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NL-339 (r, B&/04) c

MISCIBILITY ENHANCEMENT OF ALIPHATIC POLYAMIDES WITH OTHER POLYMERS THROUGH ION-DIPOLE INTERACTIONS

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by

Attila Molnár

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Department of Chemistry, McGill University, Montreal, Quebec, Canada.

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February, 1992

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To my wife,

Donna

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ABSTRACT

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Polystyrene (PS), functionalized with various ionic groups, was blended with polyamides (PA) in order to investigate the effect of ion-dipole interactions on the miscibility of PS/PA blends. Sulfonic acid groups interact strongly with amides, but catalyze the hydrolysis of the amide bonds of the PA. The neutralization of the sulfonic acid groups eliminates this reaction in the blends, and when the counterion is lithium, strong miscibility enhancement is seen between the lithium sulfonated polystyrene (LiSPS) and polyamides-6 (PA-6), -66, -610 and -11. This miscibility enhancement increases with the lithium sulfonate content of the LiSPS and the amide content of the PA, and is also dependent on the blend composition. An equilibrium thermodynamic approach is used to describe the miscibility behavior of the LiSPS blends with PA-6. When the ionic group is sodium sulfonate, lithium carboxylate or sodium carboxylate, the miscibility enhancement is negligible. As a possibly better alternative to the PS ionomers as a blend component with PAs, novel sulfonated poly(styrene-ethylene-butylene) random ionomers were synthesised and characterized.

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RÉSUMÉ

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Des mélanges de polystyrène (PS), ayant divers groupements fonctionnels, avec des polyamides (PA) ont été préparés afin d'étudier l'effet des interactions iondipôle sur la miscibilité des mélanges de PS/PA. Les groupements acide sulfoniques interagissent fortement avec les groupements amides des PA, mais cet acide catalyse l'hydrolyse des liens amides des PA. La neutralisation des groupements acide sulfoniques élimine cette réaction lors des mélanges de PS/PA. Lorsque le contre-ion est le lithium, un grand accroissement de la miscibilité a été observé pour les mélanges de polystyrène lithium sulfonés (LISPS) avec les polyamides-6 (PA-6), -66, -610 et -11. Cette amélioration de la miscibilité augmente avec l'accroissement du contenu en lithium sulfonate du LiSPS, ainsi que du conténu en groupements amides du PA. Cet accroissement de la miscibilité dépend aussi de la composition du mélange. Le comportement de la miscibilité des mélanges de LiSPS et de PA-6 a été rationalisé à l'aide d'un équilibre thermodynamique. Pour des mélanges contenant les groupements ioniques suivant; sulfonate de sodium, carboxylate de lithium, ou carboxylate de sodium, un accroissement négligeable de la miscibilité a été observé. Afin d'offrir une meilleure alternative aux ionomères de PS comme composante de mélange avec les PA, de nouveaux ionomères statistiques basés sur le poly(styrène-éthylène-butène) sulfoné ont été synthétisés et caractérisés.

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This thesis is written in the form of five papers which are preceded by a general introduction and followed by general conclusions. Four of the papers (*Chapters 2 to 5*) have been submitted for publication in scientific journals, with the research

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director, Professor Adi Eisenberg, as co-author. However, it is clear that all the work has been done by the author of this thesis, except for the normal supervision and advice given by the research director. The fifth paper (*Chapter 6*), not submitted at the present time, contains some contributions from Dr. M. Nagura (Shinshu University) in providing and analyzing the WAXS data and assistance with some of the hydrogenation reactions.

The papers have been submitted as follows:

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Chapter 2: Polymer Communications 1991, 32, 370.

Chapter 3: Polymer Engineering and Science, accepted.

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Chapter 4: Macromolecules, submitted.

Chapter 5: *Polymer*, submitted.

I hereby give copyright clearance for the inclusion of the following four papers, of which I am co-author, in the thesis of Attila Molnár:

"Compatibilization of nylon 6 and polystyrene through the functionalization of polystyrene."

"Miscibility of Polyamide-6 and Polystyrene Functionalized with Sulfonic Acid Groups."

"Miscibility of Polyamide-6 with Lithium or Sodium Sulfonated Polystyrene Ionomers."

"Miscibility of Carboxylated and Sulfonated Polystyrene Ionomers with Polyamides-66, -610 and -11."

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Date: Fol- 24 1992

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Dr. A. Eisenberg Department of Chemistry McGill University

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NOMENCLATURE

Α	=	number of amine and amide groups in the blend
В	=	effective interaction energy density (J/g)
Ь	=	ratio of the amorphous densities of the two polymers in the blend
B _c	=	interaction energy density for the LiS-PA complex formation (J/g)
Bs	=	interaction energy density for a styrene unit - PA-6 unit pair (J/g)
∆C _{pi}	=	heat capacity change at T_{gi} for polymer i (J/g K)
D ₂ O	=	deuterium oxide
DMSO-d ₆	=	deuterated dimethyl sulfoxide
DMTA	=	dynamic mechanical thermal analysis
DSC	=	differential scanning calorimetry
E'	=	storage modulus (Pa)
E"	=	loss modulus (Pa)
ΔE _a	=	apparent activation energy (kJ/mol)
EPDM	=	poly(ethylene-propylene-diene) random copolymer
FTIR	=	Fourier transform infra-red
∆G _m	=	Gibbs free energy of mixing (J/g)
ΔH _c	=	crystallization enthalpy (J/g)
$\Delta H_{\rm m}$	=	heat of mixing (J/g)
ΔH_m	=	melting enthalpy (J/g)
k	=	$\Delta C_{p2} / \Delta C_{p1}$
K	=	equilibrium constant (cm ³)
K _r	=	equilibrium constant normalized to V _r
LiS	=	lithium sulfonated styrene unit

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LiMAPS	=	poly(styrene-co-lithium methacrylate)
LiSPS	=	lithium sulfonated polystyrene
$M_{v'}M_{w'}M_n$	=	viscosity, weight and number average molecular weight (kg/mol)
MAPS	=	poly(styrene-co-metal methacrylate)
n	=	average number of chain cuts per sulfonic acid group
NaMAPS	=	poly(styrene-co-sodium methacrylate)
NaSPS	=	sodium sulfonated polystyrene
NMR	=	nuclear magnetic resonance
P _(i)	=	degree of polymerization of polymer i
PA	=	PA-6 unit
PA-6	=	polyamide-6
PA-66	#	polyamide-66
PA-610	2	polyamide-610
PA-11	=	polyamide-11
PS	=	polystyrene
PSB	=	poly(styrene-butadiene) random copolymer
PSE	=	poly(styrene-ethylene-butylene) random copolymer
PSMAA	=	poly (styrene - co - methacrylic acid)
R	=	universal gas constant (J/K mol)
S	= ^ `	number of sulfonic acid groups in the blend
SEC	=	size exclusion chromatography
SEM	=	scanning electron micrograph
$\Delta S_{\rm m}$	=	entropy of mixing (J/g K)
SPS	=	sulfonated polystyrene
SPSE	=	sulfonated PSE
Т	=	temperature at which miscibility is determined (°C or K, as indicated)

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Nomenclature

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tanδ	=	dynamic loss tangent
T _c	=	crystallization temperature (°C)
Tg	=	glass transition temperature (°C or K, as indicated)
T _{gi}	=	glass transition temperature of polymer i (°C or K, as indicated)
THF	=	tetrahydrofuran
T _m	=	polymer melting temperature (°C)
$T_{m(1)}, T_{m(2)}$	=	melting temperatures of polymers 1 and 2, respectively (K)
V _r	=	reference volume (100 cm ³)
w_{i}	=	weight fraction of polymer i in the blend
x	=	average number of cuts per chain
β	=	$B_{\rm c}/B_{\rm s}$
χ	=	Flory-Huggins interaction parameter
ф ₂ '	=	value of ϕ_2 , betwen 0 and 1, where $\Delta G_m = 0$
φ _c	=	volume fraction of LiS-PA complex in the blend
ф _і	=	volume fraction of polymer i in the blend
 ξ	=	fraction of ionomer units functionalized with lithium sulfonate groups
x(1), x(2)	=	fraction of crystallizable units for polmers 1 and 2 respectively

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Chapter 1

GENERAL INTRODUCTION : MISCIBILITY ENHANCEMENT THROUGH IONIC INTERACTIONS

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1.1 INTRODUCTION

The early investigations by Dobry and Boyer-Kawenoki $(1947)^1$ of the phase separation of polymers in solution, and later by Bohn $(1966)^2$ of the mixing of polymers in the solid state, indicated that polymers generally do not mix. These experimental studies were given a theoretical grounding by the work of Scott $(1949)^3$ and Tompa $(1949)^4$. Consequently, polymer blend technology has primarily centered around phase separated blends and the problem was often described as an attempt to move away from blend systems where the phase boundary was distinct, to systems where there was considerable interpenetration of the phases. Extremely useful polymer blends and alloys can be produced in this way. For example, high impact polystyrene (HIPS) and acrylonitrile-

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butadiene-styrene polymers (ABS) show high impact strength due to the wellbound rubbery domains and yet have sufficient rigidity and strength to be applied as engineering thermoplastics. In these blends *partial miscibility*, at least at the interface, is an important consideration in optimizing the blend properties.

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Miscibility between polymers is in many cases desirable since these blends are characterized by a single phase, with the material properties varying continuously between those of the blend components. Thus, the material properties can be controlled by simply adjusting the relative amounts of the blend components. For instance, nitrile rubber (butadiene/acrylonitrile random copolymer), which is often used as conveyor belting material, shows an improved resistance to tear, thermal aging and UV degradation upon the addition of a small amounts (20 to 40%) of polyvinylchloride (PVC)⁵. Poly(2,6dimethyl 1,4-phenylene oxide) (PPO) and polystyrene are another example of a commercially useful miscible polymer pair (commercialized in the 1960s by General Electric Co.)⁶. In these resins, the polystyrene component lowers considerably the cost as well as the glass transition temperature of the blend (which allows for easier processing) without diminishing significantly the mechanical properties afforded by the PPO component. In the PVC/nitrile rubber and PPO/polystyrene blends, total miscibility is the key to blend property optimization. ------

Ideally, it would be useful to be able to control the miscibility in order to achieve any desired extent of mixing between the two polymers i.e. *partial*, as well as *total miscibility*. Several techniques exist to enhance the miscibility between inherently immiscible polymers, some of which are listed here:

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1. addition of interfacial agents $^{7-10}$

2. random copolymerization^{5,11}

3. reactive processing^{12,13}

4. high stress shearing 14

- 5. introduction of specific interacting groups
- 6. cross linking^{15,16}

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8. salt addition 18

The introduction of specific interacting groups is a particularly versatile route to miscibility enhancement, since a large number of polymers can be functionalized with these groups. For instance, sulfonate groups can be incorporated into a variety of polymers, either through copolymerization, or post polymerization modification, as reviewed by Fitzgerald and Weiss (1988)¹⁹. The extent of the miscibility enhancement can also be easily controlled by suitably adjusting the number of these groups incorporated into the parent polymer. In addition to these benefits, specific interacting groups could be used to enhance the effect of interfacial agents, to take part in a reaction during processing, and to assist in the formation of stable interpenetrating polymer networks (1, 3, and 7 in the above list).

Many types of specific interactions are possible, the most notable of which are hydrogen bonding^{20,21} donor-acceptor complexation²², charge transfer complexation²³, dipole-dipole²⁴, ion-dipole, ion pair-ion pair, ion co-ordination and ion-ion interactions. The last four types of interactions involve the interactions of ionic groups, and this will be the focus of this chapter.

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1.2 THERMODYNAMIC CONSIDERATIONS

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The thermodynamics of mixtures is described by the Gibbs free energy of mixing $\Delta G_{\rm m}$, which can be considered to consist of a heat of mixing term $\Delta H_{\rm m}$ and an entropic term $\Delta S_{\rm m}$.

$$\Delta G_{\rm m} = \Delta H_{\rm m} - T \,\Delta S_{\rm m} \tag{1.1}$$

For the mixture to exist as a single phase at equilibrium, it is necessary that ΔG_m be negative and also that the second derivative of the Gibbs free energy with respect to composition, of either of the blend components, be positive. In mixtures of polymers, the high degree of polymerization places a severe constraint on the extent of "randomness" that mixing can bring about, so that ΔS_m is usually very small and positive. This was more clearly shown by Flory (1942)²⁵ in his derivation of an expression for the combinatorial entropy of mixing and the subsequent development of the Flory -Huggins equation to describe the Gibbs free energy of mixing a total volume of V of two polymers, A and B²⁶:

$$\Delta G_{\rm m} = B_{\rm AB} V \phi_{\rm A} \phi_{\rm B} + RTV/V_{\rm r} \left[(\phi_{\rm A}/r_{\rm A}) \ln\phi_{\rm A} + (\phi_{\rm B}/r_{\rm B}) \ln\phi_{\rm B} \right]$$
[1.2]

where V_r is a reference volume, usually taken as the molar volume of the smallest repeat unit, ϕ_i and r_i are the volume fraction and degree of polymerization of polymer i, and B_{AB} is the interaction energy density for a (polymer A unit)/(polymer B unit) pair. B_{AB} is related to the more familiar χ interaction parameter by $B_{AB} = RT\chi_{AB}/V_r$. Since the second term (the entropic part) in Equation [1.2] is negligible for blends of high polymers, the ΔH_m (= $B_{AB}V$

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 $\phi_A \phi_B$) remains as the primary contributing term to ΔG_m . Thus, ΔH_m must necessarily be either zero, or negative, as a minimum condition to ensure miscibility of the polymers.

The presence of specific intermolecular interactions can lower the heat of mixing of the two polymers in the blend, and, in some cases, lead to a negative $\Delta H_{\rm m}$ (miscibility). In this respect, specific interactions are very important in the development of miscible blends. For example, the miscibility of PPO with polystyrene has been attributed to the specific interaction of the π -orbitals of the polystyrene aromatic rings with the methylene groups of the PPO²⁷.

The specific interaction of ionic groups with polar groups, or other ionic groups, is usually a highly exothermic interaction, and, therefore, is particularly useful in lowering the heat of mixing in polymer blends. In this way polymers can be rendered miscible with only a few such interactions. This, to a large extent accounts for the wide success of ionomers in polymer blending technology. The strong interactions present in ionomer blends causes a significant deviation from randomness and consequently equations such as Equation [1.2] can no longer be applied to these blends. Several theories have been developed recently to describe the thermodynamics of blending in systems where specific interaction take place²⁸⁻³³. However, a large number of parameters, e.g. equilibrium constants, have to be determined experimentally before these equations can be successfully applied. Consequently the determination of miscibility in ionomer blends is, to a large extent, still restricted to experimental measurements.

It has been shown by a number of workers that specific interactions are not necessary to achieve a negative ΔH_m^{34-36} . In these systems, however, at least

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one of the polymers must be a random co-polymer, such that the copolymer segments interact unfavorably with each other. An example is the PVC/nitrile rubber blend, where the butadiene and acrylonitrile segments of the nitrile rubber interact more unfavorably with each other, than they do with the segment units of the PVC³⁴. Thus B_{AB} in Equation [1.2] becomes

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$$B_{\rm AB} = B_{1B}\xi_1 + B_{2B}\xi_2 - B_{12}\xi_1\xi_2$$
 [1.3]

where ξ_1 and ξ_2 are the fraction of units 1 and 2 of the random copolymer A, respectively, and B_{1B} , B_{2B} and B_{12} are the segment interaction energy densities for the segment unit pairs indicated by the subscripts. Thus, a large and positive B_{12} value can lead to a negative B_{AB} . Although ionomers can be considered as random copolymers of ionic and non-ionic units, they cannot be used in this type of theoretical treatment, since the strong self-association of the ionic groups violates the necessary random condition for Equation [1.3]; even in the pure ionomers, phase-separated ionic domains exist, suggesting the non-random distribution of segments in the bulk^{37,38}.

1.3 DETERMINATION OF MISCIBILITY

An excellent coverage of the various techniques available to study miscibility in polymer blends has been given by Olabisi, Robeson and Shaw (1979)³⁹. They generally classified the various techniques as follows: 1. T_g measuring methods, 2. microscopy, 3. scattering methods, 4. ternary solution methods and, 5. miscellaneous methods. Among the techniques using the T_g method are dynamic mechanical, dielectric and calorimetric methods. Light, phase contrast and

electron microscopy fall under the techniques utilizing microscopy. Among the scattering methods are cloud point curve measurements, small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), and conventional light scattering methods. Inverse gas chromatography and mutual-solvent methods constitute ternary solution methods. Among the miscellaneous techniques are nuclear magnetic resonance (NMR) spectroscopy, melting point depression analysis, infrared spectroscopy and heat of mixing by calorimetry.

No single technique is able to completely describe the miscibility in polymer blends and the maximum information can be gained by using a combination of methods. One of the limitations of the different techniques is the domain (phase) size that can be resolved. Thus, while a blend may seem miscible by the transparency of the blend film (resolution of phases of *ca.* 1,000Å in diameter⁴⁰), it may be immiscible when looked at by electron microscopy (ca. 50Å resolution⁴¹). T_{g} measuring methods are limited to the detection of phases large enough to give rise to an observable T_g . As suggested by Boyer (1966)⁴², the T_g involves the cooperative motion of 50-100 backbone chain atoms and hence the detection of a T_g indicates the presence of domain sizes of at least 20 or 30Å. A much larger minimum domain size of 150Å has been assigned to the T_g by Kaplan (1976)⁴³, although Bair and Warren (1981)⁴⁴ suggest that this domain size may be between 50-100Å. Some techniques can probe miscibility on a much finer level. NMR, for instance, can be used to detect heterogeneities down to about 20Å using T_{10} measurements⁴⁵, while infra-red⁴⁶ and fluorescence spectroscopy 47 can detect miscibility on the molecular scale.

The two most commonly used techniques to establish miscibility are differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA).

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Both of these techniques measure the T_g of the blend and therefore can only be used in blend systems where the T_g of the individual components are separated by at least 20°C. In semi-crystalline polymer blends, DSC is particularly useful since the crystallization and melting temperatures can be located, and thus provide some additional indirect evidence of interaction between the blend components. Typical dynamic mechanical curves are schematically shown in Figure 1.1 (top) for an immiscible (1), partially miscible (2) and "miscible" (3) polymer blend. A schematic representation of the cross-sectional compositions for these three type of blends is also shown (Figure 1.1: bottom). Note that the "miscible" blend (3) could either be a truly miscible blend, or consist of well separated microdomains smaller than ca. 50Å, which is below the resolution limit of the dynamic mechanical technique, and therefore an average response is recorded which is similar to that of a truly miscible blend. Dynamic mechanical measurements have in particular been very useful in the study of ionomers since they are able to detect a higher transition phase, called the "cluster phase", which is a characteristic of most random ionomers. One of the chief advantages of methods measuring T_g to determine miscibility is that they are also able to provide information on the purity of the phases (by the breadth of the transition), and on the extent of miscibility enhancement (by the relative T_g shifts).

1.4 IONOMER BLENDS

1.4.1 Ionomers: Ionomers are a relatively new generation of thermoplastic polymers characterized by the presence of small amounts of ionic comonomer, typically less than $10\%^{48}$, but sometimes more. This small percentage of ionic character enhances some of the properties of the polymer, such as



Figure 1.1 Schematic representation of the dynamic mechanical behavior (top) and corresponing possible cross-sectional composition (bottom) for 50:50 blends of polymers A and B when these two polymers are immiscible (1), partially miscible (2), and "miscible" (3).

adhesion and ion transport, which has led to the use of these materials in many commercial applications. One of these applications is the use of ionomers in polymer blends, either as one of the blend components, or as a compatibilizer. In this way polymer alloys and blends can be produced with improved mechanical properties. For example, blends of polyamides (nylons) with ethylene based ionomers significantly improves the impact properties of the polyamide without appreciable loss in other mechanical properties⁴⁹⁻⁵¹. Consequently, the blending of ionomer resins with polyesters, polyamides, polycarbonates, polyethers, polyolefins, polyurethanes, thermoplastic elastomers and other polymers has produced an increasing number of patents over the years. Thus, while only 17 patents on polymer blends involving ionomers were registered in the 5-year period from 1970 to 1975, 172 patents were registered in the period from 1985 to 1990.

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Although the numerous patents indicate that ionomers are a useful blend component, very few studies have been directed at understanding the extent of interaction in the blend. In this section the studies that investigate the degree of miscibility enhancement achieved with ionomers in the blend will be reviewed.

1.4.2 Ion-ion interactions: Ion-ion type interactions are typically known to take place in mixtures of cationic and anionic polyelectrolytes. In such mixtures it is found that a polyelectrolyte complex is formed which is strictly stoichiometric in composition with excess material remaining in solution⁵². Blends of polybutadienes, the one functionalized with a small amount of carboxylic acid groups, and the other with a small amount of pyridine groups, have been shown to form stable intermolecular linkages⁵³. Similarly, blends of sulfonated polystyrene and poly(styrene-4-vinyl pyridine) show evidence of

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strong interactions by having a blend T_g higher than that of the components⁵⁴. These blends are miscible, of course, since the unfunctionalized polymers are naturally also miscible.

More dramatically, Smith and Eisenberg $(1983)^{55}$ showed that two immiscible polymers polystyrene and poly(ethyl acrylate) can be rendered miscible through the incorporation of a small amount of complementary ionic groups in the two polymers, resulting in ion-ion interactions following the acid-base reaction. When the polystyrene contains about 5 mol% of styrene sulfonic acid groups and the poly(ethyl acrylate) contains about the same amount of 4-vinyl pyridine groups, a single glass transition temperature is seen by ynamic mechanical measurements (*Figure 1.2*).

This showed that the interaction between sulfonic acid and 4-vinyl pyridine is strong enough to lead to a negative ΔG_m for the blend. Polystyrene and polyisoprene can be similarly compatibilized by sulfonating the polyisoprene and copolymerizing randomly the styrene with 4-vinyl pyridine (4VP). Blends of the two ionomers containing stoichiometric quantities of functional groups again show a single glass transition when the number of ionic groups is greater than *ca*. 5 mol% in the ionomers⁵⁶.

Solution nuclear magnetic resonance (NMR) studies by Natansohn and Eisenberg (1987)⁵⁷, show that in these acid base type interactions the proton from the sulfonic acid group is transferred to the nitrogen of the 4VP group resulting in the ion-ion interaction.

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More recently Zhang and Eisenberg (1990)⁵⁸ have shown that direct ion-ion interactions, through microion elimination, are just as effective in miscibility enhancement as the proton transfer interactions. In these types of blends the acidic group, e.g. sulfonic acid of the sulfonated polystyrene, is neutralized with a group such as tetramethylammonium hydroxide, and the basic group, e.g. 4VP, is quaternized with a group such as methyl iodide. When the two polymers are solution blended, the microions, $N(CH_3)_4^+$ and Γ , are eliminated in the solution, leaving the sulfonate anion to interact directly with the quaternized pyridinium cation. Solid state NMR was also used to show that the miscibility enhancing effect of such direct ion-ion interactions are comparable, or better, than the equivalent proton transfer interactions for miscibility enhancement⁵⁹. In a separate study, Zhang and Eisenberg (1990)⁶⁰, showed that the direct ion-ion interaction between a carboxylate anion and a quaternized pyridinium cation is a much less effective interaction for miscibility enhancement than the equivalent direct ion-ion interaction with a sulfonate anion. It is worth noting that these direct ion-ion interactions can only be achieved during solution blending, since the microions are eliminated though the dissolution of these moieties by the solvent.

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The possible enhancement of miscibility of polyurethanes with polystyrene through ionic interactions was investigated by Rutkowska and Eisenberg (1984)⁶¹. A polyurethane was synthesized having chain extenders containing tertiary amines (note that the chain extenders form part of what is termed the "hard" segments of the polyurethane). These tertiary amines afford possible interaction sites for the sulfonic acid groups of a sulfonated polystyrene (SPS). In contrast to the pure polyurethane, the blend shows two glass transition temperatures; the high T_g peak increases, while the low T_g peak decreases with

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increasing SPS content or increasing sulfonation level of the SPS. The increase of the high T_g peak is due to the progressive inclusion of the polyurethane "hard" segments into the SPS phase, while the decrease of the low T_g peak is due to the resultant increasing phase purity of the "soft" polyurethane phase.

A model compound study using blends of sulfonated polystyrene with polyurethane containing just "hard" segments confirmed that a strong interaction takes place. A precipitate is formed upon mixing, and the dynamic modulus curves show a single T_g for blends containing more than 30 wt% sulfonated polystyrene (sulfonic acid content of 7.9 or 9.7 mol%).

Excellent blends were produced even when the stoichiometric ratio of the sulfonic acid to tertiary amines was exceeded, and this suggested that the sulfonic acid groups also interact with other groups on the polyurethane chain, such as the urethane, or urea groups. This possibility was further investigated using a 7.9 mol% sulfonated polystyrene blended with a polyurethane elastomer containing no tertiary amines (Rutkowska & Eisenberg, 1984)⁶². It is worth noting that the urethane and urea nitrogen groups are closely associated with the "hard" segment of the polyurethane. Dynamic mechanical studies showed that for blends containing more than 50% SPS, the high T_g (which is associated with the "hard" segment) is considerably depressed. When urethane or urea model compounds are mixed with *p*-toluene sulfonic acid (a model compound for the SPS) high melting salts (170°C and 118°C) are formed¹ confirming the interaction of the sulfonic acid groups with the urethane and urea groups.

NMR studies of proton transfer in polyurethane - sulfonated polystyrene mixtures in solution indicate that the labile proton is transferred to the secondary
structures, followed by the urethane nitrogen and then by the tertiary nitrogen, in this order⁶³.

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1.4.3 Ion pair - ion pair interactions: Using a polyurethane containing a tertiary amine in the hard segment, Rutkowska & Eisenberg (1985)⁶⁴ investigated the effect of quaternizing this nitrogen with ethyl iodide on the miscibility between this polyurethane and polystyrene ionomer containing 9.6 mol% of sodium methacrylate groups. The quaternization of the polyurethane induces phase separation of the pure material. Dynamic mechanical measurements of the blends showed that the upper T_g varied continuously from 35 °C for the pure polyurethane to 145 °C for the pure polystyrene ionomer while the low T_g remained essentially constant at about -45 °C. It was concluded that ion pair - ion pair interactions between the quaternized tertiary nitrogens of the ionomer resulted in the observed partial miscibility for this system.

Zhang and Eisenberg (1990)⁶⁰ showed that ion pair - ion pair interactions, e.g. those between sodium sulfonate and methyl pyridinium iodide groups, are less effective in miscibility enhancement than either the direct ion-ion or proton transfer interactions, at equivalent functionalization levels. In the ion pair - ion pair interactions (Na sulfonate/methyl pyridinium iodide), two separate phases could still be seen by dynamic mechanical measurements of PS/PEA blends when the ionic group content of the polymers was as high as 12 mol% each. This miscibility enhancement was found to be similar to the direct ion-ion interactions of carboxylate anions with methyl pyridinium cations.

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1.4.4 Ion co-ordination interactions: Early studies have shown that metal neutralized sulfonate groups associate with low molecular weight molecules, such as alcohols and amines^{65,66}. While alcohols form rather weak interactions, amines show nearly stoichiometric association with transition metal cations. In one study it was shown that a metal co-ordination complex is obtained when a nitrogen-containing copolymer is coagulated in an aqueous solution of a transition metal salt⁶⁷. This led to the experimental studies of Agarwal, Duvdevani, Peiffer and Lundberg (1987)⁶⁸ who investigated the possibility of miscibility enhancement of polymers though co-ordination interactions. In these studies, sulfonated ethylene-propylene-diene elastomers (EPDM) (0.65 mol% sulfonic acid) were zinc neutralized, and melt blended with a copolymer of styrene / 4-vinyl pyridine (PS4VP), containing 8.5 mol% 4-vinyl pyridine groups.

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Comparing the final blend mechanical properties it was found that near optimum properties were obtained when the blend contained about 80 wt% EPDM which corresponds to a stoichiometric ratio of interacting groups. For example it was found that at this blend ratio, the tensile strength was 3660 psi and the elongation to break 610%. When the counterion was Na, instead of Zn, the tensile strength and elongation were only 310 psi and 130% respectively. These results were rationalized in terms of the co-ordination possibility of the basic nitrogen of the pyridine group of the PS4VP with the zinc metal of the sulfonated EPDM. Viscosity data also show that the viscosity is higher in the Zn-4VP co-ordinated blends⁶⁸.

Although the mechanical properties suggest strong interactions due to ion co-

ordination, dynamic mechanical and DSC measurements indicate that these blends are phase separated.

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Recently, it has been shown by Lu and Weiss (1991)^{70,71} that transition metals such as Zn and Mn can enhance the miscibility between polystyrene and polyamide-6 (PA-6) through co-ordination type interactions. When polystyrene is functionalized with 10.1 mol% of Zn or Mn sulfonate groups, the blend of this ionomer with PA-6 is found to give a single composition dependent glass transition temperature throughout the composition range, as well as a significant melting point depression of the blend. Both of these factors suggest a strong interaction of these ionic groups with the PA-6 polymer, and spectroscopic (infrared) evidence suggests that the amide groups of the PA-6 are co-ordinated to the transition metal of the polystyrene ionomer.

1.4.5 Ion-dipole interactions; Ionomers interact with polar polymers through ion-dipole interactions. Ion-dipole interactions play an important role in the dissolution of ionic salts in water⁷². There is also evidence that polar polymers can interact strongly with small ions. For instance the glasss transition temperature of poly(propylene oxide) is increased by more than 100°C upon the addition of 25% LiClO_4^{73-75} . These experimental studies suggest that if ionic groups were chemically bound to the backbone of a polymer (e.g. polystyrene) strong interactions with polar polymers, such as poly(propylene oxide) or poly(ethylene oxide), could result.

The experimental studies of Hara and Eisenberg (1984)⁷⁶ show that this is indeed the case. Polystyrene and poly(ethylene oxide) are normally totally immiscible, as evidenced by two glass transitions of the blend at the pure component positions. However when 9.5 mol% of lithium methacrylate groups are incorporated into the polystyrene, there is a dramatic downward shift of the polystyrene ionomer T_g from 120°C to 52°C in the 50:50 blend. A similar effect is noted when poly(propylene oxide) is used instead of poly(ethylene oxide).

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The type of counterion also has a marked effect on the miscibility. The effect of the ion content and the counterion type was investigated by Hara and Eisenberg $(1987)^{77}$ using cloud point curve (CPC) measurements. As the number of ionic groups is increased, the CPC was found to move to progressively higher temperatures, indicating enhanced miscibility with increasing ion content, as would be expected. When the ion content of the ionomer was held constant at 10.4 mol%, and the counterion changed, the CPC shifted to higher temperatures as the counterion size decreased from potassium to sodium to lithium, as shown by *Figure 1.3*. When unneutralized ionomer was used in the blend (i.e. proton as the counterion) the CPC could not be located up to the decomposition temperature of the poly(propylene oxide) (*ca.* 230°C).

These results show that iniscibility enhancement is increased when the number of interacting groups is increased and also when the counterion size is decreased. The miscibility enhancing effect of the polystyrene ionomer containing 6.6 mol% lithium methacrylate groups was investigated with various other polar polymers^{78,79}. This ionomer was blended 50:50 with poly(vinyl acetate), poly(dimethyl siloxane), polycaprolactone, poly(vinyl chloride), poly(ethylene terephthalate), poly(epichlorohydrin), poly(ethylene succinate) and polysulfide. The blending (50:50) of pure polystyrene with these polar polymers all showed distinct glass transition temperatures at the pure component T_g s indicating total phase separation. The ionomer blends showed that the presence of ionic groups

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leads to enhanced miscibility in all cases except for the poly(vinyl acetate) and poly(dimethyl siloxane) blends. In these two polymers the presence of bulky side groups has been suggested to hinder the ion-dipole interaction of the ionomer. On the other hand, the blend with PVC showed a single but broad glass transition peak.

Polyurethanes are also polar polymers and the effect of ion-dipole interactions to enhance miscibility with polystyrene was studied by Rutkowska and Eisenberg (1985)⁶⁴. Polyurethanes have the advantage that the polar group content can be varied, depending on the prepolymer and the chain extender used. The polyurethanes studied were found to be immiscible with polystyrene. When a polyurethane containing ether units is blended with polystyrene ionomer containing 10.4% of lithium methacrylate groups, it is found that the miscibility enhancement depends upon the ether content of the polyurethane. For instance, when the ether unit is present only in the chain extender, no miscibility enhancement is noted. However, when the polyurethane contains polyether segments of high molecular mass (1,000 and 2,000), a considerable amount of miscibility enhancement is achieved with this "soft" segment of the polyurethane. Some of the "hard" segments containing ether moleties are however also incorporated into the polystyrene phase (Rutkowska & Eisenberg, 1987)⁶⁵.

1.5 AIMS OF THIS WORK

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As seen from the review of the miscibility enhancing effect of ion containing polymers with various other polymers, the functionalization of one or both of two immiscible polymers with ionic groups is an extremely effective way of

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enhancing the miscibility between two immiscible polymers. Some of this work has shown that the miscibility between commercial polymers, such as polyethylene oxide and PVC, can be enhanced through the use of ionic interactions.

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Polyamides constitute an important class of engineering resins as can be seen by the figures for the world demand for this resin: 500kt in 1985 vs. 300kt for the next most demanded engineering resin, i.e. polycarbonate⁸¹. Polyamides are also important in the packaging, textile fiber and fibre reinforcing industries. For instance, Kevlar[®] fiber (supplied by Du Pont), which is an aromatic polyamide, has the tensile strength of steel, at a fifth of the weight, and is consequently an important fiber reinforcing material in the aircraft, boat and tire industries. Hence, the identification of specific interacting groups with amide groups, capable of enhancing the miscibility between polyamides and other polymers, has a wide variety of applications with considerable benefit in other areas, such as dyeability, rheological modification and interfacial adhesion.

A number of patents, and a few studies, have shown that carboxylated ethylene ionomers interact favorable with polyamides. Since sulfonic acids are stronger acids than carboxylic acids, ionomers containing sulfonic acid or sulfonate groups may interact more strongly with polyamides than carboxylated ionomers. The effect of sulfonic acid or sulfonate groups in enhancing the miscibility of polymers with polyamides has not, until recently, received much attention. This thesis reports the systematic and detailed investigation of the miscibility enhancing effec: of sulfonated ionomers with aliphatic polyamides. Polystyrene was chosen as the principal polymer to compatibilize with the polyamides since this polymer is immiscible with polyamides and is relatively easy to functionalize with various ionic groups.

As pointed out in the section under ion-ion interactions, sulfonic acid groups have been found to be effective in enhancing the miscibility between polystyrene and polyurethanes, and furthermore, NMR investigations have shown that the proton from the sulfonic acid transfers to the urethane structures of the polyurethane (as well as other nitrogen containing structures). Considering the similarity of the amide and urethane structures, this type of interaction may also be operative in blends of sulfonated polystyrene with polyamides. Furthermore, the studies on blends of polystyrene ionomers with poly(alkylene oxides) suggest that the acid form is the most effective, followed by lithium and then sodium, in enhancing the miscibility between PS and poly(alkylene oxides). Consequently, in this study, the miscibility enhancing effect of sulfonic acid groups was investigated first, followed by the lithium and sodium sulfonate groups.

In *Chapter* 2 the interactions/reactions of sulfonic acid groups with the amides in blends of PS with polyamide-6 (PA-6) is presented, and it is shown that these groups can cause excellent dispersion of the PS, but some chain scission of the PA-6 occurs at processing temperatures (*ca.* 250°C). A more detailed investigation of the nature of the interaction, and extent of the hydrolysis reaction is presented in *Chapter* 3. Solution blending observations provide evidence of strong interactions, and solution NMR is used to show that the sulfonic acid groups interact with the nitrogens of the amide groups of the PA-6. Selective extraction and characterization of the PA-6 from the melt blends are

used to quantify the degradation of the PA-6. The degradation of the PA-6 in the blend at 240 °C is also followed by DSC and compared to the extraction data.

The detailed miscibility behavior of blends of sodium or lithium sulfonated polystyrene (LiSPS) ionomers with PA-6 is investigated in *Chapter 4*. It is shown that the miscibility of the LiSPS is not only dependent on the lithium sulfonate content of the ionomer, but also on the composition of the blend. This miscibility behavior is described in terms of a simple thermodynamic equation containing a specific interaction term and a random, unfavorable interaction term for the heat of mixing.

In *Chapter 5* the miscibility enhancing effect of lithium and sodium sulfonate groups are compared with those of lithium and sodium carboxylate groups. The miscibility of the LiSPS ionomer with polyamides-66, -610, -11 is also explored in order to investigate the effect of the amide content of the polyamides on the blend miscibility. A general guide to the selection of miscible pairs of LiSPS ionomers with aliphatic polyamides is given.

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One of the most sought after properties in polyamide blends is the improvement of the impact strength. Since the mixing of polystyrene with polyamides does not lead to improved mechanical properties of the blend over the material properties (the samples are brittle), the synthesis of a low T_g ionomer was developed. *Chapter 6* describes the synthesis and characterization of such a low T_g sulfonated poly(styrene-ethylene-butylene) random ionomer. Although blends of this ionomer with polyamides was not studied during the course of this work, this is part of a continuing project.

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The thesis concludes with conclusions, contributions to original knowledge and suggestions for future work (*Chapter 7*).

Finally, it must be mentioned that concurrently with (and independently of) this work, sulfonated polystyrene ionomer blends with PA-6 were also being investigated by the group of Prof. R. A. Weiss at the University of Connecticut (Dept. of Chemical Engineering). Their efforts have been directed at the detailed study of the blends with the transition metal neutralized (Zn and Mn) ionomers, and only a cursory investigation (by DSC) of the blends with acid and Li neutralized ionomers. In contrast, this thesis reports (in addition to other material) a much more detailed investigation of the latter two types of ionomer blends with PA-6.

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Chapter 2

COMPATIBILIZATION OF POLYAMIDE-6 AND POLYSTYRENE THROUGH THE FUNCTIONALIZATION OF POLYSTYRENE

2.1 ABSTRACT

Polyamide-6 (PA-6) and polystyrene are compatibilized when the polystyrene is functionalized with as little as as 2.2 mol% of sulfonic acid groups. Evidence of this is provided by scanning electron microscopy and dynamic mechanical studies. However, some hydrolysis of the PA-6 appears to take place at processing temperatures (240 - 250°C). No hydrolysis of the PA-6 is evident when the sulfonic acid groups are neutralized with lithium or sodium. The lithium neutralized material causes significant miscibility enhancement as seen from the melting point depression in the blend, suggesting a strong interaction. Sodium salts are ineffective.

2.2 INTRODUCTION

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This paper reports the results of a study of the miscibility enhancement which can be achieved between polyamide-6 (PA-6) and polystyrene when the polystyrene is lightly sulfonated. Since many polymers can be sulfonated, this interaction provides a useful avenue for the compatibilization of various polymers with the wide range of commercially available polyamides. The use of carboxylic acid groups to compatibilize various polymers with nylons has been extensively reported in the patent literature and has also been the subject of several studies¹⁻⁷. Only very recently have the sulfonates received some attention in this connection: two presentations at scientific meetings dealt with the use of sulfonic acid groups to compatibilize polystyrene with polyamides^{8,9}.

It will be shown here that the effects of carboxylates and sulfonates are quite different. While the carboxylic acid groups are shown to enhance miscibility slightly, probably by the reaction with the amine end groups^{1,2}, our solution studies show that the sulfonic acid group interacts strongly with the amide nitrogen¹⁰. This leads to strong miscibility enhancement, but unfortunately is accompanied by chain scission at elevated temperatures. The lithium salt retains the strong miscibility enhancement while avoiding the chain scission reaction. Sodium salts, on the other hand, are ineffective.

The interaction of sulfonated polystyrene with various nitrogen containing polymers has, in some cases, produced remarkable results. For instance polystyrene and poly(ethyl acrylate) blends, which are immiscible in the absence of functional groups, show a single glass transition when the parent polymers contain only 5 mol% each of styrene sulfonic acid and 4-vinylpyridine,

respectively¹¹. Blends of sulfonated polystyrene with polyurethanes also show that strong interactions take place, which leads to enhanced miscibility¹²⁻¹⁴. The observation of a proton-transfer interaction with the urethane nitrogen in these blends has raised the possibility of a similar interaction between the sulfonic acid group and the amide of a polyamide - especially in view of the similarity of the urethane and the amide structures. There is, furthermore, the possibility of interaction of the sulfonic acid group with the amine end-group of a polyamide. We therefore decided to investigate to what extent the miscibility between polystyrene and PA-6 is enhanced when the polystyrene is progressively sulfonated. We were also interested in investigating the effect of lithium neutralization of the sulfonic acid groups on the blend miscibility, since lithium salts have been shown to interact strongly with polyamides¹⁵⁻¹⁷. Here we report preliminary results of these investigations.

2.3 EXPERIMENTAL

2.3.1 Materials used: Polystyrene (PS), obtained from Aldrich ($M_v = 280,000$), was purified and homogeneously sulfonated using the method of Makowski *et.al.*¹⁸ to produce sulfonated polystyrene (SPS) containing 2.2 mol% (SPS2), 5.4 mol% (SPS5) and 9.7 mol% (SPS10) of sulfonic acid groups. Some of the SPS10 material was dissolved in benzene:methanol (80:20) and neutralized with lithium hydroxide in methanol to a phenolphthalein end point to obtain the material designated as LiSPS10. Similarly, the sodium hydroxide neutralized SPS10 gave the material designated as NaSPS10. Polyamide-6 (PA-6) was

obtained from Aldrich and was purified by precipitation from formic acid into water. All materials were dried at 80°C under vacuum for at least 4 days prior to use.

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2.3.2 Melt blends: Melt blends were prepared in a Brabender mixing head at 250°C and 90 RPM. All samples were blended for 20 minutes and showed a constant torque for at least the last 5 minutes. Blending was carried out under a constant stream of nitrogen to minimize oxidative degradation during blending.

2.3.3 Solution blends: Solution blended materials were prepared by dissolving each component in *m*-cresol:methanol (80:20) to form 5% (w/v) solutions and then mixed under constant agitation. The clear solutions were then precipitated dropwise into excess hexanes, agitated for 1 day with fresh hexanes to extract residual solvent and filtered. The material was then dried under vacuum at 100°C for 48 hrs.

2.3.4 Dynamic mechanical analysis: Dynamic mechanical properties were determined using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) instrument at a scanning rate of 1°C/min. Samples for the DMTA were prepared by compression molding at 230°C under low pressure.

2.3.5 Differential scanning calorimetry: Differential scanning calorimetry (DSC) data were recorded on a Perkin Elmer DSC II and calibrated with indium. The samples were scanned under nitrogen from 27°C to 240°C at 20°C/min. All samples were scanned once to remove differences in thermal history and then quenched at the maximum cooling rate setting of the instrument (320°C/min). The data from the second (S2) scan were recorded for all samples. Some samples

were annealed at 240 °C for 90 minutes after the second scan, then quenched and a third scan taken (S3). The recrystallization temperatures T_c and heats of recrystallization ΔH_c were obtained by quenching the samples in liquid nitrogen after the last scans and scanning again at 20°/min. The percentage crystallinity in the samples was calculated from the enthalpies of melting ΔH_m and by assuming an enthalpy of fusion of 191 J/g for 100% crystalline PA-6.

2.3.6 Scanning electron microscopy: Samples for scanning electron microscopy (SEM) were prepared by fracturing the melt-blended samples under liquid nitrogen. A JEOL-840 scanning electron microscope was used with gold sputter coating on the fracture surfaces.

2.4 RESULTS AND DISCUSSION

Figure 2.1(a) shows the SEM of the fracture surface of the PS/PA-6 blend containing 20% PS. The dispersed phase of PS domains is clearly evident in the continuous PA-6 matrix and very little adhesion if any can be seen between the two phases. Some "holes" are seen where the PS spheres have been removed with the other fracture surface. The phase separated PS domains have an average particle diameter of about 6 μ m which contrasts with the 3 μ m for the blend containing 40% PS (*Figure 2.1(b*)). The continuous phase in these blends is PA-6, as is expected from the composition ratios and as suggested by the pliability of these samples at room temperature. These samples also showed some stress whitening when flexed at room temperature, which can be attributed to microvoid formation around the loosely held PS domains. *Figure 2.1(c)* shows that the morphology of the 20% blend is dramatically changed when the polystyrene is





Figure 2.1 Scanning electron micrographs of the fracture surfaces of polyamide-6 blends containing (a) 20% PS, (b) 40% PS, (c) 20% SPS2 and (d) 40% SPS5.

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sulfonated to a level of only 2.2 mol%. Distinct phase separated domains are no longer visible, although the semi-ductile fracture surface features may suggest a certain degree of inhomogeneity. The SEMs of fracture surfaces of blends containing 20% of SPS5 and SPS10 cannot be distinguished from those containing SPS2. This indicates that increasing the sulfonation level from 2.2 to 9.7 mol% does not significantly change the blend morphology. The fracture surface of the blend containing 40% of SPS5 (*Figure 2.1(d*)) is much smoother and a more rapid brittle fracture is likely. When flexed at room temperature, the samples containing 20% SPS are all less brittle than those with 40% SPS. Stress-whitening upon room temperature flexing is not observed for any of the blends containing sulfonated polystyrene.

The tanð plots for the blends containing 40% of the polystyrene component are shown in *Figure* 2.2. The feature in the plot for the PS/PA-6 blend at about 50°C can be assigned to the glass transition (T_g) of the amorphous phase of PA-6 while the peak at 111°C is due to the T_g of PS. On mixing of the PA-6 with SPS, the glass transition of the PA-6 moves to a higher temperature and becomes increasingly merged with the tanð peak of the SPS, which also broadens considerably as the sulfonation is increased. The tanð maxima of the polystyrenic phase increase from 111°C to 117°C as the sulfonation is increased from 0 to 9.7 mol%. Since sulfonation of polystyrene increases its T_g by some 2°C per mol% sulfonation¹⁹, we can see that blending induces a progressive decrease of the T_g of the polystyrenic phase when compared with the unblended material. These DMTA data show that some compatibilization is achieved even at a low level of sulfonation of only 2.2 mol%.

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Figure 2.2 Tan δ values from DMTA runs (1Hz) for blends containing 60% polyamide-6 and 40% SPS. The level of sulfonation of the SPS is shown on the plot. The 2.2 and the 9.7% cuves have been vertically shifted by 0.1 and 0.2 units, respectively, for clarity.

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DSC shows that the melting temperature $T_{m'}$ recrystallization temperature T_c and the enthalpy of recrystallization ΔH_c are directly affected by the amount of sulfonic acid groups in the blend. For the blend containing 40% SPS10, the melting point is 22°C below that of the unfunctionalized PS/PA-6 blend and the degree of crystallinity is also reduced. At the same time, the recrystallization temperature T_c increases as the sulfonic acid group content in the blend is increased. The value of T_c is raised by as much as 69°C when going from PS to SPS10 in the blend. This suggests that the crystallization process is hindered. This suggestion is supported by the enthalpies of recrystallization ΔH_c , which are expressed as a percentage of the enthalpies of melting ΔH_m in the last column of *Table 2.1*. For the PS/PA-6 blend this value is 12%, which means that 88% of the PA-6 crystallinity was formed during the rapid liquid nitrogen quench. Similarly, the data show that in going from SPS2 to SPS10 in the blends, the amount of the crystallinity that is obtained during the rapid liquid nitrogen quench progressively decreases from 68% to 0%.

In the absence of complications, the observed behavior of $T_{m'}$, T_c and ΔH_c could be interpreted as evidence of very strong interactions. These strong interactions do indeed exist, as is confirmed by solution mixture studies¹⁰. However, the complications to be discussed below do not allow the quantitative interpretation of these DSC data in terms of interactions.

It is well known that strong acids, such as sulfuric acid, can catalyze the hydrolysis of the amide bond²³. If the sulfonic acid group is also effective in chain scission, then the decrease in the chain length of the PA-6 could also lead to the observed changes in the $T_{\rm m}$, $T_{\rm c}$ and enthalpies of recrystallization. To investigate this possibility, we compared two sets of results. In the first we

Table 2.1 DSC data obtained on blends containing 60% polyamide-6 and 40% ofpolystyrene or sulfonated polystyrene (Component Blended).

Component	DSC	Prepa-	T _m	ΔH _m	cryst.	Т _с	ΔH_c as % of ΔH_m
Blended	scan	ration ^a	(℃)	(J/g)	% b	(°С)	
PS SPS2 SPS5 SPS10	S2 S2 S2 S2 S2	m m m m	223 221 217 201	40 38 37 31	35 34 33 27	66 76 95 135	12 32 48 100
SPS10	S2	s	220	41	35	-	100
SPS10	S3	s	201	30	26	128	
LiSPS10	S2	S	214	34	29	148	
LiSPS10	S3	S	213	33	28	148	100
NaSPS10	S2	S	222	35	30	-	-
NaSPS10	S3	S	222	33	28	84	41

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^a Melt blended, m; solution blended, s

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^b Refers only to the polyamide-6 component in the blend

compared the initial DSC scan data of a solution prepared blend (SPS10 S2 s in Table 2.1) to the DSC scan of the same blend after annealing at 240°C for 90 minutes (SPS10 S3 s). Table 2.1 shows that the annealing process has a profound effect on the melting temperature and the crystallization behavior, suggesting that some time-dependent reaction occurs at 240°C. Comparison of the DSC scans of the annealed sample (SPS10 S3 s) with the scan of the sample prepared by melt blending at 250°C for 20 minutes (SPS10 S2 m) shows that these samples have comparable values for $T_{\rm m}$, $T_{\rm c}$ and enthalpies of recrystallization, indicating that this reaction has also taken place in the melt blended samples. Thus, most of the observed shifts in the T_m and T_c^{a} can be attributed to a reaction in these blends. Since these samples were found to be soluble in *m*-cresol after annealing, a cross-linking reaction can be excluded. Due to the difficulty of totally eliminating the presence of water in these blends, the acid catalyzed chain scission of the PA-6 seems the most reasonable explanation. It is known that the reduction of the PA-6 molecular weight also leads to a reduction of its melting point²⁴. Preliminary results on the extracted PA-6 from these blends indicate that the PA-6 molecular weight is indeed reduced. We are currently exploring the quantitative aspects of this reaction.

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Finally, we present DSC data for the solution prepared blends of the lithium and sodium neutralized SPS10 material. When the sulfonic acid groups are neutralized with lithium, the $T_{\rm m}$ of the PA-6 in the blend is considerably depressed (LiSPS10 S2 in *Table 2.1*). *Table 2.1* also shows that the Li neutralized sample is unaffected by annealing (LiSPS10 S3) and hence a chain scission reaction is not operative in this blend at annealing temperatures. The LiSPS10 blend shows a $T_{\rm m}$ depression of 10°C of the PA-6 in the blend, while the recrystallization of the PA-6 is strongly hindered as shown by the high $T_{\rm c}$ value

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of 148°C and the 100% recrystallization enthalpy. The invariance of the melting temperature with annealing indicates that the $T_{\rm m}$ depression can be attributed to the interaction of the blend components. Lithium salts such as LiCl and LiBr are known to interact strongly with PA-6¹⁵⁻¹⁷. LiCl has been shown to lead to a $T_{\rm m}$ depression of PA-6 attributed to its interaction with the C=O group of the amide¹⁷. Evidently a similar interaction is operative between the lithium sulfonate group of the LiSPS10 and the amide of the PA-6. *Table 2.1* also shows that sodium neutralized SPS10 (NaSPS10 S2 and S3) blend does not show these characteristics of an interacting blend, although the $T_{\rm c}$ value of 84°C shows that it is still better than the unfunctionalized PS. Again, the invariance of $T_{\rm m}$ with annealing indicates that chain scission is inoperative in this blend.

2.5 CONCLUSIONS

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The presence of sulfonic acid groups on polystyrene has been shown to compatibilize the polystyrene/polyamide-6 blend, probably via proton transfer to the amide and amine nitrogens. Annealing at high temperature (240-250 °C), either in the melt or after precipitation of the solution blended sample, leads to the hydrolysis of the polyamide-6 (PA-6). This chain scission reaction is not evident when the sulfonic acid groups are neutralized with either lithium or sodium. The sodium neutralized material does not cause any observable melting point depression in the blend. By contrast, the lithium neutralized material leads to a dramatic $T_{\rm m}$ depression and considerable hindrance of the PA-6 crystallization process in the blend, suggesting that this blend is strongly interacting. This contrasts with the studies on blends of PA-6 with carboxylic acid containing polymers where it has been found that the degree of crystallinity,

the recrystallization temperature, melting temperature and the glass transition temperature of the PA-6 component are little affected by the presence of the functionalized polymer^{1,2}. This suggests that lithium sulfonate groups interact more strongly with PA-6 than do carboxylic acid groups.

We are currently investigating the extent of the chain scission reaction in these blends and the compatibilizing efficiency of the lithium sulfonate group. These results will be published in a much more extensive treatment.

While the enhanced miscibility between PA-6 and polystyrene is not necessarily expected to produce a material with good mechanical properties⁷, it serves as a model system for the study of the interaction between the sulfonate group with the amide and amine groups in the blend.

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Chapter 3

MISCIBILITY OF POLYAMIDE-6 AND POLYSTYRENE FUNCTIONALIZED WITH SULFONIC ACID GROUPS

4

3.1 ABSTRACT

Polyamide-6 (PA-6) and sulfonated polystyrene (SPS) interact strongly in solution. Thus, solution blends of PA-6 and SPS (sulfonation levels from 0 to 12.3 mole%) in *m*-cresol form clear, hazy or gelled solutions - depending on the ratio of amide (A) to sulfonic acid (S) groups (A/S). NMR studies show that the S groups interact with the nitrogen of the amides, most probably through the transfer of the sulfonic acid protons. During melt blending, the addition of SPS to the PA-6 leads to a torque rise due to strong interactions. The glass transition temperatures of the components in the melt blended samples shift towards each other as the sulfonation level of the SPS increases, indicating enhanced miscibility. The analysis of the extracted PA-6 from these blends, however, shows that it is degraded at processing temperatures (250°C) due to some

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residual water and the catalytic activity of the sulfonic acid groups. The extent of the PA-6 degradation is inversely related to the A/S ratio. Each sulfonic acid group causes between one to two chain scissions of the PA-6. In blends with high A/S ratios, the degradation of the PA-6 is minimal; yet considerable dispersion of the SPS can be achieved, as evidenced by scanning electron micrographs of the fracture surfaces.

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3.2 INTRODUCTION

The compatibilization of various polymers with polyamides is a subject of continuing interest which can be attributed to their commercial importance. The presence of amide groups along the backbone offers sites for specific interactions, and this can be used to advantage when attempting to compatibilize polyamides with other polymers. Since acids are known to interact with the amide units of polyamides, the use of an acidic group as a compatibilizing functional group seems an obvious choice. Carboxylic acid groups have been successfully used in this way to compatibilize various polymers with polyamides; the many patents and studies attest to this fact¹⁻⁶. Since the acid strength is one of the factors controlling the extent of the interaction, a stronger acidic group, such as a sulfonic acid, may be more effective than a carboxylic acid one.

Polystyrene is relatively easy to functionalize with sulfonic acid groups to produce a sulfonated polystyrene (SPS) containing between 0 to 20 mol% of sulfonic acid groups. Unfunctionalized polystyrene is immiscible with polyamides and is therefore ideal for the study of the effect of sulfonic acid functionalization on polyamide miscibility. Furthermore, the functionalization of polystyrene with sulfonic acid groups has been demonstrated to be an effective route to compatibilize polystyrene with various other nitrogen containing polymers⁸⁻¹². Of particular relevance is the miscibility enhancement noted in blends of SPS with polyurethanes, which has been partly ascribed to the transfer of the sulfonic acid proton to the urethane nitrogen, as shown through nuclear magnetic resonance (NMR) studies¹². Due to the similarity of the urethane and the amide structures, this type of interaction may also be operative in blends of SPS with polyamides.

Recently some studies have shown that sulfonic acid groups can compatibilize polystyrene with polyamides, even at low levels of sulfonation¹³⁻¹⁵. In one study it has been suggested that the presence of sulfonic acid groups in blends of SPS with PA-6 leads to the hydrolysis of the amide groups at processing temperatures¹⁵. This is not surprising since sulfonic acids can catalyze the reactions of polyamides¹⁶ and, furthermore, strong acids are known to catalyze the hydrolysis of polyamides in the presence of water.

In this paper it will be shown that strong interactions exist between the sulfonic acid groups of the SPS and the amide groups of the polyamide-6 (PA-6). Evidence for this is provided by the formation of gel in some of the solution blends, and is confirmed by solution NMR studies. Melt and solvent-cast blends are also prepared in order to confirm that the interactions in solution persist to the solid state and enhances the miscibility of these blends. However, degradation (hydrolysis) of the PA-6 takes place at processing temperatures (240 - 250°C) due to the presence of the sulfonic acid groups. The extent of the hydrolysis reaction is inversely related to the ratio of amide to sulfonic acid groups (A/S) in the blends and this is used to identify possible A/S values

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where the SPS is adequately dispersed in the blends without severe reduction of the molecular weight of the PA-6.

The effect of water content on the hydrolysis of the PA-6 in the SPS/PA-6 blends is not reported here. In this paper the materials used for blending are subjected to a uniform drying procedure and their reactions/interactions are studied in this state.

3.3 EXPERIMENTAL

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3.3.1 Materials used: Polystyrene (PS), obtained from Aldrich ($M_v = 280 \text{ kg/mol}$), was purified and homogeneously sulfonated using the method of Makowski *et al.*¹⁷ to produce sulfonated polystyrene (SPS) containing 2.2 mole% (SPS2), 5.4 mole% (SPS5) and 9.7 mole% (SPS10) of sulfonic acid groups. These materials were used for the melt blend studies. Polystyrene obtained from Polysciences Inc. ($M_v = 50 \text{ kg/mol}$) was also sulfonated to different extents to produce sulfonation levels of 2.6, 4.5, 6.7, 9.4, and 12.3 mole% and were used for the solution and solvent cast blend studies. Polyamide-6 (PA-6) was obtained from Aldrich and analysis by size exclusion chromatography showed: $M_w = 33 \text{ kg/mol}$ and $M_n = 14 \text{ kg/mol}$. Assuming one amine end-group per chain, the amine end-group concentration was calculated as 0.071 mequivalents per gram. The PA-6 was purified by precipitation from formic acid into water. All materials were dried at 80°C under vacuum for at least 4 days prior to use.

For the NMR studies, the following materials were also used: ε -caprolactam (Aldrich) was dried in a desiccator under full vacuum for at least four days prior

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to use. PS oligomer (Pressure Chemical Co.) having $M_W = 0.450$ kg/mol was used as received. The poly(styrene-co-methacrylic acid) (PSMAA) was synthesised by free radical polymerization in conjunction with another project in this laboratory. The PSMAA contained 10.1 mol% methacrylic acid groups and was vacuum oven dried at 80°C for four days prior to use.

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3.3.2 Solution blending: Solutions (2% w/v) of PS, PA-6 and SPS were prepared in *m*-cresol (99%, Aldrich). Blends were prepared by adding the SPS (or PS) solutions dropwise to the PA-6 solutions under constant agitation. The solutions were agitated for 24 hrs and visually compared to the clear solution of pure PA-6. The solutions were classified as *hazy* when any sign of milkiness could be detected and as *gelled* when an essentially phase separated gelled mass was observed.

3.3.3 Solvent casting: Blend solutions were prepared as described above except that they were prepared directly in the solvent evaporating dish. The solutions were agitated for 12 hrs before starting solvent evaporation under partial vacuum at 50°C. The solvent was evaporated slowly over 4 days and the samples finally dried by increasing the temperature to 120°C under a full vacuum for 4 days. The films obtained were ground to a fine powder under liquid nitrogen and again dried in a vacuum oven for 4 days prior to DSC analysis.

3.3.4 Melt blending: Melt blends were prepared in a Brabender mixing head at 250 °C² and 90 RPM. Sequential addition of the components was used by adding the PA-6 first and then waiting for the torque to stabilize before adding the SPS. All samples were blended for 20 minutes and showed a constant torque



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for at least the last 5 minutes. Blending was carried out under a constant stream of nitrogen to minimize oxidative degradation during blending.

3.3.5 Dynamic mechanical analysis: Dynamic mechanical properties were determined using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) instrument at a scanning rate of 1°C/min. Samples for the DMTA were prepared by compression molding at 230°C under low pressure.

3.3.6 Differential scanning calorimetry: Differential scanning calorimetry (DSC) data were recorded on a Perkin Elmer DSC II and calibrated with indium. To study the annealing effect on the melting temperature, the samples were scanned under nitrogen purge from 27 to 240°C at 20°C/min. After the first scan to 240°C the samples were held at this temperature for ten minutes and then quenched at the maximum cooling rate setting of the instrument (320°C/min) to room temperature. Subsequent scans were recorded following the same procedure, each with a holding time of ten minutes at 240°C. The melting temperature of the PA-6 in the blend was taken at the peak of the melting endotherm.

For the analysis of the extracted PA-6 materials, the samples were scanned from 27°C at 20°C/min under nitrogen. The samples were quenched in liquid nitrogen immediately after melting was completed and then scanned again at 20°C/min to record melting (T_m) and crystallization temperatures (T_c) , respectively. This procedure was used to limit the exposure of the samples to elevated temperatures, where the condensation of the carboxylic and amine end-groups can lead to an increase of the molecular weight and subsequent changes in the T_m and T_c values.

3.3.7 Scanning electron microscopy: Samples of the blended materials were compression molded and then fractured under liquid nitrogen. One half of the samples was immersed in 88% formic acid for 24 hrs to leach out the PA-6 from the surface while the other half was used for comparison. All samples were washed with water and dried in a vacuum oven at 25°C for four days before gold sputter-coating of the fracture surfaces. A JEOL Model JSM 840 scanning electron microscope was used to record the surface features.

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**3.3.8** NMR: A 300 MHz NMR (Varian XL-300) was used to record the NMR spectra of  $\varepsilon$ -caprolactam (a monomeric model compound for PA-6) and its blends. Approximately 4 mg of  $\varepsilon$ -caprolactam in 1 ml DMSO- $d_6$  (Aldrich) was used for all the spectra, and between 30 and 40 mg of the PS oligomer, PSMAA or SPS (12.3 mol% sulfonation) was used in the blends. The PSMAA and SPS were blended with the  $\varepsilon$ -caprolactam in such a way that the functional groups and the amide groups were in stoichiometric amounts. Spectra were recorded at 50 and at 85°C. A 270 MHz NMR (JEOL Model 270-CPF) was used to analyze the PA-6 extracted from the melt blends. Approximately 60 mg of material was dissolved in 1 ml of a solvent mixture of trifluoroacetic acid -  $d_1$  (Aldrich): D<sub>2</sub>O (MSD Isotopes) (2:1).

**3.3.9** Solvent extraction: The melt blended samples were ground to pass through a sieve of mesh #12. About 2g of each material was weighed and placed in 50 ml of 88% formic acid. The samples were agitated for one week, then filtered, washed with fresh solvent, dried and weighed. The solvent was removed from the extracted materials using rotary vaporization and the solids subsequently washed and dried.

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**3.3.10** Size exclusion chromatography: A Varian DS-600 size exclusion chromatograph (SEC) was used with tetrahydrofuran as eluent and calibrated with polystyrene standards. The extracted PA-6 samples were trifluoroacetylated and prepared for SEC analysis as described in the literature<sup>18,19</sup>. The universal calibration method was used to calculate  $M_n$  of the trifluoroacetylated samples and from these values, the  $M_n$  of the PA-6 were calculated. The trifluoroacetylation reaction does not alter the degree of polymerization of the PA-6<sup>19</sup>.

# 3.4 RESULTS AND DISCUSSION

**3.4.1** Solution blends: The blending of two polymers in solution can sometimes give qualitative information about the affinity of the polymers for each other. The formation of gel upon solution blending almost always indicates strong interactions between the blend components<sup>8,9</sup>. For instance, the solution blending of SPS with poly(ethyl acrylate-co-4-vinyl pyridine) forms a gel when each polymer contains about 5 mol% of functional groups; and solid state dynamic mechanical characterization confirms that these two polymers are miscible on the 50 to 100Å level, characteristic of the measurement<sup>8</sup>.

While the solution blends of PS with PA-6 in *m*-cresol form clear solutions throughout the entire composition range, the solution blends of PA-6 with SPS can be clear, hazy or gelled, depending on the sulfonation level of the SPS and on the blend composition. The visual observations of the solutions are summarized in *Figure 3.1* and suggest that strong interactions exist between the SPS and PA-6.

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Figure 3.1 Phase diagram for solution blends of sulfonated polystyrene (SPS) with polyamide-6. The solutions are all 2% (w/v) in *m*-cresol. The lines represent the position of blends with constant amide to sulfonic acid ratio (A/S). 1  $\langle \cdot \rangle$ 

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The gelled solutions can be made to move into the *hazy* or into the *clear* parts of the diagram by adding PA-6 to the solutions. This can be reversed by adding SPS to the solutions. The interactions in solution are therefore in dynamic equilibrium. Although *Figure 3.1* does not necessarily represent a thermodynamic phase diagram, in this paper *Figure 3.1* will be referred to as "the phase diagram".

As it will be shown below, the sulfonic acid groups can interact not only with the amine end-groups of the PA-6, but also with the its amide groups. Since the PA-6 polymer contain only one amine end-group per chain (the other end-group being a carboxylic acid), the formation of gel in some of these blends provides indirect evidence that the sulfonic acid groups also interact with the amide groups. Interaction with the amine end-groups alone can not lead to gel formation. Since the relative amount of the acidic and basic functional groups is an important factor in these blends, the *clear, hazy* and *gel* sections of the phase diagram can be separated by lines of constant amide to sulfonic acid ratio (A/S). The ratio used here is actually the ratio of nitrogen containing groups (amide + amine) to sulfonic acid groups in the blend, but since the amine end-group contribution to the total nitrogen containing groups is less than 1%, it closely represents the amide to sulfonic acid ratio. In these solution blends it is more convenient to regard A/S as the amide to sulfonic acid ratio.

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The solutions begin to turn hazy when there are approximately 33 amide groups per sulfonic acid group (A/S = 33), while gelation occurs when there are less than 8 amide groups per sulfonic acid group (A/S < 8). The strongest interactions are expected for a stoichiometric amount of interacting groups (A/S

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= 1). Further decreasing the ratio should eventually lead to the clarification of the gel, because 100% SPS solutions are clear in this solvent.

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The behavior in the various regions of the phase diagram can be explained in the following way : In the clear region, there is one or more PA-6 molecular chain per sulfonic acid group, so that connectivity between different SPS chains, via PA-6 molecules, is unlikely. In this region the sulfonic acid groups are probably interacting primarily with the amine end-groups, since these are a stronger base than the amide groups. Theoretically, there is one PA-6 chain for every sulfonic acid group when A/S = 124 (calculated from  $M_n = 14 \text{ kg/mol}$  for PA-6). However, the solution blends remain clear down to a value of A/S = 33. One of the reasons for this is that, in these dilute solutions, each PA-6 molecule is more likely to interact with the same SPS chain several times rather than with two or more different SPS chains. Furthermore, the hydroxyl of the solvent, m-cresol, is also competing for interaction with both the sulfonic acid and the amide groups. The effect of the hydroxyl groups can be illustrated by the addition of 20% methanol to the blends, which moves the onset of visible haze to A/S = 10. Methanol addition, however, is limited by the precipitation of the PA-6 component in the blend when too much is added. Since the size of the scattering particles have to be at least of the order of the wavelength of the incident light before the light is scattered, this is another factor in the shifted observation of haze.

In the *hazy* section of the phase diagram, large associated particles exist, which indicates that some of the PA-6 chains are interacting with two or more SPS molecules. In this way, many SPS chains are concentrated into localized areas together with their associated PA-6 molecules. When the amide to sulfonic acid

ratio is low enough, each SPS chain is connected to at least one other SPS chain, so that a three dimensional network (gel) results.

Since the observation of haze and gel are directly governed by the functionality of the polymer chains (i.e., the number of functional groups per chain), the molecular weight of the interacting polymers is a critical factor in determining the onset of these observations. The molecular weight of the PA-6 and SPS in *Figure 3.1* is constant, but with the reduction of the PA-6 molecular weight, for instance, the onset of the *hazy* and *gel* regions is expected to shift to lower values of A/S. At one extreme, blends of SPS with monomeric PA-6 ( $\epsilon$ -caprolactam) are clear at all compositions. By contrast, if the molecular weight of the PA-6 were infinite, all blends would be expected to be *gel*.

**3.4.2 NMR studies:** NMR is a useful tool to study the nature of specific interactions. Although the formation of gel in the solution blends indicates that the sulfonic acid groups are interacting with the amide groups, it is not *a priori* clear whether the sulfonic acid is interacting with the carbonyl or the nitrogen of the amide group.

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Several NMR studies of blends of SPS with nitrogen-containing polymers have shown that the proton from the sulfonic acid group transfers to the nitrogen moiety<sup>12,20</sup>. This has been observed for the urethane group of polyurethanes<sup>12</sup>, and it is thus possible that the proton from the sulfonic acid group of the SPS also transfers to the amide nitrogen of the PA-6.

For the present study,  $\varepsilon$ -caprolactam was chosen as a model compound for PA-6 since it shows all the spectral features of the polymer without leading to gelation

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during blending. It is also soluble in common deuterated solvents such as DMSO- $d_6$ . Figure 3.2 shows the peak assignments for the  $\varepsilon$ -caprolactam and for the SPS. The  $\varepsilon$ -caprolactam peak at 3.05 ppm, which is due to the methylene protons closest to the amide nitrogen, is split into a quadruplet because of the presence of three neighboring protons (including the proton from the amide nitrogen). This is more clearly seen in the expanded region shown by Figure 3.3 (top). When the amide proton at 7.4 ppm is decoupled by irradiation, the quadruplet is reduced to a triplet, as expected (Figure 3.3: middle). However, when SPS is added to the  $\varepsilon$ -caprolactam so that there is a stoichiometric ratio of amide to sulfonic acid groups in the blend, the quadruplet at 3.05 ppm again forms a triplet, similar to the decoupled spectrum (Figure 3.3: bottom). This suggests that a rapid proton exchange is taking place between the sulfonic acid group and the nitrogen of the amide, leading to an exchange decoupling effect. This can be explained by the rapid transfer of the sulfonic acid proton to and from the amide nitrogen, represented by the equilibrium equation

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$$-SO_{3}^{-}H^{+} + -N - C - = -SO_{3}^{-} + -N - C - = [3.1]$$

After proton transfer, the protons on the amide are indistinguishable and hence either of the two could be transferred back to the sulfonic acid group. Similar equilibrium equations have been used to describe the proton transfer in other systems<sup>21</sup>.

Figure 3.4 compares the spectra (2.1 - 3.2 ppm range) for blends of  $\epsilon$ -caprolactam with polystyrene oligomer, poly(styrene-co-methacrylic acid) (PSMAA), and

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Figure 3.2 <sup>1</sup>H-NMR spectra in DMSO- $d_6$  of sulfonated polystyrene at 50 °C (top) and  $\epsilon$ -caprolactam (bottom) at 22 °C. The peak assignments are indicated. The "S" indicates peaks due to residual DMSO solvent.

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**Figure 3.3** Expanded <sup>1</sup>H-NMR spectra at 50°C of  $\varepsilon$ -caprolactam (top),  $\varepsilon$ caprolactam decoupled on the amide proton (middle), and the blend of SPS with  $\varepsilon$ -caprolactam (bottom).

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Figure 3.4 Expanded <sup>1</sup>H-NMR spectra at 85°C of blends of  $\varepsilon$ -caprolactam with polystyrene oligomer (top), poly(styrene-co-methacrylic acid) (middle), and SPS (bottom). The PSMAA and SPS blends contain a stoichiometric amount of functional groups.

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SPS. These spectra were recorded at 85°C in order to achieve solubility of the PS oligomer and the PSMAA. The splitting of the methylene signal at 3.06 ppm is unaffected by the presence of either the PS oligomer or the PSMAA, while the blend of SPS with the  $\varepsilon$ -caprolactam again shows that the sulfonic acid proton is exchanging with the amide nitrogen. Therefore, under the experimental conditions, the carboxylic acid groups are less effective than the sulfonic acid groups at proton exchange with the amide nitrogens , suggesting that proton transfer occurs less readily with carboxylic acid than with sulfonic acid groups.

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It is worth noting the unusual splitting of the triplets at *ca*. 3.05 ppm during decoupling or blending with SPS, as well as at *ca*. 2.28 ppm for all samples containing  $\varepsilon$ -caprolactam. The peak intensities of triplets usually appear in the ratio 1:2:1, and the 2:1:2 splitting seen here is probably related to the ring structure of the  $\varepsilon$ -caprolactam. Due to the unusual triplets formed, it has been suggested that the presence of a 2:1:2 triplet at 3.05 ppm for a mixture of a strong acid with  $\varepsilon$ -caprolactam would more convincingly support the mechanism proposed by Equation [1] than the 2:1:2 triplet seen in the decoupled spectrum of  $\varepsilon$ -caprolactam<sup>22</sup>. The NMR spectrum at 85°C of a stoichiometric mixture of methanesulfonic acid with  $\varepsilon$ -caprolactam in DMSO- $d_6$  (not shown) indeed gives the 2:1:2 splitting at 3.05 ppm, and is almost identical to that of the SPS blend spectrum (*Figure 3.4: bottom*), thus lending further support to the exchange decoupling mechanism depicted by Equation [1].

The influence of the interaction between the SPS and the  $\varepsilon$ -caprolactam on the chemical shift of the amide proton (7.4 ppm) of the  $\varepsilon$ -caprolactam cannot be seen due to overlap by the aromatic peaks of the SPS (6.3 - 7.5 ppm). In any event, the

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exchange decoupling is expected to "wash out" the signal of the amide proton. In this respect, quantitative NMR is not a very useful tool.

**3.4.3 Melt blends:** Since SPS and PA-6 show strong interactions in solution, it can be expected that these interactions persist in the solid state. To study the compatibilizing effect of these interactions and to analyze the effect of melt processing on the PA-6 molecular weight, several melt blends were investigated.

Reactions or interactions between two polymers in the melt sometimes result in an increase in the viscosity, and this, in turn, manifests itself as a rise in the torque during mixing23-25. Torque measurements during the melt blending of the 40:60 SPS/PA-6 blends are shown in *Figure 3.5*. Upon the addition of the SPS to the PA-6 already in the mixer, the torque increases rapidly to a maximum value, as would be expected from the filler and the cooling effects of the added SPS. The viscosity (and torque) then drops as the SPS is heated and softens. After reaching a minimum, the torque again rises slowly with time, and levels off after 10 to 15 minutes. The 20:80 SPS/PA-6 blends show a similar trend except that the torque rise is more gradual. A torque rise is typically observed for reactive blends where chemical grafting reactions take  $place^{23}$ . In the blends of SPS with PA-6 this chemical grafting is unlikely. As will be shown later, the PA-6 is hydrolyzed during melt blending so that the amine and carboxylic acid endgroup content in the blend increases. The torque rise can therefore be more readily ascribed to the strong acid-base interaction of the sulfonic acid groups of the SPS with the amine end-groups of the PA-6, despite the hydrolysis of the PA-6. This type of interaction can be viewed as a type of physical grafting resulting from ionic interactions. The interaction of the SPS with amine groups is not a new concept and has been studied in blends of SPS with amine terminated

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Figure 3.5 Torque as a function of blending time for the 40:60 SPS/PA-6 blends. Time = 0 min indicates when the SPS was added to the PA-6, already in the mixer. The numbers indicate the sulfonation level of the SPS. The torque increase at about 3 min on the 5.4% curve (indicated by the arrow), is due to a second small addition of SPS5 material to this blend, in order to bring the SPS5 content in this blend to 40%.

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poly(alkylene oxide) oligomers²⁶, and blends of SPS with short polyurethane segments containing amine groups²⁷.

The rate of torque increase from *Figure 3.5* increases with the level of sulfonation of the SPS, suggesting that the hydrolysis of, and the interactions with the PA-6 are more rapidly established with the more highly sulfonated SPS. The desulfonation of the SPS during the relatively short melt processing time is expected to be minimal²⁸.

The addition of PS instead of SPS to the PA-6 causes no torque increase after the initial rise and fall of the torque and the same is observed upon the addition of just pure PA-6. The torque profiles of the unblended SPS materials can not be obtained, since these materials cross-link at high temperatures. A cross-linking reaction of the SPS with the PA-6 does not take place since all the melt blended samples are completely soluble in *m*-cresol after melt blending.

Dynamic mechanical thermal analysis (DMTA) of blend samples are often more sensitive than DSC in identifying the glass transition temperatures of the blend components. The tanð plots from DMTA for the 20:80 melt blends are shown in *Figure 3.6.* For the 20:80 PS/PA-6 blend (*Figure 3.6: top*), two distinct tanð peaks are discernible. The lower one is due to the glass transition (T_g) of the PA-6 while the peak at 116 °C is due to the T_g of the PS. A curve, which has been synthesized by the addition of the tanð curves of the pure components, is also shown for easier comparison with the tanð profiles of the pure components. The "synthesized curve was obtained by adding and weighting the tanð plots of the pure components until the peak heights in the synthesized plot matched with the peak heights of the experimental blend. The weighting coefficients were 0.84 and

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Figure 3.6 Tan δ plots from DMTA measurements at 10 Hz for the 20:80 melt blends: PS/PA-6 (top), SPS2/PA-6 (middle), and SPS10/PA-6 (bottom). The solid lines show the blend curves synthesized from the pure component tan δ plots (see text). Points are experimental.

0.053 for the PA-6 and PS, respectively. The resultant curve does not match the peak positions of the experimental blend curve exactly, suggesting that there may be some partial miscibility of the components, even though scanning electron micrographs for these blends show distinct phase separated domains¹⁵.

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As the level of sulfonation of the SPS increases, the tan δ peaks of the two individual components shift progressively toward each other. This is shown in Figure 3.6 (middle and bottom) for the 20:80 SPS2/PA-6 and 20:80 SPS10/PA-6 blends respectively. In these plots the solid line is again obtained by adding and weighting the tan δ profiles of the pure components, using the weighting coefficients obtained from the PS/PA-6 blend. The PA-6 tanô "peak" appears as a ψ shoulder on the main tand peaks of the SPS. Two features are noteworthy: 1) the approximate maximum of the shoulder does not depend on the degree of sulfonation of the SPS since it occurs at about 75°C in the 20:80 SPS/PA-6 blends; 2) the intensity of the shoulder is very much a function of the degree of sulfonation, being highest for the SPS2 and lowest for the SPS10. This, in turn, suggests that this shoulder reflects the presence of a PA-6 rich phase, the composition of which is not very dependent on the degree of sulfonation, but the amount of which is inversely related to the sulfonation level. It is worth noting that the position of the SPS rich phase is relatively independent of the degree of sulfonation. However, since the T_g of the SPS increases with sulfonation, the T_g drop ($T_{g SPS}$ - $T_{g blend}$) increases with degree of sulfonation. The width of the peak, and therefore the total area, also increases with sulfonation, paralleling the decrease in the area of the shoulder, suggesting that more of the PA-6 is incorporated into the SPS phase as the sulfonation level increases.

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The 40:60 SPS/PA-6 blends show a similar trend to the 20:80 SPS/PA-6 blends¹⁵. The position of the glass transition temperatures for the various blends is summarized in *Table 3.1*.

These DMTA studies show that even though the SPS/PA-6 blends are compatibilized, the 20:80 and 40:60 SPS/PA-6 blends still contain two phases that are at least 100Å in dimension (reflecting the resolution limit of the DMTA instrument).

3.4.4 Extraction studies: The PA-6 can be extracted from the melt blended samples (samples containing 60% and 80% PA-6) by a specific solvent, such as formic acid, and subsequently analyzed through SEC by a method described in the literature^{18,19}. This technique has been used to analyze the PA-6 extracted from melt blends of PA-6 with poly(ethylene-acrylic acid) copolymers², and can provide useful information on the effect of processing on the molecular weight and the molecular weight distribution of the PA-6. NMR can also be used to obtain the number average molecular weight by quantifying the concentration of end-groups in the extracted PA-6.

Upon PA-6 extraction, the PS/PA-6 blends disintegrate within a few hours, leaving the PA-6 in solution and the PS as a suspended white powder. This is not surprising, since the PS appears as distinct spherical domains in the PA-6 matrix, as shown by the SEM of the fracture surfaces¹⁵. By contrast, the samples containing SPS show a decrease in their dimensions, but retain their shape upon extraction of the PA-6. This is especially remarkable considering that the major component (PA-6) is being extracted from these blends, and thus suggests the good dispersion of the SPS, even in the 20:80 SPS2/PA-6 blend where the

Table 3.1 Glass transition temperatures of pure components and blends from DMTA data taken at 10Hz. The value of the ratio A/S is also given for the blends.

PURE COMPONENTS:

| Sample | | т _g (°С) | | | |
|-------------------------------------------------|--------------------|----------------------------------|--------------------------|--|--|
| PA-6
PS
SPS2
SPS5
SPS10 | | 70
121
126
129
137 | | | |
| Sample | (A/S) | T _{g1} (℃) | T _{g2} (℃) | | |
| 20:80 wt% BLE | NDS: | | | | |
| PS/PA-6
SPS2/PA-6
SPS5/PA-6
SPS10/PA-6 | 170
71
41 | 70
>75
sh(75) *
sh(75) | 116
119
118
117 | | |
| 40:60 wt% BLE | NDS: | | <u></u> | | |
| PS/PA-6
SPS2/PA-6
SPS5/PA-6
SPS10/PA-6 |
64
27
15 | 65
sh(70)
sh(70)
sh(75) | 116
119
121
123 | | |

* sh = tan δ is a shoulder on the main peak. The number in brackets is an estimate of the maximum, after subtraction of the main peak.

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sulfonation level is only 2.2 mol%, and the PA-6 constitutes 80% of the sample by weight.

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After a one day solvent extraction, and subsequent drying, the samples containing 20% and 40% of SPS occupy about 35% and 55% of their original volumes, respectively (based upon their linear outside dimensions).

Figure 3.7 shows the SEMs of the fracture surfaces of the two samples, before and after extraction. The 20:80 SPS2/PA-6 blend (*Figure 3.7*(a)), as well as the 40:60 SPS10/PA-6 blend (*Figure 3.7*(b)), show good dispersion of the SPS component when compared to PS/PA-6 blends (not shown; see ref.15, for example), where distinct phase separated domains of 3 to 6 μ m can be seen. Even after extraction of the PA-6, the fracture surfaces still appear relatively free of large surface voids. The extracted surface of the 20:80 SPS2/PA-6 blend shows the existence of many small irregularities (*Figure 3.7*(c)), while the extracted surface of the 40:60 SPS10/PA-6 blend is smoother with larger and less distinct features (*Figure 3.7*(d)). This suggests that while both SPS2 and SPS10 are compatibilized with the PA-6, the SPS10 is better dispersed in the PA-6 matrix than the SPS2. This is also supported by the DMTA data where the miscibility is seen to improve with increasing sulfonation. of the SPS.

Table 3.2 shows the efficiency of the PA-6 extraction from the various blends. As the level of sulfonation increases, less of the PA-6 can be extracted. Thus while all of the PA-6 is extracted from the PS/PA-6 blends, only 78% of the PA-6 is extracted from the 40:60 SPS10/PA-6 blend. This decrease can be ascribed to the interaction of the SPS with the PA-6 and the greater dispersion of the SPS in blends with higher sulfonic acid content, as shown by DMTA and the fracture



Figure 3.7 SEM's of fracture surfaces for the (a) 20:80 SPS2/PA-6 blend (b) 40:60 SPS10/PA-6 blend (c) 20:80 SPS2/PA-6 blend after PA-6 extraction and (d) 40:60 SPS10/PA-6 blend after PA-6 extraction.

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surface SEMs. This makes it more difficult for the solvent to access all of the PA-6 in the well dispersed SPS10/PA-6 blends. Although the reduced extraction of the PA-6 with increasing sulfonation of the SPS apears to be a kinetic effect, the change in the extraction efficiency with extraction time was not studied to show this.

| | *AT+0% | % PA-6 | T | Т | Mn | (kg/n | nol) |
|-------------------------------------------------------------------------|------------------------------|----------------------|------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| SAMPLE | residue | extracted | ۲ _с
(°C) | 1 m
(°C) | NMR | SEC | mean |
| 20:80 PS/PA-6
20:80 SPS2/PA-6
20:80 SPS10/PA-6 | 19.5
21.5
27.0 | 100
98
91 | 66
67
84 | 220
219
216 | | | |
| 40:60 PS/PA-6
40:60 SPS2/PA-6
40:60 SPS5/PA-6
40:60 SPS10/PA-6 | 40.5
45.5
48.5
53.5 | 99
91
86
78 | 66
73
82
91 | 220
218
211
203 | 3.8
2.9
1.9
1.2 | 7.2
2.5
1.4
1.0 | 5.5
2.7
1.6
1.1 |

Table 3.2 Extraction efficiencies and characterization of the polyamide-6 extracted from the melt blended samples.

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Table 3.2 also shows the melting point (T_m) and recrystallization temperatures (T_c) of the extracted materials. Infra-red and NMR analysis shows that only the PA-6 component of the blend is extracted and, therefore, the variation of the T_m and T_c can be ascribed to differences in the molecular weights of the extracted PA-6. The decrease of the PA-6 molecular weight is known to decrease the melting temperature and the crystallization kinetics of the PA-6^{29,30}.

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Figure 3.8 shows the molecular weight distributions of the PA-6 extracted from the 20:80 and 40:60 blends. The PA-6 extracted from the 20:80 SPS2/PA-6 sample appears to be unaffected by the presence of the sulfonic acid groups in the blend

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and its distribution is comparable to that of the PA-6 extracted from the 20:80 PS/PA-6 blend. The $T_{\rm m}$ and $T_{\rm c}$ values of the PA-6 extracted from these two blends (Table 3.2), however, show that the PA-6 from the SPS2/PA-6 blend has a slightly lower $T_{\rm m}$ and a slightly higher $T_{\rm c}$ than the PA-6 from the PS/PA-6 blend. This suggests that the molecular weight of the PA-6 from the 20:80 SPS2/PA-6 blend may be slightly lower than that of the PA-6 from the 20:80 PS/PA-6 blend. At a higher sulfonation (20:80 SPS10/PA-6), degradation of the PA-6 is more evident, with the appearance of some lower molecular weight material at higher elution volumes (*Figure 3.8*) and a significant change in $T_{\rm m}$ and $T_{\rm c}$ (*Table 3.2*).

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Figure 3.8 also shows the SEC profiles for the PA-6 extracted from the 40:60 blends and it can be seen that the degradation is more extensive here than for the 20:80 blends. As expected, the degradation of the PA-6 is not only a function of the SPS sulfonation level, but also of the blend ratio. It will be shown later that the PA-6 degradation is related to the A/S ratio in the blend.

Several of the blends show a bimodal molecular weight distribution of the extracted PA-6 (20:80 SPS10/PA-6, 40:60 SPS2/PA-6 and 40:60 SPS5/PA-6). The bimodal molecular weight distributions indicate that the degradation of the PA-6 is not uniform in these blends. This can be explained by the non-uniform concentration of sulfonic acid groups, as shown by the two-phase nature of these blends from DMTA. For the PA-6 extracted from the 40:60 SPS10/PA-6 blend, however, there is a single but broad molecular weight distribution, indicating extensive degradation of the PA-6 and the predominance of the SPS rich phase from DMTA. The peaks at about 23 ml elution volume in Figure 3.8 are due to residual solvent and possibly some residual reagents from the trifluoracetylation reaction. 6.1

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Figure 3.8 SEC profiles of the PA-6 extracted from the melt blends. The blends from which the PA-6 were extracted are identified by the blend minor components.

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The number average molecular weight (M_n) of the extracted PA-6 from the blends containing 40% PS or SPS was determined using NMR and SEC (*Table 3.2*). The agreement between these two techniques is reasonable, except in the case of the PA-6 extracted from the PS/PA-6 blend. This discrepancy can be attributed to the much lower sensitivity of NMR at low end-group concentrations. The SEC value for the M_n of the PA-6 extracted from the PS/PA-6 blend should, therefore, be considered as the more correct value. Since the M_n of the PA-6 before melt blending is 14 kg/mol, the reduction in the M_n of the PA-6 blend is due to thermal and mechanical degradation during processing.

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Although not all of the PA-6 was extracted from the blends, the mean M_n values shown in *Table 3.2* provide a reasonable estimate of the number average molecular weights of the PA-6 in the 40:60 blends. Knowing the M_n of the PA-6 in the various blends, it is possible to estimate the number of chain scissions caused by the sulfonic acid groups. It is assumed that the number of chain scissions due to thermo-mechanical degradation during the 20 minute processing time is the same for all the blends, irrespective of the sulfonation level of the SPS. The M_n of PA-6 in the PS/PA-6 blend decreases from 14, before blending, to about 5.5 kg/mol, after blending, via thermo-mechanical degradation. The further reduction of the molecular weight of the PA-6 in the SPS/PA-6 blends can then be attributed to the presence of sulfonic acid groups in these blends. In this way, the number of chain scissions per sulfonic acid group can be estimated. *Table 3.3* shows the results of these calculations by using the average values for M_n given in the last column of *Table 3.2*.

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| | Chain cuts per -SO ₃ H | | |
|--------------------------------------------------------|-----------------------------------|---------------------------------|--|
| SAMPLE | mean | deviation* | |
| 40:60 SPS2/PA-6
40:60 SPS5/PA-6
40:60 SPS10/PA-6 | 1.4
1.3
1.2 | $\pm 0.8 \\ \pm 0.5 \\ \pm 0.3$ | |

Table 3.3 Chain cuts per sulfonic acid group.

* Maximum deviation from numbers obtained when using either only NMR or only SEC values of M_n in calculating the chain cuts per sulfonic acid group.

On average, therefore, every sulfonic acid group in the blend causes between one and two chain scissions of the PA-6.

3.4.5 DSC studies of solution cast blends: The relatively mild preparative conditions for blends prepared by solvent casting is not expected to cause chain scission of the PA-6. However, when these samples are heated above their melting temperatures, degradation of the PA-6 does takes place. Since the molecular weight of the PA-6 is related to its $T_{\rm m}$, the degradation of the PA-6 in the blend can be followed indirectly by observing the $T_{\rm m}$ of the blend as a function of the annealing time.

Figure 3.9 (top and bottom) shows the variation of the T_m with annealing time for SPS/PA-6 blends, where the SPS is sulfonated to 4.5 and 12.3 mol% sulfonic acid groups, respectively. As seen in these figures, there is a melting point depression in some of the blends, even before annealing (annealing time = 0 min). The source of this T_m depression can be attributed to the interaction of the SPS with the PA-6 amide groups and possibly to differences in the crystal morphology of these blends. Residual solvent may be of influence too, but the absence of a T_m

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Figure 3.9 Effect of annealing at 240°C on the melting point of the solution cast blends of SPS and PA-6. The numbers indicate weight % of the SPS in the blend.

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depression in the pure PA-6 and the increase of this T_m depression with an increase in the sulfonation level of the SPS indicates that this is only of minor influence.

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Annealing the samples at 240 °C leads to a decrease of $T_{\rm m}$ which is rapid at first, but levels off after about 90 minutes. This can be seen in *Figure 3.9*. During the initial stages of annealing, the $T_{\rm m}$ depression can be ascribed to both the interaction of the SPS with the amides of the PA-6, and to the decrease in the molecular weight of the PA-6. As the annealing continues, the concentration of the amine end-groups in the blend increases because of the hydrolysis of the PA-6. Since the amine end-groups are a stronger base than the amide groups, the sulfonic acid groups should preferentially interact with these amine end-groups. After 90 minutes of annealing, most of the sulfonic acid groups are interacted with the amine end-groups of the PA-6, leaving the rest of the PA-6 polymer chains uninteracted and free to crystallize. Therefore, it can be argued that the $T_{\rm m}$ depression after 90 min annealing is mostly due to the reduced molecular weight of the PA-6 in the blend.

The equation derived by Flory to express the T_m depression as a function of the fraction of crystallizable units can be used here to express the T_m depression. Flory's equation can be represented as follows:

$$[1/T_{m(2)}] - [1/T_{m(1)}] = -(R/\Delta H_m) \ln [x_{(2)}/x_{(1)}]$$
[3.2]

Where $T_{m(1)}$ is the melting point (in K) of a polymer having a fraction of crystallizable units of $x_{(1)}$, while $T_{m(2)}$ is the melting point (in K) of the same polymer having a fraction of crystallizable units of $x_{(2)}$, R is the universal gas

constant and ΔH_m is the melting enthalpy of 100% crystalline polymer. Since the end-groups are not crystallizable units, the $x_{(i)}$ value for a polymer having a number average degree of polymerization of $P_{(i)}$ is given by

$$x_{(i)} = (P_{(i)} - 2) / P_{(i)}$$
 [3.3]

By defining *n* as the number of chain scissions per sulfonic acid group, the degree of polymerization $P_{(2)}$ of the PA-6 after annealing can be related to its initial degree of polymerization $P_{(1)}$ through the following relationship (see Appendix A):

$$P_{(2)} = P_{(1)} / [1 + (S/A) n P_{(1)}]$$
[3.4]

Note that the sulfonic acid to nitrogen ratio (S/A) used here is the inverse of the A/S ratio used earlier. By assuming $\Delta H_m = 191 \text{ J/g}$ for the 100% crystalline PA- 6^{31} , setting $P_{(1)} = 124$ and $T_{m(1)} = 493.6$ K (220.5 °C) (obtained after annealing PA-6 for 90 minutes), the variation of the melting point $T_{m(2)}$ with S/A can be calculated from Equations [3.2] to [3.4]. The results are shown for n = 1 and n = 2 in *Figure 3.10* (top) along with the experimental points for all the solution cast blends after 90 min annealing. The T_m for all the blends fall between the calculated lines for n = 1 and n = 2, suggesting that each sulfonic acid group in the blend causes between one and two chain scissions. It can also be seen that the number of chain scissions increases slightly as the sulfonation level of the SPS is increased, indicating that extent of the hydrolysis of the PA-6 in these blends is slightly higher. This possibly reflects a higher water content for the more highly sulfonated SPS blends.

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Figure 3.10 The melting temperature of various SPS/PA-6 solution cast blends, after 90 min annealing, (top) and of the PA-6 extracted from the 40:60 melt blends (bottom) as a function of the S/A (or A/S) ratio. The solid lines represent the melting point depressions calculated from Equations [3.2] to [3.4] for one (n=1) and two (n=2) chain scissions per sulfonic acid group in the blend.

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This melting point depression analysis can also be applied to the T_m of the PA-6 extracted from the melt blended samples. In this case, $P_{(1)} = 62$ due to the mechanical and thermal degradation of the PA-6 during melt processing, as given by the M_n (SEC) of the PA-6 extracted from the 40:60 PS/PA-6 blend (*Table 3.2*). Figure 3.10 (bottom) shows that the trend is similar to that of the solution cast samples and confirms that the T_m depression in these blends is primarily due to the reduction of the PA-6 molecular weight. As for the solvent cast samples, the number of chain scissions range between one and two per sulfonic acid group, and increases slightly at higher sulfonation of the SPS in the blend.

Although $T_{\rm m}$ depressions can be caused by factors other than molecular weight effects (e.g., polymer-polymer interactions or crystal morphological changes), the extraction studies on the melt blended samples show that these are only of minor influence. Equations [3.2] to [3.4] above do not take into account any $T_{\rm m}$ depression due to interactions and thus are not meant to describe the observed $T_{\rm m}$ depressions fully. However, they illustrate that the $T_{\rm m}$ depressions in these blends are mainly due to molecular weight effects, rather than other factors.

3.5 CONCLUSIONS

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Polyamide-6 (PA-6) and lightly sulfonated polystyrene (SPS) interact strongly in solution. Evidence of this is provided by the formation of gelled or hazy solutions when PA-6 and SPS are blended in *m*-cresol. The observation of gel in some of the blends proves that the SPS interacts with the amide groups, and not only with the amine end-groups. Confirmation of the interactions are provided by NMR. The proton of the sulfonic acid interacts with the amide nitrogen, most

probably by the transfer of the proton to the nitrogen, as has been seen for other nitrogen containing polymers.

Strong interactions of the SPS with PA-6 are also seen during melt blending where a torque rise occurs upon the addition of SPS to the PA-6. The tan δ plots from dynamic mechanical analysis of the melt blended materials also show that the glass transition temperatures of the blend components shift towards each other as the sulfonation level of the SPS increases from 0 to 9.7 mol%. SEMs of the fracture surfaces show that the SPS is well dispersed in the PA-6 matrix, even at low levels of functionalization of the SPS (2.2 mol%).

Extraction and analysis of the PA-6 from the melt blended samples reveals that the presence of sulfonic acid groups in the blend causes the degradation of the PA-6, probably by hydrolysis of the amide bonds. From SEC and NMR analysis of the PA-6 extracted from the blends, and also from an equation relating the T_m of the PA-6 to its end-group concentration, it is shown that each sulfonic acid causes between one and two chain scissions of the PA-6. The extent of the PA-6 degradation is found to increase inversely with the A/S ratio. These results suggest that there are between one and two residual water molecules per sulfonic acid group in the SPS/PA-6 blends, and that the SPS is the most likely source of the water. The hygroscopic nature of the SPS as well as the PA-6 makes the total exclusion of water from these blends very difficult and the presence of some residual water per sulfonic acid group can be expected, even after vacuum oven drying.

Degradation of the PA-6 can be minimized by keeping the A/S ratio high, without compromising the good dispersion of the SPS in the PA-6. This is the

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case for the 20:80 SPS2/PA-6 blend (A/S = 170) where SEC of the extracted PA-6 shows negligible degradation, and yet good dispersion of the SPS is still achieved, as seen by SEM of the fracture surfaces.

Some current studies indicate that the neutralization of the sulfonic acid groups with some specific metals can lead to the miscibility enhancement of the SPS with PA-6, without the degradation of the PA- 6^{13} ,15,32-35. While lithium neutralized SPS (about 10 mol% functionalization) shows significant miscibility enhancement with PA-6 and other aliphatic polyamides, sodium neutralized SPS is immiscible³², ³³. The neutralization of the SPS with some transition metals, such as manganese, also leads to miscibility enhancement with PA- 6^{34} ,35. However, the neutralization of the SPS with a metal counterion (e.g. lithium) dramatically increases its melt viscosity³⁶ and consequently makes its melt processing more difficult than its unneutralized counterpart. In this respect, unneutralized SPS may be better suited for processing than when neutralized with a metal counterion.

3.6 ACKNOWLEDGEMENTS

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Chapter 4

MISCIBILITY OF POLYAMIDE-6 WITH LITHIUM OR SODIUM SULFONATED POLYSTYRENE IONOMERS

4.1 ABSTRACT

50:50 (w/w) blends of polyamide-6 (PA-6) with sulfonated polystyrene ionomers (containing 9.8 mol% of functional groups) show considerable miscibility enhancement (single glass transition at some compositions) when the counterion is Li, but are immiscible when the counterion is Na. Dynamic mechanical measurements show that there is an optimum composition of the blends of the lithium sulfonated ionomers (LiSPS) with PA-6 at which the simultaneous disruptions of the stiffening effects of crystallinity and of the "cluster phase" in the blends are at a maximum. This is manifested as a maximum in the tan δ peak height, and a minimum in the width, at this composition. At 240 - 250°C, the blends with LiSPS are either one or two-phase (on the 50 to 100Å scale), depending on the lithium sulfonate content of the ionomer and on the blend

composition. This phase behavior can be described by considering the thermodynamics of blending to be dominated by two opposing interaction enthalpies: the specific interaction of the lithium styrene sulfonate units with the amide units of the PA-6, and the random, unfavorable interaction of the styrene with the amide units.

4.2 INTRODUCTION

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While high polymers are generally immiscible due to the very low entropy of mixing, miscibility enhancement can be achieved when one or both of the polymers are functionalized with specific interacting groups. Specific intermolecular interactions lower the heat of mixing so that the thermodynamics of blending can lead to miscibility enhancement of the blend components. The functionalized on of polymers with < 15 mol% ionic groups, which produces polymers generally termed "ionomers", is particularly attractive in this respect since the ionic groups introduce the possibility of strong ion-ion, ion-pair ion-pair or ion-dipole interactions with other polymers. The miscibility enhancing effect of ionic groups has been clearly demonstrated for blends of polystyrene ionomers with various polar polymers such as poly(ethylene oxide)¹, poly(propylene oxide)^{1,2}, polycaprolactone, poly(vinyl chloride), poly(ethylene terephthalate), poly(epichlorohydrin)³, and polyurethanes⁴. Since polyamides are also polar, due to the presence of amide groups along their backbone, ionomers are usually found to interact favorably with polyamides.

Polyamides constitute an important class of commercial polymers with a wide variety of applications, from engineering thermoplastics to fibres. Hence, the

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improvement of some of the properties of polyamides (e.g., impact, dyeability, vapor permeation, anti-static) through blending is of considerable interest. The use of ionomers containing ionic carboxylate groups to compatibilize various polymers with polyamides has been the subject of several studies and many patents⁵⁻¹⁰. There are a few patents to suggest that ionomers containing ionic sulfonate groups may also be compatible with polyamides^{11,12}. However, it is only recently that some studies have demonstrated, by using differential scanning calorimetry (DSC), that there is significant miscibility enhancement between polyamide-6 (PA-6) and polystyrene ionomers when the ionomer contains lithium¹³⁻¹⁵, zinc¹⁵ or manganese^{15,16} sulfonate groups. Blends of unneutralized sulfonated polystyrene and PA-6 are also compatibilized, although the PA-6 in these blends is susceptible to hydrolysis due to the catalytic activity of the sulfonic acid groups in these blends^{14,17}. Degradation of the PA-6 is not evident when the sulfonated polystyrene is neutralized¹⁴.

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In this paper it will be shown that the choice of counterion (Li vs. Na) is critical in achieving enhanced miscibility (single glass transition) of sulfonated polystyrene with PA-6. The previous studies on blends of sulfonated polystyrene ionomers with PA-6 employed DSC to determine the miscibility. However, dynamic mechanical thermal analysis (DMTA) is often more sensitive than DSC in detecting the presence of different phases in polymer blends¹⁸. Therefore, in addition to DSC data, the phase behavior of the blends of PA-6 with lithium sulfonated polystyrene ionomer (LiSPS) as determined by DMTA is also presented here. The one or two phase behavior of these blends, as seen by DMTA, is described by considering the thermodynamics of mixing at 240 - 250°C to be dominated by two factors: the specific interaction of the lithium sulfonate groups with the polyamide units, and the random unfavorable interaction of the

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styrene with the polyamide units. The effect of the PA-6 on the "cluster phase" of the LiSPS ionomer will also be discussed and it will be shown that an optimum amide to lithium sulfonate ratio exists at which the tan δ of the blend becomes sharp and narrow.

Since DMTA can only resolve phases of at least 50 to 100Å in size, the term "miscibility", as used in this paper, implies a single phase (single glass transition) on the 50 to 100Å level. Thus "miscibility", as used here, does not necessarily imply miscibility on the molecular level. This aspect is the subject of continuing study.

4.3 EXPERIMENTAL

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4.3.1 Materials used: The PA-6 was obtained from Aldrich and was purified by dissolving in formic acid and precipitating in water. The polystyrene was also obtained from Aldrich and was sulfonated using the method of Makowski et al.¹⁹. The sulfonation level of the sulfonated polystyrene was determined by titration with methanolic NaOH to a phenolphthalein end point. The sulfonated polystyrene was dissolved in benzene/methanol (90:10) and neutralized with either LiOH or NaOH to produce the ionomers designated as LiSPS and NaSPS, respectively. The samples were subsequently freeze-dried. All materials were dried under vacuum for 2 days at 80°C prior to use. No further drying was done at this stage, since a much more thorough drying procedure was used during the preparation of the blends. In order to ensure a fair comparison between the blend properties and the pure component properties, the pure components were dissolved, precipitated, and dried following the procedure described below for

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blend preparation. *Table 4.1* lists the sample designations and characteristics of the polymers used in this study.

| Material | Mw [*]
(kg/mc!) | M _n
(kg/mol) | M _w /M _n | functional group content | |
|--------------------------------------------|--------------------------------|--------------------------------|----------------------------------------|-------------------------------|--------------------------------------|
| | | | | (mol%) | (meq./g) |
| PA-6
PS
LiSPS5
LiSPS10
NaSPS10 | 33
225
235
243
246 | 14
105
110
114
115 | 2.4
2.1
2.1
2.1
2.1
2.1 | 100
0
5.4
9.8
9.8 | 8.85
0.00
0.50
0.87
0.86 |

Table 4.1 Characteristics of the blend components.

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* The molecular weights for the PA-6 and PS were determined by size exclusion chromatography while those of the ionomers were calculated from the values for the PS.

4.3.2 Blend preparation: The blends of ionomers with PA-6 were prepared by dissolving the individual components in a solvent mixture of m-cresol/methanol (80:20) to produce 5% (w/v) solutions. The NaSPS10 ionomer is slighdy hazy in this solvent and was clarified by the addition of 10 μ l distilled water per ml of solution. To ensure a uniform solvent mixture, the same level of water was added to all the solutions. Various blend ratios were prepared by mixing different volumes of the solutions under constant agitation. The solutions were then precipitated into an excess of hexanes. The precipitated product was thoroughly washed with fresh hexanes to remove residual m-cresol. Final drying of the precipitated polymer blends was accomplished by keeping the samples under vacuum at 140°C for one week. Solid state nuclear magnetic resonance

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showed no evidence of residual solvent after this drying procedure. Loss of material during precipitation was less than 5%, as determined by the difference in weight between the polymers before blending and after precipitation and drying. Blends of PA-6 with polystyrene were prepared in a similar fashion to the ionomer/PA-6 blends, except that a m-cresol/toluene (50:50) solvent mixture was used as the solvent. Some of these PS/PA-6 solution blends had to be clarified by the addition of some toluene. All of the blend materials were stabilized with 0.1% (w/w) Irganox 1098 (kindly supplied by Ciba-Geigy Cor.) by sprinkling the ground polymer blends with a 1% (w/v) solution of the stabilizer in either methanol (for PS and LiSPS5 blends) or acetone (for Li and Na SPS10 blends). The samples were dried under vacuum for a further 2 days at 140°C prior to use.

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4.3.3 Differential scanning calorimetry: A Perkin-Elmer DSC-7 scanning calorimeter was used for the DSC measurements. All scans were run under a nitrogen purge to minimize oxidative degradation. To ensure a uniform thermal history, the samples were first heated to 250 °C and held at this temperature for 5 minuter before cooling to -10 °C at 40 °C/min. The samples were then scanned from -10° to 250°C at 20°C/min to record the T_g and T_m . The glass transition temperatures were taken as the midpoint of the heat capacity changes while the melting temperatures (T_m) and crystallization temperatures (T_c) were taken at the maximum of the enthalpy endo/exotherm peaks. The T_c values were recorded during the cooling run. The percent crystallinity of the samples was estimated by assuming an enthalpy of melting of 160 J/g for 100% crystalline PA-6²⁰.

4.3.4 Dynamic mechanical thermal analysis (DMTA): The blend samples were prepared by compression moulding at 240 - 250°C under low pressure. The samples were cooled using forced-air convective cooling. The average cooling rate was estimated at 5°C/min, with initial cooling rates as high as 10°C/min. A Polymer Laboratories DMTA instrument was used to record the dynamic mechanical properties of the samples at 1 Hz. The dual cantilever mode was used with an 8 mm free length. The samples were between two and three mm thick and approximately 11 mm wide. The samples were scanned at 1°C/min from 0°C up to the flow or melting temperature of the blends (usually about 220°C). The tan δ peaks were deconvoluted using PeakFitTM (Jandel Scientific) software and the best fits to the data were obtained by assuming an exponential baseline and an exponentially modified Gaussian distribution for the peaks. From these the characteristics (positions, widths, areas, heights) of the constituent peaks could be obtained.

4.4 RESULTS

4.4.1 Differential scanning calorimetry: Table 4.2 lists the data obtained by DSC for the various ionomer blends with PA-6. The NaSPS10 ionomer blends are clearly immiscible, as evidenced by the presence of two glass transition temperatures (T_g) and by the negligible effect on the crystalline melting temperature (T_m) of the PA-6. The LiSPS10 blends, on the other hand, show a single composition dependent T_g and a T_m depression which varies with composition, which suggests the presence of strong interactions between this ionomer and PA-6. Figure 4.1 shows the variation of T_m , T_c and T_g with composition for the LiSPS10 blend. T_m and T_c are plotted against the absolute

| polymer | polymer
(%) [*] | τ _g
(℃) | ΔH _m
(J/g) | Τ _c
(℃) | τ _m
(℃) | crst.
(%) |
|----------|-----------------------------------|-----------------------------------------------------|-------------------------------------|-------------------------------------------|-------------------------------------------|---------------------------|
| PA-6: | 100 | 54 | 69.9 | 174.4 | 220.2 | 44 |
| NaSPS10: | 10
30
50
70
90
100 | 58/132
66/130
66/129
66/132
/131
133 | 58.0
44.9
39.2
15.9
4.2 | 171.0
168.3
166.4
155.7
169.1 | 220.5
220.2
220.7
218.0
218.3 | 36
28
24
10
3 |
| LiSPS10: | 10
40
50
70
90
100 | 62
91
92
125
145
133 | 61.0
32.1
1.2

 | 170.7
141.8

 | 220.7
212.5
207.4

 | 38
20
<1
 |
| LiSPS5: | 10
30
50
70
90
100 | 58/96
68/105
110
112
120
122 | 63.3
44.6
29.5

 | 172.2
167.4
149.5

 | 221.5
220.5
217.4

 | 40
28
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 Table 4.2 DSC data for the polymers and their blends.

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* % by weight of polymer in the blend with PA-6.



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Figure 4.1 Transitions for LiSPS10 blends with PA-6 as determined by DSC.

ionomer content in the blend. Since T_g is only relevant to the amorphous phase, it is plotted as a function of the amorphous phase composition, which was calculated from the % crystallinity in the blends. For compositions greater than 50%, the LiSPS10 blends are amorphous and the T_g increases until at 90% ionomer cc:nposition, it reaches a maximum. This maximum is a reproducible feature of these blends, and is also seen by DMTA.

The DSC data in *Table 4.2* for the LiSPS5 ionomer blends show that there are two glass transition temperatures at low ionomer contents, while at high ionomer contents there appears to be a single composition dependent T_g . Considerable additional insight into the phase behavior of this blend can be gained from dynamic mechanical measurements, to be discussed later.

The progressive lowering of the crystallization temperature (T_c) of the PA-6 with increasing ionomer content, shown in *Table 4.2*, is an indication of the extent to which the PA-6 crystallization process is hindered. This, in turn, provides some insight into the level of interaction between the blend components. For the blends of PS with PA-6, T_c remains at about 174°C throughout the composition range. The order in which the polymers hinder the crystallization process is as follows: LiSPS10 > LiSPS5 > NaSPS10 > PS.

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4.4.2 Dynamic mechanical thermal analysis (DMTA): DMTA is often more sensitive in detecting T_g in blends than DSC¹⁸. It is therefore used here for the detailed analysis of the phase behavior of the ionomer blends. Since all the DMTA samples were molded at *ca*.240°C, the DMTA data can be assumed to reflect closely the phase behavior of these blends at this temperature. *Figure 4.2*





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shows the storage modulus (E'), loss modulus (E'') and tanð profiles for the 50:50 blends, and confirms the immiscibility of NaSPS10 and PS (two distinct transitions), and the miscibility (single distinct transition) of LiSPS10 with PA-6 on the 50 to 100Å level, characteristic of the DMTA measurement. The storage modulus (E') drop at about 220°C is due to the melting of the crystalline phase of the PA-6. It is worth noting that the 50:50 LiSPS10 blend sample prepared for the DMTA has a higher crystallinity (about 14%) than that shown in *Table 4.2*. This is a result of the slower cooling rate during the DMTA sample preparation than the 40°C/min used to obtain the data in *Table 4.2*. At other blend ratios (10, 30, 70, 90% ionomer or PS) the NaSPS10 and PS blends show two tanð peaks, confirming the DSC results that these blends are phase separated throughout the composition range. In contrast, the LiSPS10 and LiSPS5 ionomer blends with PA-6 are either one or two phase, depending on the blend composition.

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Figure 4.3 shows a series of tano profiles for the LiSPS5 and LiSPS10 blends respectively. Figure 4.3 (left) shows the gradual merging of the LiSPS5 and PA-6 tano peaks with increasing LiSPS5 content in the blend until, at 70% ionomer content, a single peak is seen. Compositions having more than 70% ionomer show evidence of an ionomer "cluster" peak at higher temperatures, which is a characteristic feature of the unblended ionomers. Figure 4.3 (right) shows a similar trend for the LiSPS10, except that a single (but broad) peak is already seen at a much lower ionomer content (30% ionomer).

Note that the blends containing 10% LiSPS10 and 50% LiSPS5 show two transitions by DMTA, but only a single transition by DSC (Table 4.2). It may be argued that this is a consequence of possible phase separation during the slower cooling of the DMTA sample (*vs.* faster cooling of the DSC samples). To test this,



Figure 4.3 Log tanð (1 Hz) for various blends of PA-6 with LiSPS5 (left) and LiSPS10 (right). The vertical axis refers to the bottom curve only. Subsequent curves are seperated by one log tanð unit for clarity.

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blend samples containing 10, 30 and 50% LiSPS10 were cooled at 2°C/min from 250°C and scanned by DSC as before. Single transitions were noted in all cases. Furthermore, the probable presence of a lower critical solution temperature (LCST) in these blends would also favor one-, rather than two-phase, behavior during a slow cooling process. From these considerations, DMTA can be considered to be more sensitive than DSC in detecting phase domains in these blends, with cooling rate differences being less important.

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Figure 4.4 shows the log storage modulus (E') for blends containing 50, 70 and 90% LiSPS5 ionomer. For the 70% ionomer blend, the PA-6 crystalizes during the slow heating run (1°C/min) of the DMTA experiment. This, however, is not seen in the blends containing either 50% or 90% ionomer, the 50% ionomer blend is already crystalline, and the 90% ionomer blend is, and remains, amorphous. This behavior confirms the DSC results that the lithium sulfonate groups of the ionomer strongly hinder the crystallization of the PA-6 in the blend. Again, the rapid drop in E' at about 220°C for the 50 and 70% ionomer blends is due to the melting of the PA-6 crystalline phase. The much more gradual drop of the E' for the 90% ionomer blend from 150 to 260°C is a reflection of the presence of a "cluster phase" in this blend²¹.

4.4.3 Analysis by tano peak deconvolution: Even a casual inspection of the tano profiles of the blends containing 10 and 30% LiSPS5, suggests that two overlapping tano peaks are involved which reflects the presence of two separate phases. With modern deconvolution techniques, it is possible to deconvolute such peaks to obtain semi-quantitative values for the peak positions, heights etc. This procedure, while clearly not absolutely precise, gives a useful measure of the relative tano peak positions (T_g), tano peak heights and peak widths (purity



Figure 4.4 Storage modulus (E') for blends of PA-6 with LiSPS5 recorded during the 1°C/min heating run of the DMTA experiment (1 Hz). The wt% LiSPS5 ionomer content in the blend is indicated. The experimental points are only shown for the 50% LiSPS5 blend.

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of the phases). An example of a typical deconvolution of a tan δ profile (plotted linearly) is shown in *Figure 4.5*.

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In general, the tan δ peaks can be related to three different phases: the PA-rich phase, the blend phase, and the "cluster phase" of the ionomer. The phase with the lowest T_g is a mixture of PA-6 and ionomer, and will be referred to as the PA-rich phase. The phase at intermediate T_g results from the mixture of FA-6 with much more of the unclustered ionomer, and will be referred to as the "blend" phase. At high ionomer contents, some of the blends show the presence of a high temperature transition, and this due to a "cluster phase". It is worth recalling that the polystyrene ionomers studied here show two tan δ peaks in their pure, unblended form. The one occurring at lower temperature is attributed to the unclustered phase, while the other is due to a "cluster phase" ^{21,22}. The two tan δ peaks shown in *Figure 4.5* for the blend containing 30% LiSPS5 ionomer, are thus due to a PA-rich and a blend phase.

Figure 4.6 shows the variation with temperature of the three tand peaks in the blends of LiSPS10 and LiSPS5 with PA-6. The positions of these peaks along the composition axis have been adjusted for crystallinity to represent only the amorphous phase composition. Figure 4.6 clearly shows that the cluster phases of the ionomers are plasticized by the presence of PA-6 in the blends, which is seen as a decrease in the cluster phase peak temperatures with decreasing ionomer content in the blend. Figure 4.6 also highlights the immiscible/ miscible threshold of these two ionomers, the threshold being taken between the highest composition showing two glass transition temperatures, and the lowest composition showing only one T_g . Thus, the threshold is between 17 and 43% ionomer content in the amorphous phase for the LiSPS10 (10 and 30% total

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Figure 4.5 Deconvolution of the tanδ curve (1 Hz) of the blend containing 30% LiSPS5 ionomer. The experimental points are shown by an "x" while the solid lines represent the results of the deconvolution.

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ionomer content), and between 64 and 70% amorphous phase composition for the LiSPS5 blends (50 and 70% total ionomer content). A maximum is seen in the T_g of the blend phase at 90% LiSPS10 ionomer content; this was also seen by DSC.

The peak heights of the tan δ peaks, which were identified as $T_{g(blend)}$ in Figure 4.6, are plotted in Figure 4.7. For the PS and NaSPS10 blends, only the upper transition peak heights are shown, reflecting the PS or NaSPS10-rich phases. In the immiscible blends, the tan δ peak heights of the PA-rich phase (not shown) decrease from a maximum of about 0.1 with decreasing PA-6 content in the blends. The cluster phase peak heights (also not shown) usually remain constant at of about 0.3. *Figure* 4.7 clearly shows that the variation of the peak heights with composition for the miscible blends is very different from that of the immiscible blends. In the immiscible (PS or NaSPS10) blends the peak heights increase continuously with PS or ionomer content. The miscible blends of LiSPS5 and LiSPS10, on the other hand, both show distinct maxima of the blend peak heights at compositions containing about 75% LiSPS5 and 70% LISPS10. The tand peaks are also considerably narrowed at these compositions. For instance, the peak width at half height is only 19°C for the 70% LiSPS10 blend, while this value is 50 and 39°C for the pure PA-6 and LiSPS10, respectively. This suggests that the blends are relatively homogeneous at these compositions. It is worth noting that the areas under the tand peaks parallel the trend shown by the tand peak heights.

Finally it should be mentioned that the DSC results for the blends of LiSPS10 with PA-6, shown in *Figure 4.1*, differ from those reported recently for similar blends with a comparable lithium sulfonate content of the LiSPS $(10,1 \text{ mol}\%)^{15}$. This can most probably be ascribed to differences in sample preparation and



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Figure 4.7 The tanð peak heights, as obtained from deconvolution, for blends of PA-6 with LiSPS5 (left), LiSPS10 (middle), and NaSPS10 and PS (right)

conditioning before scanning by DSC: in the present study, the blends were precipitated from solution, dried and then conditioned in the DSC apparatus at 250°C before recording T_g and T_m ; in the study of Lu and Weiss¹⁵, blend films were cast from solution at 140°C and dried at 90°C before the DSC experiment. It was also reported that the blend containing 50% LiSPS10, phase separates after heating to 250°C. This was not observed in this study, either by DSC or by DMTA (*Figure 4.2*).

4.5 DISCUSSION

4.5.1 Polymer-polymer interactions: While PS and NaSPS10 are clearly immiscible with PA-6, throughout the entire composition range, the blends of LiSPS show strong interactions with the PA-6, which results in the miscibility of both LiSPS10 and LiSPS5 at certain composition ranges. The decrease in interaction strength when going from a Li to a Na counterion is not entirely unexpected: in studies of the interaction between salts and model aliphatic amides, it has been found that Li ions interact most strongly among the alkali cations²³; cloud point curve measurements in blends of polystyrene ionomers with polypropylene oxide also show the decrease in interaction strength in the order Li> Na> K². The counterion size and the charge density is, therefore, important in determining the interaction strength of the counterion. However, the result of going from a clearly immiscible blend to a miscible blend (on the 50 to 100Å level) when switching the counterion from Na to Li, as shown by *Figure 4.2*, could not have been predicted from these considerations alone.

Considerable insight into the interaction of LiSPS ionomers with PA-6 can be gained from studies on the interaction of LiCl with various amides. Earlier studies have shown that LiCl can interact strongly with amide solutions, and in some cases, a stable complex is formed 24-27. For example, LiCl and Nmethylacetamide (NMA) has been found to form a stable crystalline adduct. Crystallographic²⁴, NMR and infrared analysis²⁵ has shown that the Li ion is coordinated to four molecules of NMA at the carbonyl oxygen and that the Cl anion is hydrogen bonded with the amide hydrogen. This mode of interaction is generally supported by many studies on the interaction of LiCl with various aromatic as well as aliphatic polyamides 28-31. Since it is improbable that lithium sulfonate and LiCl behave differently in their modes of interaction with PA-6, it is reasonable to expect that the Li ion of the LiSPS also interacts at the carbonyl oxygen of the amide, with the sulfonate anion hydrogen bonded with the amide hydrogen. However, it should be pointed out that another interaction mechanism has been suggested i.e. ion-dipole interaction between the Li cation and the amide nitrogen 15 . Further research in order to confirm the exact nature of the interaction is needed.

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4.5.2 Blend morphology: As shown by *Figure 4.7*, the tan δ peak height of the blend phase for the LiSPS10 ionomer blend reaches a maximum at around 70% ionomer content, which corresponds to a A/Li ratio of 4. It has been suggested that Li may co-ordinate to four amides in mixtures of LiCl salts with PA-6³¹. Although this may be possible in these blends too, the source of this maximum is most likely due to an optimization of two superimposable effects. Starting with pure PA-6 (0% ionomer), the addition of LiSPS10 ionomer decreases the total crystallinity of the blend because of the dilution of the crystalline PA-6 component, as well as the interaction of the LiSPS10 with the amides of the PA-6.

This causes the E' to decrease, and the tan δ (blend) peak height to increase with LiSPS10 addition (since tan $\delta = E''/E'$). At the other end of the composition scale, 100% ionomer has two phases: an unclustered phase and a cluster phase. The cluster phase of the ionomer increases E' due to the physical cross-linking by the lithium sulfonate groups, and this suppresses the measured tan δ peak height of the unclustered phase. The addition of PA-6 to the LiSPS10 ionomer disrupts the physical cross-linking effect of the cluster phase by interacting with some of the lithium sulfonate groups and thereby reduces E' and increases the measured height of the tan δ (blend) peak.

Since both these effects result in an increase of tanð, starting with the respective pure materials, a maximum of tanð is reached at some intermediate composition. The 70% ionomer blend represents a composition at which the combined disruption of the stiffening effects of the PA-6 crystalline and the ionomer cluster phases are at a maximum. Measurements of E" and E', taken at the temperature of the tanð (blend) peak positions, confirms that E' reaches a minimum at about 70% ionomer content (28 MPa vs. 650 and 158 MPa for the pure PA-6 and LiSPS10 respectively), while E" remains much less affected throughout the composition range (40-130 MPa range). Also, having eliminated the crystalline phase through the addition of LiSPS and having disrupted the cluster phase by the addition of PA-6, the 70% blend is now a one phase material (within the experimental limits) with optimum phase purity. This is supported by the narrowing of the transition width at this composition (19°C width at half height of the tanð peak as compared to 50 and 39°C for pure PA-6 and LiSPS10, respectively).

A similar though less distinct effect can be seen for the LiSPS5 ionomer blends where the tand peak heights reach a maximum for a blend containing about 75% LiSPS5. It is worth noting that at this composition A/Li is about 6, which further suggests that the maximum in the tand peak heights is not directly related to the co-ordination number of the lithium, and is rather due to the effects described above.

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At this point it is instructive to compare the effects of PA-6 with low molecular weight diluents on the two transitions of the ionomer. It has been shown that polar and non-polar diluents affect these transitions very differently: the addition of a non-polar diluent, such as diethylbenzene, to a polystyrene ionomer is found to decrease the transition temperatures of both the unclustered and the cluster phases of the ionomer; on the other hand, a polar diluent, such as glycerol, has been found to decrease rapidly the cluster phase tand peak height, and to be much less effective in decreasing the unclustered phase transition temperature 32. Polar diluents also increase significantly the unclustered phase transition $tan\delta$ peak height, as opposed to a decrease caused by non-polar diluents. Figure 4.6 shows that the addition of PA-6 to both the LiSPS5 and the LiSPS10 causes the rapid decrease of the cluster phase transition temperature $(T_{g(cl)})$ and a much more gradual decrease of the unclustered phase transition temperature of the ionomer $(T_{g(blend)})$. This, together with the sharp increase of the tan δ (blend) peak height (Figure 4.7) with small additions of PA-6 to these ionomers, indicates that the PA-6 acts in a way similar to a polar diluent. The addition of glycerol to polystyrene ionomers, as well as the addition of ethylene glycol to polyelectrolytes, increases the tand peak height at a rate of ca. 0.01/wt% of diluent^{32,33}. PA-6 increases the tan δ peak height at a rate of *ca*. 0.03 and 0.04/wt% PA-6 for the LiSPS5 and LiSPS10 ionomers, respectively. Polar diluents

for ionomers and polyelectrolytes tend to narrow the transition width of the blend phase, while non-polar diluents tend to broaden it^{32,34,35}. As mentioned earlier, PA-6 addition to the LiSPS ionomers (up to 25 wt% PA-6) results in the considerable narrowing of the transition width. It can therefore be concluded that PA-6 acts as an effective polymeric polar diluent for the LiSPS ionomers. In contrast, PA-6 acts as neither a polar nor a non-polar diluent for the NaSPS ionomer, being phase separated at all compositions.

4.5.3 Thermodynamics of blending: As was pointed out in the results section, the dynamic mechanical measurements of the lithium ionomer blends show that miscibility thresholds exist, separating one and two phase regions. When the ionomer contains 9.8 mol% of lithium sulfonate groups (LiSPS10) this miscibility threshold is between 10 and 30% ionomer content, while when the ionomer contains 5.4 mol% functional groups (LiSPS5) this miscibility threshold is found to be between 50 and 70% ionomer content. The compositions here refer to the total amorphous blend compositions at 240 - 250°C. It must be kept in mind that these miscibility thresholds are based upon the DMTA measurements and therefore reflect the phase behavior on the 50-100Å level. This phase behavior, together with the observed maximum in the T_g at 90% LiSPS10 content, can be given a theoretical interpretation. The thermodynamic treatment presented here is an approximate treatment; the limitations of DMTA and DSC in determining thermodynamic miscibility do not warrant a more fundamental approach. The derivations are merely presented to show that a simple unified treatment, even if based upon a few simplifying assumptions, can indeed correlate the miscibility thresholds and maximum in the $T_{\rm g}$ of the 90% LiSPS10 blend, and, furthermore, allow some predictions to be made about the behavior of the ionomers with other ion contents.

The Gibbs free energy of mixing, ΔG_m can be expressed in terms of the total heat of mixing, ΔH_m , and the total entropy of mixing, ΔS_m as:

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$$\Delta G_{\rm m} = \Delta H_{\rm m} - T \,\Delta S_{\rm m} \tag{4.1}$$

where T is the absolute temperature of the blend at which the miscibility is determined. For this analysis, the entropic term $-T\Delta S_m$ will be ignored due to the very low entropy of mixing for these high molecular weight polymers, relative to ΔH_m , as a result of which ΔG_m is expected to be dominated by ΔH_m . Thus, $\Delta G_m \approx \Delta H_m$. In the ensuing discussion, a negative free energy of mixing ΔG_m will be considered as a sufficient criterion for miscibility (see later for limitations of the analysis).

A) Random mixing: First, it will be shown that a random mixing approach cannot predict a composition dependent miscibility. Let the PA-6 be polymer 1 and the ionomer be polymer 2. ξ is defined as the fraction of lithium functionalized styrene units (LiS) of the ionomer, B_c as the interaction energy density associated with the complexing of a LiS unit with a PA-6 unit (PA), and B_s as the interaction energy density characteristic of a styrene unit - PA unit pair. It should be remembered that the PA and LiS units exist as associated species in the amorphous phase of the pure PA-6 and LiSPS, respectively, and therefore B_c represents the interaction energy density of a LiS - PA complex relative to these associated species. Uninteracted LiS groups are assumed to remain self associated in the blend, and therefore their contribution to the heat of mixing upon blending is zero. The random mixing enthalpy ΔH_m for polymers 1 and 2 can now be written as a sum of two van Laar type expressions³⁶:

$$\Delta G_{\rm m} \approx \Delta H_{\rm m} = B_{\rm c} \,\phi_1 \,\phi_2 \,\xi \,+\, B_{\rm s} \,\phi_1 \,\phi_2 \,(1-\xi) \qquad [4.2]$$

Here ϕ_1 and ϕ_2 represent the volume fractions of segment units, of polymers 1 and 2 in the blend and thus $\phi_1 = 1 - \phi_2$. The first term on the right reflects the contribution to ΔH_m due to the random contacts of lithium styrene sulfonate units with PA units, and the second term on the right represents the contribution due to the random interaction of styrene units (of the ionomer) with the PA units of the PA-6. The $\phi_1 \phi_2$ can be factored out, and an effective interaction energy density, defined by $B = [B_c \xi + B_s (1-\xi)]$, used to give $\Delta H_m = B \phi_1 \phi_2$. The blend is immiscible when $\Delta G_m > 0$, and can only be miscible if $\Delta G_m < 0$. A composition dependent miscibility therefore requires that ΔG_m be > 0 for some values of ϕ_2 , and $\Delta G_m < 0$ for others. Since *B* is independent of blend composition, and $\phi_1 \phi_2$ is always positive, the equation shows that the sign of ΔH_m , and hence ΔG_m , cannot be determined by changes in the relative amounts of 1 and 2. Thus, in the absence of entropic effects, a random mixing approach cannot predict a composition dependent miscibility of polymers 1 and 2.

The expression for $\Delta H_{\rm m}$ given by Equation [4.2] is similar to the equations developed to describe the miscibility of binary blends of random co-polymers³⁷⁻³⁹, with the exception that the random intramolecular interactions of LiS with styrene units are not represented. As mentioned earlier, the LiS units are strongly self associated, both in the pure ionomer and in the blend (if uninteracted), and hence the incorporation of a random intramolecular interaction term in Equation [4.2] would be unrealistic. However, even if such a term were included, the expression would still reduce to $\Delta H_{\rm m} = B \phi_1 \phi_2$, leading to the same conclusions as before.

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B) Non-random mixing: Several theories have been recently developed to describe the miscibility of polymer blends where specific interactions take $place^{40-45}$. The equation derived here has been specifically tailored to describe the blend system under study, but is similar to theories employing an equilibrium or quasichemical approach⁴³⁻⁴⁵. By assuming the interaction between the LiS units and the PA-6 units (PA) to be specific, and one to one, the equilibrium constant for the association of these two units to form an interacting LiS-PA complex is given by:

$$LiS + PA \rightarrow LiS-PA \qquad [4.3]$$

$$K = \frac{[\text{LiS-PA}]}{[\text{LiS}] [PA]} = \frac{(1/2) \phi_c V_r}{\{\phi_2 \xi - (1/2) \phi_c\} \{\phi_1 - (1/2) \phi_c\}}$$
[4.4]

where [LiS], [PA] and [LiS-PA] are the equilibrium molar concentrations of LiS, PA, and LiS-PA, respectively, while ϕ_c is the equilibrium volume fraction of the complex formed. $\phi_2\xi$ and ϕ_1 are the initial volume fractions of LiS and PA units, respectively. V_r is a reference volume and usually chosen so as to represent the molar volume of the smallest repeat unit, ca. 100 cm³/mol, for polymeric blends⁴⁶. V_r remains constant for the blend system and therefore $K_r = K/V_r$ will be used for convenience. The factor (1/2) arises in Equation [4.4] because the molar volume of the complex is approximately twice that of the reference volume. Equation [4.4] can be solved for $\phi_{c'}$ and for any given set of K_r and ξ , ϕ_c is only a function of ϕ_2 (or ϕ_1). The equation for non-random mixing can now be written as:

$$\Delta G_{\rm m} \approx \Delta H_{\rm m} = B_{\rm c} (1/2) \phi_{\rm c} + B_{\rm s} \phi_2 (1-\xi) \{1-\phi_2-(1/2)\phi_{\rm c}\}$$
[4.5]

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The first term on the right is the contribution to $\Delta H_{\rm m}$ due to the formation of the LiS-PA complex upon mixing, while the second term reflects the contribution due to the random interaction of the styrene units of the ionomer with the uncomplexed PA units of the polyamide. For any given set of values for $K_{\rm r}$, ξ , $B_{\rm c}$ and $B_{\rm s}$, the sign of $\Delta G_{\rm m}$, and hence miscibility of the blend, is now found to be a function of ϕ_2 . The miscible/immiscible threshold occurs at a composition $\phi_2 = \phi_2'$ where $\Delta G_{\rm m} = 0$ ($\phi_2' \neq 0$; $\phi_2' \neq 1$). Thus ϕ_2' at the miscibility threshold must satisfy

$$0 = \beta (1/2) \phi_{c} + \phi_{2}' (1-\xi) \{ 1-\phi_{2}'-(1/2)\phi_{c} \}$$
[4.6]

where $\beta = B_c/B_s$. For the LiSPS ionomer blends with PA-6, the lithium styrene sulfonate content of the ionomer, ξ , is known and the miscibility threshold composition, ϕ_2 ', can be reasonably well estimated from the results of the DMTA data. This leaves Equation [4.6] as a function of β and K_r (since ϕ_c is determined by the value of K_r).

The two ionomer blends (LiSPS5 and LiSPS10) provide two sets of conditions for Equation [4.6] ($\xi = 0.054$; $\phi_2'= 0.6$, and $\xi = 0.098$; $\phi_2'= 0.2$, respectively), and thus the two unknowns, β and K_r , can be estimated. Using an iterative calculating procedure, values of $\beta = -7.5$ and $K_r = 25$ fit the threshold miscibility ranges quite well. Note that ϕ_2 and the weight fraction w_2 of the ionomer in the blend are equivalent since the amorphous densities of the two polymers are about the same. It is also worth recalling that the miscibility thresholds used here are based upon the total blend compositions at 240 - 250°C, i.e. between 10 and 30wt% for LiSPS10 blends and between 50 and 70wt% for the LiSPS5 blends.

The profiles of ΔG_m as a function of composition are shown in *Figure 4.8* for various lithium sulfonate group contents of the LiSPS ionomer. As expected, ΔG_m is positive throughout the composition range for the unfunctionalized PS blends (0% in *Figure 4.8*), supporting the observed immiscibility of this blend at all compositions. On the other hand, the results of the analysis show that ΔG_m is negative throughout the composition range for an LiSPS ionomer having about 12 mol% lithium sulfonate groups, suggesting that this polymer may be miscible with PA-6 (on the DMTA scale) at all compositions. The LiSPS5 (5.4 % curve) and the LiSPS10 (9.8 % curve) ionomer blends are immiscible at compositions where $\Delta G_m > 0$, and, as can be seen from the profile of the ΔG_m - ϕ_2 curves, these blends should phase separate into an essentially pure PA-6 phase and a "blend" phase. The composition of the "blend" phase can be expected to be close to the compositions at which ΔG_m is a minimum.

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It is also worth noting that the assumed one-to-one association of the LiS with PA units does not imply that all the LiS are associated with amide units when there is a stoichiometric quantity of these groups in the blend. For instance, the LiSPS10 blend containing 90% ionomer has approximately stoichiometric quantities of the interacting groups, but by using the obtained $K_r = 25$ (and $\xi = 0.098$) and solving for ϕ_{cr} the fraction of interacted LiS ($0.5\phi_c/\phi_2\xi$) is only 0.56. The remaining uninteracted LiS units are self associated in the blend, and this is also supported by the observed presence of a cluster phase at this composition by DMTA (*Figure 4.6*). At 70% ionomer content, the calculated fraction of interacted LiS units available for the formation of a cluster phase, and consequently results in the inability of DMTA to detect such a phase at this composition.

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Figure 4.8 The predicted profile of ΔG_m using Equations [4.4] and [4.5] with $\beta = -7.5$ and $K_r = 25$ for blends of PA-6 with LiSPS ionomers having various mol% of functionalized units (as indicated).

C) T_g calculation: The blends of LiSPS10 ionomer with PA-6 show that there is a positive deviation of the blend T_g with composition, which reaches a maximum at 90% ionomer content (*Figure 4.1*). Several equations have been proposed to describe the variation of T_g with composition for miscible blends^{16,47-53}. Some of these equations are capable of predicting a positive deviation of the T_g -composition curve from the rule of mixtures^{16,51-53}, but only one of these is capable of directly relating this positive deviation of T_g to a thermodynamic parameter¹⁶:

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$$T_{g} = \frac{w_{1}T_{g1} + kw_{2}T_{g2}}{w_{1} + kw_{2}} - \frac{\chi R(T_{g2} - T_{g1})bw_{1}w_{2}}{\Delta C_{p1}(w_{1} + kw_{2})(w_{1} + bw_{2})^{2}}$$

$$[4.7]$$

where χ is the Flory-Huggins interaction parameter, ΔC_{pi} is the heat capacity change at T_{gi} for polymer i, b is the ratio of the amorphous densities of the two polymers and $k = \Delta C_{p2}/\Delta C_{p1}$. This equation has been successfully applied to ionomer blends with PA-6¹⁶, and is used here because it can be easily modified to replace the implied random mixing term $\chi R(T_{g2}-T_{g1})bw_1w_2$ with a nonrandom mixing term based upon the equations from the previous sections. As mentioned earlier, the amorphous densities of the two polymers are about the same, so b can be taken as unity, which in turn reduces the (w_1+bw_2) term to unity. Furthermore, since $\Delta H_m = \chi RTw_1w_2$ the expression for T_g can be rewritten as

$$T_{g} = \frac{w_{1}T_{g1} + kw_{2}T_{g2}}{w_{1} + kw_{2}} - \frac{\Delta H_{m}(T_{g2} - T_{g1})}{\Delta C_{p1}(w_{1} + kw_{2})T}$$
[4.8]

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where *T* is the temperature at which miscibility is determined. This equation can now be used to predict the T_g for the LiSPS10 blends with PA-6 by using Equation [4.5] for ΔH_m with $B_c = -7.5 B_s$ ($\beta = -7.5$), $T = 513 \text{ K} (240 ^{\circ}\text{C})$, $K_r = 25$, T_{g1} = 327 K (54 $^{\circ}\text{C}$), $T_{g2} = 407 \text{ K} (134 ^{\circ}\text{C})$, $\Delta C_{p1} = 0.37 \text{ J/g K}^{16}$ and $\Delta C_{p2} = 0.25 \text{ J/g K}$ (obtained from the DSC scans of the pure LiSPS10). Figure 4.9 shows that a good fit to the DSC T_g data is obtained for the essentially amorphous LiSPS10 blends (LiSPS10 content $\geq 50 \text{ wt\%}$) when $B_s = 120 \text{ J/g} (B_c = -900 \text{ J/g})$. The maximum at 90% ionomer content can thus be related to the blend interaction thermodynamics. Equations which do not take into account specific interactions, e.g. the frequently used Couchman equation⁴⁷, do not predict this type of T_g behavior.

D) Limitations of the thermodynamic treatment: The values for B_c and B_s appear quite large and these numbers should only be taken as approximations of these interaction energy densities. While the ratio of these two values, β , can be expected to be reasonable, the magnitude of B_c and B_s is essentially determined by the fit of Equation [4.8] to the experimental DSC data. The experimental limitations of DMTA and DSC, and also the assumptions of the thermodynamic treatment are bound to introduce some errors in the values obtained.

While DMTA is limited to the resolution of phases which are at least 50 - 100Å in size, the thermodynamic treatment ignores the second condition for a thermodynamically stable miscible blend: that the second derivative of the free energy with respect to composition be greater than zero $(\partial^2 \Delta G_m / \partial \phi_2^2 > 0)$. As can be seen from *Figure 4.8*, at $\phi_2 = 0.2$, for instance, the 12% curve is concave down (i.e. $\partial^2 \Delta G_m / \partial \phi_2^2 < 0$), even though ΔG_m is negative, and therefore the blend, if miscible, is thermodynamically unstable. It must be remembered that

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Figure 4.9 The T_g of blends of PA-6 with LiSPS10 as determined experimentally by DSC (hollow circles), compared to that predicted by using Equation [4.8] and the Couchman equation (solid lines).

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the thermodynamic treatment does not take the connectivity of the polymer units into account (except by ignoring the entropic effects, of course), and this connectivity may only allow micro-phase separation to take place for blends where the thermodynamic driving force for phase separation is small, i.e. blends where $\partial^2 \Delta G_m / \partial \phi_2^2 < 0$, but close to $\partial^2 \Delta G_m / \partial \phi_2^2 = 0$. Thus, while mathematically more complex, the location of the spinodal (compositions where $\partial^2 \Delta G_m / \partial \phi_2^2 = 0$) would only really be useful if miscibility could be determined on the molecular level. It is worth noting that the limerations of DMTA and the exclusion of the strict miscibility condition of $\partial^2 \Delta G_m / \partial \phi_2^2 > 0$ have the effect of balancing each other out, so that the simplified thermodynamic treatment may be closer to the true picture than one might expect.

The incorporation of the entropic term $-T \Delta S_m$ may also influence the profile of the ΔG_m - ϕ_2 curve, especially at the composition limits, but, as mentioned earlier, the influence of this term is expected to be minimal for these polymer blends where strong interactions appear to dominate the miscibility behavior.

In the equation for the prediction of T_g (Equation [4.8]), ΔH_m is assumed to vary linearly with temperature, since its true temperature dependence is unknown. Although this may be a source of some error, it is not believed to be large. The ΔC_p values in Equation [4.8] may also be a source of some inaccuracy, especially in blends with semi-crystalline polymers, since the ΔC_p at T_g of some semicrystalline polymers is not always proportional to the fraction of amorphous phase present⁵⁴. The ΔC_p of ionomers is also significantly reduced by the presence of ionic aggregation, and this is especially important at high ion contents⁵⁵. These factors may have a substantial effect on the ratio k in Equation [4.8] and may influence the $T_{\rm g}$ predicted for the semi-crystalline, ion-containing blends studied here.

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In the development of the equilibrium constant, the interaction between the LiS and the PA units is taken as one to one. Other A/Li ratios may also be possible, for example four to one, but the maximum in the T_g for the 90% LiSPS10 blend (A/Li = 1), suggests that a one to one interaction dominates the blend, at least at low PA-6 contents. The use of an equilibrium constant assumes an equilibrium state in the blend. Although the samples were held at 240 - 250°C in the melt for 5 to 10 min, and cooled relatively quickly, this may not have been adequate to establish an equilibrium state of the blends and to "freeze-in" the norphology. Since crystallization took place during the cooling of some of the blends, some re-arrangement does obviously take place. However, the driving force and kinetics for crystallization can be expected to be much higher than for phase separation (or mixing) in the amorphous phase, and therefore the experiments most probably reflect closely the amorphous phase morphology of these blends at 240 - 250°C.

Despite these limitations, the trends shown by the very simple thermodynamic analysis are expected to remain valid. It demonstrates that the composition dependent miscibility and the maximum in the T_g for the 90% LiSPS10 ionomer blend can be predicted by considering the interaction of the lithium sulfonate groups with the amide units in the blend to be specific, and the interaction of the styrene with the amide units to be random.

4.6 CONCLUSIONS

The DSC and DMTA results clearly show that the choice of counterion (Li vs. Na) is critical in determining the miscibility of polyamide-6 (PA-6) with sulfonated polystyrene ionomer. The lithium sulfonate group shows strong interaction with amide units of the PA-6, most probably with the carbonyl oxygen of the amide, and this results in strong miscibility enhancement of the lithium sulfonated polystyrene (LiSPS) ionomer with the PA-6. The sodium neutralized ionomer, on the other hand, is immiscible with PA-6 at the same level of functionalization.

PA-6 shows the characteristics of an effective polymeric polar diluent for the LiSPS ionomer, which is seen as the progressive disruption of the "cluster phase" of the ionomer and the increase of the tan δ (blend) peak height with PA-6 content. At a singular blend compositions, where the amide to lithium ratios are between 3 and 8, the tan δ (blend) peak height reaches a maximum and the transition width is also considerably narrowed. This composition represents a relatively homogeneous, single-phase blend at which the disruption of the crystallinity and the "cluster phase" are at a maximum.

The miscibility of the LiSPS ionomer with PA-6 depends on both the lithium sulfonate content of the ionomer as well as the relative quantity of the blend components. A simple non-random mixing approach is used to demonstrate that the miscibility behavior of these blends can be described by assuming a specific, non-random interaction of the lithium sulfonate groups with the amides, and a random, unfavorable interaction of the styrene units with the amide units of the PA-6. This simple thermodynamic treatment is incorporated into a recently

proposed equation for the prediction of the T_g of blends and it is shown that in this way the observed maximum in the T_g for the blend containing 90% LiSPS10 can be related to the specific interactions in the blend.

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Chapter 5

MISCIBILITY OF CARBOXYLATED AND SULFONATED POLYSTYRENE IONOMERS WITH POLYAMIDES-66, -610 AND -11

5.1 ABSTRACT

Differential scanning calorimetry (DSC) of blends of polystyrene ionomers and polyamide-66 shows that lithium sulfonate groups are more effective than lithium or sodium carboxylate groups in enhancing the miscibility between the polyamide and polystyrene. The miscibility between aliphatic polyamides and the most miscible polystyrene ionomer (containing 9.8 mol% lithium sulfonate groups) decreases as the amide content of the polyamide decreases. Thus, while blends with polyamide-66 and polyamide-610 appear miscible by DSC, the blends with polyamide-11 show evidence of some phase separation. Dynamic mechanical measurements of the 50:50 blends of this ionomer with PA-610 and PA-11 confirm the single phase and two phases behavior for these blends, respectively.

5.2 INTRODUCTION

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Miscibility enhancement between otherwise immiscible polymers is a subject of continuing academic and commercial interest 1-3. Since most polymer pairs are immiscible with each other, miscibility enhancement frequently represents a serious chalenge. Aliphatic polyamides constitute an important class of polymers with a wide variety of commercial applications, and the improvement of various mechanical, rheological and other properties of these materials is, therefore, of considerable importance. One of the ways of modifying these properties is by blending or alloying with other polymers. Although complete miscibility of the blend components is not always necessary to optimize properties, some favorable interaction between the components is almost always needed. Polyamides contain amide groups along the polymer backbone, and these offer sites amenable to specific interactions with other polymers, either through iondipole or through dipole-dipole interactions. Since ion-dipole interactions are stronger than dipole-dipole interactions, the functionalization of polymers with ionic groups is a particularly attractive way of compatibilizing various polymers with other polymers containing polar groups 7-10. The functionalization of polymers with between 0 and about 20 mol% of ionic groups, results in materials generally termed "ionomers".

A number of patents show that blends of polamides with polyethylene ionomers, containing ionic carboxylate groups (e.g. sodium methacrylate), can lead to dramatic improvements in the impact properties of polyamides¹¹⁻¹³. Numerous studies and patents show that these types of polyethylene ionomers can also be used to compatibilize blends of PA-6 with polyethylene or polypropylene¹⁴⁻¹⁸. These studies suggest that ionic carboxylate groups interact favorably with

/ 11 11 polyamides. Recently it has been shown that polyamide-6 (PA-6) can be compatibilized with polystyrene by functionalizing the polystyrene with ionic sulfonate groups¹⁹⁻²⁶ thus demonstrating that ionic sulfonate groups also inteact favorably with polyamides. Polyethylene ionomers containing ionic sulfonate groups are difficult to synthesize and, therefore, a comparison between 🕠 the miscibility enhancing effects of carboxylate vs. sulfonate ionic groups has not been made. However, polystyrene is relatively easily functionalized with both these functional groups; therefore, in this paper, the miscibility enhancement of these two groups are compared in blends of polystyrene ionomers with polyamide-66. Both Li and Na counterions are used for the ionomers since it has been previously shown, in blends of polystyrene ionomer with PA-6, that lithium sulfonate groups can lead to a single glass transition at certain blend compositions; by contrast, a two phase system results at all compositions when the ionic group is sodium sulfonate (ionic group content of 9.8 mol%) 24,28 . It will be shown that the lithium sulfonate groups interact more strongly with polyamide-66 than either the lithium or sodium carboxylate groups.

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Since the unfunctionalized polymers (i.e. polystyrene and polyethylene) are incompatible, the functional group content of the ionomer and amide content of the polyamide can be expected to play an important role in the miscibility enhancement obtained. A previous study has shown that when keeping the amide content of the polyamide constant (i.e. PA-6), the miscibility of the blend decreases as the lithium sulfonate content of the ionomer is decreased from 9.8 mol% to 5.4 mol%²⁵. In this paper the lithium sulfonate content of the ionomer is held constant at 9.8 mol% while the amide content of the polyamide in the blend is decreased. Here it is shown that, not unexpectedly, the miscibility enhancement of polyamides with lithium sulfonated polystyrene ionomers

decreases as the amide content of the polyamide decreases. Thus, while blends with polyamide-66 and polyamide-610 show a single composition dependent T_g by DSC, the blends with polyamide-11 show strong miscibility enhancement, but evidence of some phase separation. Finally, the miscibility information on blends of lithium sulfonated polystyrene ionomers with polyamides is incorporated into a "miscibility map" where areas of expected single phase behavior (on the DSC and dynamic mechanical scale) for 50:50 blends of this ionomer with various aliphatic polyamides is depicted. This is done as a function of the ionic group content of the ionomer and the amide content of the polyamide in the blend.

5.3 EXPERIMENTAL

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5.3.1 Materials used: Polyamide-66 (PA-66) and polyamide-610 (PA-610) were obtained from Aldrich and purified by dissolving in 88% fc...dc acid and precipitating into an excess of water. The polyamide-11 (PA-11) was purchased from Polysciences Inc. and purified by dissolving into trifluoroacetic acid and precipitating into an excess of water. The polyamides were dried under vacuum at 90°C for four days prior to use. Molecular weight information on these polymers is not available and thus the entropic effect on the miscibility of the blends could not be estimated. However, the strong interactions in the blends are expected to dominate, and the effects of the molecular weights on the miscibility of these polyamides with the ionomers are not considered important. The poly (styrene-co-methacrylic acid) was produced by free radical random copolymerization of styrene and methacrylic acid in conjunction with another project in this laboratory²⁷. This material contained 7.6 mol% of methacrylic acid groups and is designated as either LiMAPS8 or NaMAPS8, depending on

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whether the counterion is Li or Na, respectively. Polystyrene ($M_v = 280 \text{ kg/mol}$) was purchased from Aldrich and, after purification, was sulfonated to 5.4 and 9.8 mol% according to the method of Makowski *et. al.*²⁸. The sulfonated polystyrenes were neutralized with methanolic LiOH or NaOH, freeze dried, and dried under vacuum at 90°C for one week prior to use. The polystyrene ionomers containing 5.4 and 9.8 mol% lithium sulfonate groups will be referred to as LiSPS5 and LiSPS10, respectively. The ionomer containing 9.8 mol% sodium sulfonate groups will be referred to as NaSPS10.

5.3.2 Blend preparation: 5% (w/v) solutions of the pure materials were prepared by dissolving them in a volumetric flask using the following solvents: *m*-cresol/methanol (80:20) for all the ionomers and PA-66; *m*-cresol/methanol (88:12) for PA-610; *m*-cresol for PA-11. Volumetric amounts of the blend components were mixed under constant agitation, by the dropwise addition of the ionomer to the polyamide solutions. All of the blend solutions were clear, and were precipitated into an excess of hexanes. After thorough washing with fresh hexanes to remove the residual solvent, the precipitated blends were allowed to air dry, and then dried under vacuum at 140°C for one week. This drying procedure adequately removes residual solvent²⁵.

5.3.3 Differential scanning calorimetry: A Perkin-Elmer DSC-7 was used for the thermal analysis and was calibrated with indium. The sample cells were kept under a constant purge of dry nitrogen during the runs. The blend samples were first scanned at 100°C/min to the annealing temperature (see later), held there for 5 minutes, then cooled at 40°C/min to -10°C, held there for 2 minutes, and then scanned at 20°C/min to above the melting temperature of the blends. The annealing temperatures were chosen to be 20 to 35°C above the melting

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temperature (T_m) of the polyamide component, thus: 280°C for the blends containing PA-66 $(T_m \approx 260°C)$, 250°C for the blends containing PA-610 $(T_m \approx 220°C)$, and 225°C for blends containing PA-11 $(T_m \approx 190°C)$. The crystallization temperatures (T_c) were recorded during cooling, while the glass transition temperatures (T_g) and melting temperatures were recorded during the second heating scans. The T_g values were taken at the midpoint of the specific heat change, while T_m and T_c were recorded at the maximum of the endo/exotherms.

The amorphous phase composition of some of the semi-crystalline blends was estimated by correcting the total blend composition for the polyamide tied up in the crystalline phase. The weight fraction of crystalline material was estimated by dividing the normalized melting enthalpy of the blend, as obtained by DSC, by the heat of fusion for the 100% crytalline polyamide; the latter were taken as 196 J/g for PA-66, 200 J/g for PA-610, and 226 J/g for PA-11²⁹.

5.3.4 Dynamic mechanical thermal analysis: Samples for dynamic mechanical analysis were compression molded at 240°C (PA-610 blend) or 210°C (PA-11 blend) under low pressure. The sample dimensions were approximately 2 x 6 x 27 mm. A Polymer Laboratories DMTA instrument was used for the analysis, employing a small frame in dual cantilever mode. The samples were scanned at 1 Hz and 1°C/min from 0°C up to the sample melting points.

5.4 RESULTS

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Figure 5.1 shows the DSC data for the blends of the poly(styrene-comethacrylate) ionomers with polyamide-66 (PA-66). The presence of two



Figure 5.1 DSC data for blends of polyamide-66 with poly(styrene-co-sodium methacrylate) (left), and poly(styrene-co-lithium methacrylate) ionomers (right). The ionomers contain 7.6 mol% ionic groups.

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composition independent glass transition temperatures (T_g) and the negligible effect on the blend melting temperatures (T_m) indicate that these ionomers are not miscible with PA-66. However, the slight decrease of the crystallization temperature (T_c) with increasing ionomer content in the LiMAPS8 blends, compared to a relatively composition independent variation of T_c for the NaMAPS8 blends, does suggest that the LiMAPS8 ionomer may hinder the crystallization process marginally more than the NaMAPS8 ionomer. The slight shift of T_{g1} and T_{g2} towards each other for the LiMAPS8 ionomer blends also suggests that the Li neutralized MAPS8 ionomer may be marginally more miscible with the PA-66 than the Na neutralized ionomer. It is worth noting that the T_c values for both of the ionomer blends at 90% ionomer content were difficult to locate from the DSC runs. This is probably due to a broadening of the crystallization exotherms and the low amount of crystallizable PA-6 in the blend at these compositions, which results in a weak signal.

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The behavior of the blends of PA-66 with the lithium sulfonated polystyrene ionomers are shown in *Figure 5.2*. For the LiSPS5 ionomer blends (5.4 mol% lithium sulfonate group content), (*Figure 5.2*: *left*), the variation of $T_{m'} T_{c'} T_{g1}$ and T_{g2} are markedly different to those of the MAPS8 ionomers: the T_m and T_c both decrease with increasing LiSPS5 ionomer content until, at 90% ionomer content, the blend is amorphous (no T_m or T_c); T_{g1} and T_{g2} also shift significantly towards each other. The depression of T_m with ionomer content could be due to a less perfect crystalline structure of the PA-6 crystals³⁰ or to some miscibility of the blend components³¹, or both. In either case, some interaction of the blend components would be needed. The shifting of the blend component glass transition temperatures towards each other also implies some miscibility enhancement. Thus, the LiSPS5 ionomer shows considerably greater miscibility



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____= ______ enhancement with PA-66 than either the NaMAPS8 or LiMAPS8 ionomer, despite its lower ionic group content (5.4 mol% vs. 7.6 mol% for the MAPS8 ionomers). Increasing the ionic group content of the LiSPS ionomer to 9.8 mol% (*Figure 5.2: right*), results in a single composition dependent T_g . Furthermore, there is no crystallinity when the ionomer content is greater than 50%.

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The blends of the sodium neutralized ionomer (NaSPS10) with the PA-66 (figures not presented here) show a series of transitions by DSC similar to those for the NaMAPS8 ionomer blends (*Figure 5.1: left*), indicating that this ionomer is immiscible with PA-66.

To test the effect of decreasing the amide content of the polyamide on the miscibility of the LiSPS10 with the polyamides, DSC was used to analyse the blends of LiSPS10 ionomer with PA-610 and PA-11. The miscibility of the Li and NaMAPS8 ionomers with these polyamides was not tested, since it can be inferred, from the immiscibility of these ionomers with PA-66, that they would be also be immiscible with polyamides having an even lower amide content than PA-66. Figure 5.3 (left) shows the DSC data for the blends of LiSPS10 with PA-610. The presence of a single composition dependent $T_{g'}$ as well as the decrease of both $T_{\rm m}$ and $T_{\rm c}$ with increasing ionomer content in the blend, reflect the strong miscibility enhancement of the ionomer with this polyamide. The $T_{\rm m}$ and $T_{\rm c}$ also decrease with increasing ionomer content in the PA-11 blends (Figure 5.3: right). On the other hand, the PA-11 blends indicate the possible presence of two composition dependent glass transition temperatures: the lower $T_{\rm g}$ increases with ionomer content until, at the 50 and 70% compositions, two transitions are detectable, and only the higher $T_{\rm g}$ then persists to higher ionomer contents.

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Figure 5.3 DSC data for blends of LiSPS10 with polyamide-610 (left) and polyamide-11 (right). The * indicates that compositions refer to the amorphous phase only, as in *Figure 5.2*.

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The precise position of the glass transition temperatures is difficult to determine from the straight DSC scans, and a clearer picture can be obtained on the position and breadth of these transitions from the first derivative of the DSC traces. A series of such curves for the LiSPS10 blends with PA-11 are depicted in Figure 5.4. It is worth noting that a glass transition appears as a peak in these plots. It can be seen that the broad peak on the PA-11 curve (ranging from about 25°C to 75°C), which is associated with the T_g of the PA-11, moves to higher temperatures as the ionomer content is increased from 0 to 70%. At the same time, the transition width also narrows, until it measures about 30°C for the blend containing 70% ionomer. The transition widths are taken as T_{g} (completion) - T_{g} (onset) . In the samples containing 0, 10 and 30% ionomer, some features can be seen occuring at temperatures above the glass transition temperatures. These are most probably associated with multiple melting endotherms of different crystalline phases, as is often seen in aliphatic polyamides. This is supported by the progressive shifting of these features to lower temperatures with increasing ionomer content in the blend (dashed lines in Figure 5.4, connecting peak positions), following the trend of the principal melting endotherm (T_m in Figure 5.3: right). The up-turns of the first derivative curves occurring between 150 and 170°C, for the blends containing 0, 10, 30, and 50% ionomer, are due to the principal crystalline melting endotherms in these blends. While a second glass transition is not detectable in the blends containing 10 and 30% ionomer, the first hint of a possible second glass transition temperature is shown for the blend containing 50% ionomer and is seen as a low but broad hump centered around 115°C (shown by "a" in Figure 5.4). This second glass transition appears more pronounced for the blend containing 70% ionomer, and becomes dominant for the blend containing 90% ionomer. Note that the glass transition of the 30% blend occurs at a temperature higher than might be

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Figure 5.4 First derivative curves of the DSC scans for the LiSPS10 blends with PA-11. The numbers refer to the weight % of LiSPS10 ionomer in the blend, while the dashed lines show the position of features that are most probably due to melting of crystallites. The "a" shows the position of a possible second glass transition.

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expected from the general trend, and this is also seen for the LiSPS10 blend with PA-610 (*Figure 5.3: left*). The reason for this is not clear, but is possibly a result of the influence of crystallinity in these blends.

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Dynamic mechanical thermal analysis (DMTA) can often resolve the presence of one or two phases in a much less ambiguous way than DSC. Therefore, it can be used to confirm the single phase behavior of the 50:50 blend of LiSPS10 with PA-610, and the apparent two phase behavior of the 50:50 blend with PA-11, as seen by DSC. The results of DMTA for 50:50 blends of LiSPS10 ionomer with PA-610 and PA-11 are depicted in Figure 5.5. The PA-610 blend (Figure 5.5: left) is clearly a one phase system (on the scale accessible to DMTA), and this is shown by the single drop of the storage modulus (E') and the single peaks of both the loss modulus (E") and the tanô. The drop of E' at about 200°C is caused by the melting of the PA-610 crystalline phase, and is not associated with a glass transition, as is confirmed by the simultaneous drop in the E" at this temperature. The single glass transition temperature of this blend suggests that the blend components are miscible on the 50 to 100Å level, reflecting the resolution limit of the dynamic mechanical technique. On the other hand, the PA-11 blend (Figure 5.5: right) shows evidence of two glass transitions. This is seen as a two sloped decrease of E' with temperature at around 125°C, and the presence of humps on the E'' and $tan\delta$ curves. These humps are a result of two overlapping glass transitions and this is especially evident in the tan δ profile. Again, the simultaneous drop of E' and E" at around 180°C is due to the melting of the PA-11 crystalline phase.

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Figure 5.5 Dynamic mechanical data (1 Hz) for the 50:50 blends of LiSPS10 with PA-610 (left), and with PA-11 (right).

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5.5 DISCUSSION

The DSC results on the blends of LiSPS and MAPS8 ionomers with PA-66 unambiguously show that lithium styrene sulfonate groups are more effective in enhancing the miscibility between polystyrene and PA-66 than either lithium or sodium methacrylate groups. Some basis for this difference in interaction strength can be obtained by considering the way that the ionic groups interact with the amide groups. In one study it has been suggested that ion-dipole interactions between the Li cation and the amide nitrogen may take place²³. Based upon earlier studies on mixtures of LiCl salts with model amides³²⁻³⁶ and polyamides³⁷⁻⁴⁰ it has also been suggested that the Li cations may rather interact with the carbonyl oxygens of the amides, with the resulting sulfonate anions interacting with the amide hydrogens²⁵. Assuming that the latter interaction mechanism is the correct one, it is reasonable to expect that a similar mode of interaction also occurs in the blends of LiMAPS with polyamides. Thus, the interactions of the Li sulfonate and Li carboxylate groups with amides could be written as:

$$-SO_3^-Li^+ + HN + \dot{\zeta}O \longrightarrow -SO_3^-HN + \dot{\zeta}O Li^+$$
[1]

$$-COO^{-}Li^{+} + HN + CO \longrightarrow -COO^{-}HN + CO Li^{+}$$
[2]

The NH and CO are indicated as independent of each other because the interactions could be with the same or with different amide units in the blends. Equations [1] and [2] essentially represent the dissociation of the $-SO_3Li$ and -COOLi salts by the polar amide groups, and is akin to the dissociation of acids in water. Since the counterions (H *vs.* Li) are the same for the two types of anions in

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the acid and salt cases, dissociation constants of acids in water can provide some insight into the relative stability of the $-SO_3^-$ and $-COO^-$ anions in polar diluents, such as water or amides. Dissociation constants of acids in water at 25°C are given as follows⁴¹: benzenesulfonic is 2×10^{-1} (pK = 0.70); benzoic is 6.46×10^{-5} (pK = 4.19); acrylic is 5.6×10^{-5} (pK = 4.25). Thus the higher dissociation constant of sulfonate anions (benzenesulfonic acid) *vs.* carboxylates (benzoic and acrylic acid) suggests that the reaction given by Equation [1] is more likely to occur than that shown by Equation [2]. To some extent, this can explain the better miscibility enhancement obtained with lithium styrene sulfonate groups as opposed to lithium methacrylate groups.

It is worth noting that the marginal co-miscibility of the LiMAPS8 ionomer with PA-66 (as compared to none with NaMAPS8 ionomer), is not entirely unexpected: several studies have shown that ionomers having Li counterions are more effective in enhancing the miscibility with polar polymers than ionomers with Na counterions^{10,21,25,42}. This is generally attributed to counterion size and surface charge density differences.

The miscibility behavior of the blends of LiSPS10 and LiSPS5 ionomers with PA-66 parallel the results obtained for the blends of these ionomers with PA-6. In both cases the blends with LiSPS10 ionomer show strong miscibility enhancement (a single composition dependent T_g by DSC, and a maximum of the T_g at 90% LiSPS10 content²⁵), while the blends with LiSPS5 ionomer are only partially miscible. A notable difference is the absence of crystallinity at 70% LiSPS5 content for the blend with PA-66 as opposed to the presence of some crystallinity for the blend with PA-66, as shown by the measured T_m and T_c in *Figure 5.2* (left). The glass transition temperatures of PA-6 and PA-66 are about

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the same ($T_g \approx 50^{\circ}$ C), but the melting temperature of PA-66 is considerably higher than that of PA-6 (260 vs. 220°C). Since crystallization must take place between $T_{\rm m}$ and $T_{\rm g}$, the higher melting temperature of the PA-66 affords a larger temperature interval $(T_m - T_g)$ for the crystallization of the PA-66 during the DSC experiment than for the PA-6. Indeed, during the slow heating run (1°C/min) of the dynamic mechanical analysis of the PA-6 blend, crystallization is also found to occur 25 . Thus, the presence or absence of crystallinity in the 70% ionomer blends is most probably a kinetic rather than a miscibility effect, and, from the similarity of the glass transition behavior, it can be concluded that the extent of miscibility of the LiSPS ionomer with PA-6 or PA-66 is about the same. Furthermore, the immiscibility of the NaSPS10 ionomer with PA-66 also parallels the result found for the blend of this ionomer with PA-6. Since PA-6 and PA-66 both have the same amide content and only differ in the way that these amide groups are arranged along the polymer backbone, the results show that the miscibility is not affected by minor structural differences and is mainly dependent upon the concentration of amide and lithium styrene sulfonate groups in the blend.

As the concentration of either the lithium styrene sulfonate or amide groups decreases in the blend, the driving force for miscibility also decreases, as is seen when the lithium styrene sulfonate content is decreased from 9.4 to 5.4 mol% in the blends with PA-66. One way of describing the amide content of aliphatic polyamides is by considering one polymer "unit" to consist of two backbone atoms. Using this definition, the aliphatic polyamides then consist of regular sequences of ethylene and amide units. Thus PA-66 (or PA-6) contains 28.6 mol% amide units while PA-610, PA-11 and polyethylene contain 22.2, 16.7 and 0 mol% amide units, respectively. The DSC and DMTA results show that while the

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blends of LiSPS10 with PA-610 are single phase, the blends with PA-11 are two phase. This trend is as expected since the number of favorable interactions between the amide and the lithium sulfonate groups decreases as the amide content in the blend decreases, with a simultaneous increase in the number of unfavorable interactions between the styrene and the ethylene units.

By restricting the description of miscibility to the DMTA level (domain resolution of 50-100Å⁴³⁻⁴⁵) and to the 50:50 blends, and by taking the miscibility information into account, it is possible to roughly predict "miscible" and immiscible blends, as a function of the amide (NHCO) and lithium sulfonate (-SO₃-Li⁺) content of the polyamide and LiSPS, respectively. In this way a "miscibility map" can be drawn by considering the miscibility of functionalized polystyrene with polyamides. The blend of LiSPS5 (5.4 mol% -SO₃-Li⁺) with PA-66 (or PA-6) represents a blend on the miscibility threshold, while another miscibility threshold exists between the blends of LiSPS10 (9.8 mol% -SO₂-Li⁺) with PA-610 and PA-11, i.e. between 22.2 and 16.7 mol% NHCO, as previously discussed. Polyethylene (PE) is not expected to be miscible with LiSPS, regardless of the mol% -SO₃⁻Li⁺, due to the strong self-association of the -SO₃⁻ Li⁺ groups and the lack of polarity of PE. Unfunctionalized polystyrene is known to be immiscible with PE, and is not expected to be miscible with any of the polyamides, as has been shown for PA- 6^{22} . Therefore, the 0 mol% axes describe immiscible blends on a "miscibility map". Such a miscibility map is shown in Figure 5.6, with the shaded "miscibility" region drawn to satisfy the miscibility considerations and experimental results, as discussed. Note that the "miscible"/"immiscible" boundaries are not well defined at the 15 to 20 mol% -SO3-Li⁺ range and the 0 to 4 mol% NHCO range, and some additional experimental points would be helpful in locating the boundaries more precisely.



Figure 5.6 "Miscibility map" for 50:50 blends of lithium sulfonated polystyrene ionomers (LiSPS10) with polyamides. The shaded region represents expected single-phase behavior of the blends when analyzed by DMTA or DSC.

However, the shaded "miscible" region in *Figure 5.6* has been estimated rather conservatively, so that the miscibility region at high $-SO_3$ ^{-Li⁺} or NHCO contents, as determined by DMTA, may actually be larger than shown.

From this miscibility map, it can be predicted that 50:50 blends of polyamides-4 and -46 (40 and 33.3 mol% NHCO, respectively) should be miscible (on the DMTA scale) with LiSPS containing $\geq 5 \mod \%$ -SO₃⁻Li⁺ groups; while 50:50 blends of polyamides-4, -46, -6, -66, -69 and -610 (40, 33.3, 28.6, 28.6, 23.5, and 22.2 mol% NHCO, respectively) can all be expected to be miscible with LiSPS containing $\geq 10 \mod \%$ -SO₃⁻Li⁺. Polyamides-11 and -12 (16.7 and 15.4 mol% NHCO, repectively) may only show single phase behavior when the LiSPS10 has 15 to 20 mol% -SO₃⁻Li⁺ groups.

It must be remembered that the miscibility of the LiSPS with polyamides can be expected to be composition dependent. A detailed study, using dynamic mechanical measurements, of the phase behavior of LiSPS ionomers with PA-6 has shown that the miscibility of these two polymers is not only dependent on the ionic group content of the ionomer, but also on the blend composition²⁵. For example, if the ionomer contains 5.4 mol% lithium sulfonate groups, the blend shows a single glass transition only if the ionomer content is greater than 50 wt%. If the ionomer has 9.8 mol% ionic groups, a single phase occurs only if the ionomer content is greater than 10 wt% in the blend. Calculation has suggested that the polystyrene ionomer containing 12 mol% lithium sulfonate groups can be expected to be miscible throughout the composition range (by DMTA and DSC). These results are plotted in *Figure 5.7* which then represents a "cut" along the PA-6 line of *Figure 5.6*. In this way the two dimensional "miscibility map" of *Figure 5.6* could be extended into a third dimension, i.e. blend composition. It has

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Figure 5.7 Single phase blends (filled symbols and shaded region) of the LiSPS ionomer with PA-6 as a function of composition and lithium sulfonate content. Experimental points from ref. 22.

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also been shown that this composition dependent miscibility can be related to the specific interaction of the lithium sulfonate groups of the LiSPS with the amides of the polyamide²⁵. This can be expected to be a general rule for blends of LiSPS ionomers with aliphatic polyamides, so that miscibility would always improve with ionomer content. Taking this composition dependent miscibility into account, the shaded region of the miscibility map of *Figure 5.6*, therefore, defines a lower miscibility limit for blends containing > 50 wt% ionomer. Despite the limited experimental data, and the limitations of DMTA in resolving phases smaller than 50 - 100Å in size, this map does provide a useful guide for choosing miscible polymer pairs.

5.6 CONCLUSIONS

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It has been shown that polystyrene ionomers containing lithium or sodium methacrylate groups are much less effective in enhancing the miscibility between polystyrene ionomers and polyamide-66 than lithium styrene sulfonate ionic groups. This can be expected to be a general rule for blends of ionomers with aliphatic polyamides.

The miscibility of the lithium sulfonate functionalized polystyrene ionomer (LiSPS) with aliphatic polyamides decreases with a decrease of the functional group content of the ionomer, or a decrease of the amide content of the polyamide, or both. Thus, 50:50 blends of LiSPS_(containing 9.8 mol% lithium sulfonate groups) with polyamide-610 show a single glass transition by dynamic mechanical analysis, while the blends with PA-11 show the presence of two phases. However, even in the two phase PA-11 blends, considerable miscibility

enhancement occurs, as can be seen by the significant shifting of the glass transitions of the blend components towards each other.

A "miscibility map", defining single phase regions as a function of ionic group content of the LiSPS and the amide content of the polyamide is drawn as a guide to expected miscibility on the 50 - 100Å level for 50:50 blends of LiSPS with aliphatic polyamides.

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5.7 ACKNOWLEDGEMENTS

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Chapter 6

SULFONATED POLY (STYRENE-ETHYLENE-BUTYLENE) IONOMERS :

SYNTHESIS AND CHARACTERIZATION



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Sulfonated poly (styrene-ethylene-butylene) ionomers were obtained by the hydrogenation, and subsequent sulfonation and neutralization of poly(styrene-butadiene) random copolymers. The poly(styrene-butadiene) random copolymers, containing 5, 23, and 45 wt% styrene, were selectively hydrogenated at 50°C and 350 psi by using H₂ and Wilkinson's catalyst in *p*-xylene. The amorphous hydrogenated polymer (now containing 44 wt% styrene), was sulfonated in chloroform, using either acetyl sulfate or lauryl sulfate as a sulfonating reagent, and neutralized with various counterions to produce the ionomers. Dynamic mechanical characterization of these ionomers revealed the presence of a "low T_g " and a "ciustered" phase, which is typical of many random

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ionomers. With increasing ion content, the glass transition of the low T_g phase remains at around 0°C, while that of the clustered phase increases at about 8°C/mol%.

6.2 INTRODUCTION

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Recently it has been shown that sulfonated polystyrene ionomers can enhance considerably the miscibility between polystyrene and aliphatic polyamides¹⁻⁸. However, aliphatic polyamides are semi-crystalline polymers, and this complicates somewhat the interpretation of the phase behavior in the blends of these materials with ionomers. Amorphous polyamides are also available, and usually consist of a random distribution of aromatic and aliphatic segments which serves to break up the regular sequences in the polymer. Due to the presence of the aromatic moiety, these materials usually have a glass transition temperature of between 130 and 150°C (e.g. Selar[®] supplied by Du Pont). Since polystyrene ionomers have a glass transition temperature (T_g) falling in this same temperature range, it is difficult to study the miscibility of these ionomers with amorphous polyamides using the presence of a single glass transition temperature as a miscibility criterion. Therefore, a sulfonated ionomer having a T_{g} that is well removed from the T_{g} of the amorphous polyamide, by at least 20°C (but preferably more than 60°C), is desirable for this type of study⁹. Low T_g ionomers are particularity attractive, since they do not necessitate the use of high temperatures during thermal analysis of the blend (which could lead to degradation), and, furthermore, offer the possible advantage of improving the impact property of the blend. Thus, a low T_g , amorphous sulfonated ionomer is needed.

The sulfonation of unsaturated carbon double-bonds can be achieved readily and, a number of sulfonated rubbers have been prepared in this way¹⁰⁻¹⁵. However, the high reactivity of the unsaturated linkages leads to cross-linking and cyclization during sulfonation^{14,15}. The residual unsaturation after sulfonation also renders these polymers unstable in the solid state¹¹. This latter problem can be overcome by hydrogenating the residual unsaturation, but this often leads to semi-crystalline ionomers, as is the case for sulfonated polypentenamers¹¹.

Another way of overcoming the cross-linking/cyclization and instability problems is by limiting the amount of unsaturation in the starting polymer to the extent of the desired sulfonation. This is done in the synthesis of sulfonated ethylene-propylene-diene terpolymers (EPDM)^{10,12,13}. The principal disadvantage of this technique is that the extent of sulfonation is limited by the number of double bonds so that a broad range of ion contents cannot be obtained by using the same base polymer. Furthermore, the synthesis of these type of terpolymers is complex, and not readily performed in an academic laboratory¹⁶.

This paper reports the synthesis of a stable, amorphous, sulfonated low T_g ionomer based on hydrogenated sulfonated poly(styrene-butadiene) random copolymers. The starting material for the synthesis is a poly(styrene-butadiene) random copolymer, which is easily prepared through emulsion polymerization and is also commercially available at relatively low cost. The first step involves the removal of the unsaturation, through the selective hydrogenation of the carbon double bonds, to yield a styrene-ethylene-butylene terpolymer. The second step involves the sulfonation of the styrene groups of the terpolymer to

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the desired extent, and, finally, the neutralization of the sulfonated styrene groups to yield the ionomer. The synthetic scheme is shown in *Figure 6.1*.

6.3 EXPERIMENTAL

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6.3.1 Materials: Three poly(styrene-butadiene) random copolymers containing 5, 23 and 45 wt% styrene were purchased from Scientific Polymer Products Inc., and will be referred to as PSB-5, PSB-23 and PSB-45, respectively. These materials were purified by dissolving in toluone to 3% (w/v) solutions and precipitating into an excess of methanol. The average molecular weights of these polymers were determined by viscometry to be 250, 310 and 200 kg/mol for the PSB-5, -23, and -45, respectively (in toluene at 25°C, using Mark-Houwink coefficients of K=52.5 x 10⁻³ ml/g and a=0.667, obtained for a styrene/butadiene random copolymer containing 25 wt% styrene¹⁷). Infra-red spectroscopy indicated that about 10% of the 1,4-butadiene was in the *cis* form in these materials. The styrene, 1,4-butadiene and 1,2-butadiene content of these polymers was determined by ¹H NMR (see *Table 6.1*).

6.3.2 Hydrogenation: 30 grams of PSB were added to 600 ml of *p*-xylene (HPLC grade purchased from Aldrich) and stirred for two to three days until it dissolved. Dissolved gases were removed by three freeze-pump-thaw cycles and the solution was then placed into a two liter Parr pressure reactor (Parr Instrument Co). 20 mg Wilkinson's catalyst, tris (triphenylphosphine) rhodium (I) chloride, (Aldrich) was added for every gram butadiene in the solution, and the reactor vessel closed, purged with hydrogen gas, and pressurized up to 350 psi with H₂. The hydrogenation reaction was allowed to proceed at 50°C for 36



Figure 6.1 Schematic diagram outlining the synthetic scheme.

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hrs under constant agitation. The hydrogenated form of the PSB-5, PSB-23 and PSB-45 will be referred to as PSE-5, PSE-23 and PSE-45 respectively. The hydrogenated materials were diluted by the addition of xylenes (PSE-5 and PSE-23) or chloroform: xylenes (1:1) (PSE-45) to yield a 1% (w/v) solution, and were then precipitated into an excess of hot methanol (50°C). This was repeated three times to remove as much of the residual catalyst as possible. The polymers were dried in a vacuum oven at 80°C for 5 days, and kept in a desiccator until use.

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6.3.3 Sulfonation: A modification of the methods of Makowski *et. al.*¹⁸ and Thaler¹⁹ were used for the sulfonation of the PSE-45. Sulfonation of PSE-45 was typically carried out according to the following procedure: 3g PSE-45 was placed in 150 ml of chloroform (Aldrich, HPLC grade) and was stirred at 50°C under dry nitrogen for 24 hrs to ensure dissolution of the polymer. The appropriate amount of sulfonating reagent (see later) was charged into the solution and the reaction allowed to continue for 12 hrs at 50°C under a dry nitrogen blanket. The product was recovered by steam stripping and was purified by repeated swelling in water or methanol (*ca.* 200 ml), agitating in this solution for 24 hrs, and subsequent decanting and washing. This purification process was repeated three times. The product was stored in a "wet" form in a sealed container until further use.

One of two reagents was used for the sulfonation reaction, depending on the desired sulfonation level: reagent A consisted of 2 ml of 95% H_2SO_4 (ACP Chemicals Inc) premixed with 5.6 ml acetic anhydride (A&C American Chemicals) in 100 ml chloroform (HPLC) at 25°C; reagent B consisted of 3.7 ml of 99% CISO₃H (Aldrich) premixed with 12.8 g lauric acid (Eastman Organic Chemicals) in 100 ml chloroform (HPLC). Assuming 100% conversion the

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amount of reagent A needed was calculated to be 0.98 ml per gram of polymer, per mol percent sulfonation needed, and that for reagent B was calculated to 0.87 ml per gram of polymer, per mol percent sulfonation.

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6.3.4 Neutralization: The sulfonation level was determined by titrating a small amount of polymer with a standardized tetramethyl ammonium hydroxide (TMAH) solution in xylenes:*n*-butanol (3:1). The most consistent results were obtained by using the following procedure: to a tared flask were charged 0.5 g of wet polymer, 50 ml of xylenes: *n*-butanol (3:1) and several drops of Thymol Blue indicator solution (0.6g in 250ml absolute ethanol). The solution was titrated with 0.0218N TMAH to the first characteristic red/yellow color change. The solvents were removed using a rotary vacuum apparatus, the flask and product dried at 90°C under vacuum for 5 days, and then weighed. From the obtained weight of the product and the amount of TMAH solution used for the titration, the sulfonation level was calculated.

The bulk neutralization of the samples with various metal counterions was carried out by dissolving the "wet" sulfonated polymer in xylenes: *n*-butanol (3:1) to a 5% (w/v) solution and slowly adding the methanolic metal hydroxide (*ca*. 0.1N) to the first Thymol Blue transition. Some of the polymer solutions turned cloudy before 100% neutralization was achieved, and the addition of methanol to these solutions usually resulted in some clarification of these solutions.

The ionomers will be identified by the designation XM-SPSE-45, where X is the mol% ionic group content and M is the counterion type. Thus, 15Na-SPSE-45 represents a sulfonated PSE-45 ionomer containing 15 mol% sodium sulfonate groups.

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6.3.5 Characterization: The products and the starting materials were characterized by using nuclear magnetic resonance spectroscopy (NMR), Fourier-transform infra-red spectroscopy (FTIR), elemental analysis, differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA).

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NMR: ¹H NMR spectra were recorded on a 200 MHz Varian XL 200 spectrometer. Chloroform- d_1 (MSD Isotopes) was used as solvent for the PSE-23, PSE-45 and all three PSB materials, while *p*-xylene- d_{10} (Aldrich) was used for the PSE-5. Dimethyl sulfoxide- d_6 (MSD Isotopes) was used as solvent for the ionomers.

FTIR: An Analect model AQS-20 spectrometer was used to record the infra-red spectra. A resolution setting of 2 cm⁻¹ and 30-64 scans were utilized. Samples were cast as thin films on KBr windows.

Elemental analysis: Elemental analysis was used to determine the extent of sulfonation of the PSE-45 materials from the sulfur to carbon ratios. It was performed by Guelph Laboratories Ltd. The average of two determinations was used to establish the extent of sulfonation.

DSC: A Perkin Elmer DSC II, calibrated with indium, was used to record the glass transition (T_g) , and melting temperatures (T_m) of the PSB and PSE samples. The samples were first heated to 120°C then cooled to -100°C at 20°C/min, held at this temperature for 2-5 min and there scanned at 20°C/min. T_g and T_m were recorded during the second heating scan. The T_g was taken at the midpoint of

the heat capacity change while $T_{\rm m}$ was recorded at the maxima of the endotherms.

TGA: A Seiko 220 TG/DTA instrument was used to record the weight loss of the samples. The samples were scanned at a heating rate of 10°C/min under nitrogen (200 ml/min).

DMTA: Samples for DMTA were molded at about 200°C under low pressure. A Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) was used to record the dynamic mechanical properties of the materials using frequencies of 0.3, 1, 3, 10 and 30 Hz and a heating rate 1°C/min. To estimate the activation energies of the transitions, an Arrhenius plot of the reciprocal of the absolute transition peak temperatures against the logarithmic frequencies was used.

6.4 RESULTS AND DISCUSSION

6.4.1 Synthesis and Structural Characterization:

Hydrogenation: Several techniques exist for the selective hydrogenation of butadiene in random copolymers of butadiene with other comonomers²⁰⁻²⁶. Catalysts, such as platinum black²², *p*-toluenesulfonylhydrazide²³ and Wilkinson's²⁴⁻²⁶ have been used successfully. Since Wilkinson's catalyst was found to be extremely efficient in the selective hydrogenation of styrene/butadiene star-block copolymers²⁶, which contain the same two monomers (styrene and butadiene) as the PSB, this catalyst was also chosen for the present study. *p*-Xylene was used as the solvent for the hydrogenation ^o reactions as opposed to the methyl ethyl ketone (MEK) used for the star


copolymers. This ensured the solubility of the high molecular weight PSB materials during the reaction since *p*-xylene is a good solvent for ethylene. After the reaction, the hydrogenated PSB-5 material (PSE-5) was found to form a gel in this solvent at room temperature. The formation of polyethylene gels in various solvents including *o*-xylene, has been previously reported, and this is a function of both the concentration and the temperature of the solution²⁷. The PSE-5 gel again formed a clear solution when heated or diluted to a 1% (w/v) solution, so that subsequent purification by precipitation was easily accomplished.

The efficiency of the hydrogenation reaction was monitored by FTIR and NMR spectroscopy. The FTIR spectra of the PSB materials clearly show diene bands at 965 and 910 cm⁻¹ (*trans* form) and 995 cm⁻¹ which disappear after hydrogenation. This is shown in *Figure 6.2* (top) for PSB-45 and its hydrogenated derivative, PSE-45. As can be seen, the styrene bands at 700 and 760 cm⁻¹ remain unchanged. The proton NMR spectra show the complete elimination of the olefinic proton resonances in the 4-6 ppm region for the PSE materials (*Figure 6.2: bottom*) and suggests that the hydrogenation is essentially quantitative. *Table 6.1* lists the compositions for the PSB materials before, and after hydrogenation (PSE materials). The compositions of the PSB materials were determined by NMR from the integrated areas under the peaks corresponding to the aromatic protons (6.5 - 7.5 ppm), olefinic protons of the 1,4-butadiene (*ca.* 5.5 ppm), olefinic protons of the 1,2-butadiene (*ca.* 5.0 ppm), and aliphatic protons (1.0 - 3.0 ppm).

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Figure 6.2 Infra-red (top) and NMR spectra (bottom) of PSB-45 and PSE-45 (hydrogenated PSB-45).

The composition of the PSE materials was calculated by assuming quantitative hydrogenation of the PSB materials. Note that the mol% of styrene decreased after hydrogenation, as opposed to a negligible change in the wt%. This occurs because every butadiene unit yields two ethylene units ("y" in Figure 6.1).

Table 6.1 Composition of the polymers.

| | PSB-5 | | PSB-23 | | PSB-45 | |
|-------------------------------------------|-----------------------|---------------|----------------|----------------|----------------|----------------|
| | mol% | wt% | mol% | wt% | mol% | wt% |
| styrene
1,4-butadiene
1,2-butadiene | 3
80
17 | 5
78
17 | 13
72
15 | 23
64
13 | 30
57
13 | 45
45
10 |
| B. After hydro | genation ^t | ?: | | | | |
| | PSE | -5 | PSE | ·23 | PSE- | 45 |
| | mol% | wt% | mol% | wt% | mol% | wt% |
| styrene
ethylene
butylene | 1.5
89
9.5 | 5
78
17 | 8
84
8 | 22
65
13 | 19
73
8 | 44
46
10 |

A. Before hydrogenation^a:

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^a, determined by NMR. ^b, calculated.

DSC and wide angle X-ray scattering revealed that the PSE-5 and PSE-23 are both semi-crystalline polymers, containing about 10% and 3% crystallinity, respectively. The $T_{\rm m}$ of the PSE-5 and PSE-23 are about 70°C and 40°C, respectively. In contrast, the PSE-45 is amorphous. The hydrogenation of the PSB materials causes an increase in the polymer glass transition temperatures. The variation of the T_g with styrene content of the PSB and PSE is shown in Figure

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6.3, as determined by DMTA. The T_g values obtained by DSC parallel those by DMTA, but are about 15°C lower. The almost linear variation of T_g with composition for the hydrogenated PSB (PSE) materials is similar to that observed for other hydrogenated butadiene copolymers, e.g. those with acrylonitrile²⁴. Note that the extrapolation of the T_g for the PSB materials to 0% falls slightly above the value for polybutadiene. This is most probably due to a higher number of 1,4-butadiene units (relative to 1,2-butadiene units) in this polybutadiene than in the PSB materials.

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Sulfonation: In order to keep the sulfonation reaction as simple and as easily performable as possible, the reagents and solvents used were all used as received, as is conveniently done for the sulfonation of polystyrene^{18,19}. HPLC grade chloroform was used as the solvent since it contained amylase as a stabilizer, as opposed to the ethanol in reagent grade chloroform, which interferes with the sulfonation reaction. The polymer was found to dissolve well in this solvent at 50°C. Reagent A was successful in sulfonating the PSE-45 up to a level of approximately 9 mol%. Attempting higher sulfonations with this reagent was found to lead to a decrease in the sulfonation efficiency which can be ascribed to the precipitation of the polymer during the course of the reaction, presumably due to solvent/polymer polarity differences. The study of Thaler¹⁹ of various reagents for the sulfonation of polystyrene in a low polarity solvent (cyclohexane) showed that lauryl sulfate is quite effective in improving the sulfonation efficiency. Thus, sulfonation to higher levels of the PSE-45 was achieved by using reagent B, with the lauryl sulfate acting as a phase-transfer catalyst. Even with this reagent, however, the conversion was usually between 40-50%. These sulfonation reaction conversions are similar to those obtained for the sulfonation of the styrene/butadiene di-blocks (50 - 60% conversions)²⁸ and



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Figure 6.3 Glass transition temperatures of the PSB and PSE polymers as determined by DMTA. The T_g was taken at the temperature corresponding to the tan δ peak maximum at 1 Hz.

star-blocks (where a threefold excess of acetylsulfate is used to achieve the required degree of sulfonation)^{26,29}.

The complete removal of residual acid from the final product after sulfonation is very critical in these polymers since they can interfere with the titration results and the final product properties. The effectiveness of the repeated washing with water or methanol to remove residual acid is borne out by the unchanging sulfonation level after three repeated washings, and also by the close correspondence of the sulfonation levels obtained by titration with those obtained by elemental analysis (*Table 6.2*).

Table 6.2. Sulfonation levels.

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| | mol% Sulfonation | | | |
|---------------------------|------------------|------------------------|--|--|
| Designation ^a | titration | S/C ratio ^b | | |
| 5M-SPSE-45 | 4.5 | 5.3 | | |
| 9M-SPSE-45
10M-SPSE-45 | 8.9
10.9 | 8.9
9.9 | | |

a, 'M' denotes the counterion, either H or Cs.
b, from elemental analysis.

The highly sulfonated polymers (e.g. 15H-SPSE-45) are partially soluble in water or methanol, forming highly swollen, loose gels in these solvents, and therefore these polymers were recovered by precipitating into an excess of anhydrous ether as opposed to simply decanting the solvent. The use of anhydrous ether was also effective in removing the excess lauric acid from these polymers, as was

seen by the disappearance of the strong carbonyl band at ca. 1700 cm⁻¹ in the FTIR spectra of the polymers after purification.

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It must be noted here that the sulfonated polymers in the acid form are unstable, turning dark brown and cross-linking upon thorough drying. Therefore, these polymers have to be kept in a "wet" form, in a sealed container, until neutralized. This problem has also been found for the sulfonated star-block ionomers²⁶, and is well known to be operative in other low T_g sulfonated polymers.

Neutralization: During the neutralization of some of the sulfonated polymers with the metal hydroxide solutions, it was found that the polymer sometimes precipitated near the end-point of the titration. This was overcome to some extent by the addition of *n*-butanol or methanol to the polymer solution during titration. In all cases, however, the neutralization before precipitation was greater than 80%.

The highly sulfonated polymer, containing ca.15 mol% sulfonate groups, was found to be soluble in a 1:1 solvent mixture of methanol:THF. The complete dissolution in this solvent, however, is a slow process and can take several weeks before a clear solution is obtained. This polymer was easily titrated with a sodium hydroxide solution (~0.1N) to a phenolphthalein end-point, without any precipitation of the polymer.

Characterization: FTIR and NMR were used to confirm the sulfonation of the styrene groups of the PSE-45 polymer. Figure 6.4 shows a typical series of FTIR spectra before sulfonation, after sulfonation and after neutralization with sodium. The broad band centered around 1200 cm⁻¹ is characteristic of the لأستستستركم



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Figure 6.4 FTIR spectra of the PSE-45 polymer (top), after sulfonation to 15 mol% (middle), and after neutralization with sodium (bottom).

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O=S=O asymmetric stretching vibration,^{11,30} while that occurring at *ca*. 1040 is due to the symmetric stretching vibration. These bands are also seen for sulfonated polypentenamers, where the sulfonic acid groups are attached to olefinic carbons along the polymer backbone¹¹. However, the bands at 1130 and 1010 cm⁻¹ are characteristic of sulfonated polystyrene and are not observed for sulfonated polypentenamers. The intense absorption at *ca*. 1130 cm⁻¹ is due to the in-plane skeletal vibration of the disubstituted benzene ring³⁰. The broad hydroxy peaks at 3400 and 1650 cm⁻¹ indicate the presence of water in the sulfonated polymers, suggesting their hygroscopic nature, as is the usual case for ionomers.

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Figure 6.5 shows the NMR spectra of the highly sulfonated PSE-45 (15Na-SPSE-45). The peak at 7.5 ppm is due to the aromatic protons adjacent to the sulfonate group on the styrene unit, as indicated. The absence of any peaks between 4.0 and 5.0 ppm and at 6.6 ppm suggests that none of the sulfonate ions are attached to aliphatic or olefinic carbons¹¹. This provides further evidence of the sulfonation of the styrene units of the PSE-45. The presence of two small peaks at 7.7 and 7.9 ppm is most probably due to the presence of some styrene units containing two sulfonate groups (in the para- and ortho- positions), as suggested by the assignments in *Figure 6.5*.

Figure 6.6 shows the TGA curves for the unhydrogenated PSB-45, the hydrogenated PSB-45 (PSE-45) and two PSE-45 ionomers containing ca.15 mol% lithium or sodium sulfonate groups. The PSE-45 has a higher thermal stability than the PSB-45, due to the absence of the unstable, unsaturated linkages, present in the PSB-45. The ionomers show a small but gradual weight loss from 160°C to 400°C, followed by major decomposition at around 450°C. This initial weight loss



Figure 6.5 Solution ¹H NMR spectra for the 15Na-SPSE-45 ionomer taken in DMSO- d_6 at 21 °C.

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Figure 6.6 TGA traces for PSB-45, hydrogenated PSB-45 (PSE-45) and two ionomers containing 15mol% ionic sulfonate groups with either lithium or sodium as counterions (as indicated). í,

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can be attributed to the loss of water, since these ionomers are hygroscopic, as seen by the presence of a hydroxyl band in the FTIR spectra (*Figure 6.4*). A distinctive feature of the ionic materials is the large amount of residual material above 480°C as has also been noted for other ion containing polymers^{11,28}. The primary source of this is the inorganic component of the ion containing polymers which accounts for about 80% of this residue in these ionomers; the balance of this residue most probably due to char formation. Despite the high sulfonation levels of these ionomers, they are quite stable when compared to hydrogenated polypentenamers which show some significant decompositon at 350°C¹¹.

6.4.2 Ionomer phase behavior:

Dynamic mechanical methods have been extremely useful in the analysis of the phase behavior of random ionomers^{31,32}. By these techniques, random ionomers typically show the presence of two glass transition temperatures: the lower one is associated with a low T_g phase, and the higher one with that of a clustered phase^{32,33}. Plots of storage moduli (E') and loss tangents (tan δ) as a function of temperature are shown for PSE-45 and for a number of sulfonated PSE-45 ionomers in *Figure 6.7* at a frequency of 1 Hz. The E' curves for the sodium neutralized ionomers show the presence of a pseudo-rubbery plateau, which increases with increasing ion content. For the ionomer containing 15 mol% sodium sulfonate groups, this plateau is at least one order of magnitude higher than for the ionomer containing 5 mol% sodium sulfonate groups. Also evident in this figure is the more extended pseudo-rubbery plateau, for the ionomer containing 15 mol% of cesium sulfonate groups. This may be due to the

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Figure 6.7 Plots of E' (top) and tan δ (bottom) for unfunctionalized PSE-45 and a series of sulfonated PSE-45 ionomers. The numbers refer to the mol% sulfonation and the letters to the counterion type.

larger size of the Cs counter ion when compared to Li and Na so the the total volume fraction occupied by the ionic groups in the Cs neutralized material is higher than in the Li or Na neutralized materials. The effect of the counterion in these materials needs to be further explored.

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Figure 6.7 (bottom) shows that these ionomers have two loss tangent peaks, the one occurring at lower temperature can be ascribed to the presence of a low T_g phase, while the one occurring at higher temperature to that of a clustered phase. As the ion content of the ionomer is increased, the tan δ due to the low T_g phase decreases in height while that of the clustered phase increases in height.

These plots are very similar to those reported for poly(styrene-co-sodium methacrylate) ionomers. There are two notable differences: 1. the loss tangent maxima of the low T_g phase in the PSE-45 ionomers remains essentially constant at *ca.* 0°C as opposed to a 4-5°C/mol% increase for the polystyrene ionomers, 2. the presence of an extended pseudo-rubbery plateau, which spans almost 100°C for the cesium ionomer, and which is only seen as an inflection of the E' *vs.* temperature curve for the polystyrene ionomers. The relatively constant value of the transition temperature for the low T_g phase for the SPSE-45 ionomers is probably due to the fact that only the styrene units of the PSE-45 are functionalized with ionic groups, and this results in the incorporation of the styrene units into the multiplets with the resultant removal of these units from the multiplet-free material. Thus, the removal of styrene units from the multiplet have opposing effects on the transition temperature of this phase. This results in relatively insignificant net movement of this transition temperature.

This invariance of the low T_g phase transition temperature can also, to a certain extent, accounts for the extended pseudo-rubbery plateau seen in these ionomers.

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The increase of the transition temperature of the clustered phase with ion content in these ionomers is approximately 8°C/mol% ion content, and this corresponds closely to that seen for the polystyrene ionomers, containing sodium methacrylate ionic groups³¹.

Apparent activation energies (ΔE_a) were also determined for some of the SPSE-45 ionomers, and these are shown in *Table 6.3*. It must be remembered that the confidence limit for these numbers is ±30 kJ/mol³², and may even be larger considering that only single determinations were done per sample. They are presented here to show the relative magnitude of these values and also to show that they are considerably lower than for the poly(styrene-co-alkali methacrylate) ionomers.

| <u> </u> | ΔE_{a} (kJ/mol) | | |
|--------------------------------------------|-------------------------|-----------------|--|
| sample | low T _g | clustered | |
| 5Na-SPSE-45
9Na-SPSE-45
15Na-SPSE-45 | 280
210
250 | 110
150
a | |

Table 6.3 Apparent activation energies ΔE_a for the phases.

^a, could not be determined.

For the poly(styrene-co-alkali methacrylate) ionomers ΔE_a for the low T_g phase ranges from 500 to 650 kJ/mol while the ΔE_a for the clustered phase ranges from 200 to 450 kJ/mol³². The corresponding values for the SPSE-45 ionomers are much lower, as would be expected from the lower transition temperature of the phases in these ionomers.

6.5 CONCLUSIONS

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The synthesis of a novel sulfonated ionomer has been described. The method of synthesis consists of the hydrogenation of a poly(styrene-butadiene) random copolymer, to remove the olefinic unsaturation, followed by sulfonation and neutralization of the styrene units in the polymer to yield the ionomer. The hydrogenation of poly(styrene-butadiene) random copolymers, containing 5, 23, and 45 wt% styrene yield semi-crystalline polymers from PSB-5 and -23, but an amorphous material from PSB-45. Although this paper describes the functionalization of only the amorphous material, similar sulfonations of the -PSB-5 and -23 can be carried out to yield semi-crystalline sulfonated ionomers. The synthesized ionomer is characterized by DSC, NMR, FTIR, TGA and dynamic mechanical methods. These ionomers show the presence of a low T_{g} and a clustered phase, which are often seen in random ionomers. With increasing ion content, the transition temperature of the low T_{g} phase remains relatively constant at 0°C while the clustered phase transition temperature increases with the rate of *ca*. 8°C/mol%. An extended rubbery plateau is seen for these materials which can span almost 100°C when the ionic groups is cesium sulfonate, and the ion content is 15 mol%.

6.6 ACKNOWLEDGEMENTS

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Chapter 7

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CONCLUSIONS, CONTRIBUTIONS TO ORIGINAL KNOWLEDGE AND SUGGESTIONS FOR FURTHER WORK

7.1 CONCLUSIONS AND CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

This work shows that the functionalization of polystyrene with certain ionic groups can considerably enhance the miscibility between aliphatic polyamides and polystyrene. The choice of the ionic group is critical in determining the extent of the miscibility enhancement achieved. Thus, at equal functional group content, the polystyrene ionomer containing lithium sulfonate groups is much more effective in enhancing the miscibility between polystyrene and aliphatic polyamides than ionomers containing either sodium sulfonate, lithium carboxylate or sodium carboxylate groups. Miscibility enhancement is also seen when the polystyrene is functionalized with unneutralized sulfonic acid groups,

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although the extent of this miscibility enhancement is less than that obtained with lithium sulfonate groups.

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In the first part of this study it is shown that the unneutralized sulfonic acid groups interact strongly with amide groups, but cause the catalytic degradation of the polyamide. Thus, solution blends of polyamide-6 (PA-6) and polystyrene (PS) functionalized with sulfonic acid groups, form a gel at certain amide (A) to sulfonic acid (S) ratios (A/S). Scanning electron micrographs of fracture surfaces of the melt blended PA-6 and sulfonated polystyrene (SPS) samples show that the PS is well dispersed, even when functionalized with as little as 2.2 mol% sulfonic acid groups. Analysis of the extracted PA-6 from the melt blended samples, as well as DSC studies on solution cast blends, reveals that the sulfonic acid groups in the blend cause the catalytic hydrolysis of the PA-6 at processing temperatures (*ca*.250°C). The extent of this degradation is inversely related to the A/S ratio. Degradation of the PA-6 is not observed when the sulfonic acid groups are neutralized with either lithium or sodium.

Strong miscibility enhancement is seen between PA-6 and polystyrene ionomers containing lithium sulfonate groups (LiSPS). This is the first detailed study of these blends. It is shown that these blends are either one or two phase (on the 50-100Å scale), depending on the lithium sulfonate content of the ionomer as well as the blend composition. This phase behavior is described by a simple and novel equation which considers the heat of mixing to be dominated by two opposing interaction enthalpies: the specific interaction of the lithium sulfonate units with the amide units of the PA-6, and the random, unfavorable interaction of the styrene with the amide units. This equation adequately models the

miscibility behavior of these blends, and predicts miscibility throughout the composition range (on the 50 - 100Å level) if the LiSPS contains \geq 12 mol%.

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Numerous studies exist on the effect of low molecular weight diluents on the ionic aggregation in random ionomers. It is shown here, by dynamic mechanical measurements, that the PA-6 acts as a high molecular weight polar diluent when blended (up to 25 wt%) with LiSPS, but acts as neither a polar nor a non-polar diluent when the ionomer contains sodium sulfonate groups instead of lithium sulfonate groups. This is the first report of the polar diluent nature of PA-6 in blends with LiSPS ionomers. Furthermore, it is shown that there is a singular blend composition for the LiSPS/PA-6 blends at which the simultaneous hindering of crystallization and ionic aggregation is at a maximum. This results in a single phase material with considerable phase purity, as suggested by a sharp and narrow loss tangent at this composition.

The miscibility enhancement between LiSPS ionomers and aliphatic polyamides is also shown to depend on the amide content of the aliphatic polyamide, as expected. Thus, PA-6 and polyamide-66 (polymers which contain the same amount of amide groups) show the same extent of miscibility enhancement with LiSPS ionomers. On the other hand, the miscibility enhancement decreases when going from polyamide-610 to polyamide-11 in the blend, corresponding to a decrease in the amide content of the polyamides. Collating the miscibility information on the 50:50 blends of the LiSPS ionomers with the various aliphatic polyamides, a "miscibility map" is drawn as a function of the lithium sulfonate content of the ionomer and the amide content of the polyamide. This provides a useful guide to the level of lithium sulfonate content of the LiSPS required in

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order to observe a single glass transition temperature in a 50:50 blends of this ionomer with any selected aliphatic polyamide.

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Although this work primarily concentrates on the miscibility enhancement of blends of polystyrene with aliphatic polyamides, the miscibility enhancing effect of the lithium sulfonate groups is expected to be applicable to other polymers that can also be functionalized with these groups. With the view of showing this, and with the possibility of improving the impact strength of the polyamide component, novel sulfonated hydrogenated poly(styrene-butadiene) ionomers, having a low glass transition temperature, were synthesized and characterized. These new ionomers are thermally stable up to 450°C in the neutralized form, and show the presence of a "low T_g " phase and a "clustered" phase, as is often seen in other random ionomers.

The ease with which lithium sulfonate groups can be chemically attached to organic molecules, as well as the strong interaction of these groups with amide groups, can be expected to lead to their use in many areas of research and applications involving amide containing polymers. This is especially evident when considering the vast number of naturally occurring, as well as synthetic polymers contain amide groups. In the case of naturally occurring polymers, the amide group (often referred to as the peptide linkage), occurs in polypeptides and proteins. Among the proteins, for example, are important biological materials such as *keratin* (found in skin, hair, nails and wool), *collagen* (found in tendons), *fibroin* (found in silk), *insulin* and *hemoglobin*. Among the synthetic polyamides are aromatic polyamides (e.g., Kevlar), mixed aromatic-aliphatic polyamides (e.g., Selar) and, of course, aliphatic polyamides (e.g., polyamide-6).

Synthetic polyamides have a variety of important commercial applications, ranging from textile fibers to engineering thermoplastics.

7.2 SUGGESTIONS FOR FURTHER WORK

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7.2.1 Model compound studies: The nature of the specific interaction (by FTIR) between the lithium sulfonate and the amide groups in PA-6/LiSPS blends is currently in progress. As an aid to this study, blends of metal neutralized *p*-toluene sulfonic acid (PTSA) and N-methyl acetamide (NMA) could also be investigated. These model compound mixtures have the advantage of being easy to prepare, allowing a large number of counterions to be easily investigated, and avoiding the swamping of the spectra by non-interacting groups.

Heat of mixing experiments (using a calorimeter) of the metal neutralized PTSA with NMA could also be invaluable in comparing the interaction enthalpies of a variety of metal neutralized sulfonate groups. In this way a table of interaction enthalpies for a variety of metal sulfonates with amides could be obtained.

7.2.2 Blending thermodynamics: The equation derived in *Chapter 4* predicts that the LiSPS ionomer should be miscible with PA-6 throughout the composition range when the ionomer contains *ca.* 12 mol% ionic groups ("miscibility" being defined as a single glass transition for the blend, as seen by dynamic mechanical measurements). This prediction should be experimentally verified.

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7.2.2 Blending thermodynamics: The equation derived in *Chapter 4* predicts that the LiSPS ionomer should be miscible with PA-6 throughout the composition range when the ionomer contains *ca*. 14 mol% ionic groups ("miscibility" being defined as a single glass transition for the blend, as seen by dynamic mechanical measurements). This prediction should be experimentally verified.

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Previous work has shown that the miscibility of poly (alkalene oxide)s with poly(styrene-co-lithium methacrylate) ionomers depends on the ionic group content of the ionomer as well as on the blend composition (as has been found in this work for the LiSPS blends with PA-6). It should therefore be possible to obtain a similar equation to that presented in *Chapter 4* to predict the miscibility behavior of these blends.

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7.2.3 Polyester/LiSPS blends: Since it is believed that the lithium interacts with the carbonyl oxygen of the amide unit in the LiSPS/PA-6 blends, LiSPS may also be strongly interacting with polyesters. A whole variety of polyesters (biological as well as synthetic) are commercially available and therefore the effect of molecular parameters (e.g. ester content) on the miscibility with LiSPS could be studied.

7.2.4 Small-angle neutron scattering (SANS): SANS is a powerful tool in accurately determining the size of phases in polymer blends. It could be applied in studying the average phase size in blends of deuterated LiSPS with PA-6 as a function of composition and ionomer functionality. These results could be compared to those obtained by dynamic mechanical measurements and NMR spectroscopy, providing further insight into the morphology of these blends.

7.2.5 Semi-crystalline sulfonated PSE ionomers: The synthesis presented in *Chapter 6* of an amorphous sulfonated ethylene based ionomer should be extended to the sulfonation of the semi-crystalline poly(styrene-ethylene-butylene) (PSE) materials. The phase behavior (by DMTA) and morphology (by SAXS) of these new ionomers can then be compared to that of the amorphous PSE ionomers. This could provide some insight on the influence

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of the polymer backbone architecture on the ionomer characteristics, such as ionic aggregation numbers, distance between multiplets and apparent transition activation energies.

7.2.6 Improvement of the Impact Properties of Polyamides: The strong interaction of the lithium sulfonate group with amide units provides a way of achieving compatibility between materials possessing good impact properties and polyamides. For example, high impact polystyrene (HIPS) and polyamide-6 are both commercially available materials. LiSPS interacts strongly with the PA-6, as has been shown in this thesis, while LiSPS can be expected to be at least partially compatible with the polystyrene component of the HIPS (depending on the LiSPS functionality). Thus the compatibilization of HIPS with PA may be achieved by the addition of a small amount of the LiSPS ionomer to the blend.

In a similar way polyethylene may be compatibilized with various aliphatic polyamides by the inclusion of a small amount of lithium sulfonated PSE ionomer, synthesized according to the method described in *Chapter 6*. Alternately, the lithium sulfonated PSE ionomers could be blended directly with various aliphatic polyamides in order to improve their impact properties. Sulfonated, hydrogenated styrene-butadiene-diblocks may also be useful as interfacial agents for the compatibilization of polyethylene with aliphatic polyamides.

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Appendix A

DERIVATION OF EQUATION [3.4]

Let the original average degree of polymerization be $P_{(1)}$. Let X be the average number of cuts per chain. The final average degree of polymerization, $P_{(2)}$, after X chain cuts is given by

$$P_{(2)} = P_{(1)} / (1 + X)$$
 [A.1]

X now needs to be related to the number of sulfonic acids in the system. Let n be the number of chain cuts per sulfonic acid group. Since (S/A) is equal to the sulfonic acid to nitrogen (amide + amine) ratio in the blend,

$$(S/A)$$
 n = number of cuts per nitrogen [A.2]

Since each repeat unit of PA-6 contains one nitrogen, $P_{(1)}$ also represents the number average nitrogens per PA-6 polymer chain (amide + amine nitrogens), and so

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$$S/A$$
) $n P_{(1)}$ = number of cuts per chain = X [A.3]

Thus,

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$$P_{(2)} = P_{(1)} / [1 + (S/A) n P_{(1)}]$$
 [A.4]

which is Equation [3.4].

Appendix B

DERIVATION OF EQUATION [4.4]

The equilibrium constant K for the reaction : LiS + PA \rightarrow LiS-PA can be expressed in the usual way as

$$K = \frac{[\text{LiS-PA}]}{[\text{LiS}] [PA]} = V \frac{n_c}{(n_i - n_c)(n_1 - n_c)}$$
[B.1]

where V is the volume of the system, n_c is the equilibrium moles of LiS-PA complex formed and n_i and n_1 are the initial moles of LiS and PA units, respectively. Since $n_i = n_2\xi$, where n_2 is the total number of LiSPS polymer repeat units in the system and ξ is the fraction of these that are ionic, Equation [B.1] can be written as

$$K = V \frac{n_{\rm c}}{(n_2\xi - n_{\rm c})(n_1 - n_{\rm c})}$$
[B.2]

We need to relate the number of moles to the volume fractions of the different species in the system. The volume fractions are given by

$$\phi_c = V_c/V$$
; $\phi_2 = V_2/V$; $\phi_1 = V_1/V$ [B.3]

where V_c is the volume occupied by the LiS-PA species at equilibrium, and V_2 and V_1 are the volumes occupied by the LiSPS and PA polymer units, respectively. Let the reference volume V_r be the average molar volume of a polymer repeat unit. Note that the amorphous densities and the average repeat unit molecular weight of the PA-6 and LiSPS are about the same so that V_r closely represents the polymer repeat unit molar volume of both the LiSPS and the PA-6. We now get

$$2n_{\rm c}V_{\rm r} = V_{\rm c}$$
; $n_2V_{\rm r} = V_2$; $n_1V_{\rm r} = V_1$ [B.4]

giving

$$n_{\rm c} = V_{\rm c}/2V_{\rm r}$$
; $n_2 = V_2/V_{\rm r}$; $n_1 = V_1/V_{\rm r}$ [B.5]

Note that one mole of LiS-PA complex occupies a volume of $2V_r$ since this complex is made up of two polymer repeat units. Substituting the terms from Equation [B.5] into Equation [B.2], and factoring out the V_r terms, gives

$$K = V V_{\rm r} \frac{(1/2) V_{\rm c}}{\{V_2 \xi - (1/2) V_{\rm c}\} \{V_1 - (1/2) V_{\rm c}\}}$$
[B.6]

Using Equation [B.3], the equilibrium constant can be expressed in terms of volume fractions:

$$K = \frac{(1/2) \phi_c V_r}{\{\phi_2 \xi - (1/2) \phi_c\} \{\phi_1 - (1/2) \phi_c\}}$$
[B.7]

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which is Equation [4.4].

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SUPPLIMENTARY DATA FOR CHAPTER 4

The data are presented in the table on the next page.

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| Supplementary data. Li | | | SPS10 and LiSPS5 blends
tanδ (PA) | | 2S5 blends v

A) | with PA-6: analysis of th
 | | the DMTA | ne DMTA data.
 | | | |
|----------------------------------------------------|-----------------------------------------------------------|-------------------------------------|--------------------------------------|------------------------------------------|----------------------------------|--------------------------------------|--------------------------------------|----------------------------------------------------------|------------------------------------------------------------------|---------------------------------------------------|--------------------------------------------------------|-----------------------------------------------|
| % | E" _{max} a
(MPa) | A/Li | 7 _g
(°C) | H | ₩↔H
(℃) | Т _д
(°С) | H | T _g
(°C) | Н | W↔H
(℃) | E' ^b
(MPa) | E" ^b
(MPa) |
| LiSPS | 10 Blends | <u> </u> | | | | | | | | | | |
| 0
10
30
50
70
77
90
100 | 79
134
180
190
282
222
170
159 | 92
24
10
4
3
1
0 | 75
81

 | 0.09
0.11

 | 50
54

 |

183
208
230 |

0.51
0.39
0:45 | 107
118
130
134
140
154
150 |
0.03
0.27
0.60
1.56
1.18
0.67
0.36 |
25
37
25
19
19
32
39 | 650
524
426
136
28
30
52
158 | 70
65
134
92
52
42
52
68 |
| LiSPS | 5 Blends | | | · · · | | · · · | | | ···- | ···· | | |
| 0
10
30
50
70
82
86
90
100 | 79
94
135
243
275
264
280
222
200 | 159
41
18
8
4
3
2 | 75
78
97
103

 | 0.09
0.08
0.13
0.06

 | 50
58
56
31

 |

191
191
202
217 |

0.36
0.31
0.25
0.39 |
108
114
122
119
129
130
132
132 |
0.03
0.13
0.38
1.69
1.67
1.48
1.21
1.09 | -
23
19
23
20
17
18
19
18 | 650
615
347
310
17
29
39
30
40 | 70
57
91
142
32
52
63
40 |

Symbols: H, absolute height of deconvoluted tand peak; W \leftrightarrow H, width at half height of deconvoluted tand peak. a, maximum recorded value of E" in the experimental temperature range, 0 to about 220 °C. b, values of E' and E" taken at $T_{g(blend)}$

Appendix D

SUPPORTING DATA

The supporting data for the figures in this thesis are provided on high capacity floppy diskettes, which are formatted for use with IBM[®]PC compatible computers. The complete figures, along with data listings, can be accessed from disk # 1 using the SigmaPlot[™] software (Version 4.1) supplied by Jandel Scientific (65 Koch Rd., Corte Madera, CA 94925; phone: (415) 924-8640), and available from computer software suppliers. The figure numbers and the corresponding file names are listed here :

| Ch | apter 2: | Chapter 4:(cont'd) | | | |
|------------|--------------|-------------------------|-------------|--|--|
| Figure | File | Figure | File | | |
| 2.2 | CH2FIG2.SPG | 4.5 | CH4FIG5.SPG | | |
| | | 4.6 | CH4FIG6.SPG | | |
| Ch | apter 3: | 4.7 | CH4FIG7.SPG | | |
| Figure | File | 4.8 | CH4FIG8.SPG | | |
| 3.1 | CH3FIG1.SPG | 4.9 | CH4FIG9.SPG | | |
| 3.5 | CH3FIG5.SPG | | | | |
| 3.6 | CH3FIG6.SPG | Cha | pter 5: | | |
| 3.8 | CH3FIG8.SPG | Figure | File | | |
| 3.9 | CH3FIG9.SPG | 5.1 | CH5FIG1.SPG | | |
| 3.10 | CH3FIG10.SPG | 5.2 | CH5FIG2.SPG | | |
| | | 5.3 | CH5FIG3.SPG | | |
| Chapter 4: | | 5.5 ⁻ | CH5FIG5.SPG | | |
| Figure | File | 5.6 | CH5FIG6.SPG | | |
| 4.1 | CH4FIG1.SPG | 5.7 | CH5FIG7.SPG | | |
| 4.2 | CH4FIG2.SPG | | | | |
| 4.3 | CH4FIG3L.SPG | Chapter 6: | | | |
| | &c | Figure | File | | |
| | CH4FIG3R.SPG | 6.3 | CH6FIG3.SPG | | |
| 4.4 | CH4FIG4.SPG | 6.7 | CH6FIG7.SPG | | |

Disk # 2 contains all the above data in ASCII format, e.g. for Figure 4.2 the ASCII data file is CH4FIG2.PRN.

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