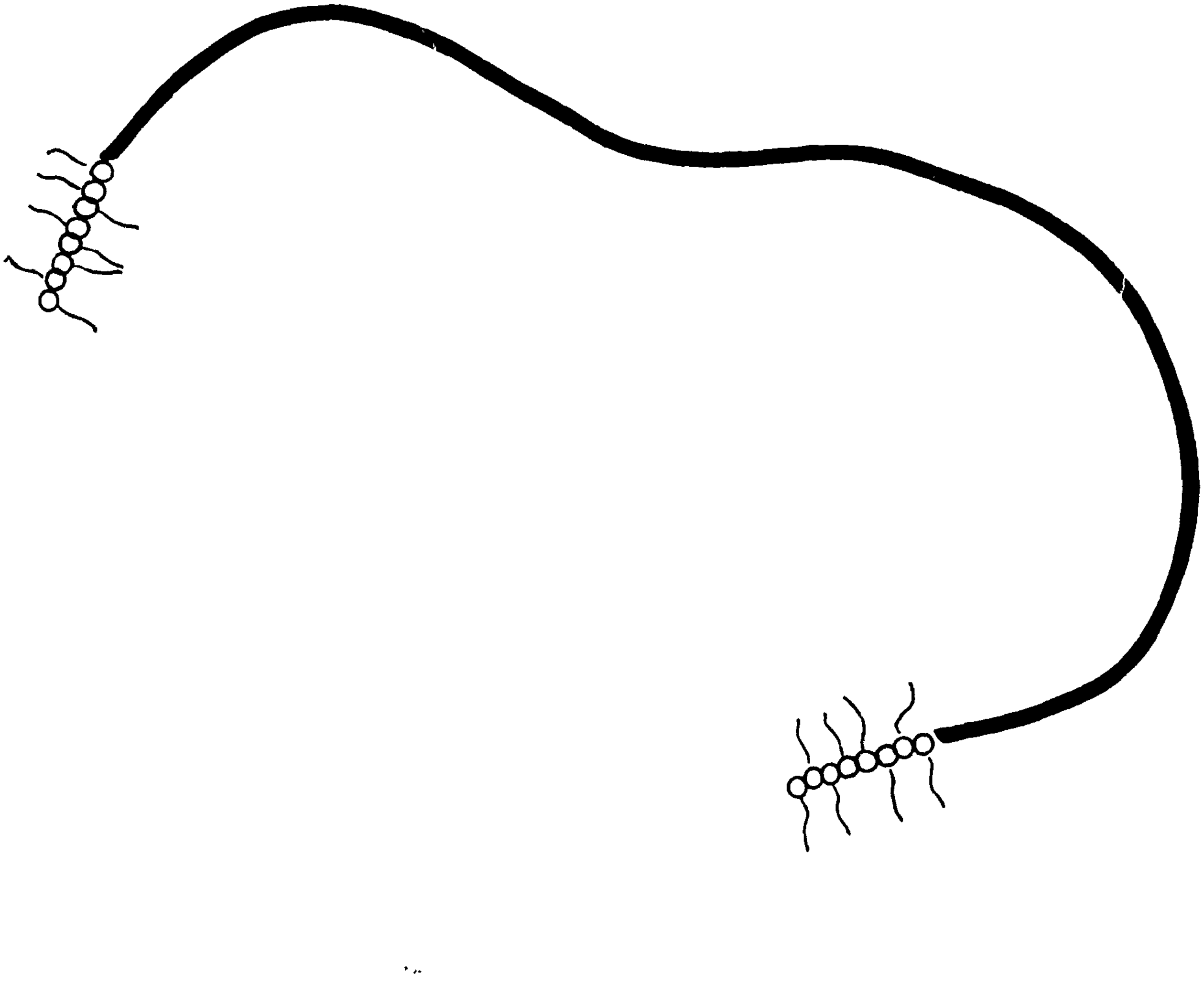

Fig. 5.1: A "bottlebrush" ionomer.

iodomethane and having the same sample treatment[8].

## 5.3 Experimental and Results

Samples of ABA block copolymers (A = 4-vinylpyridinium, B = styrene) were prepared *via* sequential anionic polymerisation[5] in three series of different styrene midblock lengths, containing 240, 590 and 1000 units. Different 4-vinylpyridine end blocks, of approximately 10, 20 and 50 units, were investigated. The styrene midblock length was determined by gel permeation chromatography. The 4-vinylpyridine content was analysed using a calibration curve based on infrared peaks[5]. The polymers were quaternised *in situ*, as previously described[5,8], in a 4/1 (v/v) solution of absolute ethanol and the freshly distilled iodoalkane. In this study, the quaternising agents ranged from iodoethane to iodododecane. In a typical quaternisation, a sample weighing approximately 1 g was immersed in 50 mL of this solution.

After refluxing under nitrogen for one week, the samples were removed from the quaternising solution. They were then soaked briefly in fresh ethanol and dried overnight at room temperature in vacuum. The ionomers were dried further at 60 °C in vacuum for at least two days. Subsequently, samples were moulded at about 130 °C and 1000 GPa pressure, yielding disks of typical dimensions 12 mm diameter and 0,8 mm thickness.

The SAXS studies were performed using synchrotron radiation on the D-22 beam line at LURE. This line is characterised by moderate flux and high resolution. The line and the experimental conditions used have been described in detail elsewhere[8], but are summarised briefly below for convenience.

The samples were run under vacuum and the experimental conditions were chosen so that data were obtained in a q-range from 0,004 to 0,15 $Å^{-1}$

($q = 4\Pi/\lambda \sin \Theta/2$ with $\Theta$ the observation angle and $\lambda$ the wavelength, equal to 1,46 Å). Typically, data were collected for 1200 s and standard corrections were applied to all scattering data.

All samples showed an intense peak in their SAXS profile ascribed to the phase separation between the ionic N-alkyl-4-vinylpyridinium iodide blocks and the styrene. From these, the $q_{max}$ and the half width for each ionomer sample were determined.

Two general profile types were observed; either, as in the previous study, a broad and asymmetric peak (Fig. 5.2) or a much narrower peak with smaller higher order peaks (Fig. 5.3). These profiles evidently result from different morphologies.

The different block ionomers studied and the type of profile they displayed are listed in Table 5.1. It is clear from this table that these systems are on the edge of organising into either one of two morphologies, thus anomalies, such as are to be found in the 49-240-49-BuI sample, are not unexpected. These results differ from those previously obtained on the samples quaternised with iodomethane which showed the morphology associated with the broad peaks, a structure similar to that observed in the nonneutralised samples[8].

## 5.4 Discussion

The profile peaks for these ionomers are ascribed to an interparticle correlation factor between pseudospherical domains and not to a spherical form factor. The same interpretation was used for the materials previously studied, because attribution of the peak to a form factor led to impossibly large radii[8].

### 5.4.1 RADIUS OF THE SCATTERING CENTRES

Additional insight concerning the phase separation in these materials may be obtained from an examination of the phase separated domains. Thus, the sizes of the aggregates were calculated from the values of $q_{max}$ using space-filling arguments, as

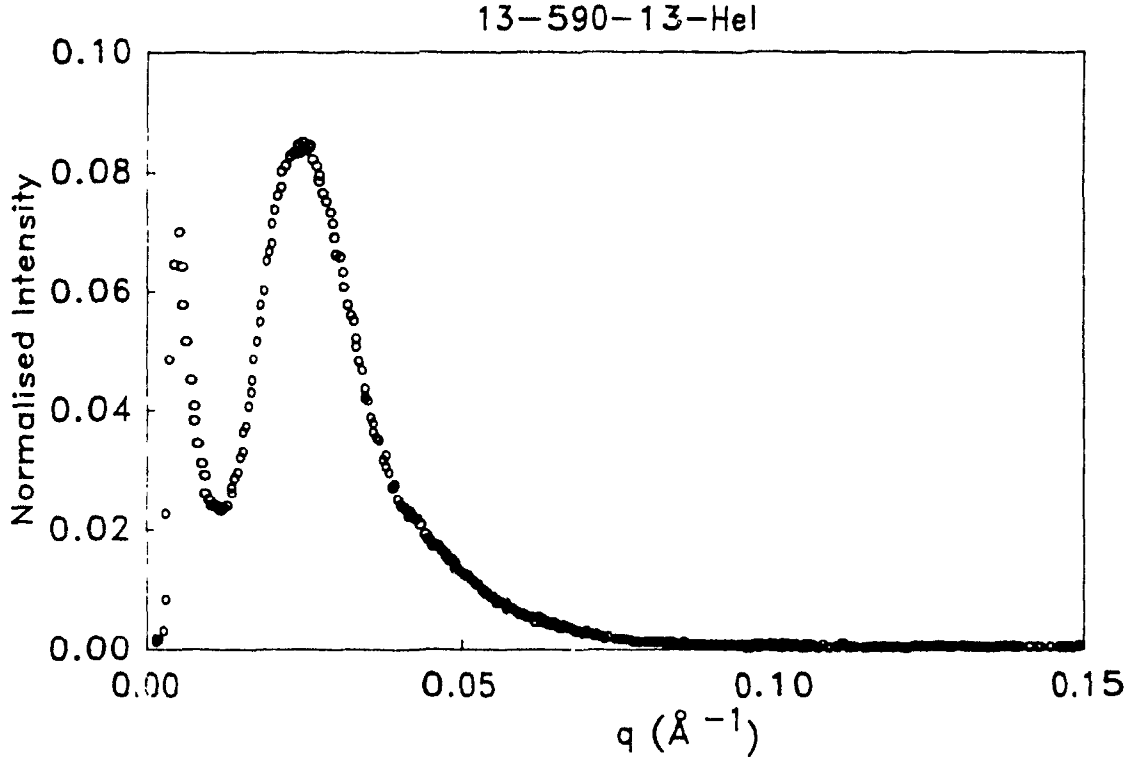

Fig. 5.2: A typical broad small angle x-ray scattering profile.

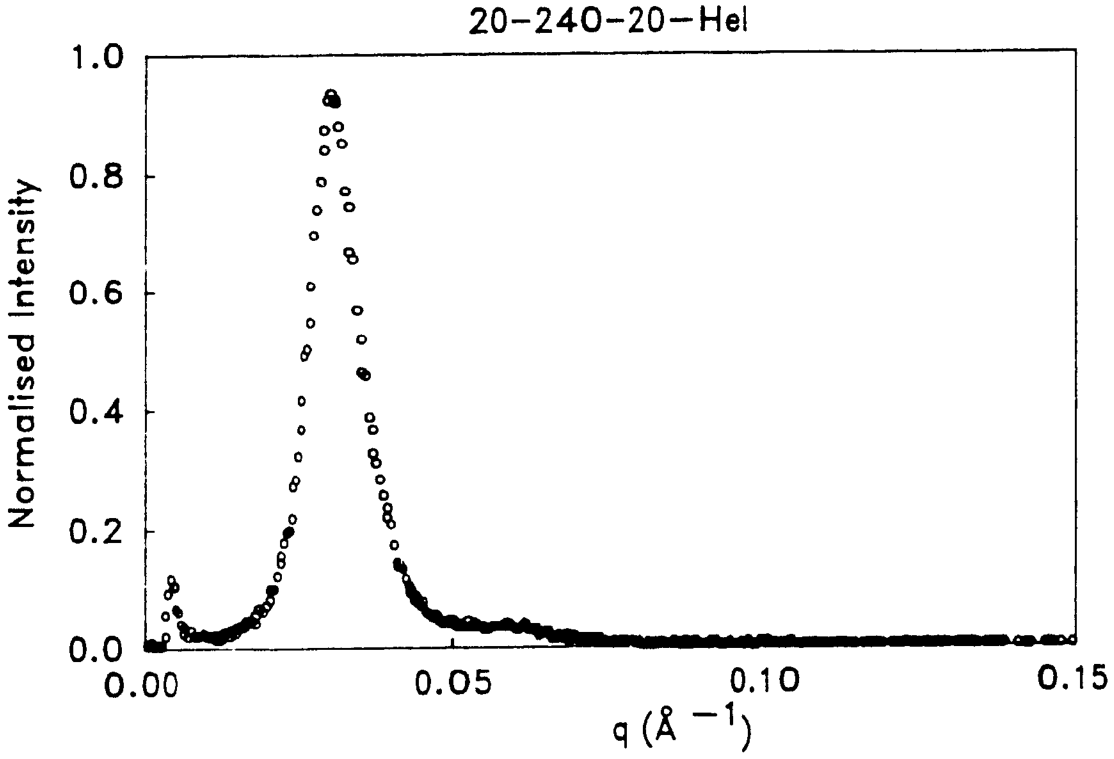

Fig. 5.3: A typical narrowed small angle x-ray scattering profile.

# Table 5.1

## Summary of the SAXS Profiles for the Different "Bottlebrush" Ionomers

| | | Midblock | | |
|---|---|---|---|---|
| | | 240 | 590 | 1000 |
| End Block | 10 | Et: **broad**<br>Bu: **broad & shoulder**<br>De: narrow & 2nd | Et: **broad & shoulder**<br>Bu: **very broad** | **broad** |
| | 20 | Et: narrow & shoulder<br>Bu: narrow & 2nd<br>He: narrow & 2nd | Et: **broad**<br>Bu: **medium broad**<br>He: **broad** | **broad** |
| | 50 | Et: narrow & 2nd<br>Bu: **broad**<br>De: narrow | Et: in beam stop | **broad** |

in the case of the styrene-N-methyl-4-vinylpyridinium iodide ABA ionomers[8]. It is assumed here that the domains are spherical for both patterns. This assumption appeared to be a valid means of treating the data in the case of the broad diffraction patterns, because in the previous study, the radii of the scattering centres increased with larger block lengths. However, while there is no reason to treat the data from the narrowed SAXS peaks in the same manner, for the sake of comparison, the same calculations were performed.

In order to calculate the radius of the scattering centres, an approximation of the volume fraction of the material due to the quaternised vinylpyridinium units had to be made. The phase separated domains in all of these systems were assumed to be spherical, without reference to their SAXS profile shapes. This assumption was based on the relative amounts of the two blocks present. Furthermore, it was assumed that the two types of units act independantly and are completely phase separated. Thus, it was possible to use the densities of the homopolymers. The volume fraction of the quaternised vinylpyridinium units was calculated from the known unit volume of styrene[8] and a unit volume estimated for the quaternised vinylpyridinium moieties. In the absence of literature values for these unit volumes, they were estimated from N-methyl-4-vinylpyridinium iodide (VP-MeI), 1.48 g/mL[8], as follows: N-ethyl-4-vinylpyridinium iodide (VP-EtI), 1.43 g/mL, N-butyl-4-vinylpyridinium iodide (VP-BuI), 1.40 g/mL, N-hexyl-4-vinylpyridinium iodide (VP-HeI), 1.37 g/mL, and N-decyl-4-vinylpyridnium iodide (VP-DeI), 1.30 g/mL.

The radii of the scattering centres were calculated based on space-filling models with different symmetry, namely simple cubic (sc), body-centred cubic (bcc) and face-centred cubic (fcc) lattices. The results of these calculations may be found in Table 5.2.

## Table 5.2
## Values of $Q_{max}$ and Radii Calculated for Different Macrolattices*

| Polymer | Quat. Agent | $Vol_{frac}$ VP | $q_{max}$ (Å$^{-1}$) | d (Å) | $R_{sc}$ (Å) | $R_{bcc}$ (Å) | $R_{fcc}$ (Å) |
|---|---|---|---|---|---|---|---|
| 12-240-12 | EtI | 0,155 | 0,0308 | 200 | 70 | 80 | 70 |
| | BuI | 0,172 | 0,0303 | 210 | 70 | 80 | 80 |
| | DeI | 0,224 | 0,0384<br>0,0744 | 160 | (60) | (60) | (60) |
| 20-240-20 | EtI | 0,235 | 0,0227<br>0,0447 | 280 | (110) | (120) | (120) |
| | BuI | 0,258 | 0,0271<br>0,0504 | 230 | (90) | (100) | (100) |
| | HeI | 0,280 | 0,0309<br>0,0599 | 200 | (80) | (90) | (90) |
| 49-240-49 | EtI | 0,429 | 0,0246 | 260 | (120) | (130) | (130) |
| | BuI | 0,459 | 0,0239 | 260 | 130 | 140 | 140 |
| | DeI | 0,542 | 0,0384 | 160 | (80) | (90) | (90) |
| 8-590-8 | EtI | 0,0475 | 0,0284 | 220 | 50 | 50 | 50 |
| | BuI | 0,0534 | 0,0271 | 230 | 50 | 60 | 60 |
| 13-590-13 | EtI | 0,0750 | 0,0214 | 290 | 80 | 90 | 80 |
| | BuI | 0,0840 | 0,0164 | 380 | 100 | 120 | 110 |
| | HeI | 0,0933 | 0,0252 | 240 | 70 | 80 | 80 |

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* The values in parentheses are those calculated for the materials whose SAXS profile showed two peaks.

### 5.4.2 SAXS PROFILES AND ORDER IN THE MATERIAL

The width of the SAXS peak and the presence of higher order peaks are known to be indications of greater uniformity of size and of regularity in the ordering of the scattering domains in a sample. The difference in position of the diffraction peaks shows a change in the symmetry of the spatial arrangement of the ionic domains. Thus, it appears that some of the materials were more highly ordered than others with the same sample history.

Results from small angle neutron scattering show that before these materials are quaternised, they are phase separated[8]. The nonionic polymers exhibit a single, broad peak in their profiles. Because they are in the solid state during quaternisation, the polymers are only swollen. Thus, rearrangement resulting from the aggregation of the ionic domains cannot take place easily and the morphology of the ionomer is expected to resemble that of the precursor. This is the case for the samples quaternised with iodomethane[8].

Several trends emerge from an examination of the profiles for the different systems in Table 5.1. The samples containing the larger midblocks all show a single, broad peak. Only the materials with a midblock of 240 styrene units show higher order peaks in the SAXS profile. Additionally, there also seems to be an effect due to the size of the end blocks. For example, in the series of 240 midblock material quaternised with iodoethane, the SAXS profiles change progressively from the broad type to the narrow one as the length of the vinylpyridinium end blocks increase. As well, the samples quaternised with longer chains tend to have small angle x-ray scattering profiles in which the narrower peaks are observed. Thus, there are probably three parameters which affect the phase separation in these materials. These are the length of the nonionic block, the length of the ionic block and the length of the quaternising agent. Each of them has a different influence on the relative time scales involved in the kinetics of the reorganisation process. It should be noted that any change in morphology during this reorganisation in the solid state requires a chain end to be detached from the ionic domains and dragged through a very incompatible medium.

The effect of the length of the quaternising agent may be understood in terms of the vapour pressures of the iodoalkanes. The longer the iodoalkane is, the higher its boiling temperature. Therefore, in the removal of solvents by evaporation, the ethanol is removed much earlier. The ionic domains are thus swollen with the iodoalkane for longer periods of time, thus allowing the domains more time to reorganise.

However, not all the materials were able to rearrange, despite the additional swelling by the quaternising agents. For an explanation of this behaviour, the differences in the polymer samples must be considered.

The midblock length governs the diffusion time of each chain through the others (because the end blocks are small, their effect is negligible). Thus, the samples with larger midblocks are prevented from reordering their domains in the available time.

The effects of the ionic blocks on the reorganisation process are quite complex. However, the vinylpyridine segments are of low molecular weight, and it is likely that secondary effects are of greater importance than rheological constraints. Thus, because a longer block will attract more of the iodoalkane, it should be plasticised for a longer time, allowing it more time to rearrange. It is evident from the table that the kinetic effects play an important role in the pattern selection, but that the influence of the different parameters is very complex, so that there is no clear-cut prediction of what these systems will do.

The variation in $q_{max}$ for the different quaternising agents is evident in Table 5.2.

It is clear that at least two different types of behaviour are observed in these samples. The majority of the peaks exhibiting a broad SAXS peak show a decrease in $q_{max}$ with increasing iodoalkane length. This indicates that the distance between the scattering centres is increasing with the quaternising agent, due to an increase in the ionic domain size. On the other hand, the $q_{max}$ of the samples whose SAXS profiles showed the narrower peak and higher order peaks increases with the chain length, an indication that the morphology of these samples is quite different.

The ratios of these narrower SAXS peaks to their higher order peaks are presented in Table 5.3. It is interesting to note that the ratios all approach the value of two, which is typical of lamellar structures, rather than close-packed spheres.

Recent studies[10] have explored the morphologies found in styrene-co-N-methyl-4-vinylpyridinium iodide materials which have been cast from dimethylformamide (DMF). This sample preparation has produced materials in which the SAXS peak is generally narrowed and accompanied by higher order peaks. The effects of solvent casting on the morphologies of the block ionomers described in this publication are currently being studied.

## 5.5 Conclusions

In ABA block ionomers of styrene-co-N-alkyl-4-vinylpyridinium iodide, the morphologies observed by SAXS are dependent on several different parameters. When the materials have identical sample histories, the sizes of all the components, i.e. the midblock, the end block and the quaternising agent, all influence the morphology. Thus, an increased styrene midblock length, shortened vinylpyridinium end block or quaternisation of the ionomer with a short, volatile iodoalkane, leads to materials which exhibit SAXS profiles with broad peaks. These materials are thought to contain deformed spherical domains on a cubic lattice. Conversely, it is

# Table 5.3

## Ratio of Peak Positions

| Sample | $q_{max(2)}/q_{max(1)}$ |
|---|---|
| 12-240-12-DeI | 1.94 |
| 20-240-20-EtI | 1.97 |
| 20-240-20-BuI | 1.86 |
| 20-240-20-HeI | 1.94 |

For reference[11]:

simple cubic: 1.41
face-centred cubic: 1.15
body-centred cubic: 1.41
hexagonally packed cylinders: 1.73
lamellae: 2.00

possible to obtain materials whose SAXS profiles show peaks that are much narrower as well as possessing higher order peaks, when the midblock is short, and the end blocks and the quaternising agents are long. The morphology of these samples is not known. Apparently, these materials are on the verge of reorganisation and it takes very little to influence them to produce either of the two morphologies observed in the SAXS studies. It is possible that other parameters, for example the moulding and annealing temperatures, or the casting solvent, would have an effect on the morphologies as well. These parameters will be investigated in other studies.

### 5.6 Acknowledgements

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### 5.7 References

(1)D. J. Meier, NATO ASI Series, Series E, **89**, 173 (1985).

(2)S. Krause and M. Iskandar, in Multiphase Polymers, S. L. Cooper, ed., ACS Symposium Series, **176**, 205 (1979).

(3)R. W. Rees and D. J. Vaughan, ACS, Div. Polym. Chem., Polym. Prepr., **6**, 287 (1965).

(4)J. Selb and Y. Gallot, in Developments in Block Copolymers, **2**, I. Goodman, ed., Elsevier Applied Scientific Publishers, 27 (1985).

(5)S. Gauthier and A. Eisenberg, Macromolecules, **20**, 760 (1987).

(6)R. D. Allen, I. Yilgor and J. E. McGrath, in Coulombic Interactions in Macromolecular Systems, ed. A. Eisenberg and F. E. Bailey, ACS Symposium Series, **302**, 79 (1986).

(7)C. D. DePorter, T. E. Long, L. N. Venkateshwaran, G. L. Wilkes and J. E. McGrath, ACS, Div. Polym. Chem., Polym. Prepr., **29**(1), 343 (1988).

(8)J.-P. Gouin, C. E. Williams and A. Eisenberg, submitted to Macromolecules.

(9)C. D. DePorter, L. N. Venkateshwaran, G. A. York, G. L. Wilkes and J. E. McGrath, ACS, Div. Polym. Chem., Polym. Prepr., **30**(1), 201 (1989).

(10)J.-P. Gouin, C. E. Williams and A. Eisenberg, mansucript in preparation.

(11)R. Richards and J. L. Thomason, Polymer, **22**, 581 (1981).

# Chapter 6

## Anomalous Glass Transitions in Styrene Block Ionomers

### 6.1 Abstract

Dynamic mechanical studies have shown that the glass transition temperature of the styrene matrix in styrene (A)-N-alkyl-4-vinylpyridinium iodide (B) ABA triblock ionomers is depressed relative to the $T_g$ of the pure styrene homopolymer. This unexpected reduction in the glass transition temperature in indepenent of both the vinylpyridine content and the iodoalkane chain length. It is proposed that packing inefficiency of the styrene chains around the ionic domains is responsible for the lowered $T_g$.

### 6.2 Introduction

Many studies have shown that phase separated block copolymers exhibit two glass transitions, one for each phase[1,2]. In this respect, block copolymers are often discussed in terms of their similarities to blends of two homopolymers. Thus, any shifts in the glass transition temperatures towards each other are generally taken to be evidence of enhanced miscibility.

However, in some block copolymers, for example styrene-butadiene and styrene-dimethylsiloxane di- and triblock materials, changes in the glass transition temperatures of both phases have been observed which have been attributed to entirely different causes[3,4,5]. Most pronounced was the reduction of the $T_g$ of the high temperature phase, which has been interpreted in terms of a thermal stress effect, caused by the extra free volume imposed on the hard phase above the glass transition of the low temperature continuous phase. In addition, however, some of these materials exhibited a substantial reduction of the lower glass transition temperature[5], while in others a slight increase in the $T_g$ of the soft phase was often observed[4,5]. In another study, the glass transition temperature of the soft phase was depressed in ABA triblock copolymers of butadiene (B) and aramid (A)[6]. In all of these investigations, the changes in the glass transition temperatures of the low temperature phases have been discussed in terms of thermal stresses present between the soft and hard phases.

In this paper, we wish to report one aspect of a dynamic mechanical study on a series of materials, *viz.* ABA block ionomers of styrene (B) and quaternized N-alkyl-4-vinylpyridinium iodide (A). These blocks are expected to be immiscible because of their very different natures, i.e. the styrene midblock is nonionic, while the vinylpyridinium end block is ionic. Thus, it is unlikely that any shift in the glass transition temperatures of the two phases could be ascribed to miscibility. The vinylpyridine contents of these materials range from 0 to *ca.* 7 mole %. The glass transition temperatures of the ionic end blocks are not known, but they are expected to be much higher than that of the high molecular weight (*ca.* $10^5$ g $\text{mol}^{-1}$) styrene midblock. Therefore, this is a system in which the low temperature phase is the major component; thus an increase in the $T_g$ of the styrene phase is anticipated. However, the glass transition temperature of the styrene matrix is depressed markedly with respect to the $T_g$ observed for a styrene homopolymer of the same molecular weight. We describe this phenomenon and offer a tentative explanation different from that proposed in the previous report on an anomalous reduction in the glass transition temperature of a soft phase matrix material[6].

The general mechanical behavior of these materials will be discussed more fully in a separate publication dealing with the mechanical behavior of plasticized styrene-vinylpyridinium block ionomers[7].

### 6.3 Experimental and Results

A series of styrene (B)-co-4-vinylpyridine (A) ABA block copolymers was prepared *via* sequential anionic polymerization, as described in detail in a separate publication[8]. Materials prepared using this technique are characterized by a common midblock (styrene) length and varying end block (vinylpyridine) lengths. The molecular weight of the styrene midblock was approximately 100,000 (*ca.* 1000 units) as determined by gel permeation chromatography of the midblock homopolymer and the vinylpyridine content ranged from 0 to 6.9 mole % (0 to 35 vinylpyridine units per block) as determined from an infrared calibration curve[8]. The materials were quaternized in a slightly swollen state with ethanol containing one of a variety of different n-iodoalkanes, ranging from methyl (1) to decyl (10), as described in another publication[9]. The ionomers were subsequently dried thoroughly and remolded at temperatures around 130-50 °C and 2 GPa, to yield blocks of approximate dimensions 12 x 36 x 2 mm. Two styrene homopolymer samples were subjected to the same quaternization method, and dried, one below the glass transition temperature of the polymer and the other above $T_g$. Finally, they were remolded under the conditions used for the ionomers. A sample of the nonionic styrene-vinylpyridine precursor was swollen with absolute ethanol as in the quaternization experiments, then dried and remolded in the same manner as the ionomers.

These molded samples were used in dynamic mechanical experiments performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyser in a dual cantilever bending mode. The samples were heated at 0.5 °C $\text{min}^{-1}$ under a light flow of nitrogen. Data were collected concurrently for up to five different frequencies. The glass transition temperatures for the different samples were determined from an analysis of the peaks in the plots of tan $\delta$ against temperature. The peaks are very narrow, thus the error in the determination of the $T_g$ was ± 0.5 °C from successive analyses. The values of the loss tangent maxima at 1 Hz for a number of samples are listed in Table 6.1 and representative loss tangent curves are plotted in Figure 6.1

The $T_g$'s of the polystyrene samples used in this study are insensitive to sample history, with an average $T_g$ of 116.1 ± 0.6 °C (average ± 2σ). The glass transition temperature of the dried unquaternized block copolymer lies in this range. In contrast, the unquaternized material which had been swollen with ethanol and then dried, has a lower $T_g$. As there was no evidence for solvent evaporation during the DMTA run, i.e. no bubbles were observed in the sample after the dynamic mechanical experiment, the existence of hydrogen-bonded pyridine is suspected. The average $T_g$ of the 16 ionomers used in this study was calculated to be 107 ± 17 °C. There is no apparent systematic variation of the glass transition temperature either with ion content or with iodoalkane length, in contrast to the results from previous studies on random styrene-co-N-alkyl-4-vinylpyridinium iodide ionomers[10].

These glass transition temperature data were first treated statistically. The $T_g$'s determined for the polystyrene and the unquaternized block copolymer, representing the glass transition temperature of the unperturbed styrene matrix, were subjected to the Q test[11]. Thus, the glass transition temperature determined for the ethanol swollen copolymer was rejected at the 90 % confidence limit. This rejection can be justified on the basis of the pyridine-ethanol complex suggested above, the presence of which could reduce the glass transition temperature of the pyridine phase by plasticization and thus lower the $T_g$ of the styrene matrix through the "soft wall" effect seen in other studies[3]. The average $T_g$ of the remaining materials was then calculated to be 116.2 ± 0.6 °C. The same statistical Q test was also applied to the glass transition temperatures of the ionomers, resulting in the rejection of one value, the $T_g$ of Sty-0.013VP(4-)-DeI (80.6 °C). The average glass transition temperature

## Table 6.1

## Styrene-Vinylpyridine Triblock Glass Transition Temperatures

| Polymer[+] |  | $T_g$ (±0.5 °C) |
|---|---|---|
| Polystyrene | (from bottle) | 116.2 |
| " | (dried) | 115.9 |
| " | (mock quaternization #1)[*] | 115.8 |
| " | (mock quaternization #2)[**] | 116.4 |
| Sty-0.069VP(4-) | (dried) | 116.5 |
| Sty-0.069VP(4-) | (swollen in ethanol) | 112.1 |
| Sty-0.013VP(4-)-MeI |  | 107.1 |
| Sty-0.013VP(4-)-DeI |  | 110.1 |
| " |  | 113.2 |
| " |  | 80.6 |
| Sty-0.033VP(4-)-MeI |  | 110.9 |
| " |  | 104.4 |
| Sty-0.033VP(4-)-DeI |  | 97.5 |
| Sty-0.045VP(4-)-MeI |  | 109.2 |
| Sty-0.045VP(4-)-EtI |  | 108.1 |
| Sty-0.045VP(4-)-DeI |  | 109.3 |
| " |  | 101.8 |
| " |  | 110.1 |
| Sty-0.069VP(4-)-MeI |  | 108.5 |
| " |  | 115.5 |
| Sty-0.069VP(4-)-DeI |  | 111.9 |
| " |  | 115.7 |

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+MeI: Iodomethane, EtI: iodoethane and DeI: iodododecane.

*Dried over ethanol (*ca.* 78 °C).

**Dried over cyclohexanone (*ca.* 132 °C).

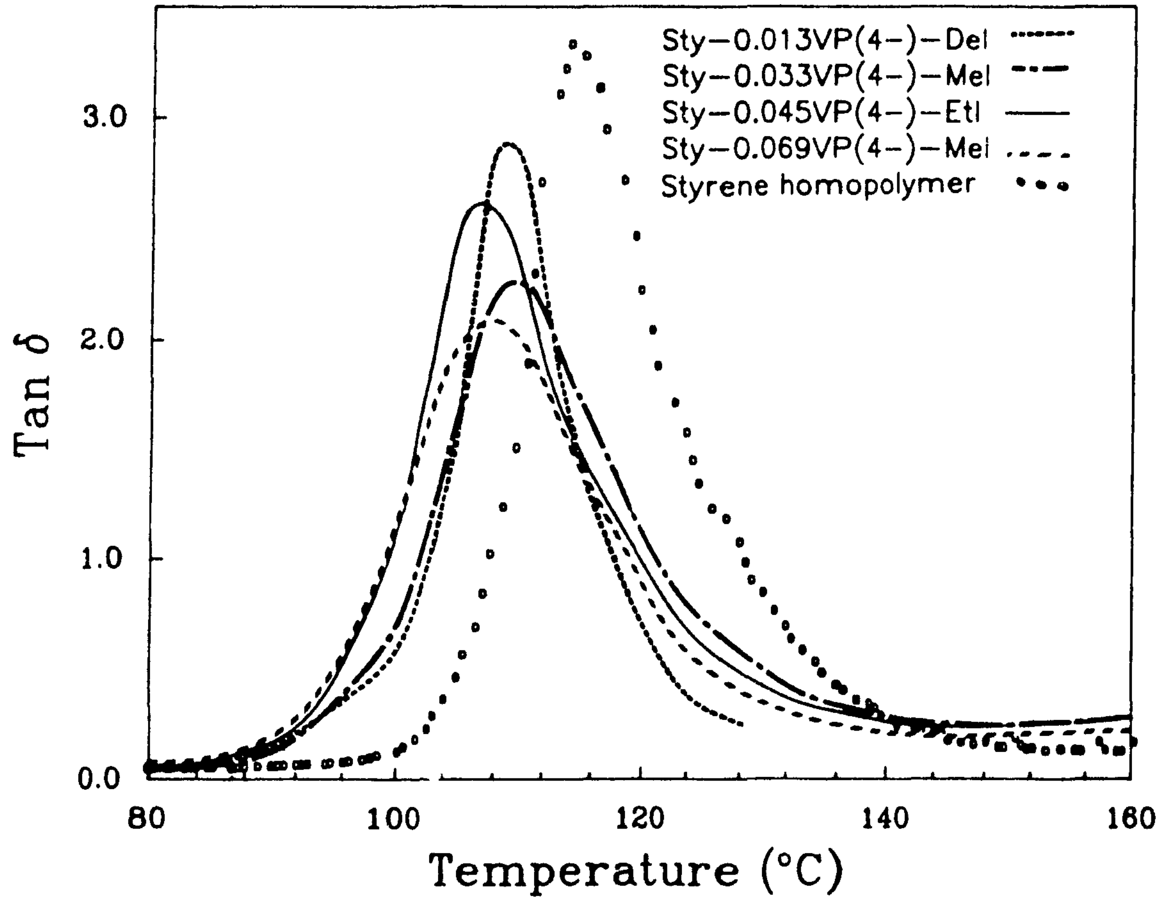

Fig. 6.1: Representative loss tangent-temperature curves at 1 Hz for styrene (A)-N-alkyl-4-vinylpyridinium iodide (B) ABA triblock ionomers.

of the remaining samples is then 109 ± 10 °C. The average $T_g$ of the nonionic materials thus lies within the range of the ionic systems at the 95% confidence level, however an analysis of the averages and variances of these samples by the Welch test indicates that the difference between the two $T_g$'s is too great for them to have come from the same population[12]. Therefore, the glass transition temperatures of the matrix of ionic systems have been significantly depressed with respect to the $T_g$'s of the nonionic materials.

In a second approach to handling the data, the statistical analysis was performed after discarding certain suspicious experimental data. First, it is apparent that the three samples with the most depressed glass transition temperatures have all been quaternized with iododecane and, therefore, it is believed that these materials could have been plasticized with residual quaternizing agent. In addition, there are two samples with much higher glass transition temperatures. Initially, it was suspected that in these two experiments the ionic blocks had perhaps dequaternized, however, no evidence for this was observed in the infrared spectra of these samples taken after the run. This anomalous behavior occurs only for the materials of highest vinylpyridine block length, and thus perhaps in the quaternization reaction, the long length of the end blocks precludes facile rearrangement from the unquaternized to the quaternized morphologies, an effect which will be discussed in the following section. When the values of the glass transition temperatures for these five samples are discounted, an average $T_g$ of 109 ± 4 °C results. As expected, results from the Welch test again indicate that, statistically, the matrix glass transition temperatures of the nonionic and ionic materials are different.

### 6.4 Discussion

It is important to establish that the observed glass transition temperature for these materials is that of the styrene matrix. There are a number of reasons why this should be so. Results from small angle X-ray scattering[13] and calculations of the $\chi$ parameter[14] indicate that even these very short end blocks are phase separated from the matrix, therefore two glass transitions should be observed. It is very unlikely that the two glass transitions superpose. As shown in Figure 6.1, the temperature range over which the transition occurs is quite narrow. If there were two $T_g$'s superposed, then it is extremely unlikely that the glass transition temperature of the ionic domains would not vary in some consistent manner, given the range of ionic block lengths and quaternizing agents, which should alter the shape of the loss tangent peak. As only one glass transition is observed in all specimens over this range and the peak shape is unchanged, the likelihood of an identity of glass transition temperatures is slim. The relative invariance of the positions of the loss tangent maxima suggests that this is the styrene midblock glass transition, and indeed, the observed glass transition is very close to that of polystyrene. Finally, it should be recalled that the $T_g$ of poly(4 vinylpyridine) is *ca.* 140 °C[15], and that ionization with the quaternizing agents used in this study has been seen to raise the glass transition temperatures of all similar random ionomers that have been explored[10].

In the majority of other "soft matrix" studies on block copolymers, the glass transition temperature of the matrix has increased[4,5]. This has been attributed to thermal stresses[4] and can be described in the following manner. One cools a system consisting of high $T_g$ inclusions in a low $T_g$ matrix from some intermediate temperature; the expansion coefficient of the soft phase is much greater than that of the inclusions, which are below their $T_g$. Compressive stresses are generated on the soft phase in the immediate vicinity of the hard inclusions. The free volume decreases and thus the glass transition temperature of the matrix increases. Surprisingly, identical arguments have been used to explain the *decrease* in the $T_g$ of the matrix in the other study where anomalous behavior was observed[6].

We propose an alternative explanation for the depression of the glass transition temperatures in our materials. Our hypothesis is concerned with the packing efficiencies at the phase boundaries and may be applicable to other systems as well. First, it is important to recall that the block ionomers show clear phase separation even at the shortest end block lengths[13]. Results from SAXS indicate that the ionic domains are smaller than those for similar nonionic block copolymers[13]. In view of these facts, and the unfavorable $\chi$, it is expected that interphase mixing is kept to a minimum in these systems. Typical radii for the phase separated regions range from *ca.* 50 to 300 Å, with the number of styrene chains emanating from these inclusions ranging from *ca.* 250 to 9000[13]. The average area per styrene chain has been calculated to be of the order of 140 Å$^2$, thus typical distances between the styrene chains are 12 Å[13]. This represents an unfavorable geometry for efficient packing, given the rigidity of the polystyrene chain, so dilation of the polystyrene close to the surface of the ionic domains is expected. The free distance between the vinylpyridine domains are of the order of 400 to 500 Å[13], thus, it is not surprising that all of the matrix is affected.

In the first publication from this laboratory on the mechanical properties of styrene-co-N-methyl-4-vinylpyridinium iodide triblock ionomers[8], this decrease in the glass transition temperature had already been observed, and at that time, the phenomenon was ascribed to water plasticization of the ionic domains. We do not feel that this possibility is a valid explanation for the results presented here because of the sample preparation techniques

## 6.5 Conclusions

The unexpected reduction in the glass transition temperatures of a series of styrene(A) N-alkyl-4-vinylpyridinium iodide(B) ABA triblock ionomers can be explained as the result of a reduced density of the styrene segments around the ionic domains. This lowering in the density is due to two factors: the relative immiscibility of the styrene and vinylpyridinium moieties, and the consequent increase in free volume of the matrix.

### 6.6 Acknowledgements

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### 6.7 References

(1)B. R. M. Gallot, Adv. Polym. Sci., **29**, 85 (1978).

(2)D. J. Meier, NATO ASI Series E, **89**, 173 (1985).

(3)S. Krause and M. Iskandar, in Multiphase Polymers, Advances in Chemistry, ed. S. L. Cooper, **79**, 205 (1979).

(4)A. T. Granger, B. Wang, S. Krause and L. J. Fetters, in Multicomponent Polymer Materials, ed. Paul and Sperling, Advances in Chemistry Series, **211**, 127 (1986).

(5)B. Wang and S. Krause, Macromolecules, **20**, 2201 (1987).

(6)T. Inoue, S. Ogata, M. Kakimoto and Y. Imai, Macromolecules, **17**, 1417 (1984).

(7)D. Wollmann and A. Eisenberg, manuscript in preparation.

(8)S. Gauthier and A. Eisenberg, Macromolecules, **20**, 760 (1987).

(9)D. Wollmann, C. E. Williams and A. Eisenberg, manuscript in preparation.

(10)D. Wollmann, S. Gauthier and A. Eisenberg, Polym. Eng. Sci., **26**, 1451 (1986).

(11)R. B. Dean and W. J. Dixon, Anal. Chem., **23**, 636 (1951).

(12)C. Mack, Essentials of Statistics for Scientists and Technologists, Plenum, New York (1967).

(13) J.-P. Gouin, C. E. Williams and A. Eisenberg, manuscript accepted by *Macromolecules*.

(14) A. Molnár, private communication.

(15) J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 2nd ed., Wiley-Interscience, New York (1975).

# Chapter 7

## Dynamic Mechanical Behaviour of Plasticised ABA Triblock Ionomers

### 7.1 Abstract

The effects of plasticisation on the dynamic mechanical behaviour of styrene (B)-N-alkyl-4-vinylpyridinium iodide (A) ABA triblock ionomers were observed for three different plasticiser types. In one case, the polar domains were plasticised internally by the quaternisation of the vinylpyridine end blocks with n-iodoalkanes. The other two plasticisers were external, i.e. they were added to the ionomer; one of these was glycerol, for plasticisation of the vinylpyridinium domains, and the other was diethylbenzene, which was used to plasticise the styrene matrix. A change in the type of plasticiser used in the ionic domains did not change the mechanical behaviour of the styrene phase. The addition of a nonpolar plasticiser, however, did reduce the $T_g$ and the apparent activation energy of the matrix comparable to the same plasticisation of a styrene homopolymer. By contrast, neither the use of n-iodalkanes nor diethylbenzene had a measurable effect on the glass transition temperature of the ionic regions. Only in the case of plasticisation with glycerol was the $T_g$ reduced to the point where they could be measured. The effect of adding glycerol was similar to the effect seen in the plasticisation of some polyelectrolytes with polar diluents, rather than the plasticisation of nonionic polymers. Thus, the rate of the depression of $T_g$ was initially very rapid, and only later did it slow down.

### 7.2 Introduction

This paper is one of a series dealing with the effects of plasticisation on the dynamic mechanical behaviour and morphologies of styrene-vinylpyridinium ionomers. The previous reports have dealt with the plasticisation of such ionomers with random architecture[1,2], and the morphologies[3] and matrix glass transition temperatures[4] of some of the ABA triblock ionomers. We present here the results of a dynamic mechanical study on styrene (B)-N-alkyl-4-vinylpyridinium iodide (A) ionomers which have been plasticised using either quaternisation with long n-iodoalkanes, or by the addition of small molecules such as diethylbenzene or glycerol.

The majority of all studies on ionomers have been concerned with random, anionic systems, and thus, such materials have been used extensively in plasticisation[5,6,7,8,9,10,11,12]. Anionic systems have been preferred over cationic ones because of the greater stability of anionic ionomers. Furthermore, many anionic materials have been found to be phase separated, while such clustering is less common in cationic systems[13,14]. In addition, ionomers with random architectures are more easily prepared than similar ionomers with blocky architectures.

It has been shown that in random anionic ionomers, plasticisation can have one of two effects. In general, the addition of a nonpolar diluent, such as diethylbenzene, reduces the glass transition temperatures of both phases[6,10,11], while plasticisation with a polar diluent, i.e. glycerol, does not affect the multiplet-containing phase, but obliterates the dynamic mechanical features associated with clusters[5,6,7]. The interactions between the diluent and the ionomer are rather complex, thus it has been shown that plasticisation using nitrobenzene, which is polar but does not hydrogen bond, is similar to plasticisation with a nonpolar diluent[12].

Studies on random styrene-N-alkyl-4-vinylpyridinium iodide ionomers[2] have shown that plasticisation with nonpolar additives can induce phase separation where none previously existed. This new behaviour was observed whether the plasticiser was mobile (external plasticisation) or attached (internal plasticisation).

The present study is concerned with a styrene-N-alkyl-4-vinylpyridinium iodide ionomer which is phase separated in the unplasticised state, because of its triblock architecture. Because of the drastic differences in polarity between the two phases, it is expected that the incoporation of a diluent should affect only one of the two phases for the majority of plasticisers. The dynamic mechanical behaviour of the other phase, i.e. the shape of its storage modulus - temperature curve, its glass transition temperature, and the activation energy of this transition, should be unchanged. Plasticisation of the ionic blocks is of particular interest, because the $T_g$ of the unplasticised N-alkyl-4-vinylpyridinium iodide segments cannot be determined, due to decomposition occuring at temperatures lower than the glass transition[13].

## 7.3 Experimental Techniques and Results

ABA triblock copolymers of styrene(B) and 4-vinylpyridine(A), containing *ca.*2 to 10 mole % 4-vinylpyridine, were synthesised *via* sequential anionic polymerisation in tetrahydrofuran with sodium naphthalenide initiator as has been previously described[15]. This method of preparation yields materials which are characterised by a common midblock length and increasing end block lengths. Following polymerisation, the materials were recovered by precipitation of a 5 % solution of the polymer into 10 volumes of methanol for the lower vinylpyridine contents, and ethanol/water for the samples containing larger amounts of vinylpyridine. The precipitates were filtered, washed with more nonsolvent, and dried in vacuum at 60 °C.

The molecular weight of the styrene midblock was determined by gel permeation chromatography The vinylpyridine content of each sample was determined relative to the midblock from an analysis of the infrared spectra, using the ratios of the intensities of the pyridine peak (1414 $cm^{-1}$) to that of styrene (1029 and 1870 $cm^{-1}$) and a previously prepared calibration curve[15].

The polymers were quaternised with a number of n-iodoalkanes, ranging from iodomethane (MeI) to iododecane (DeI), using a previously described technique, which is summarised here for convenience. After approximately 1 g of the polymer had been compression moulded (120-130 °C, 2 GPa), the sample was slightly swollen in 50 mL of a 4/1 solution of absolute ethanol and the desired iodoalkane. The mixture was refluxed under nitrogen for sufficient time to ensure complete quaternisation, from 3 days for reactions with iodomethane up to one week for quaternisations with iododecane. The materials were judged to be fully quaternised when the pyridine peak at 1414 $cm^{-1}$ in the infrared had completely disappeared. The polymers were removed from the solvent, soaked briefly in fresh ethanol, and then dried at room temperature for one day. Further drying temperatures and durations depended on the quaternising reagent; thus, polymers quaternised with iodomethane were dried for another three days at 60 °C, while those materials quaternised with iododecane were dried for a week at 90 °C.

For some of the experiments in this study, the block copolymers were plasticised externally with either a nonpolar diluent, diethylbenzene, or a polar solvent, glycerol. Plasticisation with the nonpolar material was achieved in the following manner. A dry sample was swollen and stirred in *ca.* 25 mL of benzene/methanol (90/10, v/v) for three hours. While the nonionic block copolymer dissolved quickly using this method, dissolution of the ionomer did not occur, however, even after approximately 4 mL of the diluent had been added. The polymer and plasticiser mixture was stirred for another two hours, then the benzene/methanol was removed by freezedrying. The sample was placed in a drying pistol, and excess plasticiser was removed under vacuum at *ca.* 56 °C (boiling acetone) for about 5 hours. The plasticised polymer was then remoulded at *ca.* 70 °C, weighed and used in the dynamic mechanical experiment. The polymers were also plasticised with glycerol, using a similar method. The ionic materials dissolved quickly in *ca.* 20 mL of a glycerol/benzene/methanol solution. The glycerol contents ranged from 8 x $10^{-5}$ g glycerol/mL 90/10 benzene/methanol to 2.6 x $10^{-3}$ g glycerol/mL 90/10 benzene/methanol. This range of glycerol concentrations were used to achieve plasticisation levels from *ca.* 5 to 200 mole % glycerol per mole of N-decyl-4-vinylpyridinium iodide. This solution was stirred for one hour, then the solvent was removed by freeze-drying, and the sample was remoulded at *ca.* 130-140 °C for the dynamic mechanical experiment.

Internal plasticisation of the styrene midblock *via* alkylation of the phenyl rings in the ABA copolymers was also tried as a part of this work. It was possible to alkylate the random styrene-4-vinylpyridine copolymers using a Friedel-Crafts reaction. However, repeated attempts with the triblock materials under a variety of conditions used failed due to crosslinking, presumably between the Lewis acid, $AlCl_3$, and the vinylpyridine end blocks. In view of the results from the externally plasticised ABA ionomers, it seems that results dynamic mechanical experiments would not have been especially informative.

The dynamic mechanical studies were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) over a temperature range appropriate for the particular sample. Data were collected concurrently for five different frequencies under a light flow of nitrogen and at a heating rate of 0,5 °C $min^{-1}$.

Representative storage modulus and loss tangent curves for samples of each of the plasticisation methods and a polystyrene comparison are shown in Figures 7.1 and 7.2. The glass transition temperature for each sample was taken to be the peak maximum in the loss tangent curve. These maxima were determined from a curve-fitting routine, and the values thus obtained for 1 Hz are reported in Table 7.1. The activation energies of the glass transitions and their uncertainties, also shown in Table 7.1, were calculated using a programme written by B. Hird

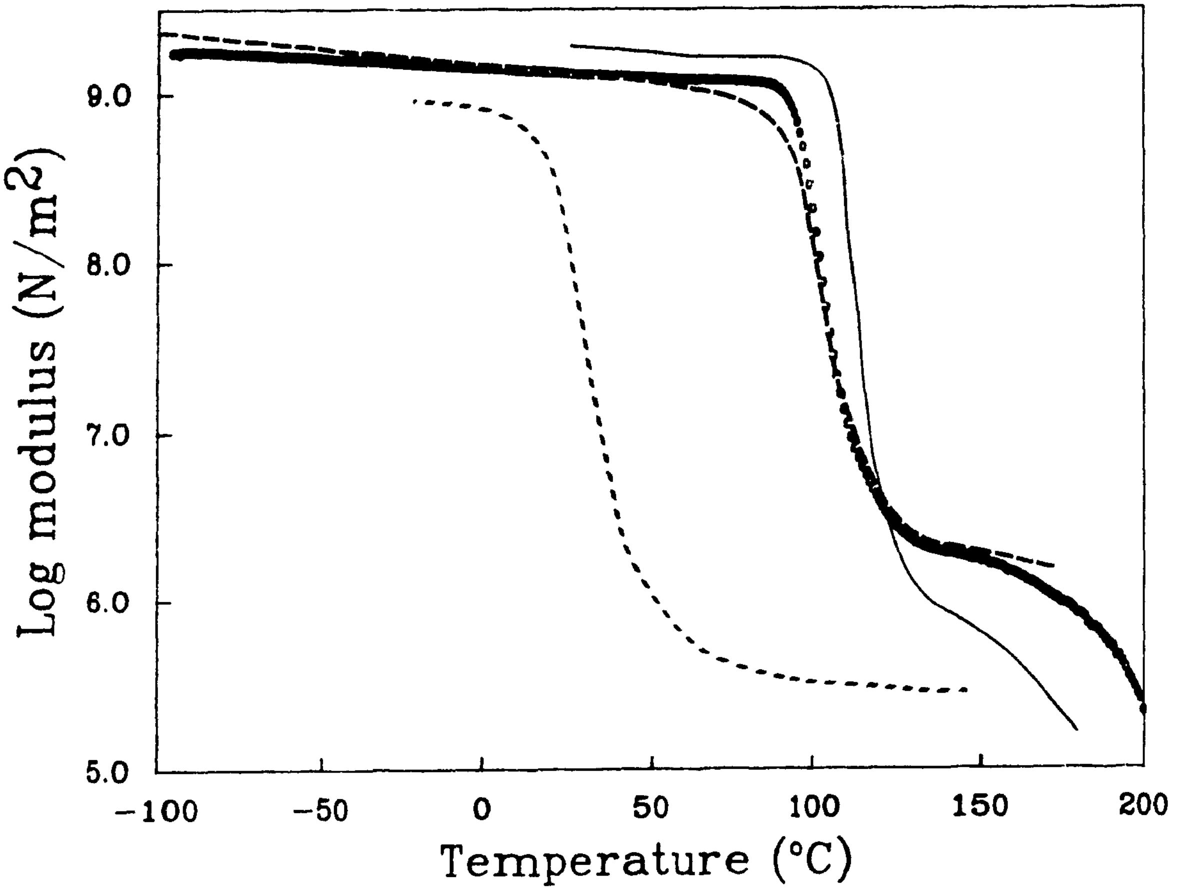


Fig. 7.1: Representative storage modulus curves at 1 Hz as a function of temperature for styrene-vinylpyridinium iodide ABA triblock ionomers. Styrene, , Sty-0.045VP(4-)-DeI, , Sty-0.045VP(4-)-MeI + 10% diethylbenzene, , Sty-0.045VP(4-)-DeI + 10% glycerol, .

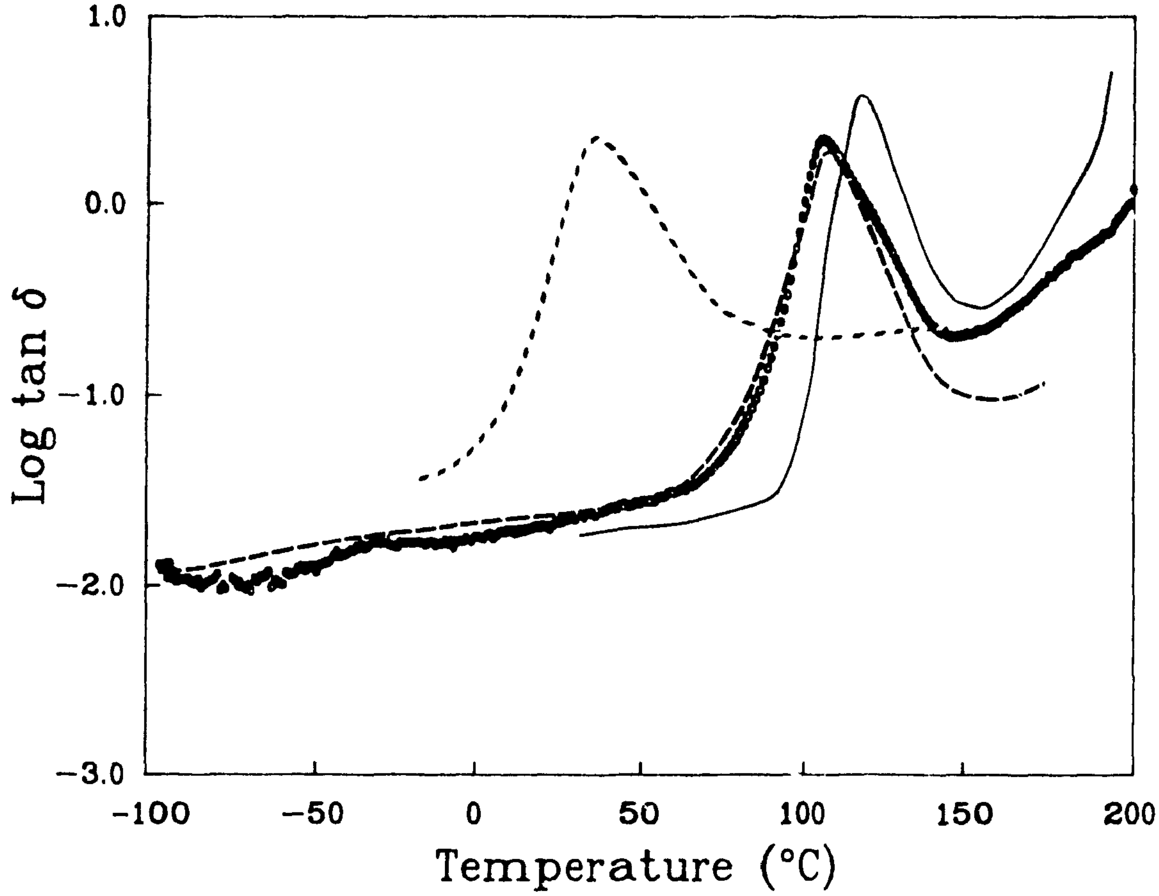


Fig. 7.2: Representative loss tangent curves at 1 Hz as a function of temperature for styrene-vinylpyridinium iodide ABA triblock ionomers. Styrene, , Sty-0.045VP(4-)-DeI, , Sty-0.045VP(4-)-MeI + 10% diethylbenzene, , Sty-0.045VP(4-)-DeI + 10% glycerol, .

## Table 7.1

## A Comparison of the Glass Transition Temperatures and Activation Energies of Selected Styrene-Vinylpyridinium ABA Triblock Ionomers Plasticised by Different Methods.

| Sample | $T_g$ (± 0.5 °C) | $E_{act}$ (± 2σkJ/mol) |
|---|---|---|
| Styrene homopolymer | 116.5 | 540 ± 100 |
| " + 10 % diethylbenzene | 48.8 | 310 ± 50 |
| Sty-0.013VP(4-)-MeI | 106.6 | 500 ± 100 |
| Sty-0.033VP(4-)-MeI | 110.9 | 440 ± 90 |
| Sty-0.045VP(4-)-MeI | 108.8 | 500 ± 100 |
| Sty-0.045VP(4-)-DeI | 109.3 | 450 ± 80 |
| Sty-0.045VP(4-)-MeI + 10% diethylbenzene | 38.8 | 290 ± 40 |
| Sty-0.045VP(4-)-DeI + 5% glycerol | 106.3 | 450 ± 110 |
| " + 10% glycerol | 107.2 | 460 ± 60 |
| " + 50% glycerol | 108.4 | 460 ± 70 |
| " +200% glycerol | 108.0 | 480 ± 70 |

## 7.4 Discussion

The glass transition temperatures that were determined for the plasticised vinylpyridinium iodide end blocks are obviously of interest in these materials, and this subject will be treated first. Another topic which will be discussed is the resemblance of the dynamic mechanical properties of these block ionomers to those of polystyrene. The final subject in this section deals with the effects of plasticisation on both the glass transition temperature depression in these materials and their activation energies.

### 7.4.1 THE GLASS TRANSITION TEMPERATURE OF THE IONIC END BLOCKS

In a previous study on the dynamic mechanical behaviour of styrene-N-methyl-4-vinylpyridinium iodide ionomers, it had not been possible to observe the glass transition temperature of the ionic blocks[15]. It was suggested at the time that the expected $T_g$ of poly(N-methyl-4-vinylpyridinium iodide) would be significantly greater than *ca* 140 °C, the glass transition temperature of unquaternised poly(4-vinylpyridine)[16]. Because dequaternisation of the vinylpyridinium had been observed in studies of random styrene-co-N-methyl-4-vinylpyridinium iodide[13], it was thought that quaternisation using n-iodoalkanes which were poorer leaving groups, for example iododecane, might be less susceptible to such decomposition The results of previous studies on random styrene vinylpyridinium ionomers quaternised with n-iodoalkanes had demonstrated that an increasing alkyl chain length acted as a plasticiser, and thus might also aid in observing the glass transition temperature of the end blocks quaternised with these materials. However, even when the block copolymers were quaternised with iodododecane, the glass transition temperature was not depressed to the extent where it could be measured, despite complete quaternisation, which implies 100 % plasticisation of the ionic regions

It had also been suggested by Gauthier and Eisenberg[15] that perhaps the glass transition of the ionic regions was superposed on that of the polystyrene midblock.

Although this possibility was considered remote, it was justifiable on the basis of the very short end block lengths in these ionomers, which would make the vinylpyridinium blocks behave like oligomers rather than polymers. An N-methyl-4-vinylpyridinium iodide oligomer might be expected to have a relatively low glass transition temperature, possibly close to that of polystyrene. Therefore, in the unlikely event that the glass transition temperatures of the midblock and the end blocks were superposed, the effects of plasticisation of the matrix by diethylbenzene were studied because only the glass transition of the nonpolar material should be affected by the addition of such a diluent. As there was no loss tangent peak left at *ca.* 110 °C after this plasticisation, superposition of the matrix and vinylpyridinium end block glass transition temperatures was ruled out.

The addition of a mobile polar diluent proved to be one way to depress the glass transition temperature of the vinylpyridinium domains to the point where the $T_g$ could be measured The decrease in the $T_g$ of the end blocks was exceptionally steep; thus, while no glass transition was observed for these domains in the unplasticised material, one is clearly evident at *ca* -30 °C for end blocks plasticised with 10 mole % glycerol relative to the vinylpyridine content. In some ways, this plasticisation level is misleading, because each mole of glycerol contains three times as many moles of hydroxyl groups, each of which can interact with one vinylpyridinium group. Because of the technique used here to introduce the plasticiser into the polymer, it was not possible to reliably achieve plasticisation levels below 5 %, and thus the number of plasticiser-polymer interactions remains relatively high.

The observation of a second glass transition temperature in these block ionomers is further evidence that these materials are phase separated, despite the small size of the end blocks This conclusion is in agreement with those obtained from small angle X-ray scattering studies[2,17]. The results of dynamic mechanical experiments for triblock ionomers with anionic end blocks show a second $T_g$ and therefore, also suggest that these materials are phase separated[18].

However, the lowering of the $T_g$ of the vinylpyridinium domains by glycerol is very different from the plasticisation of the matrix with diethylbenzene In the case of the ionic domains, the reduction of the glass transition temperature is qualitatively similar to that observed in some plasticised polyelectrolytes[19], thus, after a precipitous initial drop, the rate of change of the $T_g$ slows down and becomes linear. This observation is not very surprising considering that the vinylpyridinium block is essentially a polyelectrolyte segment.

### 7.4.2 POLYSTYRENE AND PLASTICISED IONOMERS

Before the region of viscous flow, the dynamic mechanical behaviour of the styrene matrix in the block materials is very similar to that of a styrene homopolymer of comparable molecular weight. This similarity is due to the completeness of the phase separation achieved in these plasticised block ionomers At temperatures *ca* 30-40 °C above $T_g$, homopolystyrene starts to flow These ABA ionomers do not, because the styrene matrix is crosslinked by the vinylpyridinium domains

The ABA materials are least perturbed when the copolymers have been quaternised simply with the n-iodoalkanes, because this is still a two component system, while the materials to which a mobile diluent has been added are three component systems. In the ionomers in which the plasticiser is an n-iodoalkane, the behaviour of the styrene matrix most closely resembled that of the corresponding styrene homopolymer The main difference between these ionomers and polystyrene was a slight depression of the matrix glass transition temperature, which is the subject of another paper. It is clear that this reduction in $T_g$ is not the result of increased miscibility between the polymer segments, because in the case of compatiblisation, the glass transition temperature of the styrene matrix would shift up towards the $T_g$ of dthe ionic end blocks. Instead, this glass transition temperature depression appears to be due to the inability of the styrene chains to pack efficiently around the vinylpyridinium domains.

When these ionomers are plasticised with glycerol, there is very little disruption of the styrene phase. The polymer was completely dissolved during the incorporation of the plasticiser, but reorganised to reproduce the behaviour observed for the identical, unplasticised materials, and thus the glass transition temperature of the styrene matrix is unchanged with respect to that of the unplasticised ionomer, and about 8 °C lower than that of the styrene homopolymer. At elevated temperatures, the triblock ionomers plasticised with glycerol behave like a polystyrene homopolymer, and start to flow. This indicates that the vinylpyridinium domains which were responsible for the apparent crosslinking inn the unplasticised materials are not as effective in these plasticised systems, and suggests that the glass transition seen at very low temperatures is indeed that of the ionic regions

In contrast, plasticisation of these block ionomers by diethylbenzene reduces the glass transition temperature of the matrix substantially. The addition of 10 % diethylbenzene led to a matrix $T_g$ reduced comparably (e.g. from *ca.* 108 °C to *ca.* 38 °C) with respect to a similarly plasticised styrene homopolymer ( $T_g$ reduced to *ca.* 46 °C from *ca* 116 °C).

### 7.4.3 ACTIVATION ENERGIES OF PLASTICISED BLOCK IONOMERS

The activation energies of the styrene glass transition temperatures for each of the samples were calculated, and are presented in Table 7.1. There is clearly no effect on the activation energy of the styrene matrix for materials in which the ionic domains were plasticised, either through quaternisation by n-iodoalkanes as well as those samples which were plasticised by glycerol These activation energies are within the range determined for the styrene homopolymer. In the case of the samples plasticised with diethylbenzene, the apparent activation energies are considerably lower. This result is expected as a consequence of the WLF equation, since if the constants $c_1$ and $c_2$ are unchanged, the activation energy will decrease as the glass transition temperature is reduced

## 7.5 Conclusions

The effects of plasticisation on the dynamic mechanical properties of ABA styrene-N-alkyl-4-vinylpyridinium iodide ionomers are heavily dependent on the polarity of the plasticiser as well as its method of incorporation. Thus, quaternisation of the vinylpyridine end blocks with n-iodoalkanes results in the internal plasticisation of the polar domains. The effect on the glass transition temperature of the ionic regions was not measurable using this type of plasticisation. It does, however, reduce the $T_g$ of the styrene matrix, which has been attributed to poor packing of the styrene chains immediately around the vinylpyridinium domains. The incorporation of diethylbenzene, a nonpolar diluent, into the ionomers, reduced the glass transition temperature and the activation energy of the matrix. It did not appear to have a measurable effect on the ionic phase at the level of plasticisation (*ca* 10 mole % relative to styrene) investigated. Finally, the addition of small quantities of glycerol plasticised the vinylpyridinium phase drastically, an effect similar to that seen in some plasticised polyelectrolytes, but did not disrupt the styrene matrix.

## 7.6 References

(1) D. Wollmann, S. Gauthier and A. Eisenberg, Polym. Sci. Eng., **26**, 1451 (1986).

(2) D. Wollmann, C. E. Williams and A. Eisenberg, manuscript in preparation.

(3) D. Wollmann, C. E. Williams and A. Eisenberg, manuscript submitted to J. Polym. Sci., Polym. Phys..

(4) D. Wollmann and A. Eisenberg, submitted to J. Polym. Sci., Polym. Lett. Ed..

(5) R. D. Lundberg, H. S. Makowski and L. Westerman, in Ions in Polymers, ed. A. Eisenberg, Advances in Chemistry Series, **187**, 67 (1980).

(6) C. G. Bazuin and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **24**, 1137 (1986).

(7) H. Matsuura and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **14**, 1201 (1976).

(8) R. A. Weiss, P. K. Agarwal and R. D. Lundberg, J. Appl. Polym. Sci., **29**, 755 (1984).

(9) P. Smith and A. Eisenberg, J. Polym. Sci., Polym. Phys. Ed., **26**, 569 (1988).

(10) C. G. Bazuin and S. Villeneuve, Polym. Mat. Sci. Eng., **58**, 1069 (1988).

(11) M. Gauthier and A. Eisenberg, manuscript accepted by Macromolecules.

(12) M. Gauthier and A. Eisenberg, manuscript accepted by Macromolecules.

(13) S. Gauthier, D. Duchesne and A. Eisenberg, Macromolecules, **20**, 753 (1987).

(14) D. Duchesne and A. Eisenberg, manuscript in preparation.

(15) S. Gauthier and A. Eisenberg, Macromolecules, **20**, 760, 1987.

(16) Polymer Handbook, Second Edition, eds. J. Brandrup and E. H. Immergut, Wiley-Interscience, III-155 (1975).

(17) J.-P. Gouin, C. E. Williams and A. Eisenberg, manuscript submitted to Macromolecules.

(18) A. Desjardins, unpublished results.

(19) S.C. Yeo and A. Eisenberg, J. Macromol. Sci. - Phys., **B13**, 441 (1977).

# Chapter 8
# Conclusions and Contributions to Original Knowledge

## 8.1 General Discussion

A number of different plasticisation techniques were used to reduce the glass transition temperature of styrene-vinylpyridinium ionomers having either random or ABA triblock architectures Polar and nonpolar additives were investigated and were incorporated in the material either internally, through the formation of a covalent bond between the polymer and the plasticiser, or externally, in which case the diluent was mobile, and could reside preferentially in one phase of the material.

This work is the first demonstration of the inducement of phase separation in styrene-vinylpyridinium ionomers. Random styrene-N-methyl-4-vinylpyridinium iodide ionomers are not phase separated. It was shown that the addition of very small quantities of nonpolar plasticisers could induce clustering, and that the amount of material in the clustered phase is dependent on the mobility of the plasticiser For example, a 6 mole % (vinylpyridine content) ionomer, when plasticised externally with *ca.* 10 mole % (relative to styrene) diethylbenzene, had relatively more material in the clustered phase than one internally plasticised to a comparable extent. Thus, phase separation in random styrene-vinylpyridinium ionomers is possible when the glass transition of the precursor is depressed by a nonpolar diluent

Unlike many anionic random ionomers, such as styrene-co-sodium methacrylate, plasticised styrene-vinylpyridinium ionomers with ion contents less than 6 mole % did not exhibit evidence of phase separation. However, at sufficiently high ion contents, both the cationic system studied here and anionic systems appear to undergo a phase inversion, after which the clustered domains become the continuous phase

It was also shown that excessive plasticisation, whether internal or external, disrupts the mechanical behaviour of the ionomers to the point where phase separation could not be demonstrated conclusively. The experimental results from small angle X-ray scattering, however, show that there are still two phases present in the material.

Plasticisation of the vinylpyridinium moieties in the random ionomers through quaternisation with long n-iodoalkanes did not yield phase separated materials, even though the glass transition temperature of the precursor was depressed. Instead, the linear relationship that was observed between the $T_g$, the vinylpyridine content and the length of the iodoalkane chain indicates that the quaternised ionic groups are distributed evenly throughout the matrix at all ion contents and iodoalkane chain lengths investigated.

Plasticisation of the ABA triblock styrene-vinylpyridinium ionomers did not affect the phase separation that existed in the precursors. The polarity of the plasticisers used determined whether the plasticiser resided in the matrix or the ionic domains. The glass transition temperature and the activation energy of the plasticised phase were markedly affected by the addition of a small molecule diluent, while the $T_g$ and the activation of the other phase were apparently unchanged by plasticisation.

Plasticisation of the ionic domains *via* quaternisation with n-iodoalkanes was not as effective as the addition of glycerol to reduce the glass transition temperature of the vinylpyridinium blocks to where they could be observed. The use of glycerol reduced the $T_g$ of the end blocks in a way similar to that seen for some polyelectrolytes.

The reduction in the glass transition temperature of the styrene matrix in the triblock copolymers quaternised with n-iodoalkanes was an unexpected result. The depression, although small, is reproducible, and has been explained as the result of inefficient packing of the styrene matrix immediately around the vinylpyridinium domains. The poor packing is due to the very small size of the ionic phases and the relatively large number of styrene chains emanating from these domains. This reduction in the $T_g$ of the low temperature matrix is counter to most previous experimental results, and the explanation for its occurrence is new and based on a model from recent SAXS data

The small angle X-ray scattering studies on the ABA copolymers quaternised with n-iodoalkanes yielded another novel result It is clear that the vinylpyridinium domains in the ionomers are on the verge of reorganisation. Thus, two distinct SAXS profiles, consistent with two different morphologies, were observed. In one, the ionic domains are believed to be pseudospherical. In the other, found only in materials of low styrene midblock length (240 units), the domains had clearly reorganised during the sample preparation, and were much more uniform in size and shape. This variation in morphology had not been previously reported for such a series of materials which all have the same sample histories

## 8.2 Suggestions for Future Work

The suggestions for any further projects using styrene-vinylpyridinium ionomers are divided according to the architecture of the materials which, after three Ph. D theses, has clearly become the factor differentiating the phase behaviour of the materials.

### 8.2.1 Random Ionomers

Random ionomers have been investigated now for over twenty years, and many of the basic areas of their phase behaviour have been mapped out. Many of the parameters which influence phase separation in ionomers are qualitatively understood, but there are other factors whose effects on the phase behaviour in ionomers have been not as extensively studied. Some of these, for example the effect of chain stiffness on ion aggregation would be interesting to explore.

A few experiments are suggested for the materials which have already been prepared, to further elaborate on the process of inducing phase separation in these ionomers. It might be possible to observe the spectra and the relaxation times of the iodide counterions using small angle X-ray scattering or solid state NMR. Two samples of the ionomer would be needed; one would be unplasticised and the other would be contain an excessive amount of diethylbenzene. The diluent could be removed from the second sample incrementally, until no plasticiser remained. Only one type of environment would be expected in the original, unplasticised sample, but two different iodide environments should be observed in the plasticised material. Once the sample containing the diethylbenzene was completely dried, it would be interesting to observe whether the two-phase morphology was locked in, or if the ionomer reverted to a single phase. In addition, such techniques might be useful in determining whether the ionomers with high vinylpyridinium content, for example 12 mole %, were indeed completely clustered.

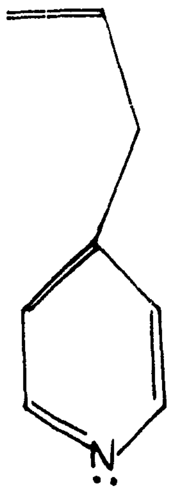
A thorough investigation into the solution properties of the alkylated ionomers is suggested. It was evident from the results of sample preparation for the work in this thesis that, after quaternisation, the ionomers were soluble in an unexpected variety of solvents, ranging from nonpolar, i.e. hexanes, to rather polar, for example methanol. It is possible that aggregates such as micelles are forming in the solutions. This aggregation could be observed through gel permeation chromatography or light scattering.

### 8.2.2 Block Ionomers

There are many investigations that could be interesting with the block ionomers which have been explored in this thesis. A small angle X-ray scattering study of the effects of casting on the morphology of the triblock ionomers is currently underway. Another area to be explored is the effect of external plasticisation of the morphologies of the ABA ionomers.

The use of novel monomers might yield information on the domain formation. It has been shown that distancing the ionic group from the main chain weakens the interactions in random ionomers. Putting the pyridine group on the end of a spacer chain might lower the glass transition temperature of the ionic phase and it would be expected to have an effect on the size of the domains that were formed. A suggested monomer is pictured below.

Novel architectures might also be of interest. The surface behaviour of AB ionomers in solution are being studied. The dynamic mechanical behaviour and morphology of styrene-vinylpyridinium star block ionomers is one possible field of work. The solution behaviour of this type of material might also be interesting.



### 8.2.3 Blends of Block and Random Ionomers

Blends of random ionomers have been the subject of a number of studies. In some cases, ion-ion interactions have been employed to achieve miscibility in otherwise immiscible systems. Other investigations have used ion-dipole interactions to obtain a miscible blend. It is suggested that blends of random and block styrene-vinylpyridinium ionomers be studied and the sizes of the ionic domains be observed, perhaps using small angle X-ray scattering.

# Appendix A:

## Glass Transition Relations in Ionomeric "Comb" Polymers

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The glass transition temperatures ($T_g$) and dynamic mechanical properties of random copolymers of styrene-4-vinylpyridine quaternized with iodoalkanes are presented for vinylpyridine contents up to ten percent and pendant alkyl chains up to ten carbons in length Two linear relationships between ion content and glass transition temperature and between pendant alkyl chain length and the $T_g$ are observed An equation is presented that can be used to predict the $T_g$ for such copolymers based on their ion contents and alkyl chain lengths

### INTRODUCTION

The properties of many industrially important polymers have been commonly modified by the use of plasticizers A wide range of these materials are used with the intention of either making the polymer more easily processable or altering the properties of the polymer to make it more suitable for its end use In either case difficulties are occasionally encountered because the plasticizer separates from the polymer over a period of time This can be due to volatility of the low molecular weight material or the poor thermodynamic miscibility between plasticizer and polymer or possibly other mechanisms Various remedies have been sought to overcome these difficulties including the use of polymeric plasticizers or the chemical attachment of the plasticizer to the polymer As might be expected both of these have their specific advantages and disadvantages

A significant problem with trying to blend two polymers is that in general polymers are immiscible due to a negligible entropy of mixing In the case of an unfavorable enthalpy of mixing immiscibility may also be a problem for some polymer—plasticizer systems Typically specific interactions are necessary to overcome this problem for example coulombic interactions Several types of interactions can be envisaged involving charged species namely ion pair—ion pair ion—ion and ion—dipole There have been many studies (1 to 7) exploring the use of coulombic interactions as miscibility enhancers in attempts to mix polymers with other polymers or with plasticizers of both low and high molecular weight

The attachment of low molecular weight groups can be achieved in three different ways using coulombic interactions For example a polymer containing pendant sulfonic acid groups can be mixed with an alkyl amine (6 7) Alternatively, it would be possible to mix polymeric amines with alkyl sulfonic acids (8) although a major difficulty is presented by the low solubility of the plasticizer which is a soap The third way, which is the subject of this paper involves the mixing of a polymeric chain containing amine or pyridine groups with alkyl halides followed by a reaction of the two This method yields a primary bond between the polymer and the plasticizer, accompanied by the formation of an ion pair

A major advantage of this last method which it shares with the first, is that the reaction and workup are very simple The creation of a true chemical bond is accompanied by further advantages not shared with the first method namely that ion hopping should not occur and that there is a greatly reduced likelihood of the plasticizer "bleeding out" of the polymer matrix under the influence of polar solvents or salt solutions A further advantage common to both the first and the last methods is that many of the plasticizing reagents are available commercially thus a wide range of structures can be envisaged and created The polymer is more a "comb" polymer (9 10) than a graft copolymer since all the side chains are of equal length This process has a further advantage in that in most graft copolymerizations a certain amount of the material to be grafted is present as unattached homopolymer (11) which is not the case for this comb polymer

Before such a plasticization technique can become a generally useful method it is advisable to be able to correlate a wide range of physical properties with the structure of the polymer-plasticizer system to be produced Perhaps the most important single parameter in plasticized polymer systems is the $T_g$ As a result, a great deal of work (12 to 19) has gone into the predictions of $T_g$

It has been recognized for a number of years that for polymers of low ion content, the $T_g$ generally increases linearly with an increase in the concentration of ions (17) It is also widely known that the presence of alkyl side chains depresses the glass transition temperature (21 to 23) In the materials described here both of these competing effects are expected to be present

Specifically this study is centered around an exploration of the $T_g$ of a styrene-co-4-vinylpyridine polymer to which alkyl halides of various chain lengths are attached thus producing ionomer "combs " The techniques involve differential scanning calorimetry and the torsion pendulum As a result of the latter technique the dynamic mechanical properties (ca 1 Hz) are also explored

## EXPERIMENTAL

Random copolymers of styrene-4-vinylpyridine containing 1 9 4 9 6 9, and 9 7 mole percent 4-vinylpyridine were synthesized in bulk using free radical initiation as described by Gauthier (24) Following isolation and drying the 4-vinylpyridine content of the materials was assessed by two methods In one the materials were titrated in chlorobenzene with a solution of $HClO_4$ and acetic acid using methyl violet as indicator In the other thin films were made by compression molding studied by infrared and the ratio of the peaks at either 1870 centimeters (cm)$^{-1}$ or 1029 cm$^{-1}$ for styrene and 1414 cm$^{-1}$ for 4-vinylpyridine was measured against a previously prepared calibration curve (24)

Straight chain iodoalkanes i e 1-iodobutane 1-iodohexane 1-iodooctane and 1-iododecane were used to quaternize the styrene-4-vinylpyridine copolymers These reagents were distilled under either nitrogen or partial vacuum to purify them

The quaternization reactions of the styrene-4 vinylpyridine copolymers were performed in the following manner a known quantity of the copolymer was dissolved in dry tetrahydrofuran to make a solution of 5 percent polymer by weight A twenty-five fold molar excess of the iodoalkane was added to the flask either by syringe or in the case of the solid iodooctadecane by weight Heating was begun and the mixture refluxed under nitrogen for 24 hours Invariably after heating started the solution turned golden yellow The intensity of the color depended on the amount and the molecular weight of the iodoalkane darker solutions were obtained as the molecular weight of the reagent increased

Once the reaction was stopped all of the polymer samples were precipitated in a ten-fold excess by volume of rapidly stirred mixed hexane isomers Each sample was filtered by suction and washed with more hexanes to remove any remaining excess iodoalkane The yellow quaternized ionomers were then dried in vacuo at 60°C to remove the solvent

The extent of quaternization in each of the styrene-based samples was checked in FTIR by the disappearance of the peak at 1414 cm$^{-1}$ Samples of each ionomer were taken, and a $T_g$ was obtained for each by DSC at a heating rate of 20°C/min

Another series of samples was then molded for use in the torsion pendulum These molded samples were further treated as follows Each sample was placed in a drying pistol and subjected to vacuum at room temperature for 24 h Then for two more days it was heated to 78°C under vacuum, to drive off as much water as possible Finally, the sample was heated to ca 130°C under nitrogen for three days to anneal it After this the sample was run in the torsion pendulum and a $T_g$ was obtained from the tan delta maximum

After the torsion pendulum run a small piece of the sample was broken off and molded to produce a film This film was studied by FTIR to determine whether any significant loss of the quaternizing agent had occurred a complication that had been observed with previous studies using iodomethane

Although iodooctadecane was used as a reagent in an attempt to quaternize the styrene-4-vinyl pyridine copolymers, the reaction was unsuccessful F the higher concentrations of vinylpyridine in particular, some degradation must have occurred due to the drastic change in the infrared spectra Thus further studies on this set of samples were abandoned

## RESULTS

### Infrared Studies

The infrared spectra of the samples following quaternization lacked the peak at 1414 cm$^{-1}$ exhibited by the procedures which is due to the unquaternized pyridine ring This indicated that within the accuracy of the measurement, all the samples were fully quaternized The infrared spectra of the samples taken after the torsion pendulum run showed a negligible dequaternization The worst sample still exhibited 98 percent quaternization after the torsion pendulum run, according to the ratio of the peaks 1414 cm$^{-1}$ and 1029 cm$^{-1}$

### DSC Studies

The DSC data obtained from these studies on the styrene-4-vinylpyridine copolymers, shown in *Table 1* for each pyridine concentration in the first row of the vinylpyridine concentration entry, clearly indicate the pattern of differing ion contents and alkyl chain lengths on the $T_g$ The values for the glass transition were confirmed by torsion pendulum and were used for the calculations that follow in the discussion section

### Torsion Pendulum

Examples of tan delta and torsion pendulum results are given in *Figs 1* and *2* The curves are all very similar, therefore all are not shown The immediate observation from these was that no clusters were present in any of the samples since there was no tan delta peak for $T > T_g$ This is consistent with previous work (24) Below the glass transition, the storage modulus of the material was typically of the order of $10^9$ N m$^2$ The initial modulus of the sample generally decreased as the chain length of the quaternizing agent increased, as in *Fig 2* The effect of the ion content on the initial modulus shows a similar trend although not as clearly Above $T_g$ the modulus of the material decreased abruptly to a level lower than that observed in other ionomers Thus it was often difficult to get very much data after $T_g$ before the experimental error became too large

The results from the torsion pendulum proved to be very sensitive to the thermal history of the sample This necessitated the elaborate annealing procedure described in experimental section

Table 1 Styrene-4 vinylpyridine Ionomers Glass Transition Temperatures °C

| Mole Percent Ions | Alkylating Agent | | | |
|---|---|---|---|---|
| | Iodobutane | Iodohexane | Iodooctane | Iododecane |
| 1 9 | 110 6 | 111 6 | 109 4 | 103 9 |
| | 111 3 | 110 3 | 109 4 | 108 4 |
| | −0 7 | 1 3 | 0 0 | −4 5 |
| 4 9 | 118 4 | 116 8 | 111 2 | 107 6 |
| | 118 8 | 116 6 | 113 8 | 111 4 |
| | −0 4 | 0 2 | −2 6 | −3 8 |
| 6 9 | 124 5 | 119 8 | 112 0 | 111 4 |
| | 123 8 | 120 3 | 116 8 | 113 4 |
| | 0 7 | −0 5 | −4 8 | −2 0 |
| 9 7 | 131 3 | 126 0 | 119 7 | 112 2 |
| | 130 8 | 125 9 | 121 0 | 115 2 |
| | 0 5 | 0 1 | −1 3 | −4 0 |

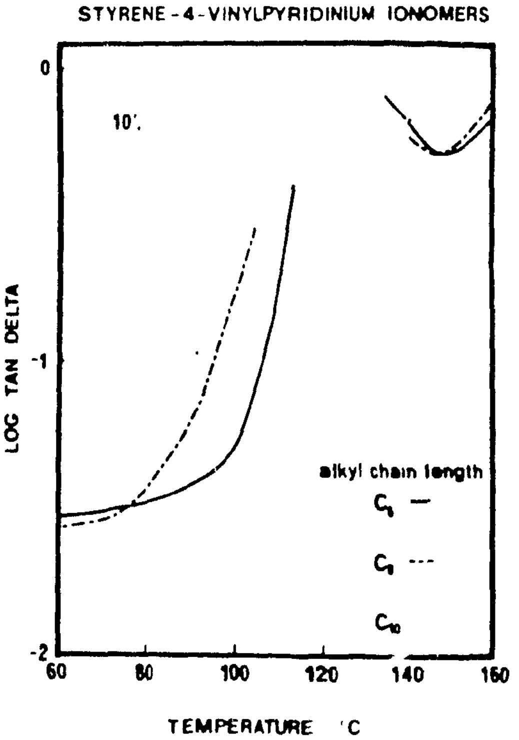

*Fig 1 Variation of tan delta with temperature for Sty 0 097VP quaternized with iodoalkanes of different lengths*

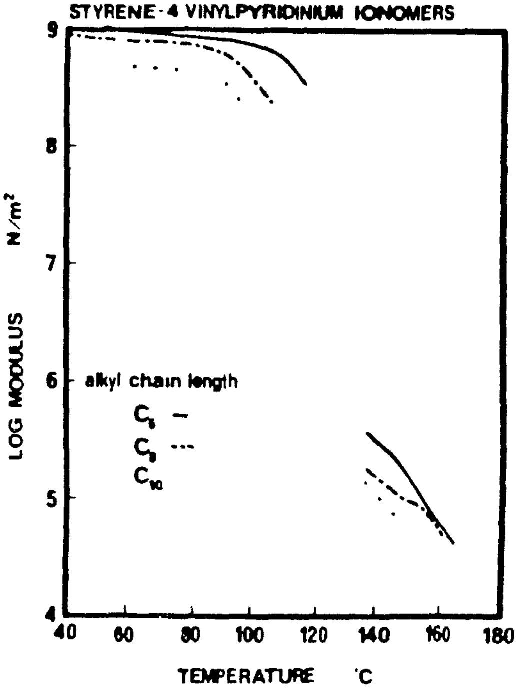

*Fig 2 Variation of the storage modulus with temperature for Sty 0 097VP quaternized with iodoalkanes of different lengths*

## DISCUSSION

It is clear from the data obtained from both the DSC and the torsion pendulum that lengthening the pendant alkyl chain lowered the $T_g$ of the ionomer Not surprisingly the effect is more pronounced at higher ion contents It has been shown elsewhere (24) that in the case of styrene-4-vinyl pyridine copolymers quaternized with iodomethane the $T_g$ increases linearly with increasing ion content This again proved to be true for the same polymer quaternized with iodobutane iodohexane iodooctane and iododecane as seen in *Fig 3* In addition, for constant ion contents, the relationship between increasing chain length and decreasing $T_g$ is linear, as shown in *Fig 4* *Figure 5* shows the relationship between the change in the $T_g$ as a function of the vinylpyridine content, from the slopes in *Fig 3* and the alkyl chain length It was found that the data could be fitted to an equation of the general form

$$T_g = T_g^{\,0} + c(k_1 - k_2 n) \qquad (1)$$

where $T_g$ is the glass transition temperature of the material and $T_g^{\,0}$ is the glass transition temperature of the nonionic starting material, in this case polystyrene The other variables in the equation are $c$ the concentration of ionic groups in mole percent $k_1$ a constant from the intercept of the plot in *Fig 5*, $k_2$ another constant for the system obtained from the slope of the plot in *Fig 5* and $n$ the number of carbons in the iodoalkane chain

The slopes of the lines for the different iodoalkanes shown in *Fig 3* were plotted on a graph against the number of carbons in the attached chains A similar slope that had been constructed for methyl iodide samples (24) was also used in the linear regression calculation

The $T_g$ of the nonionic polystyrene was determined by DSC to be 106 5°C The value of the constant $k_1$ was determined to be 3 5 ± 0 2 degrees per mole percent ions Represented by

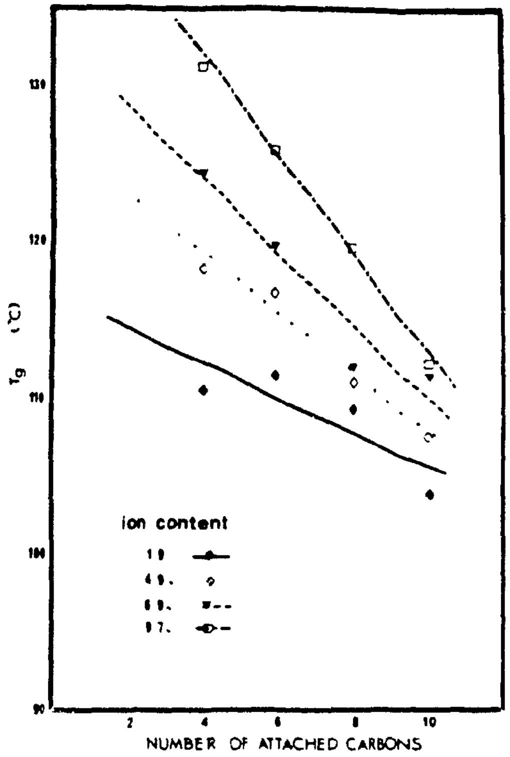

*Fig 4 Variation of the glass transition temperature with the length of the attached alkyl chain for copolymers of different ion contents*

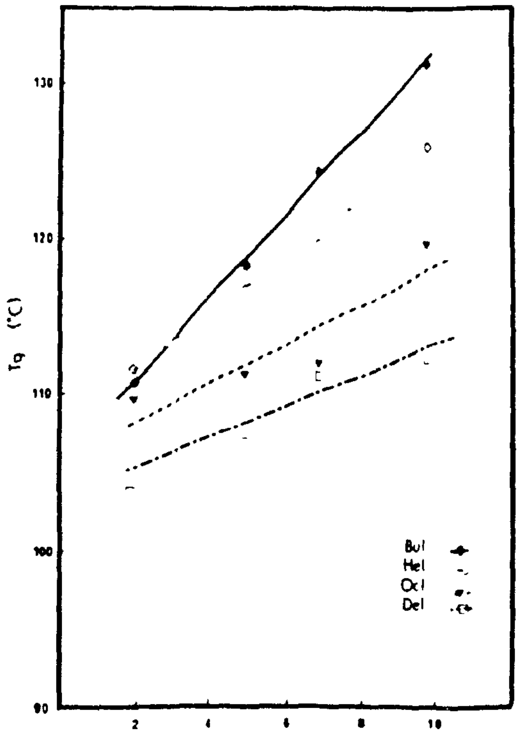

*Fig 3 Variation of the glass transition temperature with ion content for copolymers quaternized with different iodoalkanes*

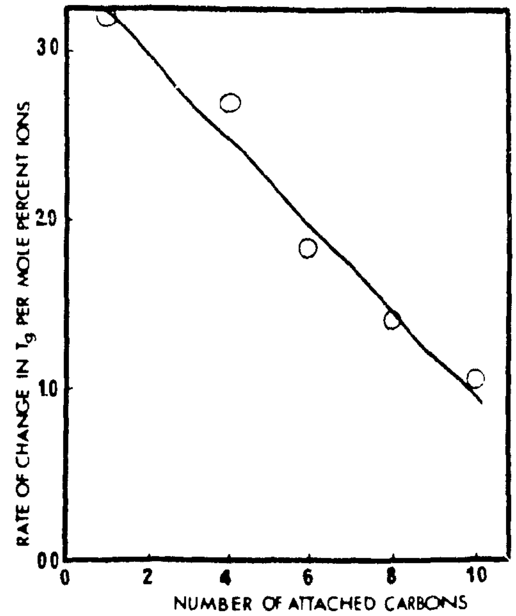

*Fig 5 Variation of the rate of change in the glass transition temperature for differing ion contents with the length of the attached alkyl chain Data for iodomethane from Ref 24*

**the slope in *Fig* 5. $k_2$ was calculated to have** the value −0 25 ± 0 02 degrees per mole percent ions per carbon atom attached Thus the general equation now takes the form

$$T_g = 106\ 5 \pm c(3\ 5 - 0\ 25n) \qquad (2)$$

The values that were obtained by the use of this equation are shown in *Table 1* in the second row In row 3 of this table are the differences between the calculated and experimental values for $T_g$ A statistical analysis shows that the average difference between these two temperatures is 1 7 degrees using absolute values of the differences

As mentioned in the introduction it has been of interest to find a means of mathematically predicting the $T_g$ Since many factors influence $T_g$ a general purpose equation describing it will have many variables related to each other in complex ways It was evident from the results obtained in this study that over the range of ion contents encountered in the polystyrene matrix the relationship between the $T_g$ and ion content as well as $T_g$ and attached side chain length was linear Yet since this relation could not be considered general on the basis of preliminary results with other systems the publications dealing with the prediction of $T_g$ by other equations were consulted to see if they were applicable to the materials in question here

These other equations could not be used for the styrene-4-vinylpyridinium-iodoalkane system given the experimental data available In particular the absence of the $T_g$ of poly-(vinylpyridinium iodoalkane) was crucial because $T_{g2}$ was called for in these other relations It was considered however that to determine these values of $T_{g2}$ was much too difficult at the present time in view of the anticipated dequaternization to warrant further study

## CONCLUSIONS

The glass transition temperatures and dynamic mechanical properties of random styrene 4-vinylpyridine ionomers quaternized with iodoalkanes have been presented The behavior of these "comb" ionomers s influenced as expected by the ion content and the length of the pendant alkyl chains Within the limits of the experimental data for example zero to ten percent vinylpyridine and one to ten carbons attached to the pyridine ring it has been possible to construct an equation that correlates the $T_g$ for such a copolymer with these variables

## APPENDIX

A linear regression (program courtesy of Mario Gauthier) was performed on each of the curves in *Figs* 3 through 5 The slope and intercept for each such curve are presented below together with their standard deviation as well as each correlation coefficient

*Figure 3*

Iodobutane
- slope 2 68 ± 0 05°C per mole percent vinylpyridine
- intercept 105 5 ± 0 4°C
- correlation coefficient 1 00

Iodohexane
- slope 1 82 ± 0 07°C per mole percent vinylpyridine
- intercept 107 9 ± 0 4°C
- correlation coefficient 1 00

Iodooctane
- slope 1 3 ± 0 3°C per mole percent vinylpyridine
- intercept 106 ± 2°C
- correlation coefficient 0 91

Iododecane
- slope 1 1 ± 0 2°C per mole percent vinylpyridine
- intercept 102 ± 1°C
- correlation coefficient 0 96

*Figure 4*

1 9% Vinylpyridine
- slope −1 1 ± 0 4°C per number of attached carbons
- intercept 117 ± 3°C
- correlation coefficient −0 84

4 9% Vinylpyridine
- slope −1 9 ± 0 2°C per number of attached carbons
- intercept 127 ± 1°C
- correlation coefficient −0 98

6 9% Vinylpyridine
- slope −2 4 ± 0 3°C per number of attached carbons
- intercept 133 ± 2°C
- correlation coefficient −0 96

9 7% Vinylpyridine
- slope −3 2 ± 0 1°C per number of attached carbons
- correlation coefficient −1 00

*Figure 5*

- slope −0 25 ± 0 02 (°C per mole percent vinylpyridine) per attached carbon
- intercept 3 5 ± 0 2°C per mole percent vinylpyridine correlation coefficient −0 98

## ACKNOWLEDGMENTS

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## REFERENCES

1 A Eisenberg P Smith and Z L Zhou *Polym Eng Sci* 22, 1117 (1982)

2 P Smith and A Eisenberg *J Polym Sci Polym Lett Ed* 21 223 (1983)

3 M Rutkowska and A Eisenberg *Macromolecules* **17**, 821 (1984)
4 M Hara and A Eisenberg *Macromolecules* 17, 1335 (1984)
5 S-D Clas and A Eisenberg *J Polym Sci Polym Phys Ed* **22**, 1529 (1984)
6 R A Weiss P K Agarwal and R D Lundberg *J Appl Polym Sci* 29, 2719 (1984)
7 P Smith Ph D thesis McGill University (1985)
8 Z I Kuvaeva A V Popov and V S Soldatov *Doklady Akademii Nauk BSSR* **28** 153 (1984)
9 F Andruzzi C Barone D Lupinacci and P L Magagnini *Makromol Chem Rapid Commun* 5 603 (1984)
10 D Lupinacci and W T Winter *J Polym Sci Poly Phys Ed* **20** 1013 (1982.
11 Y Minoura T Hanada T Kasabo and Y Ueno *J Polym Sci A 1* **4** 1665 (1966)
12 M Gordon and J S Taylor, *J Appl Chem* **2**, 495 (1952)
13 F Jenckel and R Heusch *Kolloid Z* **30**, 89 (1953)
14 T G Fox *Bull Am Phys Soc* **1**, 123 (1956)
15 P R Couchman and F E Karasz *Macromolecules* 11, 117 (1978)
16 T Czekaj and J Kapko *European Polymer Journal* 17, 1227 (1981)
17 P R Couchman *Macromolecules* **15** 770 (1982)
18 P R Couchman *Nature* **298**, 729 (1982)
19 T K Kwei *J Polym Sci Polym Lett Ed* **22**, 307 (1984)
20 A Eisenberg H Farb and L Cool *J Polym Sci* **A-2**, **4**, 855 (1966)
21 K R Dunham J Vandenberghe J W H Farber and L E Contois *J Polym Sci* 1A 751 (1963,
22 J A Shetter *Polym Letters* 1, 209 (1963)
23 W G Barb *J Polym Sci* 37, 515 (1959)
24 S Gauthier Ph D thesis McGill University (1985)

# Appendix B:

# Ionomers as Charge Additives

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## ABSTRACT

Contact electrification measurements were performed on particles containing toluenesulfonate salts both polymer bound, using a poly(styrene-co-N-methyl-4-vinylpyridinium toluenesulfonate), and a molecular salt, cetyltrimethylammonium toluenesulfonate, which is dissolved in the polymer matrix. The particles containing the ionomer become charged to a higher degree against a carrier than the particles containing the molecular salt, and have a surface salt composition, as determined by XPS, which resembles the formulation composition The surface salt composition of the particles containing the molecular salt is significantly higher than the formulation The charging results are explained in terms of ion transfer during contact and the variation in the surface ion concentration is used to estimate a relative charging capacity of the salts XPS analyses of the carriers which were used with both particles shows an S 2p signal appropriate for the toluenesulfonate anion A mechanism for charging involving the transfer of anions from the polymer particles to the carrier is proposed based on this observation

## INTRODUCTION

In the electrophotographic process used for printing and copying, toner particles (electronic ink) move from the supply bin through the machine to the designated areas on the paper.[1] The steps in the process rely heavily on the charge on the particles, characterized by the charge/mass ratio, Q/M, and the charge is activated in the storage bin by contact electrification against a second surface. The toner particles are polymeric composites containing either carbon black or color dyes and often contain a few percent of an organic salt to affect the charge. These additives are known as charge additives or charge control agents.[2,3] A fair number of organic salts, both molecular and polymer bound, have been studied for their influence on the particle charge produced by contact electrification. We now wish to report some results on contact electrification of polymer particles containing ionomers with bound quaternary ammonium toluenesulfonate salts. In comparing the charging behavior of ionomers with molecular salts, we find that the ionomers have a higher capacity for charging then structurally similar molecular salts.

## RESULTS AND DISCUSSION

The random copolymer, poly(styrene-co-4-vinylpyridine), was prepared by copolymerization of styrene and 4-vinylpyridine using published values of $r_1$ and $r_2$.[4] It has Mn of 50,000 and contains 6.0 mole percent vinylpyridine (5.1 to 6.9 mole percent as determined from the polymerization conditions. The corresponding ionomer, poly(styrene-co-N-methyl-4-vinylpyridinium toluenesulfonate), poly(S-co-MVP OTs), was obtained from the quaternization of the pyridine nitrogen with methyl toluenesulfonate in a method based on a previous report.[5] The particles used for the contact electrification measurements were prepared by melt mixing 10 % of the ionomer with 90% of a 60/40 poly(styrene-co-butylmethacrylate) random copolymer, poly(S-co-BMA), at 169 °C for 15 minutes using an HBI torque rheometer. The polymers are stable to these conditions and decompose in the temperature range 290-320 °C. Milling this mixture produced particles with irregular shapes. The particles had a size distribution ranging from 2 to 10 microns with an average size (by weight) of 9.4 microns. A complementary set of materials composed of poly(S-co-BMA) and cetyltrimethylammonium toluenesulfonate (CTMA OTs) were prepared and studied in parallel. This salt was selected for the comparison because it is a commonly known charge additive.

The capacity of the particles to charge by contact electrification was determined using a common procedure, known as total blow off[1b] In this procedure, the polymeric particles were mixed with 200 micron size irregular shaped metal particles coated with a polymer film (known as carrier), and rolled in a jar for 15 minutes to activate the charge through tribocharging We find that the charge stabilizes at a maximum value during this time The mixture was then transfered to a Faraday cage and the polymer particles were blown away from the carrier with air through a wire screen with 45 micron size openings. The Q/M for the collection of polymer particles was determined from the total charge measured across the screen using a Keithley electrometer and the weight difference of the cage before and after the blow off experiment A toner/carrier weight ratio of 0 025 was used and the particle separation was accomplished using 56 psi air pressure during 3 minutes. As can be seen in Table 1, the toners charge positive and the Q/M values are higher with the particles containing the ionomer. The values are averages of 2-5 measurements and have a 5-8% error. The salt content used in these experiments exceeds the concentration range where Q/M is a strong function of the salt content, thus, the Q/M values are fairly constant The results reveal that the particles with the ionomer salt (16-52 $\mu$mol/g) have Q/M values which are ca 1.5 times greater than the values for the particles containing CTMA OTs (4-13 $\mu$mol/g). Large particles (39 $\mu$m) of the pure ionomer charge lower than the blended particles, as is expected for larger size particles which have a lower surface to volume ratio

Our interpretation of the charging results assumes that only the salt in the surface region of the particles is active for charging Ions in the bulk must have a small effect given the highly insulating nature of these materials For example, pressed pellets of these materials (50K psi) have resistances greater than $10^{13}$ ohms at 10 V (1 mm spacing) Correspondingly, the diffusion coefficient for ions in a viscous polymer (for example, at temperatures near the Tg) can be estimated equal to $10^{16}$ $cm^2/s$[6] Thus, ion mobility is slow on the time scale of our experiments We therefore analyzed some of the toners by XPS, a surface sensitive technique (top tens of Angstroms) The toner particles were supported on indium foil and the analyses were performed on a SSX-100 model 05 XPS spectrometer, using a 600 $\mu$m spot Low energy electrons were supplied to the sample, as required, to neutralize surface charging The binding energies were referenced to the main carbon peak, taken as 284 6 eV The N 1s and S 2p signals were used to monitor the amount of ammonium and sulfonate ions in the surface region of the particles The surface atomic concentrations were estimated from the curve fit peak areas, corrected for the relative photoionization cross-sections. [7] These values are listed in Table 1. The values for C and O agree well with the calculated values in every case. The values for S are consistently higher than those for N by a factor of 1.6 to 2.0, but the differences may be at least partially due to the experimental error in the measurement of the small peaks (ca 25 % for N and ca. 15 % for S). Alternatively, the difference may reflect a preferred orientation of the sulfur species, where it may be positioned closer to the surface The N and S content for the particles with 52 $\mu$mol/g ionomer salt is in fair agreement with the amount calculated from the bulk composition. With the sample containing 26 $\mu$mol/g ionomer salt, the S value again matches the calculated amount, but to the extent that there is a signal for N, it is below the detection limit. In contrast with these results, the N and S signals for the samples with the molecular salt, CTMA OTs, are significantly higher than the amounts calculated from the formulation. This result is not too surprizing since this is a surface active salt. The salt probably becomes segregated on the surface during the milling process, but this remains to be determined

The salt in the polymer clearly controls the process which transfers charge from the toner to the carrier surface. Since the toner develops a positive charge, the $OTs^-$ anion of the salt must be the active species during the contact, but the key question remains to be answered Does the $OTs^-$ transfer to the carrier? or does it oxidize and transfer an electron? While an electron transfer process may be plausible for those cases where at least one of the surfaces involved in the contact electrification is a metal surface, [8-11] it is difficult to envision the occurrence of an electron transfer in a completely insulating system considering the known electrochemistry of these salts First, thermal electron transfer does not occur between arylsulfonate anions and neutral polymers such as, polyesters, epoxides, polyethers, etc Secondly, even in the presence of an applied electric field, the oxidation potentials for this class of ions are much higher than those for water and oxygen [12] Thus, water and oxygen are always oxidized before these ions In light of this, we suggest that charging observed with insulating polymer-polymer systems containing salts, results from the transfer of ions With the present materials, the OTs ion is the more mobile ion and is more likely to transfer XPS analysis of the carriers after 15 minutes rolling with the toner and removal of toner shows a strong S signal which is not present in carrier samples which have not been in contact with toner This is the case for the carriers used with the toners containing 26 and 52 $\mu$mol/g poly(S-co-MVP OTs) and toner containing 13 2 $\mu$mol/g CTMA OTs The observed S to "noncarrier' C ratios are in the range 0.0021-0.0035, and are 7-20 times greater than the S/C ratios of 0.0003-0.0009 observed for the toners themselves. Therefore, the toluenesulfonate anion content on the surface of the carrier is in excess of the amount expect if the carrier surface was contaminated with portions of the toner This result supports our proposal that the transfer of the $OTs^-$ anion between the two surfaces is the principal mechanism of charging. Since the polymer coating on the carrier contains nitrogen, the transfer of alkylammonium cations cannot be monitored directly. It should be stated, however, that charge separation may not be restricted to ions of the charge additive, and the involvment of moisture associated with the salt or the polymer on the surface of the particles can not be dismissed [13] The contact and separation event of the particles may promote the dissociation of adsorbed water molecules to produce $OH^-$ and $H^+$ ions which may contribute to the ion transfer process between surfaces

Regarding the different charge levels reached by the particles containing ionomer and molecular salt, we attribute it to a smaller net charge attained with the molecular salt because the ammonium cations may also transfer to reduce the net negative charge and make the toner and carrier surfaces more chemically similar Cation transfer is of course more difficult with the ionomer because the cation is bound to the polymer Finally, the Q/M values can be adjusted to reflect the salt content on the surface of the particles, as determined by XPS. This adjustment reveals that the ionomer has a surface molar charge capacity which is 5-10 times greater than that of CTMA OTs.

## ACKNOWLEDGMENTS

The authors wish to thank E Hadziioannou and J Lerczak for their assistance with various aspects of this study

## Table 1. SUMMARY OF CHARGING AND XPS RESULTS

| SALT BULK CONTENT[1] | Q/M | ATOMIC PERCENT (XPS)[2] | | |
|---|---|---|---|---|
| µMol/g | µC/g | Element | Found | Cal'd |
| **POLYMER: Poly(Styrene-co-Butylmethacrylate), no additive** | | | | |
| | | C | 93.18 | 93.43 |
| - | 0.73 | O | 6.82 | 6.57 |
| | | N,S | 0.00, 0.00 | 0.0, 0.0 |
| **IONOMER: Poly(Styrene-co-Methyl-4-vinylprydrinium Toluenesulfonate)** | | | | |
| 5.2 | 39 | | | |
| 15.6 | 79 | | | |
| | | C | 93.6 | 93.54 |
| 26.0 | 75 | O | 6.4 | 6.38 |
| | | N | 0.00 | 0.033 |
| | | S | 0.04 | 0.033 |
| 36.4 | 73 | | | |
| | | C | 92.8 | 93.72 |
| 52.0 | 81 | O | 7.1 | 6 15 |
| (52)[3] | | N | 0.05 | 0.066 |
| | | S | 0 08 | 0.066 |
| | | C | 95.9 | 96.60 |
| 520 | 42 | O | 2.7 | 2 10 |
| (520)[3] | | N | 0.50 | 0.69 |
| | | S | 0.99 | 0.69 |
| **MOLECULAR SALT: Cetyltrimethylammonium Toluenesulfonate** | | | | |
| 4.4 | 58 | | | |
| 8.8 | 55 | | | |
| | | C | 92.8 | 93.30 |
| 13.2 | 51 | O | 6 8 | 6 63 |
| (165)[3] | | N | 0 16 | 0.0161 |
| | | S | 0.25 | 0 0161 |

[1] Bulk salt content calculated from the formulation

[2] Peak position and cross-sections for the XPS signals, C, 284.6 eV (1.00); O, 532 2 eV (2.494); N, 401.7 eV (1 678); S, 167 4 eV (1.793)

[3] Salt content in the surface region calculated from XPS

## REFERENCES

1. (a) Schein, L., "Electrophotography and Development Physics", Springer Series in Electrophysics, 14, 1988; (b) Page 79.

2. Birkett, K. L.; Gregory, P., Dyes and Pigments, 1986, 7, 341.
3. Macholdt, H.-T.; A. Sieber, A., Dyes and Pigments, 1988 ,9, 119.

4. Brandrup, J.; Immergut, E. H., Eds., Polymer Handbook, 2nd Edition, Wiley-Interscience, 1975, p. 11-327

5. Gauthier, S.; Duchesne, D.; Eisenberg, A., Macromol., 1987, 20, 753.

6. Estimated by extrapolation of the data presented by Zhang, X.; Leddy, J.; Bard, A. J., J. Amer. Chem. Soc, 1985, 107, 3719.

7. Scofield, J. H., J. Electron Spectr., 1976, 8, 129.

8. Anderson, J. H.; Bugner, D. E., 4th International Congress on Non-Impact Printing Technologies, New Orleans LA, 1988, p.79.

9. Bugner, D. E.; Anderson, J. H., ACS National Meeting, Los Angeles CA, 1988, Polymer Reprints, 29, p. 463

10. Nanya, T.; Tsubuko, K , Japan Hardcopy '88, The Society of Electrophotography of Japan, 30th Conference, May 16 1988, Tokyo, Japan, p. 9.

11. Gibson, H. W , J. Amer. Chem. Soc., 1975, 97, 3832

12. Weinberg, N. L., Ed., "Technique of Electroorganic Synthesis", John Wiley and Sons, New York, 1975, Part II, Vol. 5, p 667.

13. TGA analysis in air revealed the following weight losses in the region between room temperature and 150°C: 0.07 % with poly(S-co-BMA), 0.51 % with CTMA OTs (pure), and 2.3 % with poly(S-co-MVP OTs, 520 μmol/g ionomer). We attribute this weight loss to the removal of moisture.

# Appendix C:

# Solubilities of Alkylated Styrene-Vinylpyridinium Ionomers

## C. 1: Introduction

Polymers, in general, are less readily soluble than their small molecule analogues. The thermodynamics of dissolution is often cited as the fundamental reason for the lowered polymer solubility; this is apparent from the Gibbs free energy equation

$$\Delta G = \Delta H - T\Delta S.$$

In order for dissolution to proceed spontaneously, $\Delta G$ must be negative. However, because the change in entropy, $\Delta S$, of a polymer going into solution is significantly less than the difference in entropy for a small molecule, more favourable interactions between the polymer and the solvent are often necessary to make $\Delta G$ negative. Therefore, the range of solvents for a particular polymer is often severely restricted when compared to the list of compounds in which its monomer is soluble.

Not surprisingly, the presence of two kinds of repeat unit makes it more difficult to find a common solvent. This is particularly true when the different units are on independent chains, as in the case of blends of two homopolymers. It is also a factor in block copolymers, if the blocks are long enough. For example, ABA copolymers of styrene (B) and 4-vinylpyridine (A) are not soluble in tetrahydrofuran (THF) when the 4-vinylpyridine blocks are very long[1]; although styrene, polystyrene and 4-vinylpyridine are soluble in THF, poly(4-vinylpyridine) is not, and its presence as a block in the copolymer in sufficient quantity is enough to prevent dissolution. Random copolymers tend to be more readily soluble than the blocks, and the proportion of nonsoluble comonomer to soluble comonomer often must be much greater than in the blocks before the material is no longer soluble.

Sometimes, however, random copolymers cannot dissolve even when the amount of insoluble comonomer is very low. This is true in the case when there are strong, specific interactions in the solid material, such as occur in ion-containing polymers. In these particular situations, a solution may be obtained if the dielectric constant of the solvent is increased, either by using a somewhat more polar solvent, or by using a mixture of two solvents. Thus, the solubility of an ionomer is often restricted to the higher dielectric constant compounds which are solvents for the nonionic precursor.

In the case of the alkylated styrene-N-methyl-4-vinylpyridinium iodide ionomers, a rather different phenomenon was observed. These materials were soluble in a much broader range of materials than expected, even at very high, i.e. 10 mole %, vinylpyridine content. This preliminary investigation is reported here, and is also suggested as an area of further work.

## C.2: Experimental and Results

The preparation of the alkylated ionomers has been previously described[2]. It is briefly summarised here for convenience.

Random copolymers of styrene and vinylpyridine were prepared using free radical techniques. Following isolation and characterisation to determine the vinylpyridine content, the materials were alkylated in a Friedel-Crafts reaction with 1-decene. The resulting polymers were subsequently isolated, purified and reprecipitated. The extent of alkylation was determined by NMR, the the polymers were quaternised with iodomethane in THF. The difficulties enocuntered in precipitationg the ionomer in methanol or in hexanes led to the following experiments.

Ionomers which were highly alkylated were used in this study, but similar behaviour in precipitation was observed for the 30 mole % alkylated material prepared later. Approximately 0.1 g of the ionomer was put in a testtube, 2 mL of a solvent, as received, was added, and the solubility of the material was recorded. The results are listed in Table C-1.

## C.3: Discussion

The solubility behaviour of alkylated ionomers differs from that of polystyrene in two ways. In the ionomers, the styrene matrix is highly alkylated with 1-decene. The alkylation of polystyrene is expected to slightly reduce its dielectric constant[3] from 2.85 to a value closer to that of toluene (2.38), and thus should increase the solubility of the nonionic material in nonpolar solvents, such as aliphatic hydrocarbons. At the same time, ionomers are less miscible in solvents of low polarity than are their nonionic precursors. Instead the ionomers described in this study are readily soluble in n-heptane, a nonsolvent for nonionic, unalkylated polystyrene, yet can be dissolved (with heating) in acetone, even at ion concentrations of less than 3 mole %. Apparently, instead of two competing effects, the presence of a nonpolar internal plasticiser and ionic groups in one material results in an overall cooperative effect with respect to the solubility of the ionomers.

The alkylation of the phenyl rings probably has a two-fold effect on the solubility. Thus, in addition to the reduction in the dielectric constant described above, the incorporation of long alkyl chains increases the free volume of the material, and presumably partially solvates it before any solvent is added.

From the results of small angle X-ray scattering studies[2], it is known that the highly alkylated, low vinylpyridine content materials do not appear to be clustered, while materials with vinylpyridine contents equal to or greater than 8 mole %, and possessing similar levels of alkylation do exhibit evidence of phase separation. Consequently, the dissolution of the ionomer is not affected by the presence of domains of different ion contents, although these domains are of great significance in dynamic mechanical studies.

While these ionomers are not soluble in methanol going from the solid state, the

**Table C.1: Solution Behaviour of Alkylated Ionomers**

| Material | Solvent | Dielectric* Constant | Solubility** Parameter $[J/m^3]^{1/2}*10^{-3}$ | Behaviour |
|---|---|---|---|---|
| Sty[p-C10]-.027VP-MeI | n-Heptane | 1.9 | 15.1 p | soluble |
| " " | $CCl_4$ | 2.24 | 17.6 p | " |
| " " | Toluene | 2.38 | 18.2 p | " |
| " " | $CS_2$ | 2.64 | 20.5 p | " |
| " " | Diethyl ether | 4.34 | 15.1 m | " |
| " " | $CHCl_3$ | 4.81 | 19.0 p | " |
| " " | Chlorobenzene | 5.71 | 19.4 p | " |
| " " | THF | 7 | 18.6 m | " |
| " " | Pyridine | 12.3 | 21.9 s | " |
| " " | Cyclohexanone | 18.3 | 20.3 m | "[a] |
| " " | Methyl ethyl ketone | 18.4 | 19.0 m | " |
| " " | Acetone | 20.7 | 20.3 m | "[b] |

Continued on next page.

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*Values of the dielectric constants taken from CRC, 63d Edition and from Pine, Hendrickson, Cram and Hammond, Organic Chemistry, 4th Edition, McGraw-Hill, New York, 1980, p.388.

**Values of the solubility parameters taken from Polymer Handbook, 2 ed., eds. J. Brandrup and E. H. Immergut, Wiley-Interscience, New York, iv-341 (1975).

a Slowly

b On heating

**Table C.1 (continued)**

| Material | Solvent | Dielectric Constant | Solubility Parameter<br>$[J/m^3]^{1/2}*10^{-3}$ | Behaviour |
|---|---|---|---|---|
| Sty[p-C10]-.027VP-MeI | Methanol | 32.6 | 29.7 s | not soluble |
| " " | DMF | 37 | 24.8 m | " |
| " " | DMSO | 45 | 24.6 m | " |
| " " | Water | 81 | 47.9 s | " |
| Sty[p-C10]-.10VP-MeI | n-Heptane | 1.9 | 15.1 p | soluble |
| " " | Acetone | 20.7 | 20.3 m | soluble[c] |

For reference, polystyrene is soluble in solvents ranging from toluene and chloroform to methyl ethyl ketone and carbon disulfide. It is not soluble in aliphatic hydrocarbons, acetone or diethyl ether[4]. This corresponds to a solubility range of 16,400 - 21,700 $[J/m^3]^{1/2}$ for poorly hydrogen-bonded solvents and to a range of 16,600 to 20,300 $[J/m^3]^{1/2}$ for moderately hydrogen-bonded materials[5]. Thus the solvents in which the alkylated ionomers extend the solubility range over that of polystyrene are n-heptane, diethyl ether, pyridine and acetone.

---

c Cloudy

5 % solution of ionomer in THF could not be precipitated in 20 volumes of methanol, and the solution had to be concentrated to *ca.* 20 % ionomer before any precipitation was possible. Thus, very little solvent is required to keep such an ionomer is solution in what is, for the unalkylated ionomers, a nonsolvent.

## C.4: Conclusions

The alkylation of an ionomer and resultant lowering of the dielectric constant of the matrix does not diminish the solubility of the polymer in polar solvents However, this same alkylation increases the solubility of the ionomer in nonpolar solvents. This leads to the situation in which the highly alkylated styrene-N-methyl-4-vinylpyridinium iodide ionomers are soluble in solvents which are so nonpolar that polystyrene cannot dissolve in them Thus, the presence of ionic groups and nonpolar internal plasticisers confers solubility over a wider range of solvents to these ionomers than either one of these factors alone.

## C.5 References

(1) S. Gauthier, Ph. D. Thesis, McGill University, 1985.

(2) D. Wollmann, C. E. Williams and A. Eisenberg, in preparation.

(3) O. Yaro and Y. Wada, J. Polym. Sci., **9**, 686 (1971).

(4) Polymer Handbook, 2d Ed., eds. J. Brandrup and E. H. Immergut, Wiley-Interscience, New York, iv-241 (1975).

(5) Polymer Handbook, 2d Ed., eds. J. Brandrup and E. H. Immergut, Wiley-Interscience, New York, p. 352 (1975).

# Appendix D

## Supporting Data

The supporting data for this dissertation is organised in the following manner. The data from the torsion pendulum is printed out and listed according to the experiments that were performed. This data is listed in the first section of this appendix.

The data for the DMTA runs and the SAXS experiments are on floppy diskettes. The DMTA data may be accessed using the programme READDMTA, written by Mario Gauthier, and included on diskette #1. The user should enter READDMTA and he will be prompted for the name of the DMTA file to access

The small angle X-ray scattering data is already in ASCII files, which can be read by using the DOS command TYPE [filename].

Name RBU22.DAT

STY-0.0193VP(4 ) BU1(R)
NOV. 5, 1984

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 36.2 | 0.01478 | 9.155E+08 | 1.353E+07 | 2.4408 |
| 38.0 | 0.01528 | 9.146E+08 | 1.397E+07 | 2.4396 |
| 40.3 | 0.01537 | 9.097E+08 | 1.398E+07 | 2.4331 |
| 42.7 | 0.01526 | 9.055E+08 | 1.382E+07 | 2.4275 |
| 43.4 | 0.01537 | 9.044E+08 | 1.390E+07 | 2.4260 |
| 44.9 | 0.01574 | 9.055E+08 | 1.425E+07 | 2.4275 |
| 46.2 | 0.01575 | 9.014E+08 | 1.419E+07 | 2.4219 |
| 48.4 | 0.01569 | 9.040E+08 | 1.419E+07 | 2.4254 |
| 52.0 | 0.01659 | 8.917E+08 | 1.480E+07 | 2.4088 |
| 54.4 | 0.01624 | 8.931E+08 | 1.451E+07 | 2.4107 |
| 58.6 | 0.01656 | 8.825E+08 | 1.461E+07 | 2.3964 |
| 62.3 | 0.01708 | 8.757E+08 | 1.496E+07 | 2.3872 |
| 64.7 | 0.01685 | 8.772E+08 | 1.478E+07 | 2.3892 |
| 68.2 | 0.01695 | 8.690E+08 | 1.473E+07 | 2.3780 |
| 70.1 | 0.01701 | 8.662E+08 | 1.473E+07 | 2.3742 |
| 72.6 | 0.01692 | 8.631E+08 | 1.460E+07 | 2.3699 |
| 74.8 | 0.01724 | 8.564E+08 | 1.476E+07 | 2.3607 |
| 76.0 | 0.01739 | 8.559E+08 | 1.488E+07 | 2.3600 |
| 77.3 | 0.01750 | 8.528E+08 | 1.493E+07 | 2.3558 |
| 81.9 | 0.01758 | 8.458E+08 | 1.487E+07 | 2.3460 |
| 83.1 | 0.01813 | 8.440E+08 | 1.530E+07 | 2.3436 |
| 84.5 | 0.01802 | 8.423E+08 | 1.517E+07 | 2.3412 |
| 89.4 | 0.01875 | 8.294E+08 | 1.555E+07 | 2.3233 |

STY-0.0193VP(4-) BU1(R)
NOV. 5, 1984

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 90.6 | 0.01945 | 8.273E+08 | 1.609E+07 | 2.3203 |
| 92.9 | 0.01899 | 8.219E+08 | 1.561E+07 | 2.3127 |
| 96.2 | 0.01971 | 8.152E+08 | 1.607E+07 | 2.3032 |
| 95.5 | 0.02011 | 8.127E+08 | 1.635E+07 | 2.2997 |
| 97.4 | 0.01979 | 8.144E+08 | 1.611E+07 | 2.3021 |
| 99.0 | 0.02039 | 8.086E+08 | 1.649E+07 | 2.2939 |
| 100.1 | 0.02104 | 8.038E+08 | 1.691E+07 | 2.2870 |
| 100.5 | 0.02229 | 8.005E+08 | 1.785E+07 | 2.2824 |
| 100.9 | 0.02211 | 7.953E+08 | 1.759E+07 | 2.2750 |
| 102.2 | 0.02240 | 7.961E+08 | 1.783E+07 | 2.2761 |
| 104.5 | 0.02368 | 7.867E+08 | 1.863E+07 | 2.2627 |
| 106.3 | 0.02514 | 7.697E+08 | 1.935E+07 | 2.2380 |
| 107.9 | 0.02626 | 7.637E+08 | 2.005E+07 | 2.2293 |
| 108.4 | 0.03598 | 7.424E+08 | 2.671E+07 | 2.1978 |
| 110.2 | 0.04298 | 7.304E+08 | 3.139E+07 | 2.1798 |
| 116.2 | 0.12027 | 4.627E+08 | 5.566E+07 | 1.7327 |
| 120.1 | 0.54270 | 3.987E+08 | 2.164E+08 | 1.5459 |
| 143.2 | 0.86690 | 3.712E+05 | 3.218E+05 | 0.0769 |
| 143.8 | 0.63479 | 4.386E+05 | 2.784E+05 | 0.0801 |
| 147.5 | 0.47205 | 4.899E+05 | 2.313E+05 | 0.0824 |
| 148.6 | 0.77719 | 2.470E+05 | 1.920E+05 | 0.0722 |
| 148.8 | 0.50048 | 3.595E+05 | 1.799E+05 | 0.0773 |
| 152.4 | 0.42503 | 2.858E+05 | 1.215E+05 | 0.0743 |

STY-0.0193VP(4-)-RUI(F)
NOV. 5, 1984

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 153.5 | 0.44610 | 2.534E+05 | 1.130E+05 | 0.0729 |
| 156.2 | 0.38749 | 2.618E+05 | 1.014E+05 | 0.0733 |
| 155.3 | 0.24646 | 3.151E+05 | 7.766E+04 | 0.0757 |
| 155.2 | 0.46034 | 2.102E+05 | 9.675E+04 | 0.0710 |
| 158.6 | 0.43372 | 2.024E+05 | 8.778E+04 | 0.0706 |
| 160.2 | 0.38278 | 1.978E+05 | 7.572E+04 | 0.0704 |
| 160.6 | 0.59308 | 1.338E+05 | 7.938E+04 | 0.0674 |
| 163.9 | 0.71678 | 1.064E+05 | 7.623E+04 | 0.0661 |
| 166.0 | 0.73167 | 9.553E+04 | 6.990E+04 | 0.0656 |
| 167.0 | 0.61160 | 1.079E+05 | 6.602E+04 | 0.0662 |
| 170.5 | 0.99210 | 6.622E+04 | 6.570E+04 | 0.0641 |
| 173.4 | 0.75229 | 7.784E+04 | 5.856E+04 | 0.0647 |
| 177.6 | 0.86671 | 6.500E+04 | 5.634E+04 | 0.0641 |
| 179.9 | 1.54954 | 3.427E+04 | 5.310E+04 | 0.0625 |
| 181.6 | 1.79881 | 2.769E+04 | 4.981E+04 | 0.0621 |
| 182.9 | 1.95231 | 2.357E+04 | 4.601E+04 | 0.0619 |
| 186.0 | 3.29584 | 1.221E+04 | 4.025E+04 | 0.0613 |

STY 0.0486VP(4 ) BHT(6)
DEC. 3, 1984

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 22.2 | 0.01431 | 1.229E+09 | 1.760E+07 | 2.8765 |
| 30.0 | 0.01588 | 1.210E+09 | 1.921E+07 | 2.8537 |
| 31.5 | 0.01598 | 1.207E+09 | 1.929E+07 | 2.8504 |
| 33.8 | 0.01650 | 1.204E+09 | 1.986E+07 | 2.8464 |
| 35.8 | 0.01662 | 1.201E+09 | 1.996E+07 | 2.8436 |
| 37.0 | 0.01684 | 1.193E+09 | 2.010E+07 | 2.8341 |
| 38.5 | 0.01649 | 1.191E+09 | 1.964E+07 | 2.8313 |
| 39.8 | 0.01649 | 1.190E+09 | 1.963E+07 | 2.8302 |
| 40.8 | 0.016[illegible] | 1.188E+09 | 1.980E+07 | 2.8280 |
| 42.4 | 0.01708 | 1.182E+09 | 2.019E+07 | 2.8202 |
| 42.8 | 0.01737 | 1.179E+09 | 2.048E+07 | 2.8169 |
| 44.2 | 0.01752 | 1.175E+09 | 2.059E+07 | 2.8125 |
| 45.8 | 0.01743 | 1.175E+09 | 2.048E+07 | 2.8125 |
| 47.2 | 0.01742 | 1.172E+09 | 2.042E+07 | 2.8092 |
| 48.9 | 0.01788 | 1.166E+09 | 2.085E+07 | 2.8016 |
| 50.2 | 0.01745 | 1.161E+09 | 2.025E+07 | 2.7950 |
| 51.7 | 0.01854 | 1.155E+09 | 2.141E+07 | 2.7885 |
| 52.5 | 0.01822 | 1.156E+09 | 2.107E+07 | 2.7896 |
| 52.9 | 0.01840 | 1.152E+09 | 2.119E+07 | 2.7842 |
| 53.1 | 0.01798 | 1.153E+09 | 2.074E+07 | 2.7864 |
| 54.0 | 0.01836 | 1.150E+09 | 2.111E+07 | 2.7921 |
| 55.5 | 0.01866 | 1.151E+09 | 2.149E+07 | 2.7857 |
| 56.5 | 0.01865 | 1.145E+09 | 2.133E+07 | 2.7735 |

STY 0.0486VP-4 [illegible]
DEC. 3, 1984

| TEMP. | TAN DELTA | G | G' | FREQ. |
|---|---|---|---|---|
| 57.0 | 0.01868 | 1.142E+09 | 2.132E+07 | 2.7719 |
| 58.0 | 0.01868 | 1.140E+09 | 2.130E+07 | 2.7703 |
| 58.5 | 0.01828 | 1.139E+09 | 2.081E+07 | 2.7687 |
| 59.0 | 0.01915 | 1.137E+09 | 2.176E+07 | 2.7666 |
| 60.4 | 0.01902 | 1.135E+09 | 2.159E+07 | 2.7639 |
| 61.0 | 0.01923 | 1.131E+09 | 2.175E+07 | 2.7586 |
| 62.0 | 0.01934 | 1.130E+09 | 2.184E+07 | 2.7576 |
| 62.2 | 0.01935 | 1.128E+09 | 2.183E+07 | 2.7555 |
| 63.0 | 0.01950 | 1.126E+09 | 2.195E+07 | 2.7528 |
| 63.5 | 0.01987 | 1.123E+09 | 2.231E+07 | 2.7491 |
| 64.0 | 0.01967 | 1.121E+09 | 2.205E+07 | 2.7465 |
| 65.6 | 0.01983 | 1.118E+09 | 2.217E+07 | 2.7434 |
| 66.5 | 0.02017 | 1.115E+09 | 2.250E+07 | 2.7397 |
| 67.2 | 0.01994 | 1.112E+09 | 2.218E+07 | 2.7361 |
| 70.0 | 0.02045 | 1.100E+09 | 2.250E+07 | 2.7216 |
| 71.8 | 0.02093 | 1.093E+09 | 2.289E+07 | 2.7129 |
| 73.0 | 0.02075 | 1.095E+09 | 2.273E+0 | 2.7149 |
| 73.5 | 0.02134 | 1.090E+09 | 2.326E+07 | 2.7088 |
| 75.5 | 0.02222 | 1.082E+09 | 2.403E+07 | 2.6981 |
| 76.8 | 0.02258 | 1.075E+09 | 2.427E+07 | 2.6896 |
| 78.8 | 0.02291 | 1.071E+09 | 2.454E+07 | 2.6851 |
| 80.8 | 0.02345 | 1.055E+09 | 2.473E+07 | 2.664 |
| 81.6 | 0.02437 | 1.053E+09 | 2.566E+0 | 2.6617 |

STY-0.0485[illegible]
DEC. 3, 1984

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 83.0 | 0.02483 | 1.046E+09 | 2.597E+07 | 2.6[illegible]29 |
| 85.3 | 0.02614 | 1.035E+09 | 2.704E+07 | 2.6389 |
| 86.2 | 0.0[illegible]24 | 1.024E+09 | 2.[illegible]89E+07 | 2.6[illegible] |
| 8[illegible] | 0.028[illegible] | 1.016E+09 | 2.87[illegible]E+07 | 2.6148 |
| 89.4 | 0.02908 | 1.010E+09 | 2.938E+07 | 2.60[illegible] |
| 90.5 | 0.03135 | 1.002E+09 | 3.140E+07 | 2.59[illegible] |
| 92.8 | 0.0343[illegible] | 9.905E+08 | 3.399E+07 | 2.5818 |
| 94.2 | 0.04060 | 9.581E+08 | 3.890E+07 | 2.5[illegible]92 |
| 95.9 | 0.04665 | 9.368E+08 | 4.3[illegible]E+07 | [illegible] |
| 97.3 | 0.05163 | 9.202E+08 | 4.751E+07 | 2.488[illegible] |
| 98.8 | 0.06141 | 8.949E+08 | 5.496E+07 | 2.4534 |
| 101.9 | 0.13[illegible]1 | 7.5[illegible]1E+08 | 1.003E+08 | 2.2[illegible] |
| 103.2 | 0.16[illegible] | [illegible].299E+08 | 1.184E+08 | [illegible] |
| 10[illegible].6 | 0.1[illegible]698 | 7.095E+08 | 1.256E+08 | [illegible] |
| 10[illegible].6 | 0.1940[illegible] | 6.649E+08 | 1.290E+08 | [illegible].1059 |
| 12[illegible].0 | 0.505[illegible] | [illegible]E+05 | [illegible].015E+05 | [illegible] |
| 132.9 | 0.424[illegible] | 5.281E+05 | 2.24[illegible]E+05 | 0.083[illegible] |
| 1[illegible].5 | 0.45646 | 4.5[illegible]E+05 | 2.084E+05 | [illegible].0811 |
| 134.4 | 0.44251 | 4.09[illegible]E+05 | 1.811E+05 | 0.0[illegible]1 |
| 135.2 | 0.4[illegible] | 4.235E+05 | 1.[illegible]95E+05 | [illegible] |
| 138.3 | 0.360[illegible] | 3.680E+05 | 1.328E+05 | 0.0[illegible]5 |
| 139.0 | 0.3[illegible]382 | 3.35[illegible]E+05 | 1.255E+05 | 0.0[illegible]61 |
| 141.[illegible] | 0.[illegible]8628 | 2.982E+05 | 1.15[illegible]E+05 | 0.0[illegible]44 |

STY-0.0486VP4 2-BUT(R)
DEC. 3, 1984

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 14[illegible] | 0.38158 | 2.792E+05 | 1.062E+05 | 0.0736 |
| 144.5 | 0.41126 | 2.442E+05 | 1.004E+05 | 0.0729 |
| 147.0 | 0.42742 | 2.080E+05 | 8.889E+04 | 0.0703 |
| 150.5 | 0.49771 | 1.814E+05 | 9.028E+04 | 0.0690 |
| 151.5 | 0.51223 | 1.593E+05 | 8.160E+04 | 0.0677 |
| 153.0 | 0.56109 | 1.385E+05 | 7.771E+04 | 0.0669 |
| 154.2 | 0.63449 | 1.183E+05 | 7.506E+04 | 0.0669 |
| 156.4 | 0.76242 | 9.051E+04 | 6.901E+04 | 0.0645 |
| 157.0 | 0.77671 | 8.852E+04 | 6.875E+04 | 0.0644 |
| 159.0 | 0.76041 | 7.827E+04 | 5.952E+04 | 0.0638 |
| 163.0 | 0.82626 | 6.866E+04 | 5.672E+04 | 0.0633 |
| 165.0 | 0.83791 | 6.279E+04 | 5.261E+04 | 0.0630 |
| 167.0 | 1.01415 | 4.920E+04 | 4.990E+04 | 0.0626 |
| 170.0 | 1.25135 | 3.434E+04 | 4.297E+04 | 0.0615 |
| 171.0 | 1.32449 | 2.860E+04 | 3.787E+04 | 0.0612 |
| 172.0 | 1.55989 | 2.179E+04 | 3.398E+04 | 0.0608 |
| 173.0 | 1.84824 | 1.692E+04 | 3.127E+04 | 0.0606 |

Jan 10, 1985

Ref RBUI10.DAT

SIYO.09/[illegible]
[illegible]

| T [illegible] | [illegible] | G | [illegible] | [illegible] |
|---|---|---|---|---|
| [illegible] | [illegible] | 1.[illegible]E+09 | [illegible]72E+07 | 3.4568 |
| [illegible] | [illegible] | 1.2[illegible]8E+09 | 1.[illegible]89E+07 | 3.4[illegible]4 |
| [illegible] | 0.01539 | 1.292E+09 | 1.750E+07 | 3.4423 |
| [illegible].8 | 0.01[illegible]8 | 1.257E+09 | 1.920E+07 | 3.3956 |
| [illegible] | 0.01539 | 1.253E+09 | 1.928E+07 | 3.3898 |
| 33.0 | 0.01595 | 1.247E+09 | 1.988E+07 | 3.3812 |
| 36.2 | 0.01609 | 1.247E+09 | 2.006E+07 | 3.3812 |
| 38.1 | 0.01664 | 1.232E+09 | 2.050E+07 | 3.3613 |
| 40.0 | 0.01678 | 1.228E+09 | 2.060E+07 | 3.3557 |
| 42.3 | 0.01729 | 1.220E+09 | 2.109E+07 | 3.3445 |
| 44.5 | 0.01713 | 1.214E+09 | 2.081E+07 | 3.3372 |
| 47.5 | 0.01825 | 1.205E+09 | 2.200E+07 | 3.3250 |
| 49.3 | 0.01847 | 1.192E+09 | 2.200E+07 | 3.3058 |
| 49.6 | 0.01840 | 1.193E+09 | 2.194E+07 | 3.3075 |
| 52.1 | 0.01861 | 1.191E+09 | 2.216E+07 | 3.3045 |
| 54.4 | 0.01899 | 1.182E+09 | 2.245E+07 | 3.2928 |
| 56.0 | 0.01912 | 1.172E+09 | 2.241E+07 | 3.2787 |
| 56.5 | 0.01916 | 1.172E+09 | 2.245E+07 | 3.2787 |
| 58.2 | 0.01895 | 1.174E+09 | 2.225E+07 | 3.2812 |
| 61.4 | 0.01985 | 1.157E+09 | 2.297E+07 | 3.2581 |
| 63.9 | 0.01990 | 1.149E+09 | 2.287E+07 | 3.2468 |
| 66.6 | 0.02031 | 1.141E+09 | 2.318E+07 | 3.2354 |
| 68.5 | 0.02037 | 1.133E+09 | 2.309E+07 | 3.2242 |

STYO.0971VP(4-)-BUI (R)
GOOD LUCK, KID!

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 70.5 | 0.02177 | 1.124E+09 | 2.447E+07 | 3.2103 |
| 70.7 | 0.02167 | 1.122E+09 | 2.431E+07 | 3.2075 |
| 72.0 | 0.02192 | 1.118E+09 | 2.450E+07 | 3.2020 |
| 73.0 | 0.02188 | 1.116E+09 | 2.442E+07 | 3.1992 |
| 75.1 | 0.02262 | 1.103E+09 | 2.494E+07 | 3.1800 |
| 80.1 | 0.02542 | 1.073E+09 | 2.727E+07 | 3.1571 |
| 82.2 | 0.02647 | 1.059E+09 | 2.802E+07 | 3.1160 |
| 84.0 | 0.02803 | 1.046E+09 | 2.932E+07 | 3.0972 |
| 86.1 | 0.02900 | 1.033E+09 | 2.996E+07 | 3.0771 |
| 88.2 | 0.03402 | 1.007E+09 | 3.427E+07 | 3.0395 |
| 91.5 | 0.03880 | 9.744E+08 | 3.781E+07 | 2.9892 |
| 93.6 | 0.04217 | 9.544E+08 | 4.025E+07 | 2.9582 |
| 95.1 | 0.04357 | 9.463E+08 | 4.123E+07 | 2.9455 |
| 96.4 | 0.04770 | 9.256E+08 | 4.415E+07 | 2.9130 |
| 98.3 | 0.05037 | 9.070E+08 | 4.569E+07 | 2.8836 |
| 100.0 | 0.06087 | 8.732E+08 | 5.315E+07 | 2.8289 |
| 101.9 | 0.07321 | 8.318E+08 | 6.090E+07 | 2.7605 |
| 102.5 | 0.07561 | 8.341E+08 | 6.306E+07 | 2.7642 |
| 104.8 | 0.12690 | 7.252E+08 | 9.203E+07 | 2.5742 |
| 132.5 | 0.72461 | 3.985E+05 | 2.888E+05 | 0.0834 |
| 134.7 | 0.69636 | 3.366E+05 | 2.344E+05 | 0.0804 |
| 143.3 | 0.60059 | 1.821E+05 | 1.093E+05 | 0.0720 |
| 147.1 | 0.56941 | 1.614E+06 | 9.193E+05 | 0.0707 |

STY0.0971VP(4-)-BUI (R)
GOOD LUCK, KID!

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 151.0 | 0.64509 | 1.365E+05 | 8.803E+04 | 0.0691 |
| 154.0 | 0.77641 | 8.611E+04 | 6.685E+04 | 0.0658 |
| 157.0 | 1.13167 | 4.728E+04 | 5.351E+04 | 0.0631 |
| 160.0 | 3.01569 | 1.340E+04 | 4.040E+04 | 0.0606 |
| 162.0 | 2.67613 | 1.315E+04 | 3.519E+04 | 0.0606 |

RCEI2 DAT

Jan 31, 1985

A modified edition (minus data 794-91.5°C) is ROEI22 DAT

[illegible]

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| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

STY-0.0193VP(4-)-DEI (R)

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 62.8 | 0.04732 | 7.670E+08 | 3.630E+07 | 2.5922 |
| 63.8 | 0.05156 | 7.390E+08 | 3.811E+07 | 2.5443 |
| 69.0 | 0.08351 | 6.410E+08 | 5.353E+07 | 2.3684 |
| 69.5 | 0.08448 | 6.265E+08 | 5.293E+07 | 2.3415 |
| 70.4 | 0.09301 | 6.088E+08 | 5.663E+07 | 2.3077 |
| 70.2 | 0.10235 | 5.986E+08 | 6.127E+07 | 2.2878 |
| 71.1 | 0.11757 | 5.679E+08 | 6.677E+07 | 2.2274 |
| 72.7 | 0.13643 | 5.504E+08 | 7.509E+07 | 2.1916 |
| 73.2 | 0.13808 | 5.361E+08 | 7.403E+07 | 2.1628 |
| 74.8 | 0.20651 | 4.849E+08 | 1.001E+08 | 2.0508 |
| 75.5 | 0.18468 | 4.595E+08 | 8.486E+07 | 1.9986 |
| 76.2 | 0.22929 | 4.275E+08 | 9.803E+07 | 1.9233 |
| 76.4 | 0.27317 | 4.300E+08 | 1.175E+08 | 1.9233 |
| 78.0 | 0.31048 | 3.714E+08 | 1.153E+08 | 1.7823 |
| 78.8 | 0.24800 | 2.627E+08 | 6.515E+07 | 1.5063 |
| 79.4 | 0.47667 | 7.837E+08 | 3.736E+08 | 2.5405 |
| 79.6 | 0.29475 | 6.172E+08 | 1.819E+08 | 2.3002 |
| 80.0 | 0.21877 | 5.360E+08 | 1.173E+08 | 2.1546 |
| 81.2 | 0.21825 | 3.866E+08 | 8.438E+07 | 1.8302 |
| 81.3 | 0.03572 | 5.434E+08 | 1.941E+07 | 2.1822 |
| 95.1 | 0.11090 | 2.174E+08 | 2.411E+07 | 1.3793 |
| 105.2 | 0.77688 | 2.494E+05 | 1.938E+05 | 0.0749 |
| 106.0 | 0.76570 | 2.264E+05 | 1.733E+05 | 0.0737 |

STY-0.0193VF(4-)-DEI (R)

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 106.8 | 0.69235 | 1.988E+05 | 1.376E+05 | 0.0723 |
| 107.2 | 0.80279 | 1.775E+05 | 1.425E+05 | 0.0710 |
| 108.3 | 0.72963 | 1.564E+05 | 1.141E+05 | 0.0698 |
| 109.2 | 0.70386 | 1.573E+05 | 1.107E+05 | 0.0699 |
| 110.0 | 0.74087 | 1.381E+05 | 1.023E+05 | 0.0688 |
| 111.5 | 0.71187 | 1.256E+05 | 8.939E+04 | 0.0680 |
| 112.3 | 0.69514 | 1.285E+05 | 8.936E+04 | 0.0682 |
| 113.0 | 0.66766 | 1.242E+05 | 8.289E+04 | 0.0680 |
| 113.4 | 0.66436 | 1.246E+05 | 8.276E+04 | 0.0680 |
| 113.8 | 0.68562 | 1.152E+05 | 7.900E+04 | 0.0674 |
| 114.5 | 0.67378 | 1.066E+05 | 7.186E+04 | 0.0669 |
| 114.8 | 0.71221 | 1.017E+05 | 7.243E+04 | 0.0665 |
| 115.0 | 0.67339 | 1.037E+05 | 6.984E+04 | 0.0667 |
| 116.6 | 0.66344 | 9.340E+04 | 6.197E+04 | 0.0660 |
| 118.7 | 0.73727 | 7.449E+04 | 5.492E+04 | 0.0648 |
| 121.4 | 0.71944 | 7.099E+04 | 5.107E+04 | 0.0646 |
| 123.5 | 0.86597 | 5.814E+04 | 5.035E+04 | 0.0637 |
| 125.5 | 0.83813 | 5.753E+04 | 4.822E+04 | 0.0637 |
| 128.6 | 0.81358 | 6.106E+04 | 4.968E+04 | 0.0639 |
| 134.0 | 1.02664 | 5.145E+04 | 5.282E+04 | 0.0632 |
| 134.6 | 0.91557 | 5.877E+04 | 5.381E+04 | 0.0637 |
| 136.4 | 1.01207 | 5.653E+04 | 5.722E+04 | 0.0626 |
| 137.4 | 0.76049 | 7.141E+04 | 5.616E+04 | 0.0646 |

STY-0.0486VP(4-)-DEI (R)

| TEMP. | TAN DELTA | G | G'' | FREQ. |
|---|---|---|---|---|
| 24.4 | 0.01611 | 1.305E+09 | 2.104E+07 | 2.4863 |
| 23.3 | 0.01565 | 1.305E+09 | 2.042E+07 | 2.4856 |
| 33.6 | 0.01739 | 1.284E+09 | 2.234E+07 | 2.4662 |
| 35.3 | 0.01695 | 1.277E+09 | 2.166E+07 | 2.4595 |
| 37.2 | 0.01735 | 1.273E+09 | 2.209E+07 | 2.4553 |
| 39.0 | 0.01803 | 1.265E+09 | 2.280E+07 | 2.4471 |
| 41.4 | 0.01829 | 1.257E+09 | 2.300E+07 | 2.4401 |
| 42.8 | 0.01845 | 1.251E+09 | 2.308E+07 | 2.4340 |
| 44.8 | 0.01927 | 1.244E+09 | 2.397E+07 | 2.4268 |
| 46.7 | 0.01922 | 1.237E+09 | 2.378E+07 | 2.4204 |
| 48.8 | 0.01952 | 1.234E+09 | 2.409E+07 | 2.4177 |
| 50.9 | 0.02047 | 1.219E+09 | 2.495E+07 | 2.4023 |
| 53.2 | 0.02114 | 1.208E+09 | 2.554E+07 | 2.3914 |
| 55.6 | 0.02307 | 1.191E+09 | 2.747E+07 | 2.3747 |
| 58.3 | 0.02382 | 1.179E+09 | 2.809E+07 | 2.3631 |
| 60.3 | 0.02586 | 1.162E+09 | 3.006E+07 | 2.3459 |
| 62.2 | 0.02676 | 1.146E+09 | 3.067E+07 | 2.3296 |
| 64.7 | 0.02720 | 1.137E+09 | 3.092E+07 | 2.3202 |
| 66.4 | 0.02933 | 1.120E+09 | 3.283E+07 | 2.3024 |
| 69.4 | 0.03283 | 1.096E+09 | 3.598E+07 | 2.2779 |
| 72.1 | 0.03465 | 1.085E+09 | 3.760E+07 | 2.2666 |
| 74.2 | 0.03636 | 1.069E+09 | 3.887E+07 | 2.2499 |
| 76.2 | 0.03955 | 1.042E+09 | 4.123E+07 | 2.2214 |

STY-0.0486VP(4-)-DEI (R)

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 78.3 | 0.04184 | 1.033E+09 | 4.324E+07 | 2.2119 |
| 79.2 | 0.04271 | 1.022E+09 | 4.363E+07 | 2.1992 |
| 81.5 | 0.04532 | 1.016E+09 | 4.605E+07 | 2.1932 |
| 84.5 | 0.05736 | 9.586E+08 | 5.499E+07 | 2.1300 |
| 86.8 | 0.06225 | 9.373E+08 | 5.835E+07 | 2.1060 |
| 88.8 | 0.07605 | 8.946E+08 | 6.804E+07 | 2.0570 |
| 90.3 | 0.07830 | 8.919E+08 | 6.983E+07 | 2.0538 |
| 92.8 | 0.08910 | 8.746E+08 | 7.793E+07 | 2.0334 |
| 93.7 | 0.10582 | 8.165E+08 | 8.641E+07 | 1.9640 |
| 95.8 | 0.12644 | 7.577E+08 | 9.580E+07 | 1.8909 |
| 98.4 | 0.17514 | 6.441E+08 | 1.128E+08 | 1.7402 |
| 101.1 | 0.26321 | 6.936E+08 | 1.826E+08 | 1.7968 |
| 129.0 | 0.53011 | 2.756E+05 | 1.461E+05 | 0.0696 |
| 134.2 | 0.50489 | 2.615E+05 | 1.320E+05 | 0.0691 |
| 135.6 | 0.60003 | 2.097E+05 | 1.258E+05 | 0.0673 |
| 136.7 | 0.54740 | 1.796E+05 | 9.832E+04 | 0.0663 |
| 138.7 | 0.54074 | 1.728E+05 | 9.347E+04 | 0.0661 |
| 139.4 | 0.76345 | 1.254E+05 | 9.577E+04 | 0.0644 |
| 139.0 | 0.64505 | 1.314E+05 | 8.473E+04 | 0.0646 |
| 141.4 | 0.78148 | 9.659E+04 | 7.548E+04 | 0.0633 |
| 147.8 | 1.25668 | 5.812E+04 | 7.304E+04 | 0.0619 |
| 153.0 | 1.65506 | 3.997E+04 | 6.616E+04 | 0.0612 |
| 151.0 | 1.11750 | 5.461E+04 | 6.102E+04 | 0.0617 |

STY-0.0486VP(4-)-DEI (R)

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 155.0 | 2.25510 | 2.363E+04 | 5.328E+04 | 0.0606 |

STY-0.0689VP(4-)-MET (R)
FEB. 21, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 22.4 | 0.01485 | 1.198E+09 | 1.779E+07 | 2.0190 |
| 40.8 | 0.01733 | 1.152E+09 | 1.996E+07 | 1.9797 |
| 45.6 | 0.01897 | 1.134E+09 | 2.150E+07 | 1.9642 |
| 47.0 | 0.01911 | 1.132E+09 | 2.164E+07 | 1.9630 |
| 49.0 | 0.01911 | 1.126E+09 | 2.153E+07 | 1.9574 |
| 51.3 | 0.01973 | 1.121E+09 | 2.211E+07 | 1.9530 |
| 53.6 | 0.02013 | 1.114E+09 | 2.243E+07 | 1.9473 |
| 55.0 | 0.02094 | 1.109E+09 | 2.322E+07 | 1.9429 |
| 57.1 | 0.02151 | 1.101E+09 | 2.368E+07 | 1.9353 |
| 60.5 | 0.02274 | 1.083E+09 | 2.463E+07 | 1.9198 |
| 63.0 | 0.02434 | 1.070E+09 | 2.604E+07 | 1.9082 |
| 64.4 | 0.02483 | 1.064E+09 | 2.642E+07 | 1.9026 |
| 66.2 | 0.02576 | 1.051E+09 | 2.706E+07 | 1.8907 |
| 68.2 | 0.02735 | 1.039E+09 | 2.841E+07 | 1.8800 |
| 70.3 | 0.02860 | 1.026E+09 | 2.933E+07 | 1.8681 |
| 72.4 | 0.02959 | 1.017E+09 | 3.010E+07 | 1.8605 |
| 73.3 | 0.03024 | 1.010E+09 | 3.053E+07 | 1.8535 |
| 74.4 | 0.03102 | 9.980E+08 | 3.096E+07 | 1.8428 |
| 75.0 | 0.03165 | 9.927E+08 | 3.142E+07 | 1.8379 |
| 76.1 | 0.03248 | 9.843E+08 | 3.197E+07 | 1.8301 |
| 78.0 | 0.03475 | 9.729E+08 | 3.380E+07 | 1.8195 |
| 80.1 | 0.03665 | 9.502E+08 | 3.482E+07 | 1.7981 |
| 82.2 | 0.03738 | 9.359E+08 | 3.499E+07 | 1.7845 |

STY-0.0689VP(4-)-DEI (R)
FEB. 21, 1985

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 84.5 | 0.04163 | 9.065E+08 | 3.774E+07 | 1.7562 |
| 85.9 | 0.04328 | 8.956E+08 | 3.876E+07 | 1.7456 |
| 88.0 | 0.04617 | 8.709E+08 | 4.020E+07 | 1.7213 |
| 90.8 | 0.05372 | 8.380E+08 | 4.501E+07 | 1.6884 |
| 92.2 | 0.05527 | 8.215E+08 | 4.540E+07 | 1.6716 |
| 94.2 | 0.06652 | 7.866E+08 | 5.232E+07 | 1.6355 |
| 95.6 | 0.07029 | 7.686E+08 | 5.402E+07 | 1.6166 |
| 96.4 | 0.07577 | 7.524E+08 | 5.701E+07 | 1.5994 |
| 97.5 | 0.08199 | 7.253E+08 | 5.947E+07 | 1.5701 |
| 98.6 | 0.09174 | 7.017E+08 | 6.437E+07 | 1.5441 |
| 100.0 | 0.10037 | 6.779E+08 | 6.804E+07 | 1.5174 |
| 100.6 | 0.11389 | 6.558E+08 | 7.469E+07 | 1.4920 |
| 101.2 | 0.12865 | 6.181E+08 | 7.951E+07 | 1.4478 |
| 101.6 | 0.14116 | 5.890E+08 | 8.315E+07 | 1.4129 |
| 103.0 | 0.16368 | 5.737E+08 | 9.391E+07 | 1.3932 |
| 103.4 | 0.19388 | 5.327E+08 | 1.033E+08 | 1.3408 |
| 104.3 | 0.21773 | 5.203E+08 | 1.133E+08 | 1.3234 |
| 105.2 | 0.28141 | 4.400E+08 | 1.238E+08 | 1.2121 |
| 106.5 | 0.30116 | 4.321E+08 | 1.301E+08 | 1.1994 |
| 107.1 | 0.32184 | 4.524E+08 | 1.456E+08 | 1.2251 |
| 139.0 | 0.58565 | 2.130E+05 | 1.248E+05 | 0.0654 |
| 140.3 | 0.59612 | 1.952E+05 | 1.164E+05 | 0.0649 |
| 142.8 | 0.61073 | 1.638E+05 | 1.001E+05 | 0.0641 |

STY-0.0689VP(4-)-DEI (R)
FEB. 21, 1985

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 144.0 | 0.61070 | 1.512E+05 | 9.234E+04 | 0.0638 |
| 145.5 | 0.62758 | 1.358E+05 | 8.521E+04 | 0.0634 |
| 148.0 | 0.72611 | 1.205E+05 | 8.748E+04 | 0.0630 |
| 149.1 | 0.71617 | 1.108E+05 | 7.937E+04 | 0.0627 |
| 151.2 | 0.85671 | 9.017E+04 | 7.725E+04 | 0.0621 |
| 152.0 | 0.90927 | 7.993E+04 | 7.268E+04 | 0.0619 |
| 152.9 | 0.97291 | 7.926E+04 | 7.711E+04 | 0.0618 |

STY-0.0971VP(4-)-DEI (R)
FEBRUARY 28, 1985

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 22.4 | 0.02128 | 1.142E+09 | 2.429E+07 | 2.2091 |
| 26.5 | 0.02215 | 1.118E+09 | 2.477E+07 | 2.1866 |
| 27.8 | 0.02273 | 1.114E+09 | 2.531E+07 | 2.1819 |
| 30.3 | 0.02214 | 1.104E+09 | 2.444E+07 | 2.1724 |
| 31.7 | 0.02302 | 1.105E+09 | 2.543E+07 | 2.1730 |
| 33.8 | 0.02397 | 1.091E+09 | 2.616E+07 | 2.1599 |
| 37.2 | 0.02347 | 1.079E+09 | 2.533E+07 | 2.1476 |
| 40.0 | 0.02441 | 1.071E+09 | 2.615E+07 | 2.1400 |
| 41.5 | 0.02451 | 1.059E+09 | 2.596E+07 | 2.1279 |
| 44.0 | 0.02543 | 1.047E+09 | 2.662E+07 | 2.1152 |
| 46.1 | 0.02630 | 1.041E+09 | 2.739E+07 | 2.1100 |
| 48.6 | 0.02590 | 1.027E+09 | 2.660E+07 | 2.0953 |
| 50.4 | 0.02775 | 1.019E+09 | 2.826E+07 | 2.0866 |
| 52.8 | 0.02859 | 1.006E+09 | 2.876E+07 | 2.0737 |
| 54.2 | 0.02890 | 1.000E+09 | 2.891E+07 | 2.0680 |
| 57.0 | 0.02985 | 9.872E+08 | 2.946E+07 | 2.0542 |
| 59.2 | 0.03079 | 9.694E+08 | 2.985E+07 | [illegible] |
| 58.8 | 0.03031 | 9.748E+08 | 2.955E+07 | 2.0414 |
| 61.0 | 0.03140 | 9.617E+08 | 3.020E+07 | 2.0276 |
| 63.5 | 0.03371 | 9.426E+08 | 3.178E+07 | 2.0075 |
| 65.2 | 0.03566 | 9.326E+08 | 3.326E+07 | 1.9966 |
| 66.5 | 0.03601 | 9.227E+08 | 3.323E+07 | 1.9860 |
| 69.1 | 0.03739 | 9.067E+08 | 3.390E+07 | 1.9687 |

STY-0.0971VP(4-)-DE1 (R)
FEBRUARY 28, 1985

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 71.2 | 0.03790 | 8.905E+08 | 3.374E+07 | 1.9510 |
| 71.8 | 0.03840 | 8.885E+08 | 3.412E+07 | 1.9488 |
| 73.2 | 0.03966 | 8.786E+08 | 3.484E+07 | 1.9380 |
| 76.8 | 0.04303 | 8.563E+08 | 3.684E+07 | 1.9161 |
| 80.2 | 0.04601 | 8.434E+08 | 3.880E+07 | 1.8986 |
| 82.2 | 0.04821 | 8.278E+08 | 3.991E+07 | 1.8809 |
| 87.2 | 0.07091 | 7.457E+08 | 5.288E+07 | 1.7848 |
| 88.2 | 0.07623 | 7.274E+08 | 5.545E+07 | 1.7625 |
| 89.2 | 0.09112 | 7.042E+08 | 6.417E+07 | 1.7337 |
| 90.1 | 0.10930 | 6.627E+08 | 7.244E+07 | 1.6812 |
| 91.9 | 0.12971 | 6.340E+08 | 8.224E+07 | 1.6434 |
| 93.5 | 0.15338 | 5.069E+08 | 7.775E+07 | 1.4684 |
| 94.7 | 0.22069 | 4.719E+08 | 1.042E+08 | 1.4124 |
| 96.2 | 0.27408 | 4.391E+08 | 1.203E+08 | 1.3578 |
| 98.0 | 0.26300 | 4.313E+08 | 1.134E+08 | 1.3466 |
| 98.2 | 0.27103 | 3.867E+08 | 1.048E+08 | 1.2747 |
| 123.6 | 0.91719 | 3.166E+05 | 2.904E+05 | 0.0695 |
| 126.8 | 0.89594 | 2.209E+05 | 1.979E+05 | 0.0668 |
| 131.7 | 0.72009 | 2.005E+05 | 1.444E+05 | 0.0665 |
| 133.6 | 0.76485 | 1.641E+05 | 1.255E+05 | 0.0651 |
| 134.7 | 0.79814 | 1.314E+05 | 1.049E+05 | 0.0641 |
| 135.2 | 0.69966 | 1.515E+05 | 1.060E+05 | 0.0648 |
| 137.6 | 0.83866 | 1.280E+05 | 1.073E+05 | 0.0640 |

STY-0.0971VP(4 )-DEI (R)
FEBRUARY 28, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 139.0 | 0.70125 | 1.478E+05 | 1.037E+05 | 0.0646 |

STY-0.0193VP(4-)-HCl (R)
MARCH 14, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 22.8 | 0.01438 | 1.211E+09 | 1.741E+07 | 3.8023 |
| 27.7 | 0.01563 | 1.197E+09 | 1.871E+07 | 3.7807 |
| 30.2 | 0.01610 | 1.194E+09 | 1.923E+07 | 3.7760 |
| 32.3 | 0.01638 | 1.181E+09 | 1.934E+07 | 3.7547 |
| 35.0 | 0.01748 | 1.173E+09 | 2.051E+07 | 3.7430 |
| 37.2 | 0.01824 | 1.162E+09 | 2.120E+07 | 3.7244 |
| 39.5 | 0.01849 | 1.153E+09 | 2.132E+07 | 3.7106 |
| 41.7 | 0.01865 | 1.153E+09 | 2.151E+07 | 3.7106 |
| 44.0 | 0.01949 | 1.139E+09 | 2.220E+07 | 3.6878 |
| 46.5 | 0.02003 | 1.127E+09 | 2.257E+07 | 3.6675 |
| 50.1 | 0.02055 | 1.116E+09 | 2.293E+07 | 3.6496 |
| 51.0 | 0.02121 | 1.112E+09 | 2.358E+07 | 3.6430 |
| 53.5 | 0.02226 | 1.102E+09 | 2.453E+07 | 3.6276 |
| 54.6 | 0.02263 | 1.090E+09 | 2.468E+07 | 3.6079 |
| 56.6 | 0.02340 | 1.081E+09 | 2.530E+07 | 3.5928 |
| 58.8 | 0.02420 | 1.072E+09 | 2.595E+07 | 3.5778 |
| 60.9 | 0.02600 | 1.058E+09 | 2.752E+07 | 3.5545 |
| 62.8 | 0.02669 | 1.046E+09 | 2.792E+07 | 3.5336 |
| 65.2 | 0.02898 | 1.030E+09 | 2.985E+07 | 3.5067 |
| 66.2 | 0.02803 | 1.023E+09 | 2.867E+07 | 3.4945 |
| 67.0 | 0.02967 | 1.023E+09 | 3.035E+07 | 3.4945 |
| 68.2 | 0.03084 | 1.006E+09 | 3.104E+07 | 3.4662 |
| 71.2 | 0.03372 | 9.950E+08 | 3.355E+07 | 3.4463 |

STY-0.0193VP(4-)-HEI (R)
MARCH 14, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 73.2 | 0.03848 | 9.715E+08 | 3.738E+07 | 3.4052 |
| 74.2 | 0.04160 | 9.541E+08 | 3.969E+07 | 3.3746 |
| 75.3 | 0.04517 | 9.457E+08 | 4.272E+07 | 3.3595 |
| 79.4 | 0.06899 | 8.686E+08 | 5.992E+07 | 3.2186 |
| 115.0 | 0.45276 | 3.778E+05 | 1.710E+05 | 0.0892 |
| 116.0 | 0.46417 | 3.042E+05 | 1.412E+05 | 0.0843 |
| 120.5 | 0.42484 | 2.620E+05 | 1.113E+05 | 0.0815 |
| 122.0 | 0.44890 | 2.466E+05 | 1.107E+05 | 0.0803 |
| 123.6 | 0.45819 | 2.247E+05 | 1.030E+05 | 0.0787 |
| 125.6 | 0.42676 | 2.064E+05 | 8.809E+04 | 0.0774 |
| 126.0 | 0.42268 | 1.800E+05 | 7.608E+04 | 0.0754 |
| 127.0 | 0.46855 | 1.742E+05 | 8.163E+04 | 0.0749 |
| 128.5 | 0.43839 | 1.612E+05 | 7.068E+04 | 0.0739 |
| 129.0 | 0.46701 | 1.584E+05 | 7.399E+04 | 0.0737 |
| 130.1 | 0.52118 | 1.368E+05 | 7.131E+04 | 0.0719 |
| 133.0 | 0.53977 | 1.122E+05 | 6.059E+04 | 0.0699 |
| 134.2 | 0.55928 | 1.049E+05 | 5.869E+04 | 0.0693 |
| 135.5 | 0.62906 | 9.598E+04 | 6.038E+04 | 0.0685 |
| 137.0 | 0.63785 | 8.584E+04 | 5.475E+04 | 0.0677 |
| 139.6 | 0.80245 | 6.273E+04 | 5.033E+04 | 0.0656 |
| 140.2 | 0.73371 | 6.334E+04 | 4.647E+04 | 0.0657 |
| 143.1 | 1.02637 | 4.199E+04 | 4.309E+04 | 0.0637 |
| 145.0 | 1.06943 | 3.783E+04 | 4.045E+04 | 0.0633 |

STY-0.0193VP(4-)-HCI (R)
MARCH 14, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 150.5 | 1.84572 | 1.793E+04 | 3.309E+04 | 0.0615 |

STY-0.0486VP(4-)-HCl (R)
MARCH 19,1985

| TEMP. | TAN DELTA | E' | E'' | FREQ. |
|---|---|---|---|---|
| 21.2 | 0.01874 | 1.264E+09 | 2.369E+07 | 3.2653 |
| 26.7 | 0.02064 | 1.239E+09 | 2.557E+07 | 3.2330 |
| 28.9 | 0.02159 | 1.233E+09 | 2.660E+07 | 3.2244 |
| 30.3 | 0.02204 | 1.225E+09 | 2.699E+07 | 3.2143 |
| 32.4 | 0.02289 | 1.213E+09 | 2.776E+07 | 3.1886 |
| 36.6 | 0.02412 | 1.192E+09 | 2.874E+07 | 3.1704 |
| 41.0 | 0.02494 | 1.178E+09 | 2.938E+07 | 3.1524 |
| 42.8 | 0.02577 | 1.167E+09 | 3.007E+07 | 3.1373 |
| 44.6 | 0.02658 | 1.155E+09 | 3.069E+07 | 3.1209 |
| 46.2 | 0.02708 | 1.143E+09 | 3.095E+07 | 3.1048 |
| 48.6 | 0.02760 | 1.132E+09 | 3.125E+07 | 3.0901 |
| 50.5 | 0.02829 | 1.123E+09 | 3.178E+07 | 3.0782 |
| 52.2 | 0.02985 | 1.100E+09 | 3.283E+07 | 3.0457 |
| 54.5 | 0.03044 | 1.093E+09 | 3.328E+07 | 3.0367 |
| 56.5 | 0.03197 | 1.077E+09 | 3.443E+07 | 3.0138 |
| 58.0 | 0.03400 | 1.056E+09 | 3.592E+07 | 2.9851 |
| 60.2 | 0.03504 | 1.037E+09 | 3.633E+07 | 2.9569 |
| 63.5 | 0.03751 | 1.017E+09 | 3.793E+07 | 2.9280 |
| 67.3 | 0.04113 | 9.914E+08 | 4.078E+07 | 2.8916 |
| 68.2 | 0.04471 | 9.844E+08 | 4.401E+07 | 2.8819 |
| 71.4 | 0.04683 | 9.462E+08 | 4.431E+07 | [illegible] |
| 73.8 | 0.05464 | 9.207E+08 | 5.031E+07 | 2.7861 |
| 74.0 | 0.05839 | 9.131E+08 | 5.331E+07 | 2.7745 |

STY-0.0486VP(4-)-HLI (R)
MARCH 19,1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 75.0 | 0.06249 | 9.136E+08 | 5.709E+07 | 2.7750 |
| 76.9 | 0.06999 | 8.726E+08 | 6.107E+07 | 2.7117 |
| 79.2 | 0.07997 | 8.475E+08 | [illegible] | [illegible] |
| 81.5 | 0.0688 | 8.032E+08 | 7.124E+07 | 2.5000 |
| [illegible] | 0.10412 | 7.861E+08 | 8.107E+07 | [illegible] |
| 82.0 | 0.10303 | 7.815E+08 | 8.446E+07 | [illegible] |
| 84.2 | 0.1210 | 7.394E+08 | [illegible] | [illegible] |
| 86.0 | 0.15807 | 6.825E+08 | 1.079E+08 | 2.3926 |
| 88.5 | 0.22196 | [illegible] | [illegible] | [illegible] |
| 90.0 | 0.31456 | 5.006E+08 | 1.575E+08 | [illegible] |
| 110.5 | 0.51062 | 4.313E+05 | 2.202E+05 | [illegible] |
| 118.0 | 0.54548 | 3.564E+05 | 1.944E+05 | 0.0806 |
| 120.4 | [illegible] | 3.319E+05 | 1.635E+05 | [illegible] |
| [illegible] | [illegible] | 2.943E+05 | 1.305E+05 | [illegible] |
| 126.0 | [illegible] | 2.548E+05 | 1.117E+05 | [illegible] |
| 127.3 | 0.44636 | 2.150E+05 | 9.597E+04 | [illegible] |
| 128.8 | 0.45002 | 1.975E+05 | 8.888E+04 | [illegible] |
| 130.1 | [illegible] | 1.733E+05 | 8.139E+04 | 0.0708 |
| 131.2 | [illegible] | 1.605E+05 | 7.518E+04 | 0.0701 |
| 132.8 | 0.51148 | 1.366E+05 | 6.985E+04 | [illegible] |
| 134.0 | 0.54088 | 1.342E+05 | 7.261E+04 | 0.0585 |
| 135.1 | [illegible] | 1.117E+05 | 6.559E+04 | [illegible] |
| 137.5 | 0.65861 | 9.008E+04 | [illegible] | [illegible] |

STY-0.0486VP(4 ) HEI (K)
MARCH 19,1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 136.6 | 0.65089 | 9.190E+04 | 5.982E+04 | 0.0658 |
| 138.5 | 0.63120 | 9.366E+04 | 5.912E+04 | 0.0660 |
| 140.4 | 1.02804 | 6.221E+04 | 6.385E+04 | 0.0657 |
| 142.3 | 1.51660 | 4.655E+04 | 7.060E+04 | 0.0658 |

STY-0.0971VF(4 )-HEI (R)
MARCH 21, 1985

| TEMP. | TAN DELTA | G | G" | FREQ. |
|---|---|---|---|---|
| 108.0 | 0.12772 | 6.110E+08 | 7.814E+07 | 2.3000 |
| 109.5 | 0.14364 | 5.963E+08 | 8.565E+07 | 2.2701 |
| 110.0 | 0.16492 | 5.723E+08 | 9.438E+07 | 2.2227 |
| 110.3 | 0.18077 | 5.084E+08 | 9.190E+07 | 2.0931 |
| 111.3 | 0.18822 | 5.040E+08 | 9.487E+07 | 2.0833 |
| 111.8 | 0.23052 | 4.863E+08 | 1.121E+08 | 2.0419 |
| 112.8 | 0.31721 | 3.962E+08 | 1.257E+08 | 1.8015 |
| 113.2 | 0.37493 | 3.219E+08 | 1.207E+08 | 1.6420 |
| 136.6 | 0.74339 | 4.616E+05 | 3.431E+05 | 0.0853 |
| 138.0 | 0.71434 | 3.462E+05 | 2.473E+05 | 0.0800 |
| 141.4 | 0.59883 | 3.057E+05 | 1.830E+05 | 0.0783 |
| 142.0 | 0.57463 | 2.964E+05 | 1.703E+05 | 0.0778 |
| 143.3 | 0.59746 | 2.716E+05 | 1.623E+05 | 0.0765 |
| 144.4 | 0.55641 | 2.580E+05 | 1.435E+05 | 0.0758 |
| 145.4 | 0.53566 | 2.426E+05 | 1.300E+05 | 0.0750 |
| 146.0 | 0.53017 | 2.337E+05 | 1.239E+05 | 0.0745 |
| 148.0 | 0.48826 | 1.996E+05 | 9.744E+04 | 0.0726 |
| 148.3 | 0.51767 | 1.881E+05 | 9.735E+04 | 0.0719 |
| 149.5 | 0.54451 | 1.612E+05 | 8.780E+04 | 0.0703 |
| 149.7 | 0.53456 | 1.529E+05 | 8.174E+04 | 0.0698 |
| 151.1 | 0.51609 | 1.540E+05 | 7.950E+04 | 0.0699 |
| 152.0 | 0.55746 | 1.347E+05 | 7.507E+04 | 0.0687 |
| 153.2 | 0.60817 | 1.171E+05 | 7.122E+04 | 0.0676 |

STY-0.0971VP(4-)-HEI (R)
MARCH 21, 1985

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 69.8 | 0.03150 | 9.163E+08 | 2.887E+07 | 2.8209 |
| 71.7 | 0.03159 | 9.146E+08 | 2.889E+07 | 2.8182 |
| 73.1 | 0.03190 | 9.019E+08 | 2.877E+07 | 2.7985 |
| 77.0 | 0.03275 | 8.969E+08 | 2.937E+07 | 2.7907 |
| 78.8 | 0.03326 | 8.853E+08 | 2.945E+07 | 2.7726 |
| 80.6 | 0.03330 | 8.853E+08 | 2.948E+07 | 2.7726 |
| 81.5 | 0.03398 | 8.764E+08 | 2.978E+07 | 2.7586 |
| 82.4 | 0.03380 | 8.723E+08 | 2.948E+07 | 2.7523 |
| 84.6 | 0.03446 | 8.692E+08 | 2.995E+07 | 2.7473 |
| 86.0 | 0.03514 | 8.628E+08 | 3.032E+07 | 2.7372 |
| 88.1 | 0.03650 | 8.527E+08 | 3.112E+07 | 2.7211 |
| 89.9 | 0.03709 | 8.481E+08 | 3.146E+07 | 2.7137 |
| 91.6 | 0.03942 | 8.300E+08 | 3.272E+07 | 2.6846 |
| 93.2 | 0.03986 | 8.234E+08 | 3.282E+07 | 2.6738 |
| 93.8 | 0.04171 | 8.183E+08 | 3.413E+07 | 2.6655 |
| 94.1 | 0.04189 | 8.161E+08 | 3.419E+07 | 2.6619 |
| 96.0 | 0.04405 | 8.011E+08 | 3.529E+07 | 2.6374 |
| 98.6 | 0.04952 | 7.771E+08 | 3.848E+07 | 2.5974 |
| 99.8 | 0.05181 | 7.665E+08 | 3.971E+07 | 2.5795 |
| 100.9 | 0.05218 | 7.560E+08 | 3.945E+07 | 2.5618 |
| 102.0 | 0.05942 | 7.397E+08 | 4.395E+07 | 2.5338 |
| 105.5 | 0.07877 | 6.840E+08 | 5.381E+07 | 2.4556 |
| 106.7 | 0.1026 | 6.510E+08 | 6.686E+07 | 2.375 |

STY-0.0971VP(4-)-HEI (R)
MARCH 21, 1985

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 21.6 | 0.01720 | 1.063E+09 | 1.828E+07 | 3.0380 |
| 27.4 | 0.01819 | 1.050E+09 | 1.910E+07 | 3.0196 |
| 29.2 | 0.01865 | 1.046E+09 | 1.950E+07 | 3.0136 |
| 31.3 | 0.01925 | 1.042E+09 | 2.005E+07 | 3.0075 |
| 33.4 | 0.01982 | 1.038E+09 | 2.058E+07 | 3.0030 |
| 36.0 | 0.02038 | 1.029E+09 | 2.097E+07 | 2.9895 |
| 37.8 | 0.02071 | 1.023E+09 | 2.119E+07 | 2.9806 |
| 39.4 | 0.02153 | 1.023E+09 | 2.202E+07 | 2.9806 |
| 41.0 | 0.02192 | 1.017E+09 | 2.229E+07 | 2.9718 |
| 42.9 | 0.02249 | 1.010E+09 | 2.271E+07 | 2.9615 |
| 44.5 | 0.02298 | 1.006E+09 | 2.312E+07 | 2.9557 |
| 46.5 | 0.02383 | 1.001E+09 | 2.386E+07 | 2.9484 |
| 48.1 | 0.02413 | 9.912E+08 | 2.392E+07 | 2.9340 |
| 49.8 | 0.02465 | 9.883E+08 | 2.436E+07 | 2.9297 |
| 51.6 | 0.02534 | 9.807E+08 | 2.485E+07 | 2.9183 |
| 54.0 | 0.02635 | 9.721E+08 | 2.561E+07 | 2.9056 |
| 55.8 | 0.02685 | 9.675E+08 | 2.598E+07 | 2.8986 |
| 57.4 | 0.02750 | 9.619E+08 | 2.645E+07 | 2.8902 |
| 59.8 | 0.02911 | 9.481E+08 | 2.760E+07 | 2.8694 |
| 61.8 | 0.02926 | 9.409E+08 | 2.754E+07 | 2.8585 |
| 63.9 | 0.02953 | 9.365E+08 | 2.765E+07 | 2.8517 |
| 66.1 | 0.03049 | 9.276E+08 | 2.828E+07 | 2.8382 |
| 67.9 | 0.03096 | 9.181E+08 | 2.842E+07 | 2.8235 |

STY-0.097IVP(4-)-HEI (R)
MARCH 21, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 15[illegible].0 | 0.62741 | 1.098E+05 | 6.886E+04 | 0.0671 |
| 155.1 | 0.60034 | 1.068E+05 | 6.500E+04 | 0.0670 |
| 155.5 | 0.64294 | 9.887E+04 | 6.358E+04 | 0.0665 |
| 15[illegible] | 0.6235[illegible] | 9.787E+04 | 6.103E+04 | 0.0664 |
| [illegible] | [illegible] | [illegible] | 5.907E+04 | 0.0662 |
| [illegible] | [illegible] | 7.45[illegible]E+04 | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | 5.373E+04 | 0.0641 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

STY-0.0193VP(4-)-DCI (R)
ANNEALED SAMPLE; MAY 2, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 28.1 | 0.01449 | 9.767E+08 | 1.415E+07 | 3.8119 |
| 31.0 | 0.01509 | 9.668E+08 | 1.459E+07 | 3.7927 |
| 33.2 | 0.01539 | 9.595E+08 | 1.476E+07 | 3.7783 |
| 35.0 | 0.01553 | 9.559E+08 | 1.485E+07 | 3.7712 |
| 37.4 | 0.01592 | 9.500E+08 | 1.512E+07 | 3.7594 |
| 39.4 | 0.01624 | 9.476E+08 | 1.539E+07 | 3.7547 |
| 41.2 | 0.01651 | 9.417E+08 | 1.555E+07 | 3.7430 |
| 42.8 | 0.01654 | 9.382E+08 | 1.552E+07 | 3.7360 |
| 45.1 | 0.01690 | 9.289E+08 | 1.570E+07 | 3.7175 |
| 47.1 | 0.01722 | 9.254E+08 | 1.593E+07 | 3.7106 |
| 50.0 | 0.01738 | 9.197E+08 | 1.598E+07 | 3.6991 |
| 54.2 | 0.01808 | 9.063E+08 | 1.639E+07 | 3.6720 |
| 57.1 | 0.01802 | 9.008E+08 | 1.623E+07 | 3.6608 |
| 59.4 | 0.01803 | 8.910E+08 | 1.606E+07 | 3.6408 |
| 61.3 | 0.01894 | 8.888E+08 | 1.683E+07 | 3.6364 |
| 68.0 | 0.01990 | 8.830E+08 | 1.748E+07 | 3.6244 |
| 68.7 | 0.01968 | 8.773E+08 | 1.726E+07 | 3.6127 |
| 70.7 | 0.02082 | 8.672E+08 | 1.805E+07 | 3.59[illegible] |
| 74.2 | 0.02324 | 8.501E+08 | 1.976E+07 | 3.5562 |
| 82.8 | 0.05659 | 7.337E+08 | 4.152E+07 | 3.3028 |
| 86.1 | 0.10006 | 6.333E+08 | 6.337E+07 | 3.0661 |
| 89.2 | 0.16672 | 5.299E+08 | 8.834E+07 | 2.79[illegible] |
| 114.0 | 0.58939 | 4.244E+05 | 2.926E+05 | 0.09[illegible] |

STY-0.0193VP(4-)-OCI (R)
ANNEALED SAMPLE; MAY 2, 1985

| TEMP. | TAN DELTA | G′ | G′′ | FREQ. |
|---|---|---|---|---|
| 118.5 | 0.70736 | 3.042E+05 | 2.152E+05 | 0.0882 |
| 119.0 | 0.55632 | 2.229E+05 | 1.518E+05 | 0.0864 |
| 123.3 | 0.60966 | 2.063E+05 | 1.258E+05 | 0.0807 |
| 124.6 | 0.56045 | 2.024E+05 | 1.134E+05 | 0.0805 |
| 125.0 | 0.52174 | 1.919E+05 | 1.001E+05 | 0.0796 |
| 127.8 | 0.60313 | 1.563E+05 | 9.430E+04 | 0.0763 |
| 129.0 | 0.51391 | 1.508E+05 | 7.752E+04 | 0.0759 |
| 131.2 | 0.57069 | 1.425E+05 | 8.130E+04 | 0.0750 |
| 133.5 | 0.62948 | 1.075E+05 | 6.769E+[illegible] | 0.0716 |
| 134.0 | 0.68162 | 1.014E+05 | 6.911E+04 | 0.0709 |
| 137.5 | 0.60492 | 8.617E+04 | 5.212E+04 | 0.0695 |
| 138.8 | 0.80990 | 7.657E+04 | 6.201E+04 | 0.0683 |
| 139.0 | 0.88345 | 6.840E+04 | 6.043E+04 | 0.0674 |

STY-0.0486VP(4-)-OCI (R)
ANNEALED; MAY 9, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 21.8 | 0.01527 | 8.798E+08 | 1.374E+07 | 2.9938 |
| 40.5 | 0.01750 | 8.677E+08 | 1.519E+07 | 2.9400 |
| 42.8 | 0.01732 | 8.649E+08 | 1.498E+07 | 2.9352 |
| 45.0 | 0.01731 | 8.600E+08 | 1.488E+07 | 2.9268 |
| 47.2 | 0.01762 | 8.572E+08 | 1.510E+07 | 2.9221 |
| 49.7 | 0.01764 | 8.518E+08 | 1.502E+07 | 2.9129 |
| 50.8 | 0.01787 | 8.490E+08 | 1.517E+07 | 2.9080 |
| 52.6 | 0.01767 | 8.433E+08 | 1.490E+07 | 2.8983 |
| 55.0 | 0.01797 | 8.416E+08 | 1.512E+07 | 2.8954 |
| 57.0 | 0.01812 | 8.416E+08 | 1.525E+07 | 2.8954 |
| 59.3 | 0.01839 | 8.371E+08 | 1.540E+07 | 2.8877 |
| 61.1 | 0.01856 | 8.349E+08 | 1.550E+07 | 2.8839 |
| 63.2 | 0.01872 | 8.332E+08 | 1.560E+07 | 2.8810 |
| 67.0 | 0.01902 | 8.234E+08 | 1.566E+07 | 2.8639 |
| 69.2 | 0.01925 | 8.190E+08 | 1.576E+07 | 2.8563 |
| 71.0 | 0.01987 | 8.121E+08 | 1.614E+07 | 2.8442 |
| 72.9 | 0.02069 | 8.089E+08 | 1.673E+07 | 2.8386 |
| 75.2 | 0.02027 | 8.020E+08 | 1.625E+07 | 2.8266 |
| 78.2 | 0.02200 | 7.891E+08 | 1.736E+07 | 2.8037 |
| 80.3 | 0.02309 | 7.826E+08 | 1.807E+07 | 2.7920 |
| 82.0 | 0.02523 | 7.706E+08 | 1.944E+07 | 2.7706 |
| 83.5 | 0.02585 | 7.643E+08 | 1.976E+07 | 2.7571 |
| 85.8 | 0.02765 | 7.566E+08 | 2.091E+07 | 2.7452 |

STY-0.0486VP(4-)-OCI (R)
ANNEALED: MAY 9, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 86.6 | 0.02875 | 7.469E+08 | 2.147E+07 | 2.7275 |
| 89.0 | 0.03281 | 7.250E+08 | 2.379E+07 | 2.6872 |
| 91.3 | 0.03567 | 7.170E+08 | 2.557E+07 | 2.6722 |
| 91.8 | 0.03735 | 7.062E+08 | 2.638E+07 | 2.6520 |
| 93.0 | 0.04108 | 6.925E+08 | 2.845E+07 | 2.6261 |
| 94.9 | 0.05075 | 6.615E+08 | 3.357E+07 | 2.5665 |
| 98.0 | 0.07757 | 6.064E+08 | 4.704E+07 | 2.4561 |
| 99.5 | 0.10041 | 5.743E+08 | 5.767E+07 | 2.3891 |
| 100.1 | 0.11816 | 5.452E+08 | 6.442E+07 | 2.3267 |
| 103.0 | 0.21389 | 4.715E+08 | 1.009E+08 | 2.1552 |
| 104.4 | 0.30502 | 3.928E+08 | 1.198E+08 | 1.9550 |
| 105.0 | 0.22984 | 3.576E+08 | 8.219E+07 | 1.8753 |
| 105.3 | 0.27176 | 3.852E+08 | 1.047E+08 | 1.9406 |
| 106.2 | 0.28161 | 4.104E+08 | 1.156E+08 | 2.0020 |
| 124.2 | 0.82712 | 3.256E+05 | 2.691E+05 | 0.1078 |
| 129.0 | 0.67844 | 4.031E+05 | 2.735E+05 | 0.0857 |
| 130.0 | [illegible] | 2.901E+05 | 2.056E+05 | 0.0797 |
| [illegible] | 0.58255 | 2.703E+05 | 1.575E+05 | 0.0785 |
| 136.4 | [illegible] | 2.304E+05 | 1.228E+05 | 0.0762 |
| [illegible] | [illegible] | 2.135E+05 | 1.160E+05 | 0.0751 |
| [illegible] | [illegible] | 1.945E+05 | 1.057E+05 | 0.0739 |
| [illegible] | [illegible] | 1.704E+05 | 1.019E+05 | 0.0736 |
| [illegible] | [illegible] | [illegible] | 9.291E+04 | [illegible] |

STY-0.0486VP(4-)-OCI (R)
ANNEALED; MAY 9, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 142.0 | 0.56127 | 1.512E+05 | 8.485E+04 | 0.0710 |
| 144.5 | 0.54577 | 1.498E+05 | 8.176E+04 | 0.0710 |
| 147.0 | 0.59040 | 1.256E+05 | 7.414E+04 | 0.0693 |
| 150.0 | 0.65575 | 1.195E+05 | 7.834E+04 | 0.0688 |
| 151.9 | 0.72069 | 1.055E+05 | 7.606E+04 | 0.0678 |
| 152.8 | 0.68846 | 9.450E+04 | 6.506E+04 | 0.0670 |
| 153.7 | 0.74488 | 8.043E+04 | 5.991E+04 | 0.0660 |
| 155.7 | 0.77805 | 7.401E+04 | 5.758E+04 | 0.0655 |
| 156.8 | 0.94759 | 5.822E+04 | 5.517E+04 | 0.0643 |
| 157.4 | 0.94150 | 5.618E+04 | 5.289E+04 | 0.0642 |
| 160.0 | 0.96848 | 5.046E+04 | 4.887E+04 | 0.0637 |

STY-0.0971VP(4-)-OCI (R) ANNEALED
MAY 16, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 23.5 | 0.01977 | 9.251E+08 | 1.829E+07 | 3.3296 |
| 29.5 | 0.02032 | 9.119E+08 | 1.853E+07 | 3.3058 |
| 31.0 | 0.02169 | 9.109E+08 | 1.976E+07 | 3.3040 |
| 33.6 | 0.02178 | 9.029E+08 | 1.967E+07 | 3.2895 |
| 35.5 | 0.02222 | 8.990E+08 | 1.998E+07 | 3.2823 |
| 37.5 | 0.02291 | 8.902E+08 | 2.040E+07 | 3.2662 |
| 39.7 | 0.02325 | 8.873E+08 | 2.063E+07 | 3.2609 |
| 41.7 | 0.02352 | 8.787E+08 | 2.067E+07 | 3.2450 |
| 43.4 | 0.02422 | 8.749E+08 | 2.119E+07 | 3.2380 |
| 45.4 | 0.02441 | 8.693E+08 | 2.122E+07 | 3.2275 |
| 47.4 | 0.02476 | 8.655E+08 | 2.143E+07 | 3.2206 |
| 49.5 | 0.02499 | 8.554E+08 | 2.138E+07 | 3.2017 |
| 51.3 | 0.02531 | 8.536E+08 | 2.160E+07 | 3.1983 |
| 53.7 | 0.02591 | 8.446E+08 | 2.189E+07 | 3.1813 |
| 56.3 | 0.02685 | 8.392E+08 | 2.253E+07 | 3.1712 |
| 57.3 | 0.02657 | 8.339E+08 | 2.216E+07 | 3.1612 |
| 59.5 | 0.02678 | 8.287E+08 | 2.219E+07 | 3.1513 |
| 61.6 | 0.02748 | 8.200E+08 | 2.253E+07 | 3.1348 |
| 63.8 | 0.02755 | 8.149E+08 | 2.245E+07 | 3.1250 |
| 65.6 | 0.02808 | 8.065E+08 | 2.265E+07 | 3.1086 |
| 67.7 | 0.02849 | 8.025E+08 | 2.286E+07 | 3.1008 |
| 69.4 | 0.02855 | 7.974E+08 | 2.276E+07 | 3.0912 |
| 71.4 | 0.02906 | 7.868E+08 | 2.286E+07 | 3.0706 |

STY-0.0971VF(4-)-UC1 (R) ANNEALED
MAY 16, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 73.6 | 0.02994 | 7.757E+08 | 2.323E+07 | 3.0488 |
| 76.0 | 0.03098 | 7.671E+08 | 2.376E+07 | 3.0318 |
| 78.0 | 0.03258 | 7.548E+08 | 2.459E+07 | 3.0075 |
| 82.3 | 0.03926 | 7.170E+08 | 2.815E+07 | 2.9311 |
| 84.2 | 0.04203 | 7.033E+08 | 2.956E+07 | 2.9028 |
| 88.8 | 0.05509 | 6.569E+08 | 3.619E+07 | 2.8050 |
| 92.0 | 0.06591 | 5.993E+08 | 3.950E+07 | 2.6789 |
| 94.6 | 0.09242 | 5.957E+08 | 5.505E+07 | 2.6693 |
| 95.8 | 0.11277 | 5.032E+08 | 5.675E+07 | 2.4526 |
| 97.5 | 0.12553 | 4.710E+08 | 5.912E+07 | 2.3715 |
| 100.0 | 0.16822 | 4.091E+08 | 6.882E+07 | 2.2069 |
| 104.3 | 0.26538 | 2.786E+08 | 7.394E+07 | 1.8116 |
| 141.0 | 0.57207 | 1.355E+05 | 7.751E+04 | 0.0718 |
| 146.0 | 0.28784 | 1.022E+06 | 2.942E+05 | 0.1250 |
| 148.4 | 0.59129 | 1.072E+05 | 6.337E+04 | 0.0695 |
| 150.7 | 0.54956 | 1.068E+05 | 5.870E+04 | 0.0695 |
| 153.5 | 0.62114 | 9.747E+04 | 6.055E+04 | 0.0687 |
| 154.0 | 0.56969 | 1.005E+05 | 5.725E+04 | 0.0690 |
| 156.0 | 0.64252 | 7.828E+04 | 5.030E+04 | 0.0670 |
| 158.3 | 0.74291 | 6.269E+04 | 4.657E+04 | 0.0656 |
| 161.0 | 0.85454 | 5.744E+04 | 4.909E+04 | 0.0651 |
| 163.2 | 0.85672 | 4.977E+04 | 4.263E+04 | 0.0645 |

STY-0.0193VP(4-)-BUI (R)
ANNEALED SAMPLE, MAY 23, 1985

| TEMP. | TAN DELTA | G' | G'' | [illegible] |
|---|---|---|---|---|
| [illegible] | 0.01762 | 1.016E+09 | 1.790E+07 | [illegible] |
| 76.2 | 0.01782 | 1.014E+09 | 1.807E+07 | 2.9954 |
| 77.0 | 0.01803 | 1.013E+09 | 1.826E+07 | [illegible] |
| 81.0 | 0.02050 | 9.924E+08 | 2.035E+07 | [illegible] |
| [illegible] | 0.02254 | [illegible] | 2.219E+07 | [illegible] |
| 84.8 | 0.02333 | 9.719E+08 | 2.267E+07 | [illegible] |
| 87.1 | 0.02442 | 9.543E+08 | 2.331E+07 | [illegible] |
| [illegible] | [illegible] | 9.372E+08 | [illegible] | [illegible] |
| 91.6 | 0.03156 | 9.184E+08 | [illegible] | [illegible] |
| 93.6 | 0.03680 | 9.072E+08 | [illegible] | [illegible] |
| 95.0 | [illegible] | 8.655E+08 | 4.113E+07 | [illegible] |
| 95.3 | 0.05121 | 8.616E+08 | 4.413E+07 | [illegible] |
| 96.0 | 0.06093 | 8.374E+08 | 5.103E+07 | [illegible] |
| 96.3 | 0.06871 | 8.218E+08 | 5.646E+07 | 2.6633 |
| 96.7 | 0.07716 | 7.949E+08 | 6.134E+07 | [illegible] |
| 97.4 | 0.08413 | 7.825E+08 | 6.583E+07 | 2.5864 |
| 97.7 | 0.09533 | 7.675E+08 | 7.316E+07 | [illegible] |
| 98.2 | 0.09978 | 7.538E+08 | 7.522E+07 | 2.5397 |
| 98.8 | 0.11551 | 7.256E+08 | [illegible] | [illegible] |
| 99.0 | 0.12879 | 7.032E+08 | 9.057E+07 | 2.4510 |
| 99.7 | 0.15350 | 6.425E+08 | 9.863E+07 | 2.3408 |
| 100.3 | 0.17598 | [illegible] | 1.093E+08 | [illegible] |
| 100.5 | 0.18450 | 6.389E+08 | 1.179E+08 | 2.3310 |

STY-0.0193VP(4-)-BUI (R)
ANNEALED SAMPLE; MAY 23, 1985

| TEMP. | TAN DELTA | G' | G '' | FREQ. |
|---|---|---|---|---|
| 100.6 | 0.20496 | 6.017E+08 | 1.233E+08 | 2.2599 |
| 101.0 | 0.21298 | 5.597E+08 | 1.192E+08 | 2.1786 |
| 103.1 | 0.29425 | 5.271E+08 | 1.551E+08 | 2.1030 |
| 103.2 | 0.43009 | 4.063E+08 | 1.748E+08 | 1.8215 |
| 104.4 | 0.41463 | 8.930E+08 | 3.702E+08 | 2.7045 |
| 121.2 | 0.70163 | 5.571E+05 | 3.909E+05 | 0.0894 |
| 123.5 | 0.64635 | 5.239E+05 | 3.386E+05 | 0.0883 |
| 124.4 | 0.56889 | 4.206E+05 | 2.393E+05 | 0.0839 |
| 125.8 | 0.56659 | 3.516E+05 | 1.992E+05 | 0.0875 |
| 127.3 | 0.48776 | 3.263E+05 | 1.591E+05 | 0.0794 |
| 130.0 | 0.44738 | 2.711E+05 | 1.213E+05 | 0.0765 |
| 131.1 | 0.43703 | 2.504E+05 | 1.094E+05 | 0.0754 |
| 134.9 | 0.41132 | 2.143E+05 | 8.816E+04 | 0.0734 |
| 136.4 | 0.41893 | 2.129E+05 | 8.920E+04 | 0.0736 |
| 137.5 | 0.44478 | 1.528E+05 | 6.796E+04 | 0.0698 |
| 139.6 | 0.46702 | 1.424E+05 | 6.651E+04 | 0.0691 |
| 142.6 | 0.54541 | 1.258E+05 | 6.863E+04 | 0.0681 |
| 144.0 | 0.66390 | 9.917E+04 | 6.584E+04 | 0.0669 |
| 147.3 | 0.71539 | 7.291E+04 | 5.216E+04 | 0.0647 |
| 151.5 | 0.96291 | 4.837E+04 | 4.657E+04 | 0.0651 |

STY-0.0486VP(4-)-DE1 (R)
ANNEALED; MAY 30, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 30.7 | 0.01800 | 6.813E+08 | 1.226E+07 | 2.2670 |
| 31.7 | 0.01871 | 6.758E+08 | 1.265E+07 | 2.2578 |
| 35.3 | 0.01892 | 6.745E+08 | 1.276E+07 | 2.2556 |
| 37.0 | 0.01927 | 6.699E+08 | 1.291E+07 | 2.2479 |
| 39.9 | 0.01946 | 6.657E+08 | 1.295E+07 | 2.2409 |
| 42.6 | 0.02001 | 6.645E+08 | 1.330E+07 | 2.2388 |
| 44.6 | 0.01945 | 6.612E+08 | 1.285E+07 | 2.2355 |
| 44.8 | 0.01988 | [illegible] | 1.308E+07 | [illegible] |
| 46.[illegible] | 0.01965 | 6.571E+08 | 1.307E+07 | 2.2265 |
| 48.7 | 0.01951 | 6.556E+08 | 1.302E+07 | 2.2209 |
| 49.5 | 0.02009 | 6.486E+08 | 1.303E+07 | 2.2170 |
| 51.4 | 0.02042 | 6.466E+08 | 1.320E+07 | 2.2066 |
| 53.1 | 0.02050 | 6.466F+08 | 1.326E+07 | 2.2086 |
| 55.0 | 0.02065 | 6.403E+08 | 1.322E+07 | 2.1978 |
| 57.2 | 0.02070 | 6.376E+08 | 1.320E+07 | 2.1931 |
| 58.0 | 0.02090 | 6.353E+08 | 1.328E+07 | 2.1891 |
| 60.0 | 0.02106 | 6.311E+08 | 1.329E+07 | 2.1818 |
| 62.4 | 0.02154 | 6.246E+08 | 1.345E+07 | 2.1706 |
| 64.5 | 0.02170 | 6.186E+08 | 1.342E+07 | 2.1602 |
| 66.1 | 0.02180 | 6.120E+08 | 1.334E+07 | 2.1486 |
| 68.1 | 0.02235 | 6.083E+08 | 1.359E+07 | 2.1422 |
| 70.8 | 0.02340 | 5.973E+08 | 1.397E+07 | 2.1226 |
| 72.3 | 0.02426 | 5.903F+08 | 1.432E+07 | 2.1102 |

STY-0.0486VP(4-)-DEI (R)
ANNEALED; MAY 30, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 74.5 | 0.02549 | 5.801E+08 | 1.479E+07 | 2.0918 |
| 76.6 | 0.02659 | 5.691E+08 | 1.513E+07 | 2.0719 |
| 77.0 | 0.02738 | 5.658E+08 | 1.549E+07 | 2.0660 |
| 78.5 | 0.02900 | 5.572E+08 | 1.616E+07 | 2.0501 |
| 80.2 | 0.03060 | 5.462E+08 | 1.672E+07 | 2.0299 |
| 81.0 | 0.03246 | 5.398E+08 | 1.752E+07 | 2.0179 |
| 82.6 | 0.03506 | 5.306E+08 | 1.860E+07 | 2.0006 |
| 85.6 | 0.05194 | 4.940E+08 | 2.566E+07 | 1.9300 |
| 86.3 | 0.05407 | 4.897E+08 | 2.648E+07 | 1.9216 |
| 86.8 | 0.06217 | 4.783E+08 | 2.973E+07 | 1.8988 |
| 87.7 | 0.07462 | 4.612E+08 | 3.442E+07 | 1.8643 |
| 88.2 | 0.08234 | 4.512E+08 | 3.715E+07 | 1.8436 |
| 89.3 | 0.08832 | 4.334E+08 | 3.828E+07 | 1.8068 |
| 90.0 | 0.11057 | 4.137E+08 | 4.566E+07 | 1.7644 |
| 90.2 | 0.11437 | 4.116E+08 | 4.707E+07 | 1.7596 |
| 91.0 | 0.12830 | 4.059E+08 | 5.207E+07 | 1.7466 |
| 91.2 | 0.13864 | 3.924E+08 | 5.441E+07 | 1.7169 |
| 92.0 | 0.15298 | 3.749E+08 | 5.764E+07 | 1.6771 |
| 93.2 | 0.19571 | 3.580E+08 | 7.007E+07 | 1.6360 |
| 93.9 | 0.23054 | 3.190E+08 | 7.308E+07 | 1.5414 |
| 94.1 | 0.24922 | 3.037E+08 | 7.571E+07 | 1.5024 |
| 94.7 | 0.32603 | 2.680E+08 | 8.657E+07 | 1.4050 |
| 124.0 | 0.66886 | 1.096E+06 | [illegible] | 0.0002 |

STY-0.0486VF(4-)-DEI (R)
ANNEALED MAY 30, 1985

| TEMP. | TAN DELTA | G' | G" | FREQ. |
|---|---|---|---|---|
| 125.2 | 0.65083 | 1.038E+05 | 6.[illegible]E+04 | 0.0659 |
| 126.5 | 0.7[illegible]006 | 9.134E+04 | [illegible].034E+04 | 0.065[illegible] |
| 128.0 | 0.65028 | 8.469E+04 | 5.389E+04 | 0.0648 |
| 129.5 | 0.59695 | 8.459E+04 | 5.050E+04 | [illegible] |
| 129.8 | [illegible] | 9.2[illegible]E+04 | 4.9[illegible]E+04 | [illegible] |
| 131.0 | 0.45[illegible] | 9.459E+04 | 4.555E+04 | 0.06[illegible] |
| 133.5 | 0.56189 | [illegible] | 4.488E+04 | [illegible] |
| 135.0 | 0.61175 | 7.456E+04 | 4.5[illegible]E+04 | 0.0643 |
| 136.1 | 0.60085 | [illegible].214E+04 | 4.5[illegible]E+04 | 0.0641 |
| 13[illegible].0 | 0.62938 | 6.984E+04 | 4.186E+04 | 0.0640 |
| 138.7 | 0.[illegible] | [illegible].549E+04 | [illegible]E+04 | 0.061[illegible] |
| 142.0 | [illegible].76[illegible] | 5.05[illegible]E+04 | 2.994E+04 | 0.06[illegible] |
| 14[illegible].0 | 0.7[illegible]526 | 5.2[illegible]E+04 | 4.0[illegible]E+04 | [illegible] |
| 146.0 | 1.09906 | 5.008E+04 | 5.[illegible]E+04 | 0.0616 |

STY-0.0689VP(4-)-BUI (R)
ANNEALED; JUNE 6, 1985

| TEMP. | TAN DELTA | G | G'' | FREQ. |
|---|---|---|---|---|
| 55.2 | 0.02116 | 9.718E+08 | 2.056E+07 | 3.3241 |
| 56.7 | 0.02191 | 9.664E+08 | 2.118E+07 | 3.3149 |
| 58.2 | 0.02210 | 9.629E+08 | 2.128E+07 | 3.3088 |
| 60.2 | 0.02211 | 9.576E+08 | 2.118E+07 | 3.2997 |
| 62.3 | 0.02216 | 9.550E+08 | 2.116E+07 | 3.2952 |
| 66.2 | 0.02292 | 9.429E+08 | 2.161E+07 | 3.2742 |
| 70.5 | 0.02348 | 9.327E+08 | 2.190E+07 | 3.2564 |
| 72.2 | 0.02398 | 9.276E+08 | 2.224E+07 | 3.24[illegible] |
| 74.5 | 0.02402 | 9.210E+08 | 2.213E+07 | 3.2370 |
| 78.1 | 0.02[illegible] | 9.095E+08 | 2.3[illegible]E+07 | 3.215[illegible] |
| 80.7 | 0.02518 | 9.016E+08 | 2.274E+07 | 3.20[illegible] |
| 84.9 | 0.02714 | 8.841E+08 | 2.399E+07 | 3.1704 |
| 87.4 | 0.02862 | 8.687E+08 | 2.486E+07 | 3.1427 |
| 90.2 | 0.03250 | 8.461E+08 | 2.750E+07 | 3.1014 |
| 92.1 | 0.03324 | 8.430E+08 | 2.802E+07 | 3.0979 |
| 94.2 | 0.03701 | 8.213E+08 | 3.04[illegible]E+07 | 3.0555 |
| 97.5 | 0.04382 | 7.9[illegible]1E+08 | 3.471E+07 | 3.0006 |
| 99.1 | 0.04611 | 7.834E+08 | 3.613E+07 | 2.9811 |
| 100.0 | 0.04564 | 7.717E+08 | 3.5[illegible]E+07 | 2.[illegible] |
| 100.8 | 0.04909 | 7.559E+08 | 3.711E+07 | 2.9[illegible]11 |
| 101.8 | 0.05287 | 7.[illegible]55E+08 | 3.994E+07 | 2.9302 |
| 103.6 | 0.05770 | 7.365E+08 | 4.250E+07 | 2.8929 |
| 103.7 | 0.05750 | 7.343E+08 | 4.222E+07 | 2.888[illegible] |

STY-0.0689VP(4-)-BUI (R)
ANNEALED; JUNE 6, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 104.6 | 0.06285 | 7.248E+08 | 4.555E+07 | 2.8696 |
| 105.0 | 0.06527 | 7.146E+08 | 4.664E+07 | 2.8493 |
| 105.8 | 0.07023 | 7.026E+08 | 4.935E+07 | 2.8251 |
| 106.8 | 0.07164 | 6.953E+08 | 4.981E+07 | 2.8103 |
| 108.0 | 0.07931 | 6.785E+08 | 5.382E+07 | 2.7758 |
| 109.0 | 0.09268 | 6.517E+08 | 6.040E+07 | 2.7195 |
| 110.3 | 0.09722 | 6.433E+08 | 6.254E+07 | 2.7018 |
| 111.0 | 0.10764 | 6.259E+08 | 6.737E+07 | 2.6641 |
| 111.8 | 0.12539 | 5.788E+08 | 7.258E+07 | 2.5608 |
| 112.5 | 0.12598 | 5.813E+08 | 7.323E+07 | [illegible] |
| 113.5 | 0.15980 | 5.242E+08 | 8.377E+07 | 2.4341 |
| 114.2 | 0.17402 | 5.012E+08 | 8.722E+07 | 2.3786 |
| 115.2 | 0.19898 | 4.761E+08 | 9.473E+07 | 2.3155 |
| 116.1 | 0.24200 | 4.752E+08 | 1.150E+08 | 2.3077 |
| 117.0 | 0.34908 | 3.868E+08 | 1.350E+08 | 2.0645 |
| 118.0 | 0.41049 | 6.838E+08 | 2.807E+08 | 2.7267 |
| 140.0 | 0.57031 | 4.889E+05 | 2.788E+05 | 0.0941 |
| 145.0 | 0.49527 | 3.929E+05 | 1.946E+05 | 0.0888 |
| 147.8 | 0.49037 | 3.654E+05 | 1.792E+05 | 0.0871 |
| 148.1 | 0.49892 | 3.195E+05 | 1.594E+05 | 0.0842 |
| 149.4 | 0.48383 | 3.053E+05 | 1.477E+05 | 0.0833 |
| 151.2 | 0.47006 | 2.893E+05 | 1.360E+05 | [illegible] |
| 152.5 | 0.47262 | 2.491E+05 | 1.177E+05 | 0.0796 |

STY-0.0689VF(4-)-BUI (R)
ANNEALED; JUNE 6, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 154.7 | 0.46717 | 2.504E+05 | 1.170E+05 | 0.0797 |
| 155.3 | 0.46505 | 2.238E+05 | 1.041E+05 | 0.0779 |
| 158.0 | 0.46969 | 1.967E+05 | 9.239E+04 | 0.0759 |
| 145.0 | 0.51468 | [illegible] | 6.842E+04 | 0.0711 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 8.991E+04 | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | 0.0670 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | 1.14490 | [illegible] | [illegible] | [illegible] |

STY-0.0689VF(4-)-DEL (R)
ANNEALED. ONLY #3THERMOCOUPLE. JUNE 11.

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 28.6 | 0.01758 | 7.095E+08 | 1.248E+07 | 1.7261 |
| 30.5 | 0.01771 | 7.026E+08 | 1.244E+07 | 1.7178 |
| 33.0 | 0.01836 | 6.966E+08 | 1.279E+07 | 1.7104 |
| 37.2 | 0.01883 | 6.874E+08 | 1.294E+07 | 1.6990 |
| 39.2 | 0.01911 | 6.811E+08 | 1.302E+07 | 1.6944 |
| 41.1 | 0.01918 | 6.752E+08 | 1.295E+07 | 1.6840 |
| 43.5 | 0.01933 | 6.750E+08 | 1.305E+07 | 1.6857 |
| 45.4 | 0.01961 | 6.706E+08 | 1.315E+07 | 1.6786 |
| 47.4 | 0.01989 | 6.662E+08 | 1.325E+07 | 1.6726 |
| 49.7 | 0.02006 | 6.602E+08 | 1.324E+07 | 1.6632 |
| 53.6 | 0.02059 | 6.494E+08 | 1.337E+07 | 1.6514 |
| 55.5 | 0.02113 | 6.425E+08 | 1.358E+07 | 1.6427 |
| 57.4 | 0.02164 | 6.354E+08 | 1.375E+07 | 1.6336 |
| 59.3 | 0.02173 | 6.291E+08 | 1.367E+07 | 1.6255 |
| 61.2 | 0.02266 | 6.213E+08 | 1.408E+07 | 1.6154 |
| 64.6 | 0.02357 | 6.078E+08 | 1.433E+07 | 1.5977 |
| 66.7 | 0.02462 | 5.980E+08 | 1.472E+07 | 1.5849 |
| 68.2 | 0.02577 | 5.890E+08 | 1.518E+07 | 1.5729 |
| 70.5 | 0.02660 | 5.779E+08 | 1.534E+07 | 1.5606 |
| 72.4 | 0.02854 | 5.645E+08 | 1.611E+07 | 1.5596 |
| 74.3 | 0.03011 | 5.595E+08 | 1.685E+07 | 1.5540 |
| 77.[illegible] | [illegible] | 5.593E+08 | 1.762E+07 | 1.5[illegible] |
| 79.6 | 0.03770 | 5.184E+08 | 1.954E+07 | 1.42[illegible] |

STY-0.0689VF(4-)-III (R)
ANNEALED, ONLY #3THERMOCOUPLE; JUNE 11,

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 81.3 | 0.03866 | 5.062E+08 | 1.957E+07 | 1.4581 |
| 82.7 | 0.04112 | 4.971E+08 | 2.044E+07 | 1.4449 |
| 83.7 | 0.04421 | 4.846E+08 | 2.143E+07 | 1.4267 |
| 84.6 | 0.04704 | 4.745E+08 | 2.231E+07 | 1.4115 |
| 85.8 | 0.04900 | 4.641E+08 | 2.274E+07 | 1.3962 |
| 86.9 | 0.05131 | 4.547E+08 | 2.334E+07 | 1.3815 |
| 88.0 | 0.05642 | 4.465E+08 | 2.534E+07 | 1.3690 |
| 89.1 | 0.0572 | 4.372E+08 | 2.500E+07 | 1.3550 |
| 90.[illegible] | 0.06019 | [illegible] | 2.562E+07 | 1.[illegible]355 |
| 90.[illegible] | 0.06608 | 4.151E+08 | 2.751E+07 | 1.3171 |
| 91.1 | 0.07250 | 4.051E+08 | 2.966E+07 | 1.3008 |
| [illegible] | [illegible] | 3.940E+08 | [illegible] | 1.2850 |
| 92.7 | 0.08086 | 3.816E+08 | [illegible] | 1.2654 |
| 93.5 | [illegible] | 3.788E+08 | 3.308E+07 | 1.2608 |
| [illegible] | [illegible] | [illegible] | [illegible] | 1.2509 |
| [illegible]4.4 | 0.09556 | [illegible] | 3.450E+07 | [illegible] |
| 95.[illegible] | [illegible] | 3.436E+08 | 3.851E+07 | 1.2006 |
| 95.[illegible] | [illegible] | [illegible] | 4.065E+07 | 1.1871 |
| [illegible] | [illegible] | [illegible]187E+08 | 4.100E+07 | [illegible] |
| [illegible] | [illegible] | 3.073E+08 | 4.636E+07 | [illegible] |
| [illegible] | [illegible] | [illegible] | 4.555E+07 | [illegible] |
| [illegible] | [illegible] | [illegible] | 5.192E+07 | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

STY-0.0689VF (4-)-DE1 (R)
ANNEALED, ONE #5THERMOCOUPLE, JUNE 11,

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 98.6 | 0.23115 | 2.669E+08 | 6.169E+07 | 1.0526 |
| 99.1 | 0.2611[illegible] | 2.590E+08 | 6.762E+07 | 1.0549 |
| 99.6 | 0.2[illegible] | 2.5[illegible]E+08 | 6.758E+07 | 1.0257 |
| 100.5 | 0.38106 | 2.349E+08 | 8.951E+07 | 0.9756 |
| 102.8 | 0.[illegible] | 2.0[illegible]E+08 | 8.08[illegible]E+07 | 0.9124 |
| 12[illegible] | 0.88185 | 1.6[illegible]E+05 | 1.45[illegible]E+05 | 0.[illegible] |
| [illegible] | [illegible] | 1.512E+05 | 1.[illegible] | 0.[illegible] |
| 130. | 0.[illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | 1.[illegible]E+05 | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | 5.404E+0[illegible] | 0.[illegible] |
| [illegible] | [illegible] | [illegible] | 5.491E+0[illegible] | 0.[illegible] |

[illegible] DELTA VS
ANNEALED [illegible] VERY SHORT SAMPLE

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 62.1 | 0.03162 | 5.805E+08 | 1.847E+07 | 1.7794 |
| 65.0 | 0.03194 | 5.754E+08 | 1.839E+07 | 1.7725 |
| 67.3 | 0.03201 | 5.716E+08 | 1.850E+07 | 1.7660 |
| 70.0 | 0.03296 | 5.668E+08 | 1.866E+07 | 1.7585 |
| 70.5 | 0.03287 | 5.480E+08 | 1.801E+07 | 1.7291 |
| 72.5 | 0.03337 | 5.281E+08 | 1.762E+07 | 1.6975 |
| 74.1 | 0.03406 | 5.218E+08 | 1.777E+07 | 1.6875 |
| 76.0 | 0.03476 | 5.016E+08 | 1.744E+07 | 1.6559 |
| 76.6 | 0.03516 | 5.001E+08 | 1.758E+07 | 1.6519 |
| 78.0 | 0.03544 | 4.957E+08 | 1.757E+07 | 1.6446 |
| 80.0 | 0.03531 | 4.919E+08 | 1.737E+07 | 1.6384 |
| 82.0 | 0.03681 | 4.897E+08 | 1.803E+07 | 1.6347 |
| 84.2 | 0.03697 | 4.854E+08 | 1.794E+07 | 1.6274 |
| 86.4 | 0.03752 | 4.817E+08 | 1.807E+07 | 1.6213 |
| 88.0 | 0.03779 | 4.781E+08 | 1.808E+07 | 1.6157 |
| 90.3 | 0.03801 | 4.753E+08 | 1.807E+07 | 1.6104 |
| 92.1 | 0.03984 | 4.715E+08 | 1.878E+07 | 1.6055 |
| 94.2 | 0.04012 | 4.692E+08 | 1.882E+07 | 1.6000 |
| 98.1 | 0.04204 | 4.589E+08 | 1.927E+07 | 1.5719 |
| 100.1 | 0.04602 | 4.477E+08 | 2.060E+07 | 1.5650 |
| 102.0 | 0.04863 | 4.425E+08 | 2.143E+07 | 1.5507 |
| 104.2 | 0.05082 | [illegible] | 2.176E+07 | 1.5285 |
| 106.2 | [illegible] | [illegible] | [illegible] | 1.5246 |

STY-0.0971U(4-)-DLI (R)
ANNEALED, VERY SHORT SAMPLE

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 108.2 | 0.05862 | 4.213E+08 | 2.470E+07 | 1.5186 |
| 110.1 | 0.06569 | 4.102E+08 | 2.695E+07 | [illegible] |
| 112.2 | 0.07285 | 3.940E+08 | 2.870E+07 | 1.4656 |
| 114.2 | 0.08421 | 3.809E+08 | 3.206E+07 | 1.4110 |
| 116.0 | 0.09851 | 3.596E+08 | 3.542E+07 | 1.4001 |
| 118.1 | 0.12619 | 3.536E+08 | 4.462E+07 | 1.3669 |
| [illegible] | [illegible] | 3.166E+08 | 4.404E+07 | 1.3038 |
| [illegible] | [illegible] | 3.011E+08 | 5.012E+07 | 1.2782 |
| [illegible] | 0.19016 | 2.835E+08 | 5.410E+07 | 1.2411 |
| [illegible] | [illegible] | [illegible] | 6.186E+07 | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | 1.0371 |
| [illegible] | [illegible] | [illegible] | 1.118E+08 | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | 1.011E+05 | 0.0626 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | 0.87062 | [illegible] | 1.475E+05 | 0.0066 |
| 158.4 | [illegible] | 1.610E+05 | 1.526E+05 | 0.0675 |
| [illegible] | [illegible] | [illegible] | 9.076E+04 | [illegible] |
| [illegible] | [illegible] | [illegible] | 8.415E+04 | 0.0650 |
| 166.8 | 0.91166 | 9.360E+04 | 8.536E+04 | 0.0638 |
| [illegible] | [illegible] | 5.601E+04 | 4.782E+04 | 0.0625 |
| 172.0 | 0.80626 | 6.270E+04 | 5.056E+04 | 0.0629 |
| 175.5 | 1.16896 | 5.880E+04 | 6.874E+04 | 0.0623 |

[illegible] 0.05/[illegible] DLT [illegible] ANN.
JUNE 1, 1985; MINUS 25 DEG

| TEMP. | TAN DELTA | [illegible] | U | FREQ. |
|---|---|---|---|---|
| [illegible] | 0.063[illegible] | 5.80[illegible]E+08 | 1.641E+07 | 1.7794 |
| [illegible] | 0.061[illegible] | 5.7[illegible]E+08 | 1.8[illegible]E+07 | 1.7725 |
| [illegible] | [illegible] | [illegible] | 1.850E+07 | 1.7[illegible] |
| [illegible] | [illegible] | [illegible] | 1.8[illegible]E+07 | 1.7580 |
| [illegible] | [illegible] | 5.660E+08 | 1.801E+07 | 1.7291 |
| [illegible] | 0.06[illegible] | 5.2[illegible]E+08 | 1.7[illegible]E+07 | 1.6975 |
| [illegible] | [illegible] | [illegible]E+08 | 1.7[illegible]E+07 | 1.6875 |
| 51.0 | 0.064[illegible] | 5.013E+08 | 1.744E+07 | 1.6539 |
| 51.6 | 0.05516 | 5.001E+08 | 1.758E+07 | 1.6519 |
| 53.0 | 0.055[illegible] | 4.957E+08 | 1.757E+07 | 1.6446 |
| 55.0 | 0.055[illegible] | 4.919E+08 | 1.757E+07 | 1.6384 |
| 57.0 | 0.05681 | 4.897E+08 | 1.805E+07 | 1.6337 |
| 59.2 | 0.05697 | 4.854E+08 | 1.794E+07 | 1.6274 |
| 61.4 | 0.057[illegible] | 4.817E+08 | 1.807E+07 | 1.6216 |
| 63.0 | 0.057[illegible] | 4.784E+08 | 1.808E+07 | 1.6157 |
| [illegible] | 0.05801 | [illegible]E+08 | 1.807E+07 | 1.6104 |
| 67.1 | 0.05984 | 4.715E+08 | 1.878E+07 | 1.6069 |
| 67.2 | 0.06012 | 4.692E+08 | 1.885E+07 | 1.6000 |
| 70.1 | [illegible] | [illegible]E+08 | 1.9[illegible]E+07 | 1.57[illegible] |
| [illegible] | [illegible] | [illegible]E+08 | 2.060E+07 | 1.5650 |
| [illegible] | [illegible] | [illegible] | 2.19[illegible]E+07 | [illegible] |
| [illegible] | [illegible] | [illegible] | 2.176E+07 | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible]E+07 | 1.5240 |

STY 0.0571UP(4 + DET (R) ANN.
JUNE 14, 1985, MINUS 25 DEG

| TEMP. | TAN DELTA | G | G'' | FREQ. |
|---|---|---|---|---|
| 83.2 | 0.05862 | 4.213E+08 | 2.470E+07 | 1.5160 |
| 85.4 | 0.06569 | 4.102E+08 | 2.695E+07 | 1.4957 |
| 87.2 | 0.07280 | 3.930E+08 | 2.870E+07 | 1.4658 |
| 89.2 | 0.08421 | 3.809E+08 | 3.208E+07 | 1.4410 |
| 91.0 | 0.09861 | 3.591E+08 | 3.541E+07 | 1.4001 |
| 93.1 | 0.12549 | 3.556E+08 | 4.462E+07 | 1.3869 |
| 94.1 | 0.14316 | 3.133E+08 | 4.484E+07 | 1.3048 |
| 93.8 | 0.16645 | 3.011E+08 | 5.012E+07 | 1.2782 |
| 95.5 | 0.19016 | 2.845E+08 | 5.410E+07 | 1.2411 |
| 97.7 | 0.27108 | 2.282E+08 | 6.186E+07 | 1.1065 |
| 99.0 | 0.33657 | 2.065E+08 | 6.950E+07 | 1.0471 |
| 100.2 | 0.41859 | 2.670E+08 | 1.118E+08 | 1.1799 |
| 127.5 | 0.98771 | 2.092E+05 | 2.066E+05 | 0.0682 |
| 129.6 | 0.79494 | 2.279E+05 | 1.811E+05 | 0.0690 |
| 130.5 | 0.86338 | 1.712E+05 | 1.478E+05 | 0.0669 |
| 131.5 | 0.87062 | 1.695E+05 | 1.475E+05 | 0.0668 |
| 133.4 | 0.73107 | 1.810E+05 | 1.323E+05 | 0.0675 |
| [illegible] | 0.63756 | 1.423E+05 | 9.076E+04 | 0.0659 |
| 140.1 | 0.69431 | 1.212E+05 | 8.415E+04 | 0.0650 |
| 141.8 | 0.91136 | 9.366E+04 | 8.536E+04 | 0.0638 |
| 145.6 | 0.84922 | 5.631E+04 | 4.782E+04 | 0.0623 |
| 147.0 | 0.80862 | 6.970E+04 | 5.636E+04 | 0.0629 |
| 150.5 | 1.16905 | 5.880E+04 | 6.874E+04 | 0.0625 |

STY-0.0689VP(4-)-HL1 (R)
ANNEALED; JUNE 18, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 44.2 | 0.03318 | 6.601E+08 | 2.190E+07 | 1.0650 |
| 47.0 | 0.03526 | 6.458E+08 | 2.277E+07 | 1.0534 |
| 48.7 | 0.03535 | 6.404E+08 | 2.264E+07 | 1.0490 |
| 50.6 | 0.03601 | 6.332E+08 | 2.280E+07 | 1.0431 |
| 52.5 | 0.03634 | 6.242E+08 | 2.268E+07 | 1.0356 |
| 54.9 | 0.03750 | 6.176E+08 | 2.316E+07 | 1.0302 |
| 56.2 | 0.03704 | 6.107E+08 | 2.262E+07 | 1.0245 |
| 58.9 | 0.03821 | 5.983E+08 | 2.286E+07 | 1.0132 |
| 60.9 | 0.03841 | 5.918E+08 | 2.279E+07 | 1.0086 |
| 65.5 | 0.04071 | 5.742E+08 | 2.338E+07 | 0.9935 |
| 67.5 | 0.04220 | 5.637E+08 | 2.379E+07 | 0.9843 |
| 69.5 | 0.04365 | 5.505E+08 | 2.403E+07 | 0.9727 |
| 71.5 | 0.04690 | 5.358E+08 | 2.513E+07 | 0.9597 |
| 75.4 | 0.05613 | 5.060E+08 | 2.840E+07 | 0.9326 |
| 77.5 | 0.07955 | 4.493E+08 | 3.574E+07 | 0.8787 |
| 83.3 | 0.15502 | 3.109E+08 | 4.819E+07 | 0.7300 |
| 86.0 | 0.25251 | 2.282E+08 | 5.763E+07 | 0.6231 |
| 86.3 | 0.31221 | 1.838E+08 | 5.738E+07 | 0.5574 |
| 87.5 | 0.39758 | 1.380E+08 | 5.488E+07 | 0.4801 |
| 111.0 | 1.02959 | 2.689E+05 | 2.769E+05 | 0.0634 |
| 113.0 | 1.40171 | 1.414E+05 | 1.982E+05 | 0.0617 |
| 115.0 | 0.79072 | 1.388E+05 | 1.097E+05 | 0.0617 |
| 117.0 | 0.61369 | 1.425E+05 | 8.747E+04 | 0.0618 |

STY-0.0689VP(4-)-HET (R)
ANNEALED; JUNE 18, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 119.0 | [illegible] | [illegible] | 5.4[illegible]1E+04 | 0.0616 |
| 121.0 | 0.43760 | [illegible].058E+04 | 2.161E+04 | 0.0605 |
| [illegible].0 | 0.3[illegible] | [illegible].911E+0[illegible] | 3.029E+0[illegible] | 0.0599 |
| [illegible] | [illegible] | [illegible] | 7.036E+04 | 0.0617 |
| [illegible] | [illegible] | 3.1[illegible] | [illegible] | 0.0602 |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible].03 |

STY-0.0689VF(4-)-OCI (R)
ANNEALED; AUG. 21, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 22.2 | 0.02711 | 7.266E+08 | 1.970E+07 | 2.5487 |
| 33.4 | 0.02733 | 6.957E+08 | 1.901E+07 | 2.4939 |
| 35.3 | 0.02932 | 6.876E+08 | 2.016E+07 | 2.4793 |
| 37.8 | 0.02969 | 6.806E+08 | 2.021E+07 | 2.4666 |
| 39.9 | 0.03026 | 6.741E+08 | 2.040E+07 | 2.4548 |
| 42.1 | 0.03157 | 6.623E+08 | 2.091E+07 | 2.4333 |
| 44.1 | 0.03152 | 6.574E+08 | 2.072E+07 | 2.4242 |
| 46.3 | 0.03397 | 6.456E+08 | 2.193E+07 | 2.4024 |
| 47.9 | 0.03469 | 6.375E+08 | 2.212E+07 | 2.3873 |
| 50.5 | 0.03731 | 6.242E+08 | 2.329E+07 | 2.3622 |
| 51.8 | 0.03966 | 6.145E+08 | 2.437E+07 | 2.3437 |
| 53.2 | 0.04450 | 5.997E+08 | 2.669E+07 | 2.3151 |
| 54.2 | 0.04761 | 5.888E+08 | 2.803E+07 | 2.2941 |
| 55.4 | 0.05284 | 5.739E+08 | 3.032E+07 | 2.2646 |
| 57.0 | 0.06488 | 5.451E+08 | 3.537E+07 | 2.2068 |
| 59.1 | 0.09229 | 4.963E+08 | 4.580E+07 | 2.1045 |
| 60.0 | 0.11325 | 4.641E+08 | 5.256E+07 | 2.0341 |
| 62.4 | 0.16622 | 4.020E+08 | 6.682E+07 | 1.8898 |
| 63.0 | 0.18783 | 3.411E+08 | 6.407E+07 | 1.7391 |
| 63.9 | 0.18701 | 3.194E+08 | 5.973E+07 | 1.6830 |
| 64.4 | 0.21598 | 3.194E+08 | 6.900E+07 | 1.6807 |
| 65.3 | 0.21285 | 2.837E+08 | 6.038E+07 | 1.5842 |
| 65.6 | 0.26232 | 2.596E+08 | 6.809E+07 | 1.5109 |

STY-0.0689VP(4-)-OCI (R)
ANNEALED; AUG. 21, 1985

| TEMP. | TAN DELTA | G' | G'' | FREQ. |
|---|---|---|---|---|
| 100.0 | 0.75203 | 1.110E+06 | 8.348E+05 | 0.1112 |
| 100.5 | 0.80775 | 8.588E+05 | 6.937E+05 | 0.1016 |
| 104.0 | 0.66385 | 4.740E+05 | 3.146E+05 | 0.0869 |
| 107.0 | 0.59559 | 1.420E+06 | 8.457E+05 | 0.1238 |
| 115.5 | 0.17571 | 1.998E+05 | 3.510E+04 | 0.0732 |
| 120.0 | 0.46430 | 6.690E+04 | 3.106E+04 | 0.0646 |