THERMO-CHEMICAL RECOVERY OF STYRENE FROM POLYSTYRENE WASTE

by

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ABSTRACT

Styrene was recovered from polystyrene by thermo-chemical treatment in a nitrogen atmosphere carried out at 330°C to 410°C, for 30 to 60 minutes. Up to 70% of the polystyrene was converted to styrene at a reaction temperature of 406°C and reaction time of 45 minutes. The styrene yield increased with temperature. At the lower temperatures, the molecular weight of the polystyrene was reduced from 138 000 to 8 900. At the higher temperatures, the polystyrene residue obtained consisted mainly of styrene dimer and trimer. The use of catalysts was evaluated. The catalysts were mixed with the polystyrene in 10% by weight mixtures. They were: silica-alumina, poly(α-methylstyrene), an antioxidant (2,2'-Methylenebis(4-methyl-6-tert-butyl phenol)), and zeolite. The above catalysts were found to have no effect on the thermal degradation of polystyrene under the conditions of the present study. The initial rate of thermal degradation of polystyrene was found to fit a first order model. The activation energy obtained was 181 kJ/mol, which is in accordance with literature values.

RESUME

Le styrène a été récupéré du polystyrène par un traitement thermo-chimique sous un atmosphère d'azote à 330°C jusqu'à 410°C, pour 30 à 60 minutes. Jusqu'à 70% du polystyrène a été converti en styrène à une température de 406°C et un temps de réaction de 45 minutes. Le rendement de styrène augmentait avec la température. Aux températures basses, la masse moléculaire du polystyrène a été réduite de 138 000 à 8 900. Aux températures hautes, le résidue de polystyrène obtenu était compris principalement de dimère et trimère de styrène. L'utilization de catalyseurs a été évaluée. Les catalyseurs étaient mélangés avec le polystyrène dans des mélanges à 10% par masse. Ils étaient: silica-alumina, poly(α-methylstyrène), un antioxidant (2,2'-Methylènebis(4-methyl-6-ter-butyl phénole)), et zéolite. Ces catalyseurs n'avaient aucun effet sur la dégradation thermique du polystyrène sous les conditions de notre étude. Le taux initial de la dégradation thermique du polystyrène se trouvait à suivre une réaction de premier ordre. L'énergie d'activation obtenu était de 181 kJ/mol, ce qui est en accord avec les valeurs dans la litérature.

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1. INTRODUCTION

1.1 Solid Waste Problem

North America is a throw-away society and as a result, we have a mounting solid waste crisis. From municipal sources, 145 million tonnes of solid waste were generated in the U.S. in 1986 [1]. This amounts to about 1.8 kg per person per day. In Quebec, 2.2 million tonnes of municipal solid waste (MSW), or 0.9 kg per person per day, were generated in 1988 [2].

1.1.1 Municipal Solid Waste Composition

Figures 1.1.1 and 1.1.2 show the estimates of the composition (by weight) of MSW in the U.S., in terms of materials and products. As seen in Figure 1.1.1, plastics constitute only 7% by weight of the MSW. Despite this small amount, the population at large views plastic materials as the main culprits of the solid waste problems being faced today. This is due to the high visibility of plastics and the false perceptions that plastics cannot be recycled.

As seen in Figure 1.1.2, approximately one third of the MSW is packaging materials, consisting mainly of paper (48%), glass (27%), and plastics (11%) [3]. The durables are comprised of: major appliances, furniture, rubber tires, miscellaneous. The nondurables are: newspapers, books, magazines, tissue paper, office and commercial paper, clothing, footware, miscellaneous.

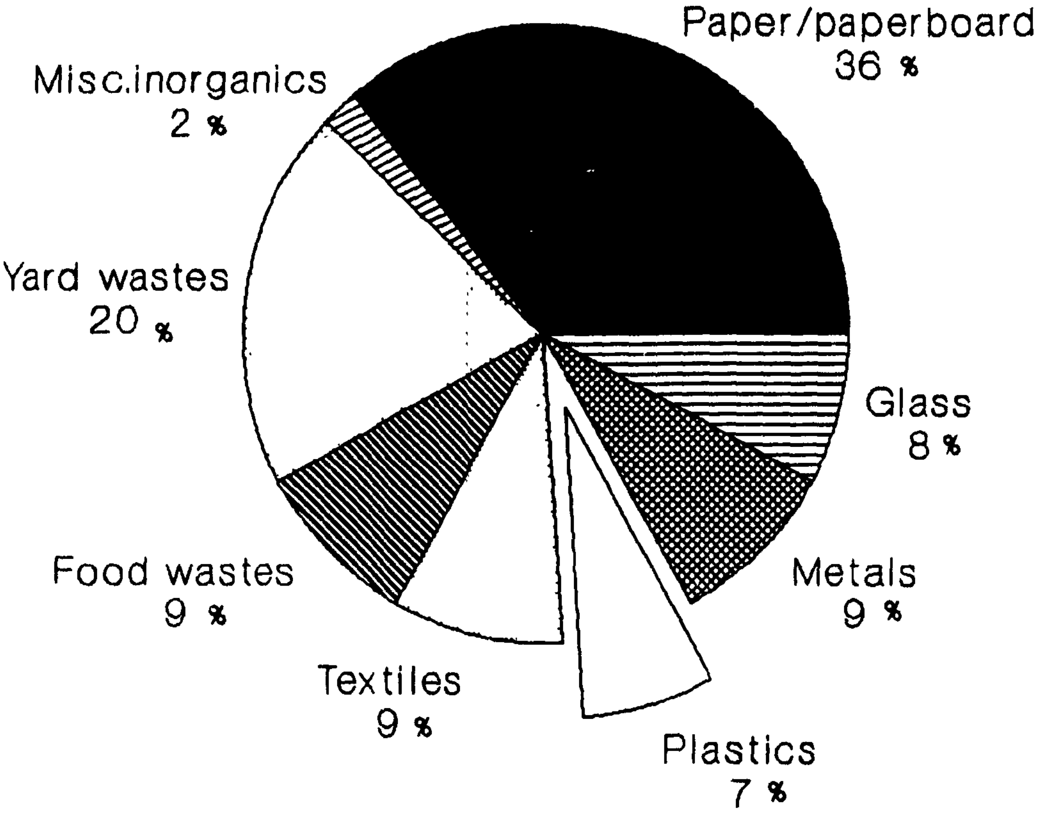


Figure 1.1.1 Composition (%wt) of municipal solid waste by materials, 1986 [1]

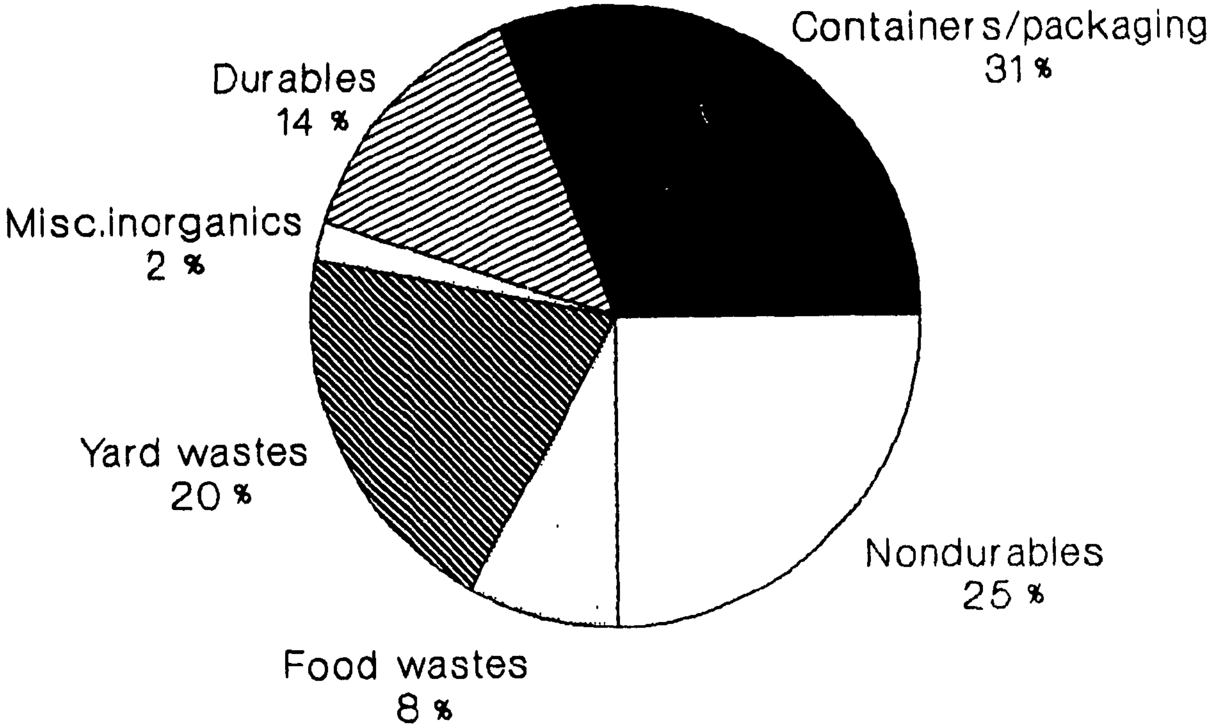


Figure 1.1.2 Composition (%wt) of municipal solid waste by products, 1986 [1]

1.1.2 Municipal Solid Waste Management

The three basic methods of managing MSW are: landfilling, incineration, and recycling. As can be seen in Table 1.1.1, the U.S. and Europe landfill most of their MSW, whereas in Japan, incineration is favoured.

Table 1.1.1 Municipal Solid Waste Management (in % of MSW) [4]

Method	Europe[a]	Japan[b]	U.S.A.[c]
Landfilling	60	30	73
Incineration	33	>65	14
Recycling	<1	<5	11
Composting	7	NA	2

1.1.3 Plastics Waste Management

Figure 1.1.3 illustrates a hierarchy for the management of plastics waste. The 3 R's are emphasized. These are: reduction at source, reuse of materials, and recycling. Recycling involves collection and segregation of the materials. Following the different types of recycling there is incineration from which energy may be recovered and the volume of the waste reduced. Lastly, the least favoured method is landfilling [1]. The focus of this report will be on chemical recycling of polystyrene.

(a) 1987 estimates from European Parliament Committee.

(b) Estimated. NA=Not available

(c) 1988 EPA figures.

- Reduction at Source
- Reuse of Materials
- Collection, Segregation
  - Material Recycling
    - Generic material reclamation
    - Mixed plastics waste recycling
  - Chemical Recycling
    - Hydrolysis
    - Pyrolysis
    - Hydrocracking
      - recovery as monomers
- Incineration
  - Energy recovery
  - Volume reduction
- Landfilling

Figure 1.1.3 Hierarchy of plastics waste management

The recycling of post-consumer plastics is just beginning. Plastics have the lowest recycling rate among MSW components- only about 1%. This can be seen in Figure 1.1.4 which shows the recycling rates for particular materials of the MSW stream.

1.2 Plastics Recycling

In the late 1970s, much attention was given to the recycling of plastics as part of the environmental awareness movement. A strong economy, a shortage of new resin supplies, and the Arab oil embargo incited efforts to establish plastics recycling plants [5].

However, in the early 1980s, when the North American economy went into a recession and new resin capacity came on line, and world oil shortages subsided, the recycling of plastics lost its momentum.

Now, in the 1990s, many opportunities lie in plastics recycling, based not only upon economics but also upon changes in attitudes [4,6]. The world's largest chemical companies are now setting up their own recycling ventures.

There is a growing realization that recycling in general is required if we are to uphold our standard of living. Economically, the residual value of recycled plastics is higher than it was before [6]. This increase in value has ensued from higher costs of waste plastics disposal, declining recycling costs, and increasing consumer willingness to pay more for products that promote recycling.

Government involvement is also very important [7]. Increased legislation, increased regulatory initiatives, deposits on containers, and post-consumer plastics collection programs are all examples of incentives to the recycling of waste plastics.

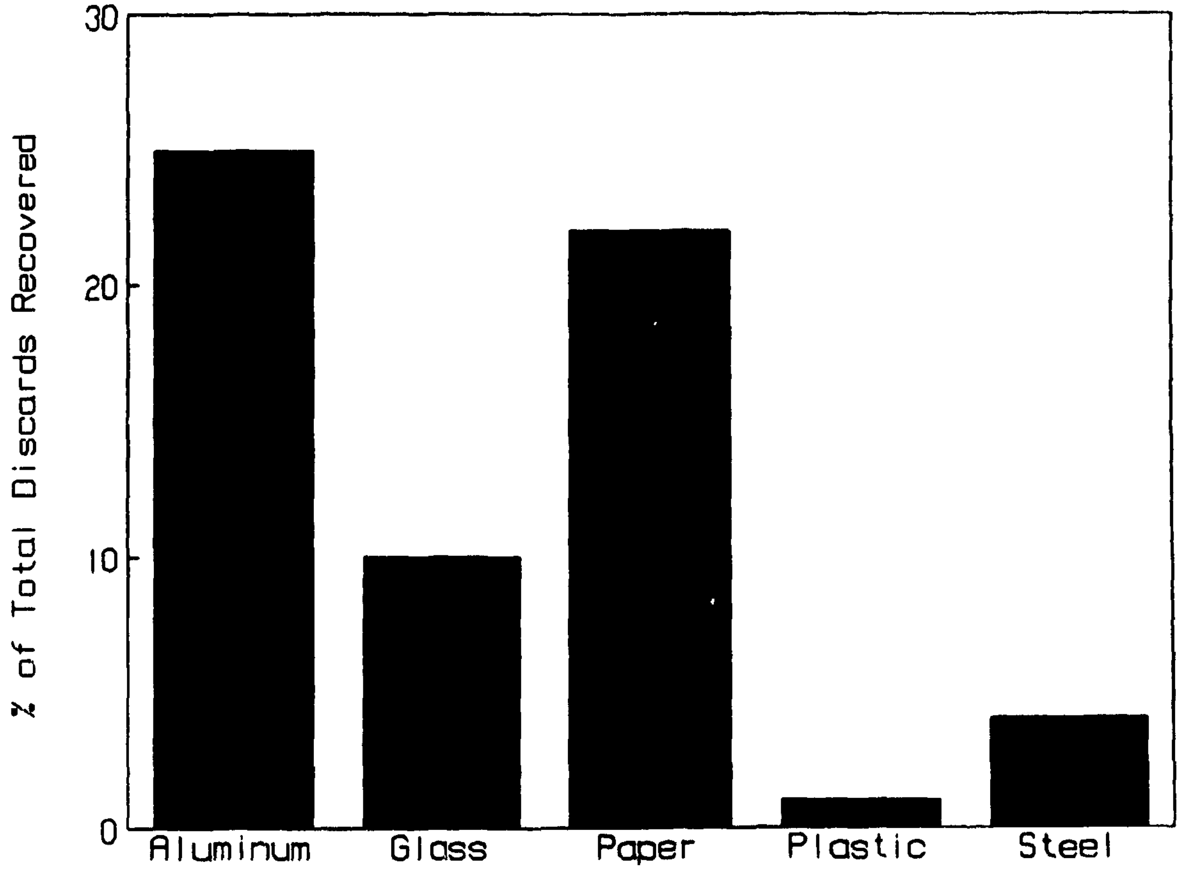


Figure 1.1.4 Municipal solid waste recycling rates, 1986 [1]

1.2.1 Types

There are four types of plastics recycling: primary, secondary, tertiary, and quaternary. Table 1.2.1 defines these types of recycling and Figure 1.2.1 illustrates them.

Table 1.2.1 Types of Plastics Recycling [8]

Recycling Type	Definition
Primary	Processing of plastics waste into a product with characteristics similar to those of the original product, i.e. industrial recycling
Secondary	Processing of plastics waste into products with characteristics that are inferior to the original product (e.g. plastic lumber)
Tertiary	Recovery of basic chemicals and fuels from plastics waste, i.e. chemical recycling
Quaternary	Recovery of heat content from plastics waste by incineration

1.2.2 Production and Growth

Listed in Table 1.2.2 are the five most important resins by production and the amounts produced in the U.S. in recent years. The descending order of production is: low density polyethylene (LDPE), polyvinyl chloride (PVC), high density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS).

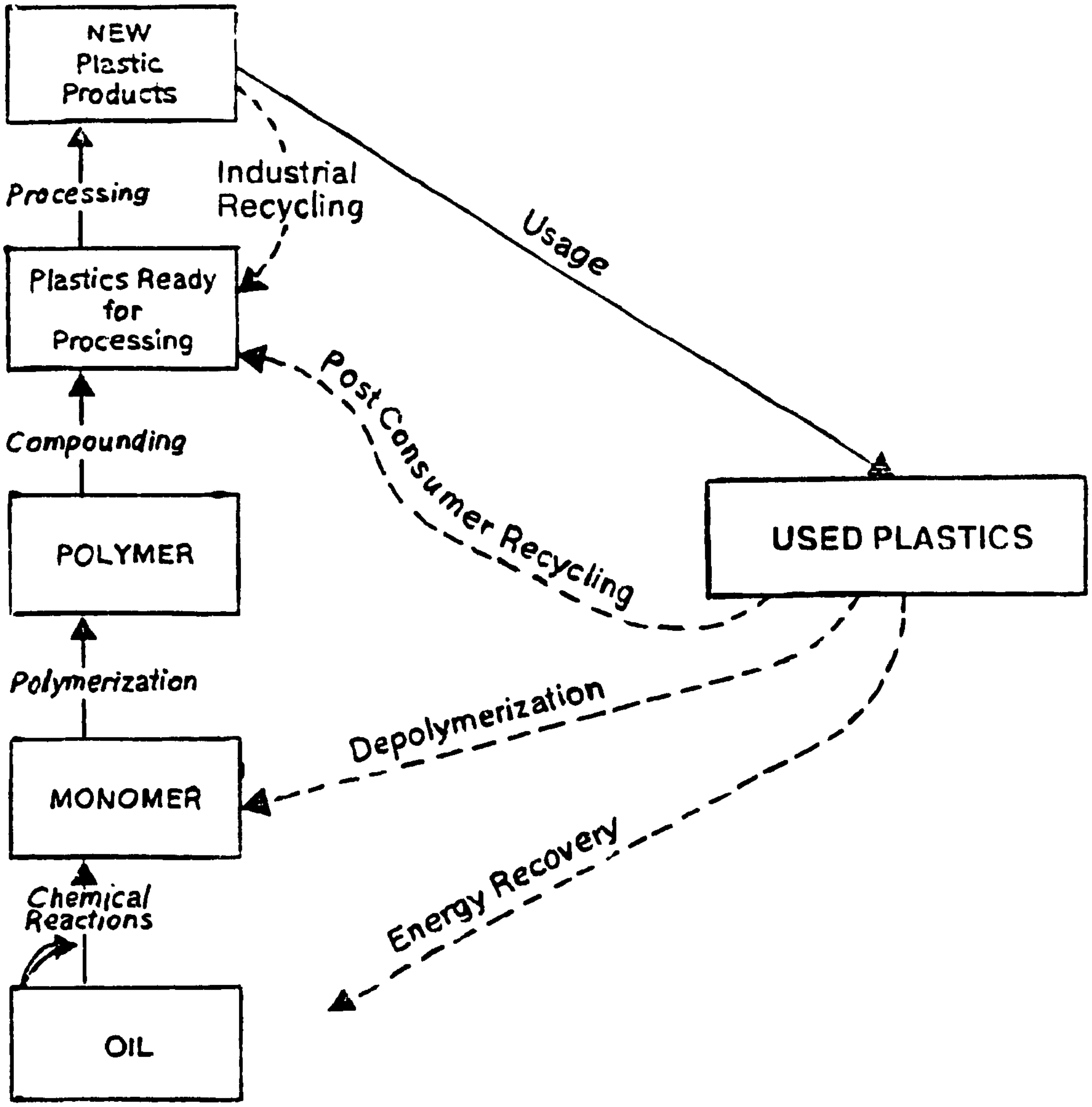


Figure 1.2.1 Plastics recycling flowchart [9]

Table 1.2.2 Production of Plastics in the U.S. in Millions of Tonnes [10]

Plastic	1989	1990	1991	1992
HDPE	3.7	3.8	4.0	4.1
LDPE	4.4	5.1	5.3	5.4
PP	3.3	3.8	3.8	3.8
PS	2.3	2.3	2.2	2.2
PVC	3.8	4.1	4.1	4.2
TOTAL	17.5	19.1	19.4	19.7

By the year 2000, it is estimated that as much as 1.6 million tonnes of plastic resin will be recycled in the U.S. [10]. This is three times that of 1990 figures. By the year 2000, stocks of potentially recyclable plastics will total 25.3 million tonnes, up from 16.6 million tonnes in 1990. These figures suggest that the recycling rate will reach 6.4% by the end of the decade, up from a rate of 2.9% in 1990.

In terms of largest amounts of potentially recyclable plastics, i.e., commodity platics, LDPE accounted for over 4.4 million tonnes in 1990, although the recycling rate was only 1.1% (49 000 tonnes). Rates for PVC and PS are estimated to remain fairly constant. Recycling of potentially reusable PVC will grow from a 1990 rate of 1.1% to 1.5% by 2000. PS recycling is expected to increase from a rate of 1.7% in 1990 to 2.9% by the year 2000.

The focus of this study is the tertiary recycling (chemical recycling) of polystyrene waste, that is, conversion of plastics waste into higher value products. More specifically, the objective is to recover styrene by the thermo-chemical treatment of polystyrene at moderate temperatures. The use of catalysts for the degradation of polystyrene is also evaluated.

2. BACKGROUND

2.1 Polymer degradation

Polymer degradation involves changes in a polymer caused by chemical reactions where bond scission occurs in the macromolecule. Various modes of degradation occur simultaneously in certain circumstances, for example, thermoplastic polymers will undergo oxidative degradation during processing which involves the combined actions of heat, mechanical forces, and oxygen.

Thermal degradation, in the strictest sense, refers to the situation where the polymer undergoes chemical changes at elevated temperatures, without another compound being involved at the same time [11].

There are two principal modes of thermal degradation: random chain scission and depolymerization. Both modes can occur at the same time in the polymer chain.

Depending on its structure, the temperature, the initiating agent, etc., the polymer breaks down randomly, that is, chain scission takes place at random points along the chain. Very little monomer is formed but the molecular weight decreases rapidly.

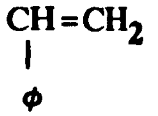
When depolymerization occurs, the polymer degrades at the chain ends. An appreciable amount of monomer is evolved before the molecular weight of the remaining polymer is greatly changed. Depolymerization proceeds via an unzipping mechanism whereby monomer molecules are successively peeled off the chain ends until an entire polymer molecule has been converted to monomer. Intramolecular transfer may produce dimer and trimer unless steric factors interfere. Depolymerization occurs frequently with vinyl polymers and polymers produced from cyclic monomers [11].

Bond scissions under the influence of heat are the result of overcoming bond dissociation energies. Polymer degradation takes place when a temperature is reached at which the majority of bonds in the polymer fail, leading to a change in the overall structure. This results in the formation of a volatile fraction and a polymer chain residue.

2.2 Chemistry of Styrene and Polystyrene

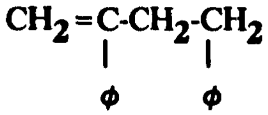
Illustrated below are the structures and the molecular weights (MW) of styrene monomer, dimer (2,4-diphenyl-1-butene), and trimer (2,4,6-triphenyl-1-hexene):

Monomer
(MW=104)



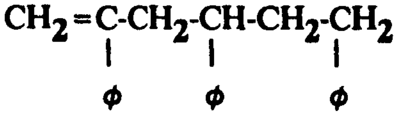
$$\underset{\substack{| \\ \phi}}{\mathrm{CH}}=\mathrm{CH_2}$$

Dimer
(MW=208)



$$\mathrm{CH_2}=\underset{\substack{| \\ \phi}}{\mathrm{C}}\text{-}\mathrm{CH_2}\text{-}\underset{\substack{| \\ \phi}}{\mathrm{CH_2}}$$

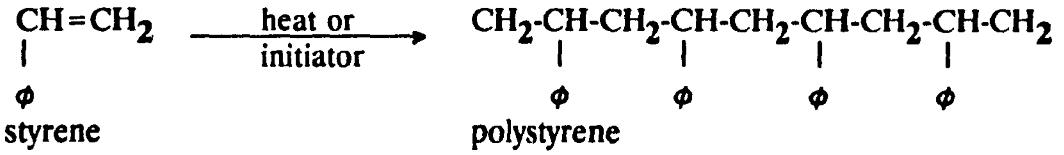
Trimer
(MW=312)



$$\mathrm{CH_2}=\underset{\substack{| \\ \phi}}{\mathrm{C}}\text{-}\mathrm{CH_2}\text{-}\underset{\substack{| \\ \phi}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{-}\underset{\substack{| \\ \phi}}{\mathrm{CH_2}}$$

Polystyrene is a commodity thermoplastic, that is, produced at low cost in high volumes. Its important characteristics are ease of processing, high transparency and rigidity, and low moisture absorption. It is used in many applications, for example: appliances, furniture, toys, cutlery, medical supplies, and assorted packaging [12].

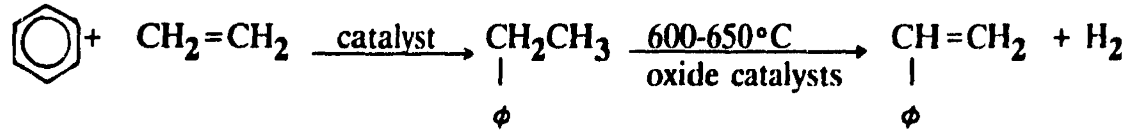
Polystyrene is an addition polymer formed by the polymerization of styrene:



$$\underset{\substack{|\\ \phi}}{\mathrm{CH}}{=}\mathrm{CH_2} \xrightarrow[\text{initiator}]{\text{heat or}} \mathrm{CH_2}\text{-}\underset{\substack{|\\ \phi}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{-}\underset{\substack{|\\ \phi}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{-}\underset{\substack{|\\ \phi}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{-}\underset{\substack{|\\ \phi}}{\mathrm{CH}}\text{-}\mathrm{CH_2}$$

Styrene polymerizes spontaneously on heating in an oxygen-free atmosphere. The first polymerization is credited to E. Simon in 1839 [13]. He gave the name of styrol to the solid compound obtained after steam distillation from a resinous gum.

Commercial production of styrene is performed by conversion of benzene to ethylbenzene (usually by direct alkylation of benzene with ethylene), followed by dehydrogenation [14]:



The fully condensed reaction product typically contains (in % weight): 35-40% styrene, 59-61% ethylbenzene, 1-2% toluene, 0.5-2% benzene, 0.2-0.5% tars [15].

The recovery of styrene is carried out by vacuum distillation using specially designed columns and suitable non-volatile polymerization inhibitors for the styrene. p-tert-butylcatechol (TBC) is used as an inhibitor and antioxidant for the storage of styrene.

Styrene readily polymerizes by free radical, anionic, and cationic mechanisms. This is due to the aromatic ring which is able to stabilize the propagating species, be it a free radical, anion, or cation. Free radical initiation is the most important industrial method of synthesizing polystyrene. In general, free radical polymerized polystyrene is less thermally stable than polystyrene obtained by anionic polymerization [16].

2.3 Literature Review

2.3.1 Thermal Degradation of Polystyrene

There have been many studies examining the mechanisms of the thermal degradation of polystyrene. However, unsolved problems remain and conflicting views are still not fully resolved [16-31].

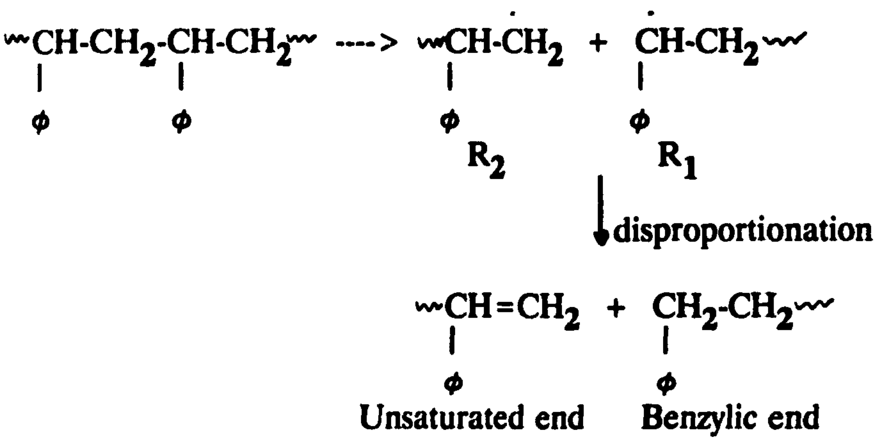
The general features of the degradation process are now widely accepted and are shown in Table 2.3.1. The thermal degradation of polystyrene is a radical chain process which involves initiation, propagation, transfer, and termination steps. Degradation of polystyrene is an endothermic reaction. Many competitive elementary reactions and side reactions exist, and the process complexity increases with increasing temperature.

Table 2.3.1 **General Features of the Radical Chain Scission Degradation Process [18]**

ELEMENTARY REACTION	CHAIN REACTION STEP	MODE
C-C Scission	Initiation	Weak points Chain end Random
ß-Scission	Propagation	Depolymerization Chain scission
Hydrogen abstraction	Transfer	Intramolecular Intermolecular
Mutual destruction	Termination	Coupling Disproportionation Evaporation

Between 280°C and 300°C, the molecular weight of polystyrene decreases but no volatile products are evolved. Random scission occurs whereby free radicals are generated [32]. Two types of radicals may form, namely the normal polystyryl radical (R_1) and the methylene end group radical (R_2). These radicals either recombine or undergo intramolecular hydrogen abstraction (disproportionation) giving rise to two chain ends, a saturated benzylic chain end and an unsaturated thermally unstable end (double bond chain end). This is illustrated in Scheme 1.

Random Scission

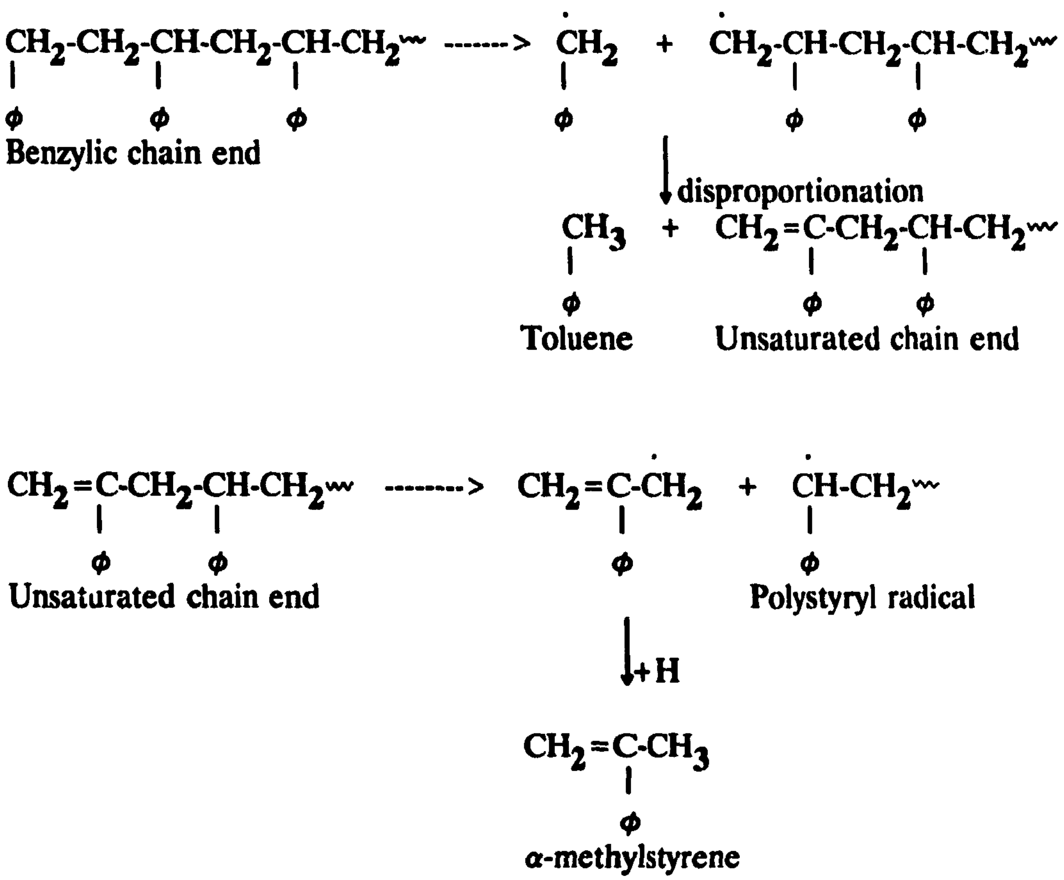


$$\sim\underset{\phi}{CH}\text{-}CH_2\text{-}\underset{\phi}{CH}\text{-}CH_2\sim \;\text{---->}\; \underbrace{\sim\underset{\phi}{\dot{C}H}\text{-}CH_2}_{R_2} + \underbrace{\underset{\phi}{\dot{C}H}\text{-}CH_2\sim}_{R_1} \xrightarrow{\text{disproportionation}} \underset{\text{Unsaturated end}}{\sim\underset{\phi}{CH}=CH_2} + \underset{\text{Benzylic end}}{\underset{\phi}{CH_2}\text{-}CH_2\sim}$$

Scheme 1. Random scission followed by disproportionation.

Above 300°C, the unsaturated chain ends are believed to be the primary initiation sites for thermal degradation [29]. The formation of volatile products is observed when polystyrene is heated above 300°C [17]. They consist mainly of styrene monomer, dimer, and trimer, and smaller amounts of toluene and α-methylstyrene [32].

Between 330°C and about 450°C, the primary sites for radical generation are the chain ends [32]. Initiation at a chain end with a benzyl group produces a tolyl radical and a polystyryl radical. At unsaturated end groups, α-methylstyryl and polystyryl radicals are formed. Coupling of the tolyl and α-methystyryl radicals with hydrogen yields toluene and α-methylstyrene. This is illustrated in Scheme 2.

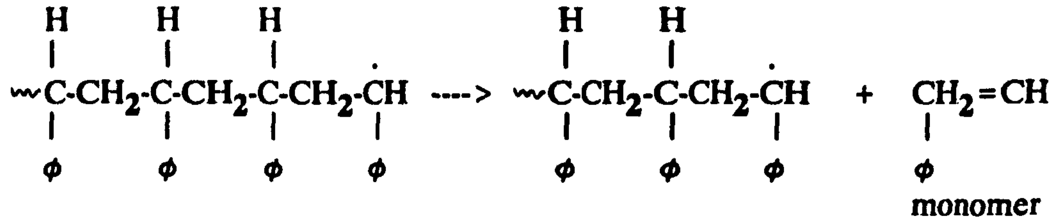


Scheme 2. Chain end initiation.

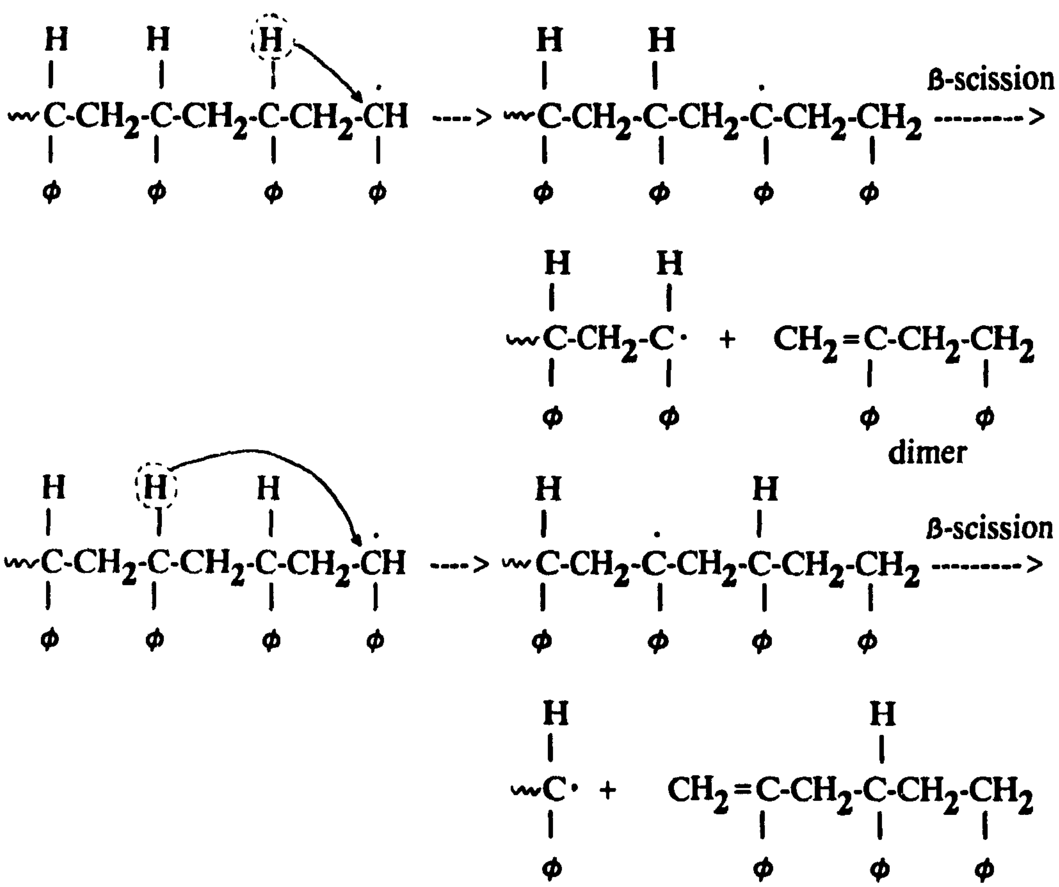
The initiation reaction is associated with the different amounts of irregular structures in the polymer [16]. These are called weak points , that is structural irregularities whereby scission can take place. The identities of these points have not yet been established [32] but structures investigated include chain branches, double bonds, internal unsaturations, head-to-head links, and initiator residues. Even the positions of these weak points remain elusive. Some workers expect them to be randomly distributed along the polymer chain [16,19,33-35], and others expect them to occur at the chain ends [36-38].

Once a polystyryl chain end radical (R_1) forms at higher temperatures (>350°C), the volatiles can escape and molecular motion is fast. Three series of propagation and transfer reactions account for the major volatile products observed [38]. These are : ß-scission, intramolecular hydrogen transfer, and intermolecular hydrogen transfer. They are shown in Scheme 3.

ß-Scission

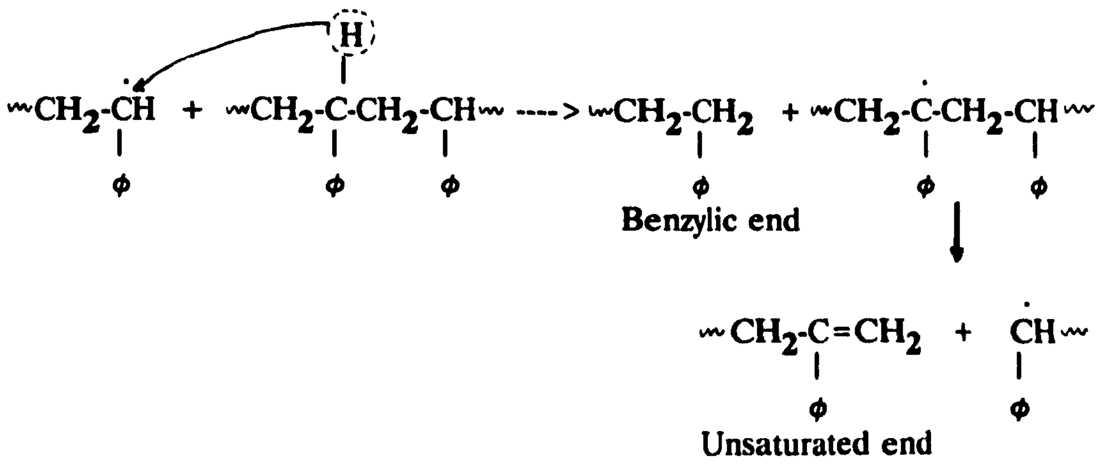


Intramolecular hydrogen abstraction



Scheme 3. Propagation and transfer mechanisms.

Intermolecular hydrogen abstraction



Scheme 3. Propagation and transfer mechanisms (cont'd).

ß-scission is the most frequent reaction, involving the polystyryl chain end radical (R_1) with the resultant formation of styrene and a polystyryl radical one unit shorter (unzipping). Hydrogen abstraction in the main chain is the second most important reaction [31]. Intramolecular abstraction of a tertiary hydrogen one unit away from the chain end precedes scission of the ß carbon carbon bond farther from the chain end. The products are styrene dimer and another polystyryl radical. Trimer is formed when hydrogen abstraction occurs two units away followed by ß-scission farther from the chain end. These hydrogen abstractions are called back-biting reactions. Intermolecular abstraction results in a benzylic chain end, an unsaturated chain end, and another polystyryl chain end radical.

An alternative mechanism for the formation of oligomers has been proposed by Dean et al. [39]. They obtained evidence to suggest that dimers and trimers are possibly formed by monomer recombination, occurring both within the molten polystyrene and in the vapour phase above it.

The termination step has been shown to be a first order reaction [19,38]. One would expect a second order reaction if the termination reaction was by mutual destruction of the free radicals. A first order reaction can be explained if one assumes that the radicals may escape from the reaction medium by evaporation when they are small enough. The most probable process involves intramolecular transfer with subsequent scission to give an oligomer radical which is small enough to diffuse readily from the system without further reaction [38].

In the late twenties and early thirties, Staudinger et al. [40,41] investigated the thermal degradation of polystyrene and the nature of its degradation products. They thermally degraded polystyrene in nitrogen at 0.1 torr, at 290-320°C, and at atmospheric pressure, at 310-350°C. Their results are summarized in Table 2.3.2. The yield of monomer, in percent of the volatilized part, is greater in the presence of an atmosphere of nitrogen than in a vacuum of nitrogen. They did not analyze the residues.

Table 2.3.2 Distribution of Products Formed in the Thermal Degradation of Polystyrene [41]

Pressure of N2	Temp. °C	Duration hr	Monomer %	Dimer %	Trimer %	Tetramer %	Residue %	Total %
atm.	310-350	6	62	19	4	--	10	95
0.1 torr	290-320	12	38	19	23	4	12	96

In the fifties and sixties, many studies were carried out on the thermal degradation of polystyrene in a vacuum and at temperatures up to approximately 400°C [36,37,42-52]. These experiments involved measuring the molecular weight of the degraded polystyrene. Results obtained by Jellinek [42,43], Grassie and Kerr [36,37], and Madorsky et al. [44,45] are in fairly good agreement even though polystyrene samples of different molecular weights and properties were used. In all cases, the molecular weight dropped abruptly during the first 10% loss of weight of sample. Beyond this, the drop was gradual. The initial drop in molecular weight may be due partially to scissions at weak links in the polymer, but is mainly caused by thermal scissions in the chain. This continues to a point where the drop in weight caused by random scissions is counterbalanced by the disappearance of smaller chains through unzipping, mainly into monomers [45,46].

Madorsky et al. [45-52] analyzed the composition of the products of polystyrene degradation. The volatile products were separated by molecular distillation into several fractions and analyzed using a mass spectrometer. Results are summarized in Table 2.3.3. The composition of the volatile fraction did not change significantly with temperature or duration of reaction. The average styrene content of the volatilized part was 41%.

Table 2.3.3. Distribution of Fractions in the Thermal Degradation of Polystyrene in Vacuum [48,49]

Temp. °C	Duration hr	Volatilization %	Residue %	Volatile Composition (in wt.% of volatilized part)		
				Styrene	Toluene	Other
336	1.0	22.1	77.9	39.0	3.0	58.0
336	2.0	40.6	59.4	39.3	2.1	58.6
339	3.0	78.5	21.5*	37.6	1.4	61.0
339	4.0	91.4	8.6	34.6	2.0	63.2
354	0.5	47.2	52.8	47.8	2.0	50.2
373	0.5	91.1	8.9	44.2	1.8	54.0
375	0.5	88.5	11.5	41.0	2.0	56.7
375	0.5	94.7	5.3	40.7	1.9	57.4
				Aver: 40.6	2.0	57.4

* Mw=2078

In the seventies, Malhotra et al. [53] carried out kinetic studies on the decomposition of polystyrene using differential thermogravimetric and differential scanning calorimetric techniques in nitrogen atmosphere. They did not analyze the components of the products of degradation but they did measure the changes in the molecular weight distributions of the degraded polystyrene (residue) by gel permeation chromatography (GPC). They compared the GPC distributions of the undecomposed polystyrene with its decomposed counterparts obtained at different temperatures for 50 minute periods. They obtained similar results to Jellinek [42,43], Grassie and Kerr [36,37], and Madorsky et al. [44,45] in terms the molecular weight decrease as a function of % volatilization.

Due to the environmental awareness movement of the seventies, there was much research in the recycling of plastics waste for the recovery of material and/or recovery of energy. The thermal degradation of polystyrene at higher temperatures was studied [54-60].

2.3.2 Catalytic Degradation of Polystyrene

The use of suitable catalysts can improve the thermal degradation of synthetic polymers [61-72]. Recently, catalysts for polystyrene degradation have been screened by Audisio et al. [64]. The catalysts they studied were silica-aluminas and zeolites mixed with powdered polystyrene in 10% by weight mixtures. The degradations were performed under vacuum at 350°C and 550°C for 1 hour. They obtained different product distributions compared to thermal degradation of polystyrene without catalyst. The catalytic degradation gave rise to many fewer olefinic products than the thermal degradation. The amount of styrene formed increased with temperature. They also studied the effect of vacuum using polystyrene alone, and found that a change from 0.1 to 0.2 torr resulted in a 20% increase in the residue. This is reasonable since the lower the vacuum, the less amount of the volatile fraction will be removed from the reaction zone and therefore more residue will result.

Simionescu et al. [65] found that if the thermal degradation of styrenic polymers was catalyzed, the proportions of oligomers were very much lower and the content of valuable products became important. The catalysts they used were the following:

- aluminum bronze
- MnO_2 on fire bricks
- CuO on fire bricks and asbestos
- amorphous silica-alumina
- silica-alumina crystals with 10-20% molecular sieves
- ZSM-5 zeolites

The pyrolysis experiments they carried out were in two steps, one at 400-500°C and the second at 420-500°C. The catalysts were used as a fixed bed. In other words, first the polystyrene was thermally degraded, then its degradation products were reacted over a catalyst. This is different from Audisio et al. [64], whose experiments involved pre-blending polystyrene powder with catalyst followed by thermal degradation.

Besides the well known radical decomposition, the catalysts can induce many secondary reactions, such as intermolecular hydrogen extraction, isomerization at double bonds, branchings, alkylation, cyclization and aromatization, dehydrogenation, secondary crackings and destructive scission, polymerization, and coking [65].

Ide et al. [66-69] have carried out many studies on the catalytic thermal degradation of polystyrene.

The catalytic degradation of polystyrene wastes over an active charcoal catalyst gave useful products [66]. Cis-1,3-diphenyl-2-butene, trans-1,3-diphenyl-2-butene, 1,3-diphenyl-1-butene, and 1,3-diphenylbutane (all dimer derivatives) were detected as the main products. Their selective recovery by catalytic reaction of polystyrene was possible by controlling the contact time and activity of the catalyst.

Catalysts containing 13% highly acidic or 88% weakly acidic Al_2O_3 were used for thermal decomposition of polystyrene at 170-270°C for 0.25-5 hours [67]. Highly acidic catalysts gave large amounts of benzene, cumene, and methylindanes, while weakly acidic catalysts gave mainly benzene.

Catalytic degradation of polystyrene in the presence of silica-alumina catalyst at

190-230°C made it possible to control the decrease in molecular weight and to obtain styrene oligomer having a molecular weight of 500-3000 [68].

The recovery of indan derivatives from polystyrene was studied by degrading polystyrene in a fixed bed flow reactor consisting of two sections: the upper part of the reactor tube was for the thermal decomposition of polystyrene and the bottom part was for the catalytic reaction of the thermal decomposition products of polystyrene [69]. In this study, the thermal decomposition of polystyrene was carried out at 420°C for 2.4 hours so as to obtain styrene (62 wt.%), dimer (10 wt.%), and trimer (9 wt.%). These were then reacted over silica-alumina catalyst at 300°C to obtain indan derivatives as the degradation products.

Yamamoto et al. [70] carried out catalytic degradation of polystyrene on silica-alumina under a nitrogen atmosphere by a batch process. In the absence of catalyst, the volatile fraction was obtained at >310°C and consisted mainly of styrene (70 wt.%), α-methylstyrene (2 wt.%), and toluene (1 wt.%). In the presence of the catalyst, the volatile fraction consisted mainly of benzene (35-53 wt.%), cumene (15 wt.%), ethylbenzene (10 wt.%), and many unidentified products having high boiling points. With increasing reaction temperature or relative amount of catalyst to polystyrene, the yield of the volatile fraction increased. With increasing flow rate of nitrogen, the yield of benzene decreased and that of the high-boiling products increased while that of other products remained constant.

Richards and Salter [71] used poly(α-methylstyrene)(PMS) as a catalyst for the thermal degradation of polystyrene at 260-287°C. PMS was thus used as a radical producing agent. In their study, the quantities of monomers evolved were very low since their main focus was on the rates of monomer evolution as a function of PMS and its molecular weight.

Substances such as:

- 2,2,4-trimethyl-1,2-dihydroquinoline
- 2,2'-methylenebis(4-methyl-6-tert-butylphenol)
- hydroquinone monobenzyl ether
- 2,5-di-tert-butylhydroquinone
- p,p'-methylenedianiline
- lauryl mercaptan
- p-(p-tolysulfonyl amide)diphenylamine

and other antioxidants of this general type are thought to accelerate the depolymerization of styrene polymers by preventing the recombination of the free radicals resulting from the scission of the polymer chains while, at the same time, also preventing the side reactions which result in branching and cross-linking [72]. Other substances may be used which are known as initiators of free radical type polymerizations or chain transfer agents, that is, aromatic peroxides and hydroperoxides, azo compounds, mercaptans, etc.

2.3.3 Overall Findings

Table 2.3.4 summarizes the main results of past work in the field of polystyrene degradation. The yields of styrene range from 1 to 77 % of the polystyrene. In general, styrene yield increases with temperature.

Table 2.3.5 gives a comparison of activation energies for polystyrene degradation found in literature. The activation energies are between 163 and 243 kJ/mol.

Table 2.3.4 Summary of Polystyrene Degradation Results

Authors Year	Set-Up	Temp. (°C)	Time (hrs)	Styrene Yield (%wt of PS)
Staudinger et al, 1929 [41]	N_2 atm. N_2 0.1 mm	310-350 290-320	6 12	62 38
Madorsky & Straus, 1948 [48]	vacuum	354 375	0.5 0.5	23 39
Wall et al, 1955 [73]	vacuum	350 to 378	1.5	43
Straus & Madorsky, 1962 [52]	vacuum	400 500 800	0.5 0.5 0.5	50 56 48
Tokushige et al, 1974 [54]	vacuum,screw extruder,30rpm	500 600	not avail.	72 77
Sekiguchi et al, 1977 [74]	N_2 atm.	350 400 450 500	1.2 1.2 1.2 1.2	35 50 59 65
Ogawa et al, 1981 [69]	N_2 atm.	420	2.4	62
Ide et al, 1984 [68]	N_2 atm. PS + active charcoal	300 350	2.4 2.4	49 43
Saido et al, 1985 [75]	vacuum	340	2	49
Costa et al, 1985 [76]	N_2 atm.	348	0.5	36
Costa et al, 1986 [30]	N_2 atm.	334	1	41
Scott et al, 1990 [77]	N_2 atm.	532 615 708	0.5 0.5 0.5	76 72 76
Audisio et al, 1990 [64]	vacuum PS + silica-alumina PS + zeolite	350 550 350 550	1 1 1 1	1 4 3 28
Carniti et al, 1991 [78]	vacuum	360 380 400	1.5 1.0 0.5	7 4 3

Table 2.3.5 Comparison of Activation Energies for Polystyrene Degradation

Authors, Year	Conditions	E_a (kJ/mol)
Jellinek et al, 1949 [43]	vacuum, 348-398 °C	187
Madorsky, 1952 [44]	vacuum, 360-420 °C	243
Madorsky & Straus, 1959 [51]	vacuum, 299-348 °C	230
Anderson & Freeman, 1961 [79]	vacuum, 250-430 °C	222
Boon & Chella, 1965 [80]	vacuum, 269-317 °C	163
Nakajima et al, 1966 [81]	vacuum, 265-320 °C	176
Wall et al, 1966 [82]	vacuum, < 350 °C	230
Richards & Salter, 1967 [71]	vacuum, 260-290 °C	180
Cameron & Kerr, 1968 [16]	vacuum, 280-320 °C	205
Wegner & Patat, 1970 [83]	vacuum, 250-300 °C	201
Kokta et al, 1973 [84]	nitrogen flow, 300-500 °C	176
Malhotra et al, 1975 [53]	nitrogen flow, 280-390 °C	201
Still & Whitehead, 1976 [85]	nitrogen flow, 360-415 °C	180
Dickens, 1980 [86]	nitrogen flow & vacuum, 350-415 °C	188
Cameron & McWalter, 1982 [34]	vacuum, 280-300 °C	204
Cameron et al, 1984 [35]	vacuum, 280-300 °C	227, 232
Carniti et al, 1989 [87]	vacuum, 350-420 °C	185
Carniti et al, 1991 [78]	vacuum, 360-420 °C	195

3. OBJECTIVES

The present work is part of a more general program in the area of plastics waste chemical recycling. The program covers the recovery of useful products from waste plastics through the use of thermo-chemical conversions.

The objectives of this Master's project are as follows:

1. To set up a system to thermally degrade polystyrene at moderate temperatures.
2. To characterize the starting polymer and its degradation products.
3. To study the effect of potential catalysts, temperature, and reaction time on the process.
4. To investigate the kinetics of polystyrene thermal degradation
5. To utilize the system (recovery method) on consumer polystyrene.
6. To compare the results of this work to other research in the same field.

4. EXPERIMENTAL

4.1 Materials

Polystyrene (STYRON 688) produced by free radical polymerization by Dow Chemical Canada Inc. was employed in powder form. Its number average molecular weight ($\overline{M}n$) and its polydispersity index ($\overline{M}w/\overline{M}n$) were 138 000 and 2.6, respectively. A sample of consumer polystyrene was also utilized in the form of a clear polystyrene cup.

The catalysts utilized and respective suppliers are listed in Table 4.1.1. They were all in powder form, except for poly(α-methylstyrene) (PMS) which was in the form of small beads. The butyl phenol was an antioxidant (CYANOX 425). To form the mixtures of polystyrene and catalyst, 10% by weight of the catalyst was combined with polystyrene by vigourously shaking the mixture in a bag.

Table 4.1.1 Catalysts Utilized

Catalyst	Supplier
silica-alumina	Strem Chemicals, Inc.
poly(α-methylstyrene)	Polysciences, Inc.
2,2'-Methylenebis (4-methyl-6-tert-butyl phenol)	American Cyanamid Company
zeolite	American Chemicals, Ltd.

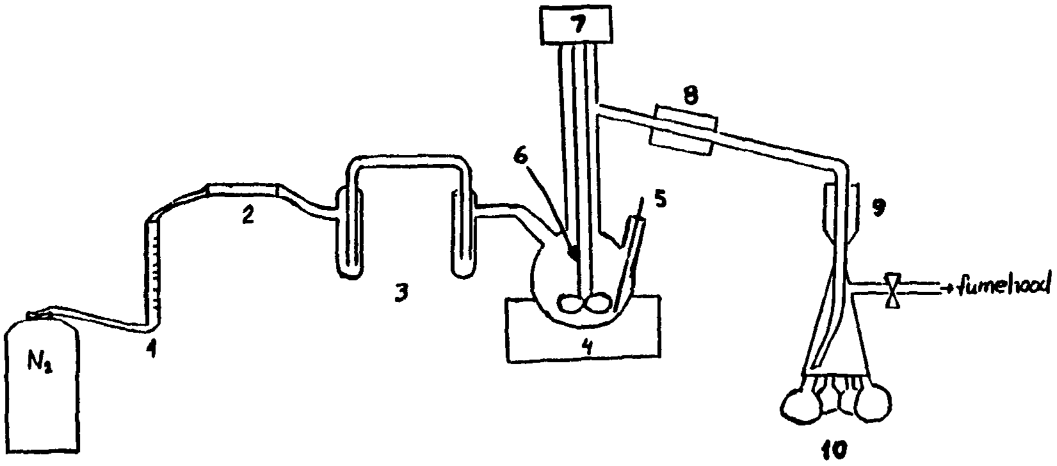
4.2 Apparatus

The apparatus utilized is shown in Figure 4.2.1. All the parts are made of Pyrex glass. All joint sizes are $\overline{\$}$24/40.

4.3 Procedure

Samples weighing 3g were mixed by a paddle connected to a motorized shaft in a 100 ml three-necked round bottomed flask (reaction vessel) under a nitrogen atmosphere. The motor for the stirrer was from Caframo Ltd. Heating was provided by a spherical flask heating mantle from Glas-Col. It allowed full view of the contents of the flask while heating and its maximum temperature allowable was 650 °C. Heating was controlled by a temperature controller from Omega Engineering Inc. A type J thermocouple also from Omega Engineering Inc. was used. The temperature range was 330-410°C and reaction times employed were 30, 45, and 60 minutes. The volatiles were condensed and collected in a special rotating vessel comprising four 50 ml flasks which allowed the flasks to be turned with time and thus collect the liquid at different stages of the reaction.

High purity nitrogen from Liquid Carbonic Inc. was used. The flowmeter was from Gilmont Instruments Inc. The drying tube was filled with Drierite. The bubblers were filled with mineral oil from Fisher Scientific. A water condenser and a cooler filled with ice were utilized.



1. Flowmeter
2. Drying Tube
3. Bubblers
4. Heating Mantle
5. Temperature Probe
6. Stirrer
7. Motor
8. Condenser
9. Cooler
10. Collection Vessels

Figure 4.2.1 Apparatus

Prior to an experimental run, the reaction vessel and the flasks on the rotating receiving vessel were weighed. After setting up the apparatus, the system was purged for 15 minutes with nitrogen. The nitrogen flow was then lowered to a constant flow rate of 50 ml/min, and the heating mantle and mixer were turned on.

The temperature was monitored during the reaction. A typical temperature profile for an experimental run is shown in Figure 4.3.1. It took approximately 5 to 10 minutes for the polymer to reach the desired temperature. An average reaction temperature was calculated for the constant region of the temperature profile. On average, the standard deviation was 6°C.

At the end of an experiment, both the mixer and heater were turned off, and the reaction vessel was allowed to cool to room temperature. Then, the nitrogen flow was stopped, the apparatus was disassembled, and the individual parts were weighed. The degradation products (condensed volatile fractions and residue) were stored in glass vials in the refrigerator under nitrogen.

4.4 Analytical Techniques

The condensed volatile fractions obtained in the collection flasks were analyzed by gas chromatography (GC) and the residue in the reaction vessel was analyzed by gel permeation chromatography (GPC). Tables 4.4.1 and 4.4.2 show the GC and GPC conditions utilized, respectively.

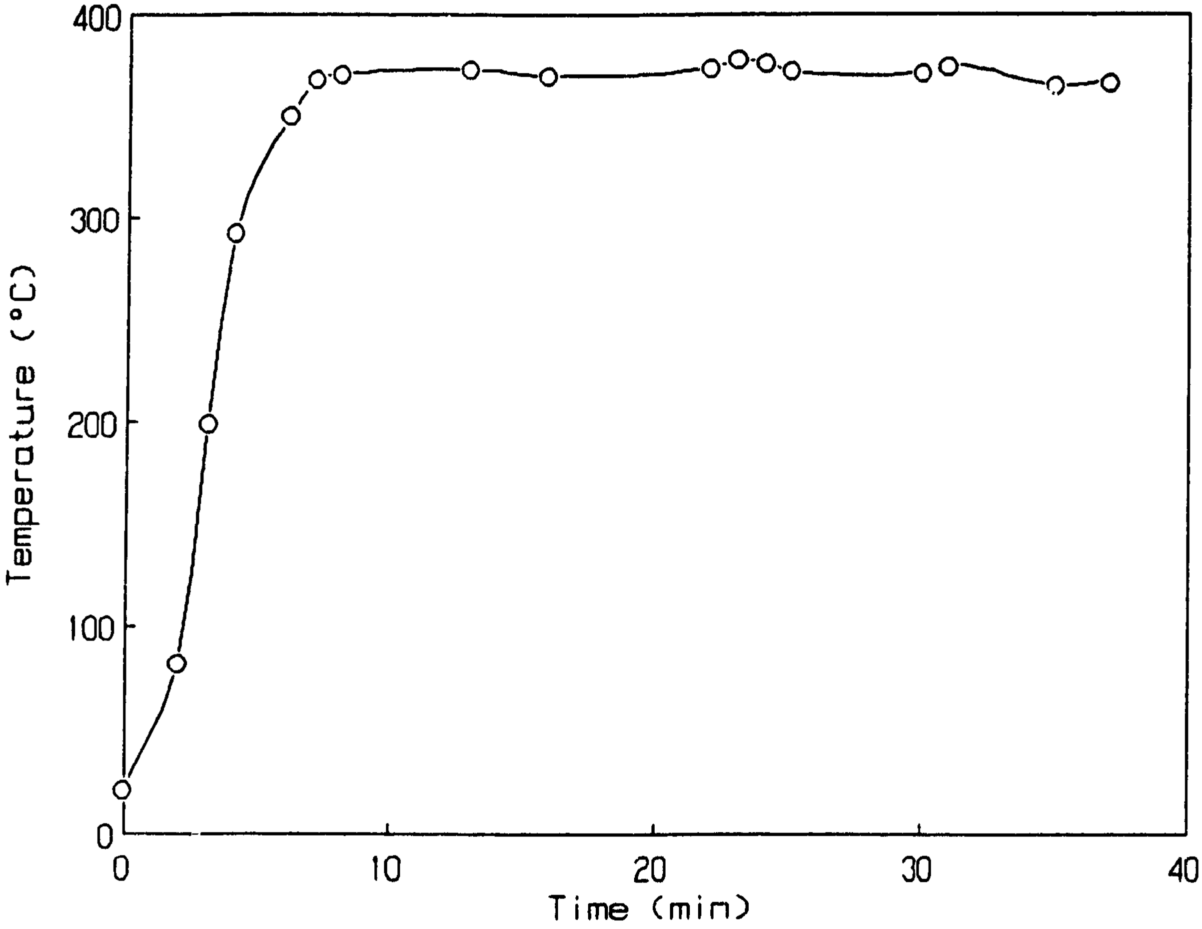


Figure 4.3.1 Typical temperature profile

Table 4.4.1 Gas Chromatograph Conditions

Chromatograph	Hewlett Packard 5890A
Detector	Flame ionization
Column	6' x 1/8" stainless steel
Packing	5.0% SP-1200/1.75% Bentone 34 on 100-120 mesh Supelcoport
Column temperature	120°C
Injector temperature	250°C
Detector temperature	300°C
Helium flow	30 ml/min
Hydrogen flow	30 ml/min
Air flow	300 ml/min
Sample size	0.05 μl

Table 4.4.2 Gel Permeation Chromatograph Conditions

Chromatograph	Varian 5010
Detector	Varian RI-4
Columns	Ultrastyragel 100,500,10^3,10^4Å
Temperature	35°C
Solvent	Tetrahydrofuran
Flow rate	1 ml/min
Type of calibration	Series of narrow PS standards

The volatile fraction was characterized using GC. For the quantitative results, it was assumed that the area under each peak was directly proportional to the corresponding amount of component and independent of its chemical structure. This assumption is reasonable because the correction factors were found to be 1.0 ± 0.05.

GPC was used to determine the molecular weights and molecular weight distributions for the original polystyrene and for the polystyrene degradation reaction residue. The calibration curves are shown in the appendix.

5. RESULTS

5.1 Mass Balances

In all, thirty six experiments were carried out, using polystyrene alone, mixtures of polystyrene with catalysts, and consumer polystyrene in the form of a clear polystyrene cup. The degradation products formed were the condensed volatile fraction in the collection vessels and the residue in the reaction vessel. Mass balances for all the experiments are summarized in Table 5.1.1 and are illustrated in Figure 5.1.1. This is a graph of the amount of the volatile fraction formed versus the amount of weight lost from the reaction vessel. The losses were consistent between experiments as seen by the linearity of the experimental data. On average, the losses were equal to 22% (standard deviation = 7%) of the weight of the original polystyrene.

Table 5.1.1 Mass Balances for all Experiments

Experiment	Temp.	Yields (%wt of PS):			
Number	(°C)	Residue	Volatiles	Styrene	Losses
1	355	42.6	30.8	30.0	26.6
2	357	20.8	62.4	57.9	16.8
3	353	46.5	41.5	38.5	12.0
4	351	73.3	7.1	6.8	19.6
5	352	72.6	5.9	5.6	21.5
6^d	353	67.5	10.9	10.5	21.6
7	357	54.7	17.9	17.4	27.4
8	368	12.9	54.7	53.8	32.4
9	354	54.5	15.6	15.4	29.9
10	350	26.9	26.9	26.2	46.2
11	331	67.6	6.1	5.9	26.3
12	333	75.6	7.7	7.4	16.7
13	335	67.2	26.8	26.3	6.0
14	391	5.4	72.1	63.2	22.5
15	407	18.7	69.5	64.2	11.8
16	348	66.2	13.0	12.9	20.8
17	408	8.2	58.3	50.5	33.5
18	403	6.9	67.6	60.6	25.5
19	406	6.9	78.0	70.8	15.1
20	371	59.4	21.4	20.7	19.2
21	372	39.2	33.4	31.8	27.4
22	385	14.8	66.6	60.8	18.6
23^e	385	22.9	71.2	60.6	6.0
24^f	392	29.7	60.0	56.0	10.3
25^g	391	31.1	57.7	51.4	11.2
26	383	33.5	44.0	40.2	22.5
27	376	39.4	36.9	31.9	23.7
28	391	20.4	55.9	52.3	23.7
29	408	12.8	71.3	65.8	15.9
30	344	71.3	9.5	9.3	19.2
31	408	8.9	71.1	64.4	20.0
32	387	14.7	63.6	58.7	21.7
33	395	11.1	70.2	63.6	18.7
34	402	3.7	75.9	65.9	20.4
35	392	15.2	67.7	58.2	17.1
36^h	383	33.6	40.1	37.6	26.3

(d) PS + silica-alumina

(e) PS + poly(α-methylstyrene)

(f) PS + antioxidant

(g) PS + zeolite

(h) PS cup

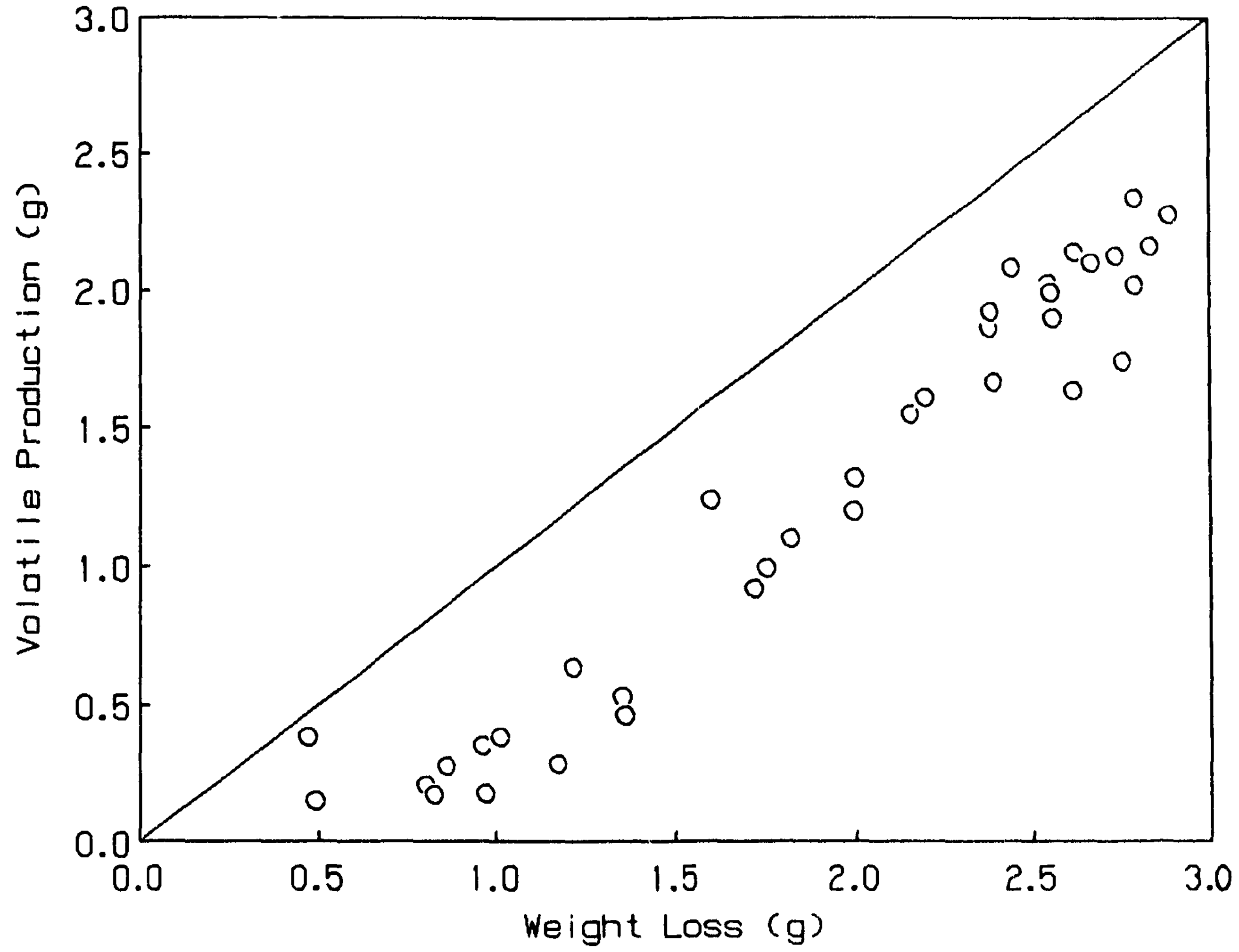


Figure 5.1.1 Mass balances: volatile production versus weight loss for all experiments: — ideal mass balance; ○ experimental values.

5.2 Volatile Fraction

Figure 5.2.1 shows a typical gas chromatogram obtained for the collected volatile fraction. The main components are: styrene, toluene, α-methylstyrene, and ethylbenzene. Trace components are benzene and styrene oligomers.

The composition of the volatile fraction did not change significantly over the temperature range investigated, as can be seen in Table 5.2.1. Figure 5.2.2 gives a typical composition of the volatile fraction, namely, 97.7% styrene, 1.2% α-methylstyrene, 0.9% toluene, 0.1% ethylbenzene, and 0.1% oligomers.

Table 5.2.1 Composition of the Volatile Fraction in % Weight

Temp.(°C)	344	350	355	371
Styrene	98.7(± 0.5)	97.7(±0.5)	97.3(±0.5)	97.0(±0.5)
α-Methylstyrene	0.5(±0.01)	1.2(±0.05)	1.2(±0.05)	1.2(±0.05)
Toluene	0.6(±0.01)	0.3(±0.01)	1.3(±0.05)	1.4(±0.05)
Ethylbenzene	0.1(±0.01)	0.1(±0.01)	0.1(±0.01)	0.3(±0.01)
Oligomers	0.1(±0.01)	0.7(±0.01)	0.1(±0.01)	0.1(±0.01)

The composition of the volatile fraction did change with reaction time. Figure 5.2.3 shows that the styrene and toluene contents decreased with time, while the contents of α-methylstyrene and ethylbenzene increased with time.

Figure 5.2.4 shows the variation of styrene content in the volatile fraction as a function of time for different starting materials, namely, consumer polystyrene (PS cup), polystyrene alone, mixtures of polystyrene with antioxidant, polystyrene with zeolite, and polystyrene with poly(α-methylstyrene)(PMS). There was no difference between the results obtained with polystyrene and with the polystyrene cup. Catalyst addition resulted in lower contents of styrene.

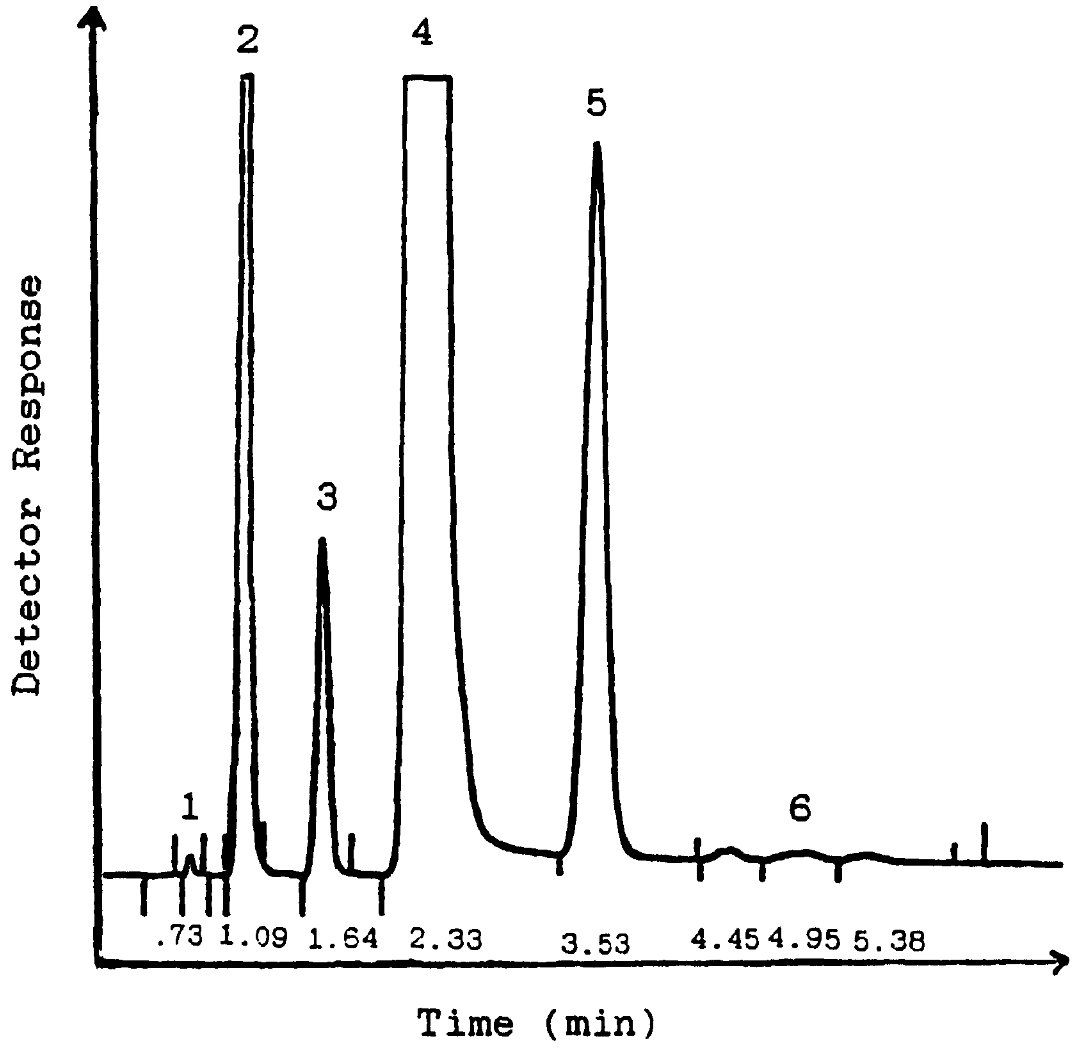


Figure 5.2.1 **Identification of components in volatile fraction by gas chromatography: 1.Benzene 2.Toluene 3.Ethylbenzene 4.Styrene 5.α-methylstyrene 6.Oligomers**

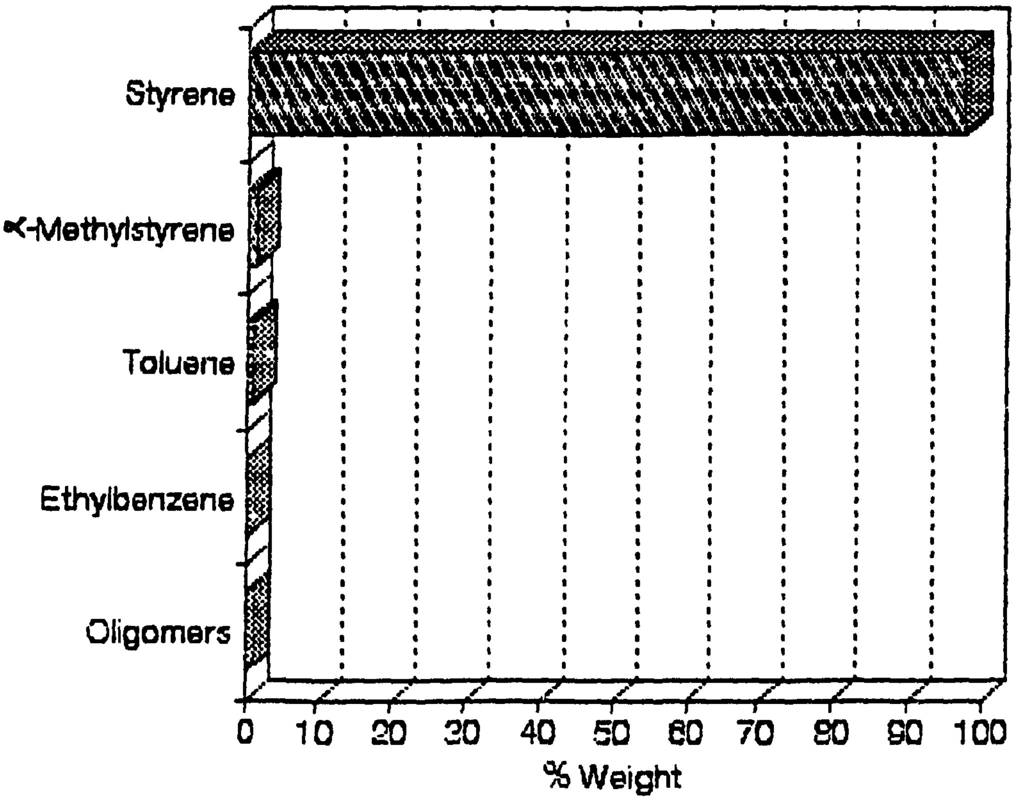


Figure 5.2.2 Typical composition of the volatile fraction

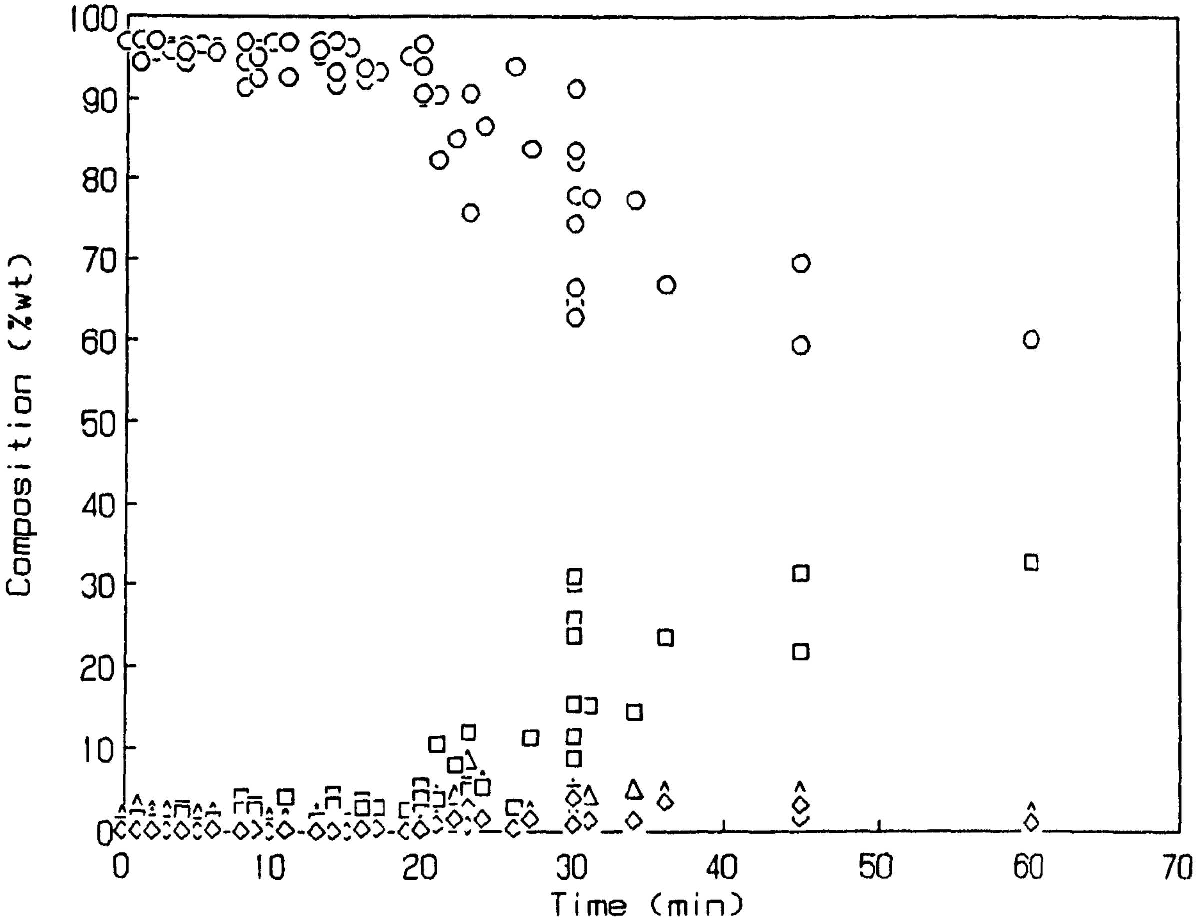


Figure 5.2.3 Composition of the volatile fraction with time:
○ styrene; △ toluene; □ α-methylstyrene; ◇ ethylbenzene

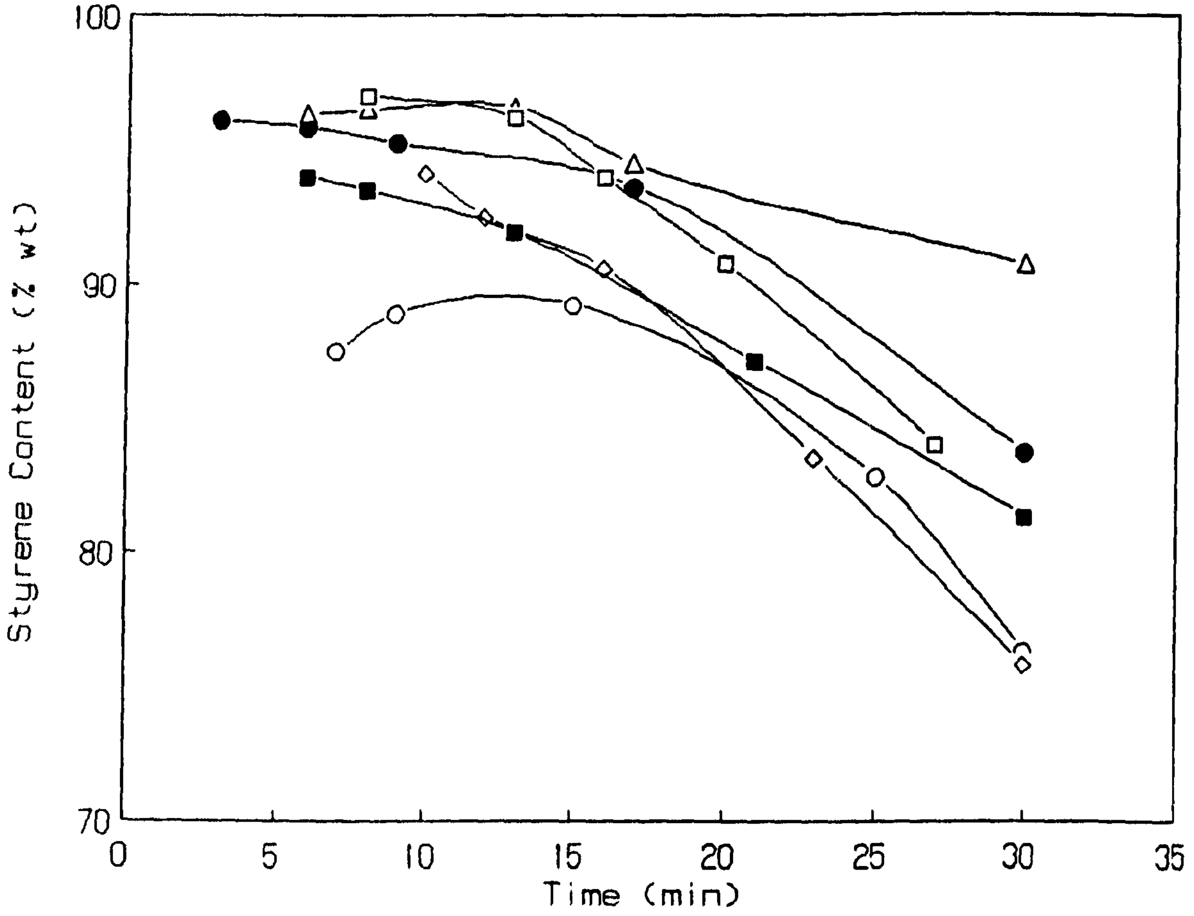


Figure 5.2.4 Styrene content of volatile fraction with time for different starting materials: △ PScup,383°C; □ PS,391°C; ● PS,383°C; ◇ PS+antioxidant,392°C; ■ PS+zeolite,391°C; ○ PS+PMS,385°C

5.3 Residue

Figure 5.3.1 shows the decrease in molecular weight of the polystyrene residue in the reaction vessel as a function of time at a reaction temperature of 354°C. There is a sudden initial drop in molecular weight from 138 000 to 22 000 in the first 30 minutes, followed by a more gradual decrease from 22 000 to 8 900 in the subsequent 30 minutes. The residues obtained were gelatinous in nature.

Figure 5.3.2 shows the molecular weight distribution (MWD) of the original polystyrene and the polystyrene degraded after 30 and 60 minutes of reaction at 354°C. The MWD undergoes dramatic change within 30 minutes. The MWD shifts to the lower molecular weight region. However, a further significant decrease takes place in the subsequent 30 minutes.

Figure 5.3.3 shows the molecular weight distribution of the original polystyrene and the polystyrene degraded after 60 minutes at different reaction temperatures. It can be seen that the MWD has shifted to the lower molecular weight region as the temperature increased.

The polystyrene residues obtained at the higher reaction temperatures (391, 407°C, reaction time=30 minutes) consist mainly of styrene dimer and trimer, and traces of tetramer, monomer, α-methylstyrene, and ethylbenzene. This can be seen in Figure 5.3.4 which illustrates the GPC results for these residues. These residues were liquid and oily in nature.

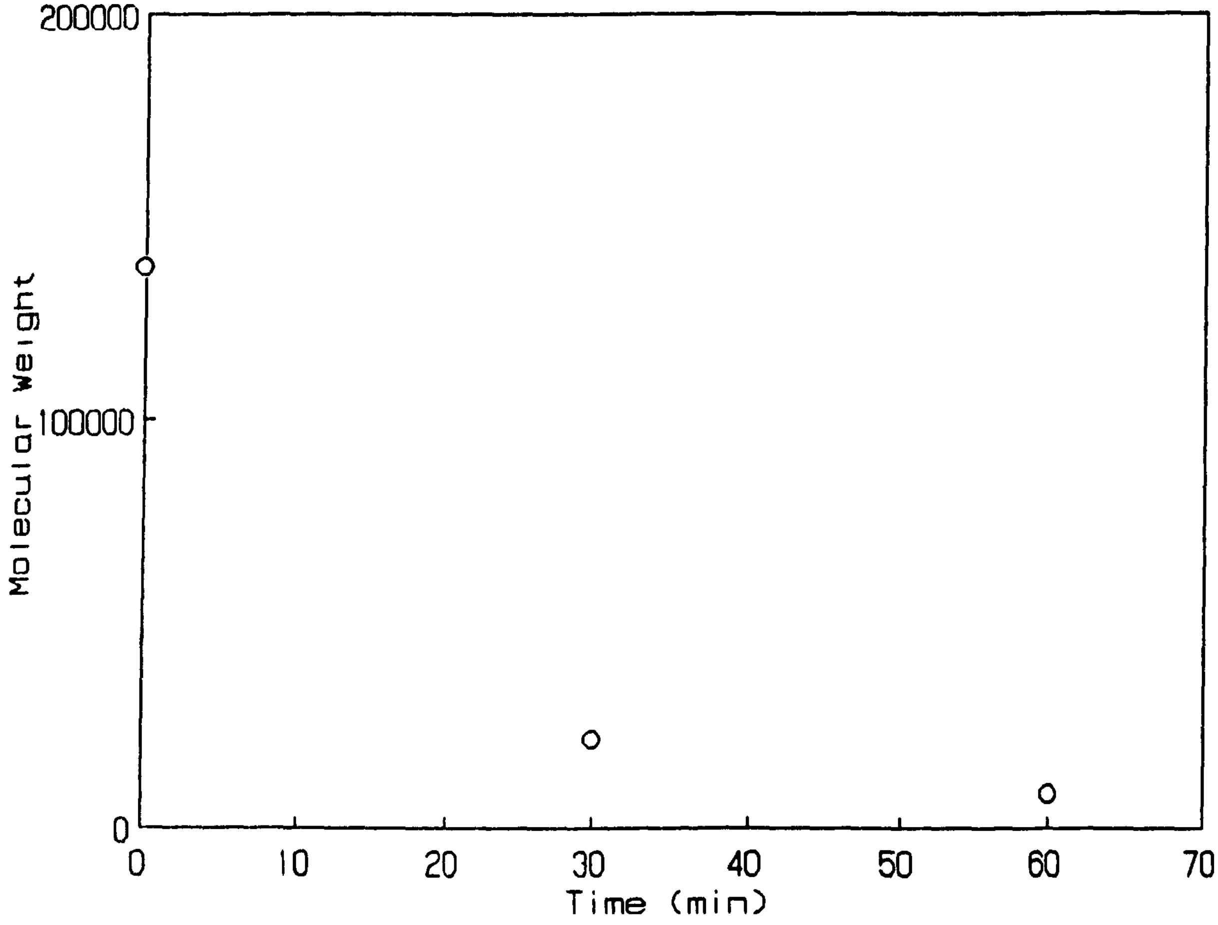


Figure 5.3.1 Molecular weight versus time, T=354°C

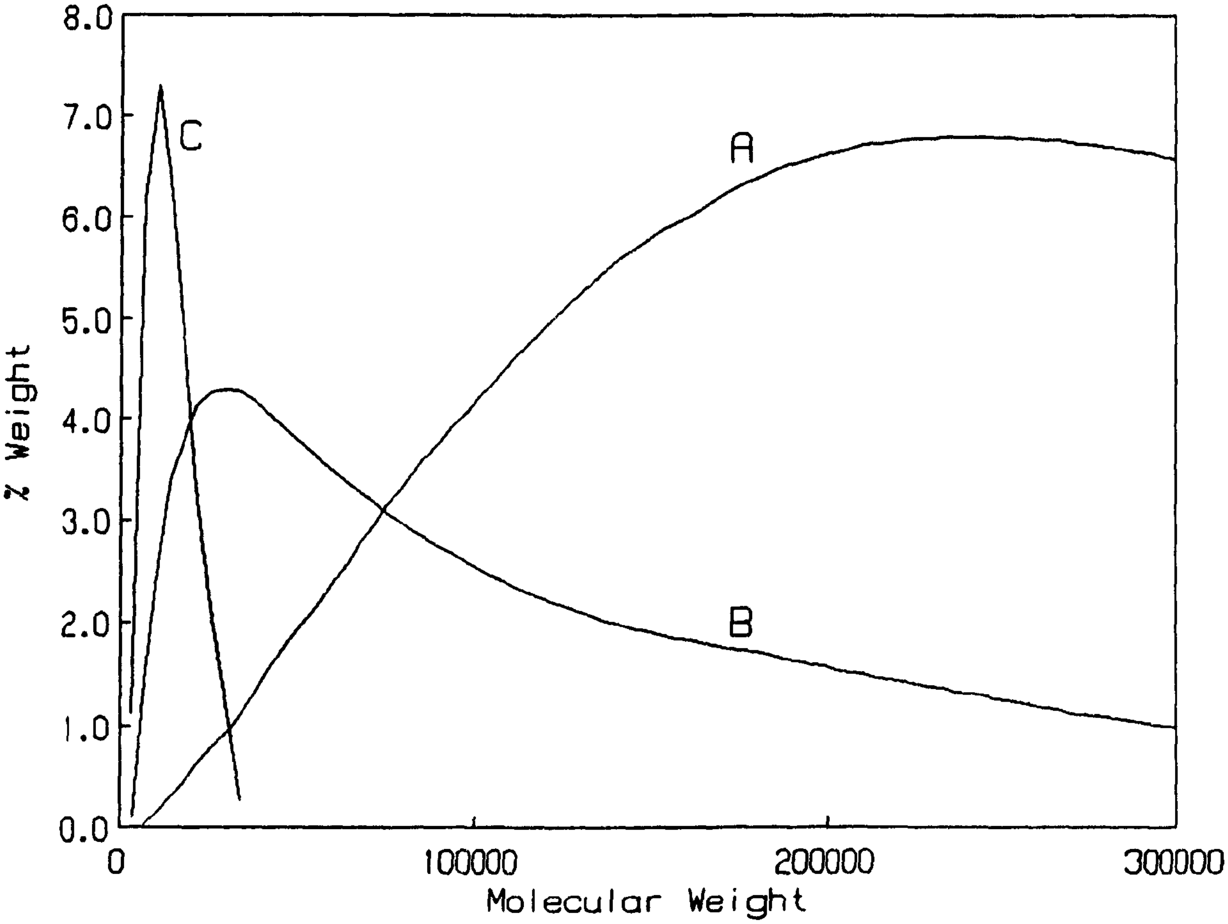


Figure 5.3.2 Change in molecular weight distribution with reaction time: (A)original; (B)30 min; (C)60 min.

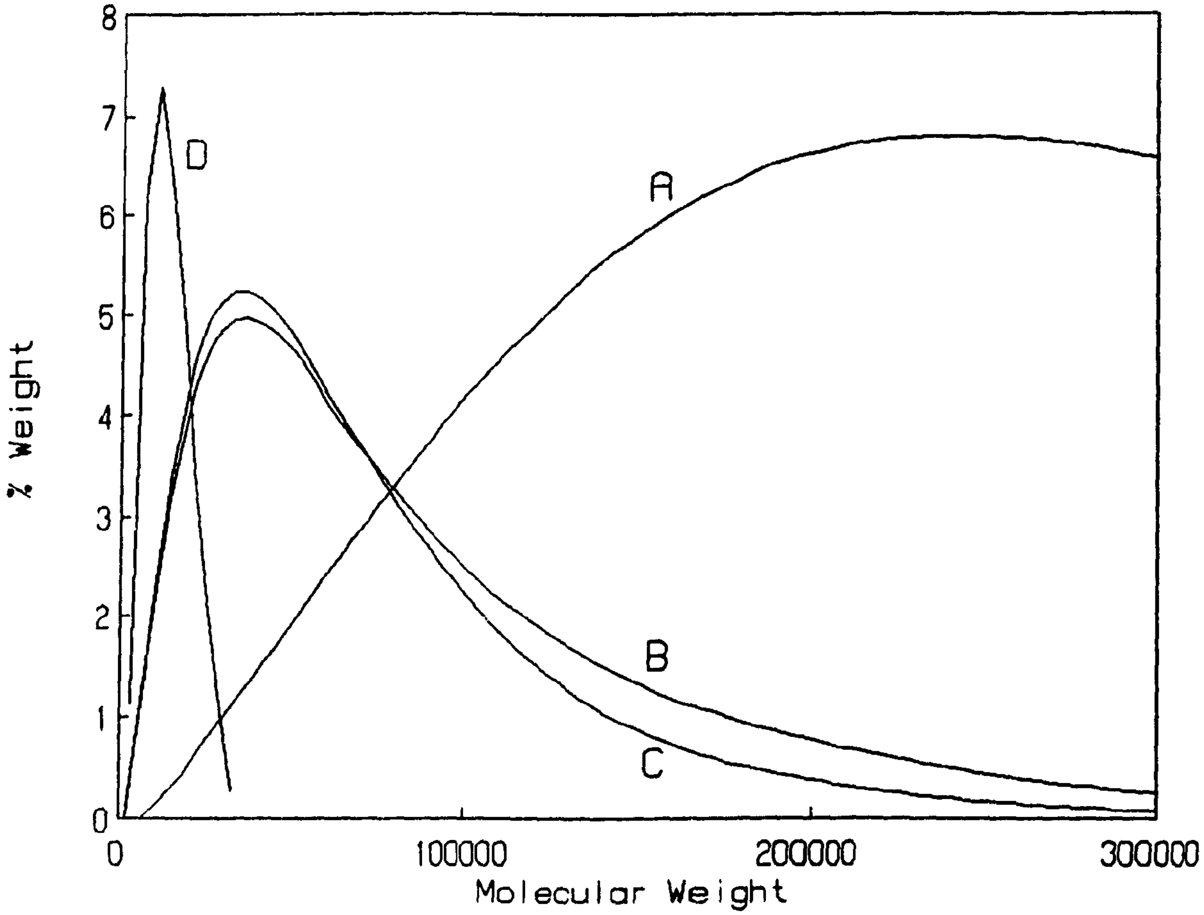


Figure 5.3.3 **Change in molecular weight distribution with reaction temperature: (A)original; (B)341°C; (C)346°C; (D)353°C.**

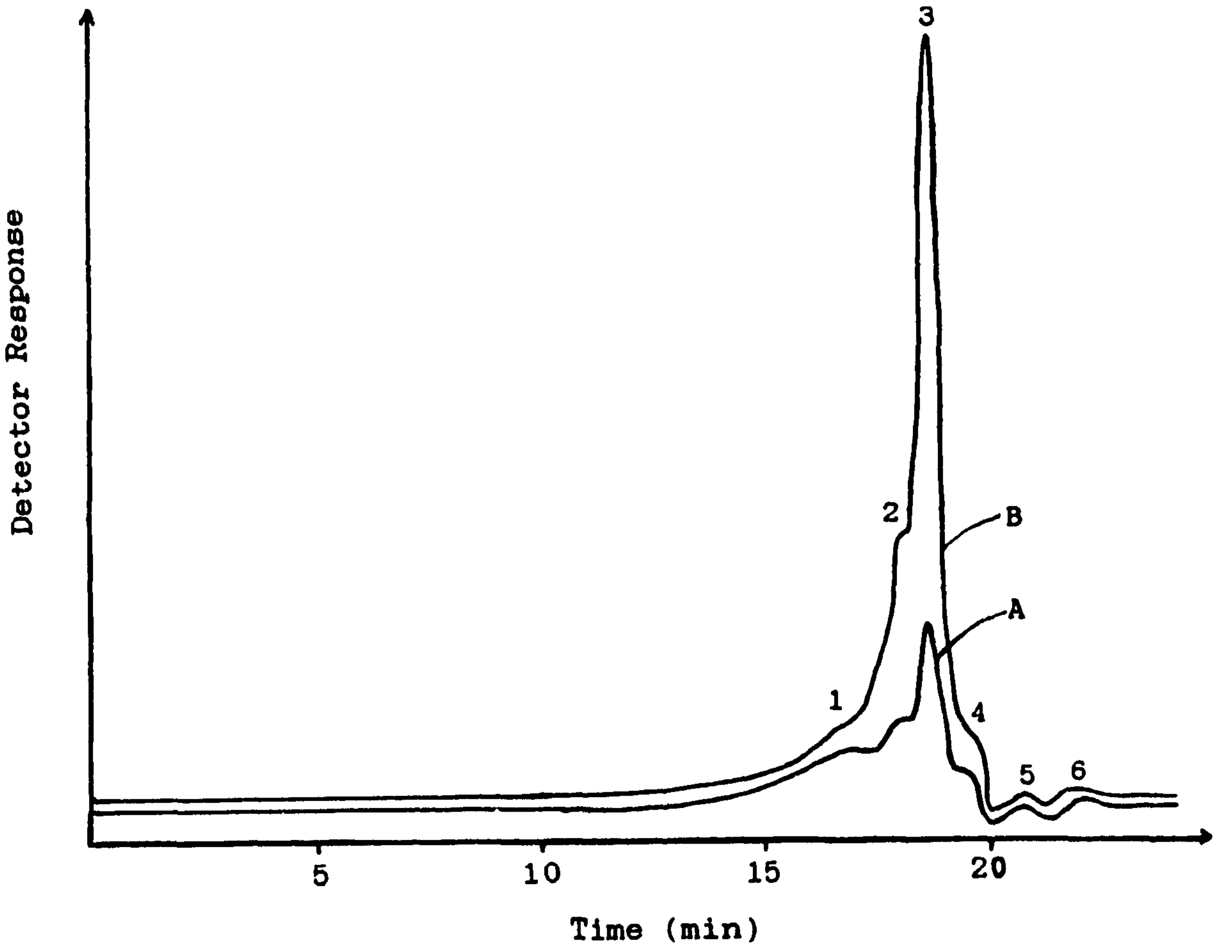


Figure 5.3.4 Composition of residues obtained at the higher temperatures: (A)391°C; (B)407°C; 1.tetramer 2.trimer 3.dimer 4.monomer 5.α-methylstyrene 6.ethylbenzene

5.4 Yields

Figures 5.4.1 and 5.4.2 show the yields (as % weight of the original polystyrene) of styrene and of residue as a function of reaction temperature for different reaction times. It can be seen that there is no difference between the results for the different reaction times. The figures also include the results of the experiments performed with mixtures of polystyrene and catalysts, and with a clear polystyrene cup. It can be seen that there is no difference in the results using these and using polystyrene alone. The yield of styrene increases and the yield of residue decreases with reaction temperature as illustrated in Figure 5.4.3. Up to 70% of the polystyrene was converted to styrene after reacting at 406°C for 45 minutes. After 30 minutes of reaction at 402°C, 66% of the polystyrene was converted to styrene.

5.5 Kinetics

Figure 5.5.1 shows the yield of styrene (as % weight of the original polystyrene) as a function of time for six different reaction temperatures.

$\ln(1-X)$ versus time for six different temperatures was plotted where X is the conversion of polystyrene to styrene. This is shown in Figures 5.5.2 to 5.5.7. The slopes of the lines give the rate constants for the different temperatures. These are reported in Table 5.5.1.

Table 5.5.1 Rate Constants at Different Temperatures

Temp.(°C):	408	402	395	392	383	376
k(min^{-1}):	0.396	0.119	0.071	0.056	0.025	0.011

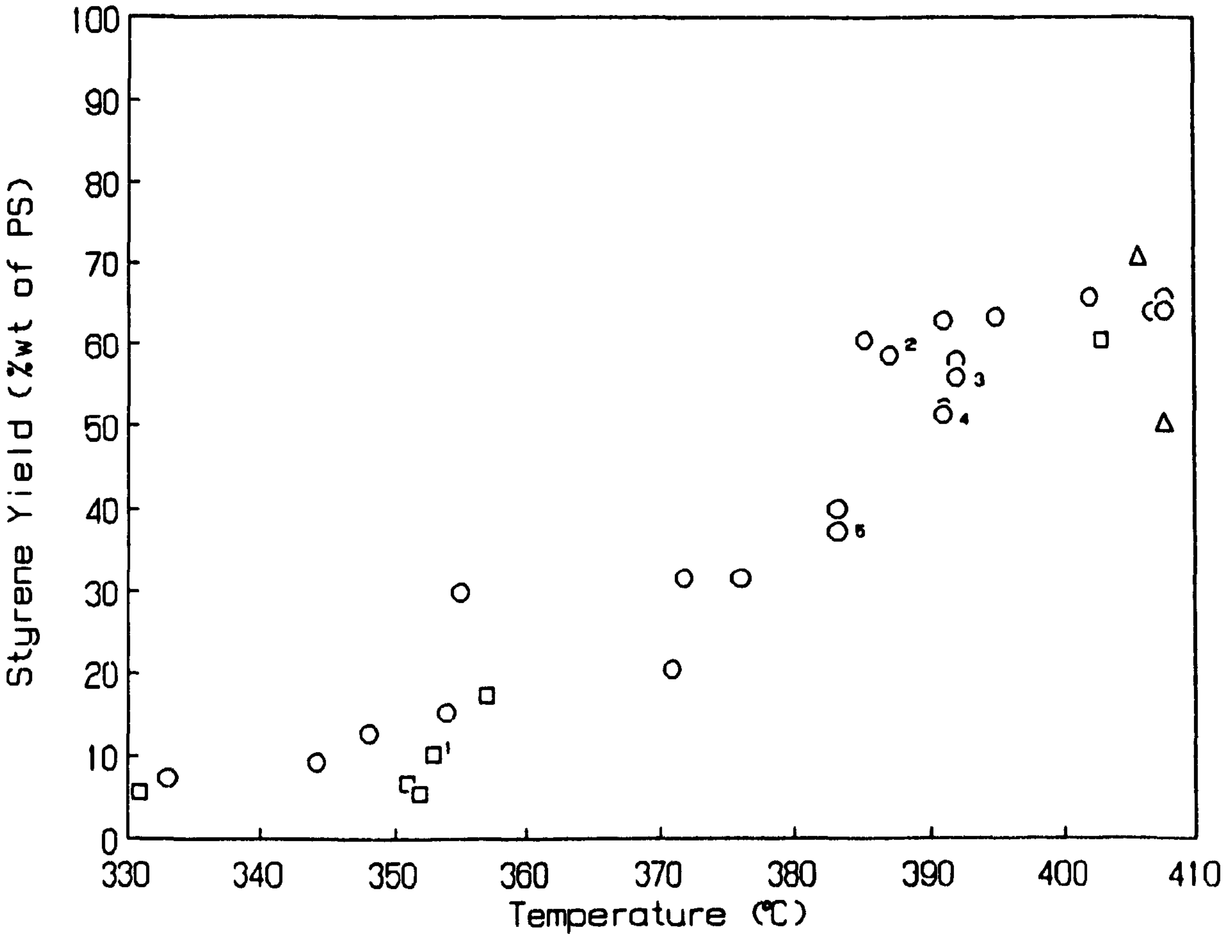


Figure 5.4.1 Styrene yield versus temperature for different reaction times: ○ 30 min; △ 45 min; □ 60 min; 1.PS+silica-alumina 2.PS+PMS 3.PS+antioxidant 4.PS+zeolite 5.PScup.

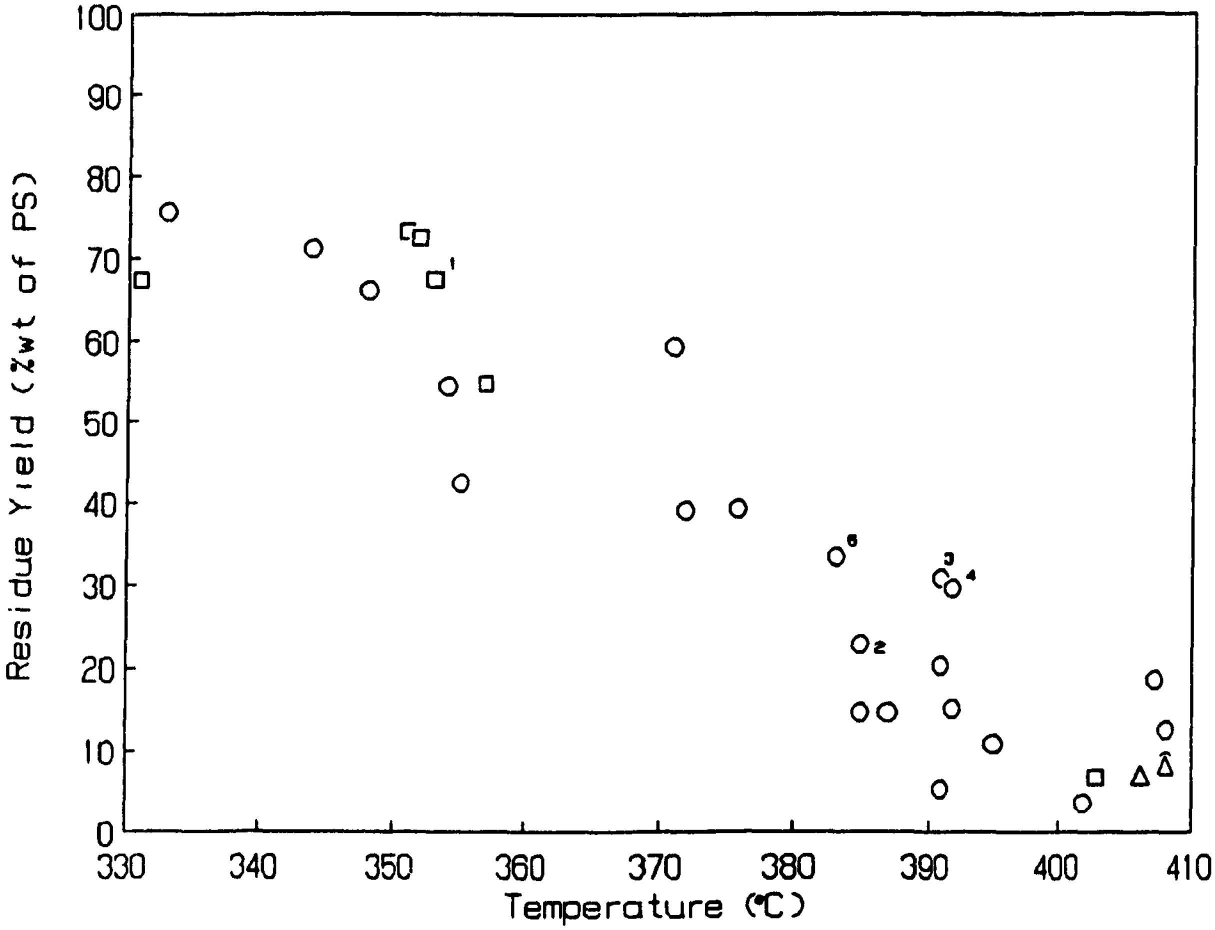


Figure 5.4.2 Residue yield versus temperature for different reaction times: ○ 30 min; △ 45 min; □ 60 min; 1.PS+silica-alumina 2.PS+PMS 3.PS+antioxidant 4.PS+zeolite 5.PScup.

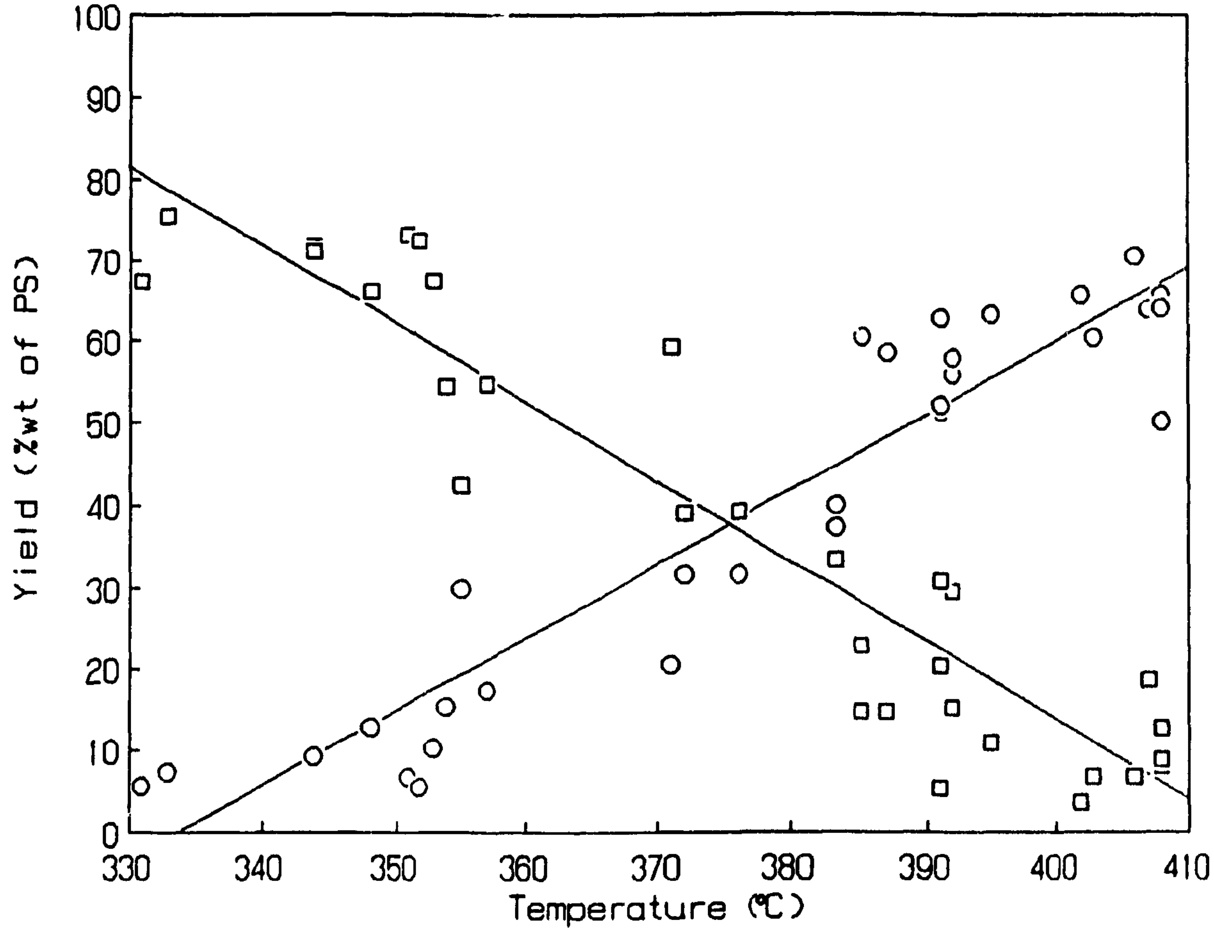


Figure 5.4.3 Yields of products versus temperature: ○ styrene; □ residue

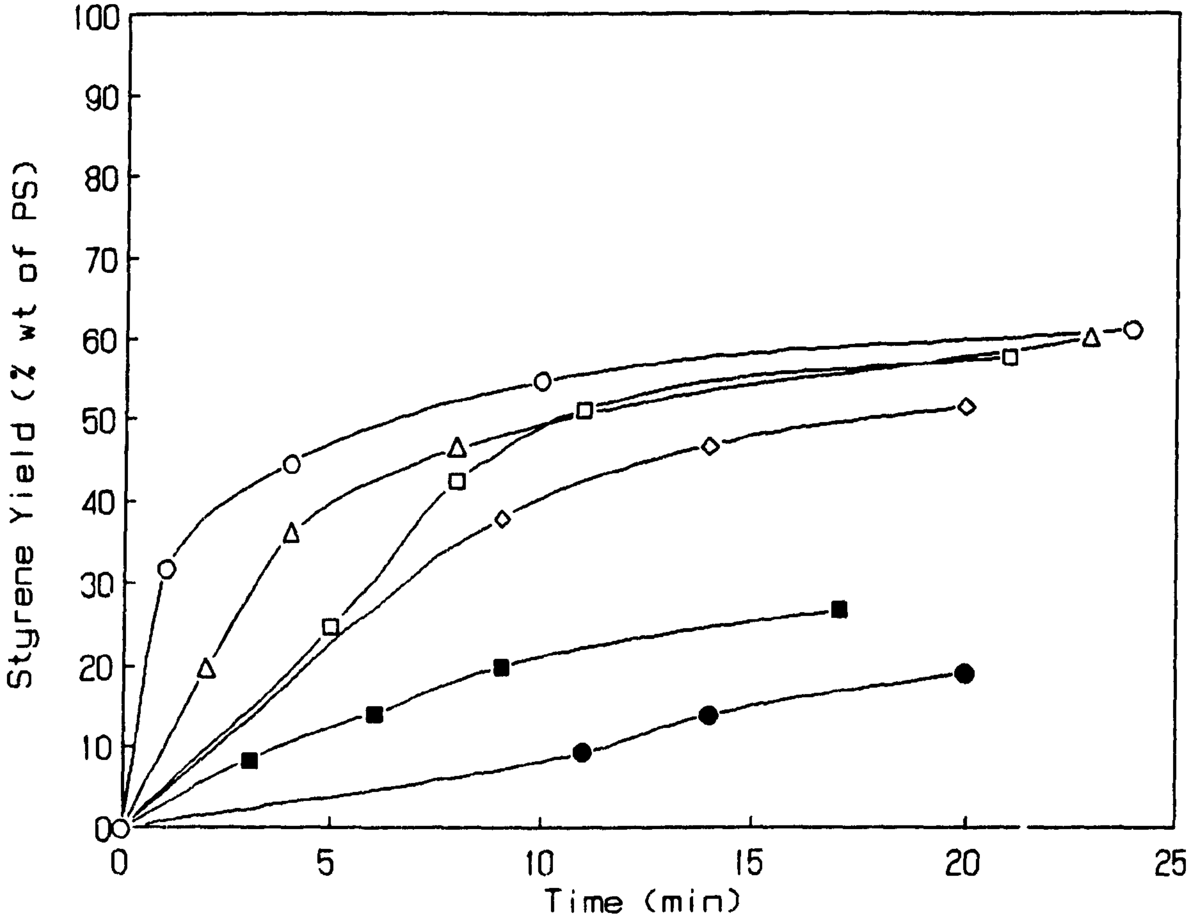


Figure 5.5.1 Styrene yield with time at various temperatures: ○ 408•C; △ 402•C; □ 395•C; ◇ 392•C; ■ 383•C; ● 376•C

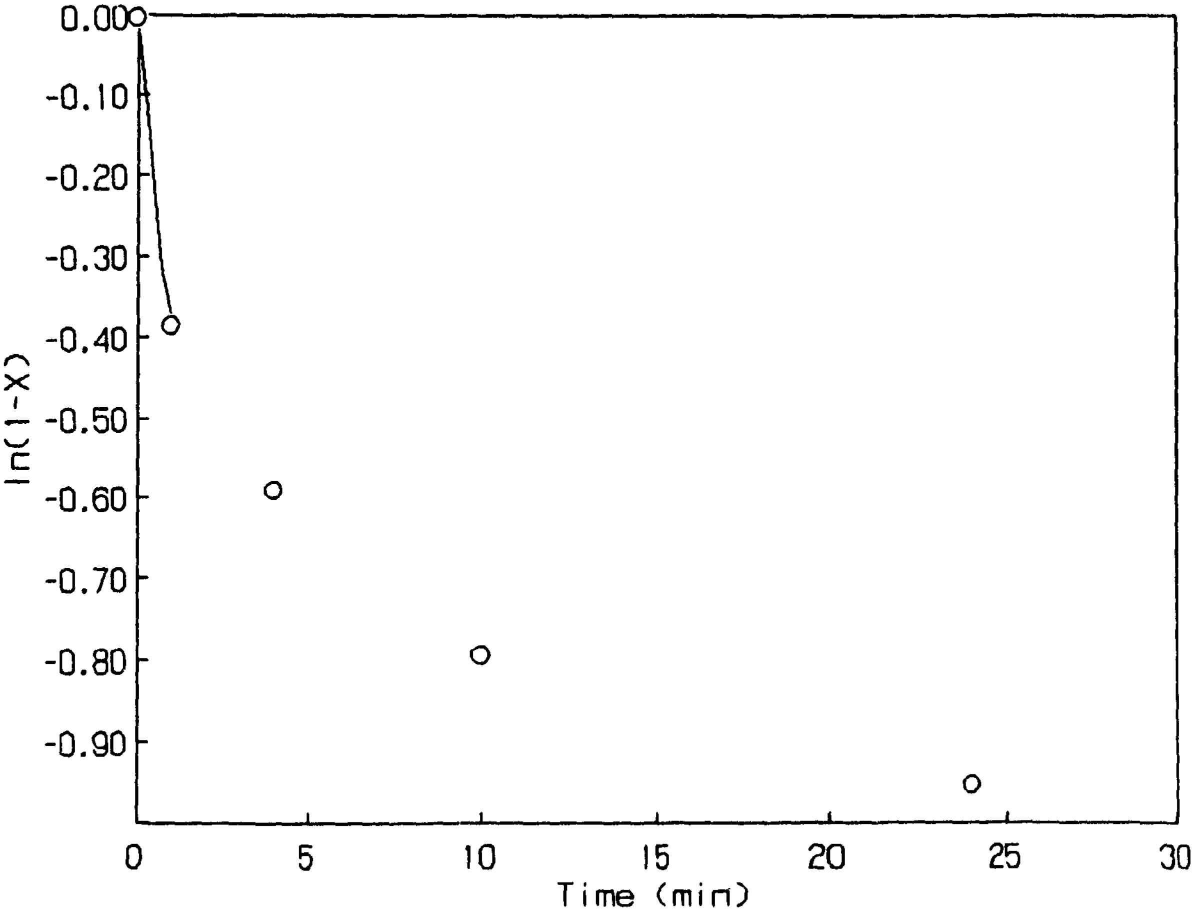


Figure 5.5.2 First order model, ln(1-X) versus time, T=408 °C

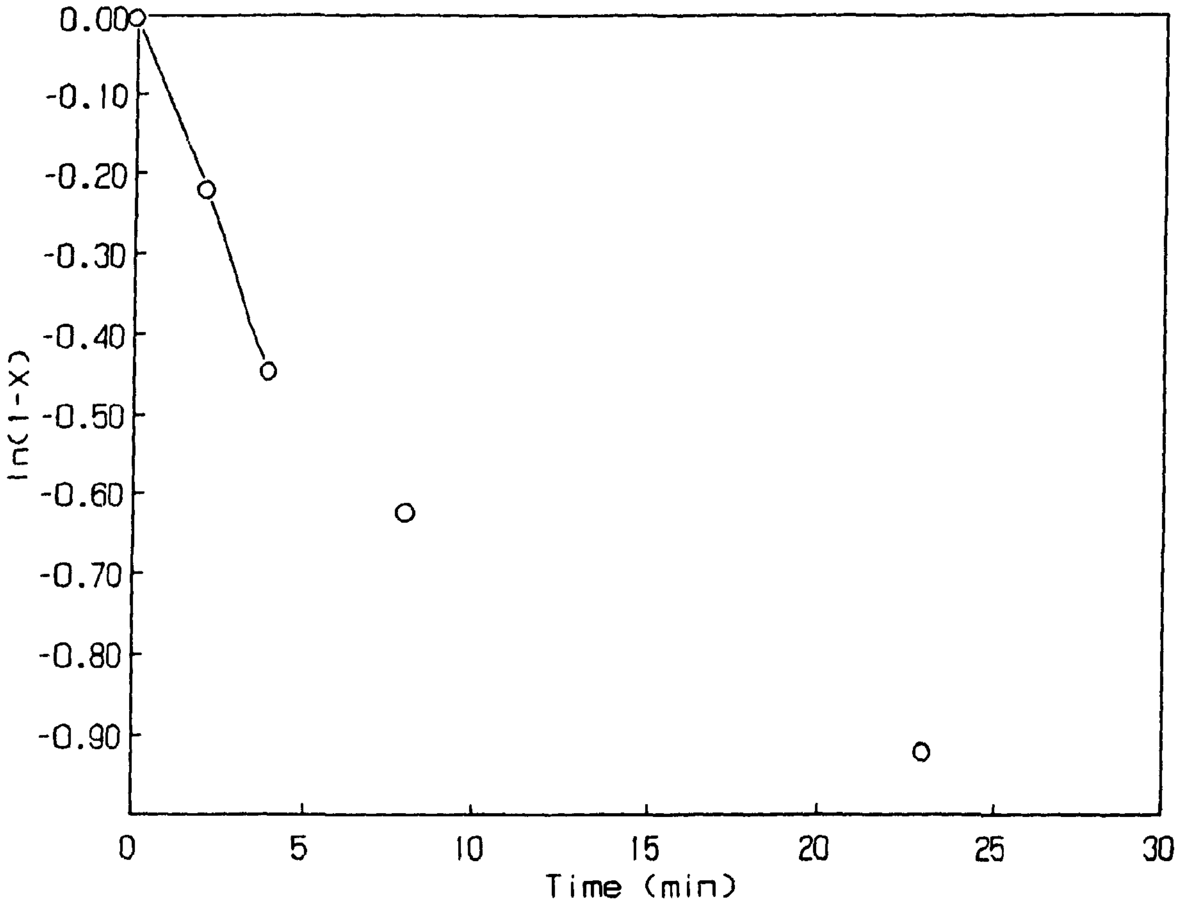


Figure 5.5.3 First order model, ln(1-X) versus time, T=402°C

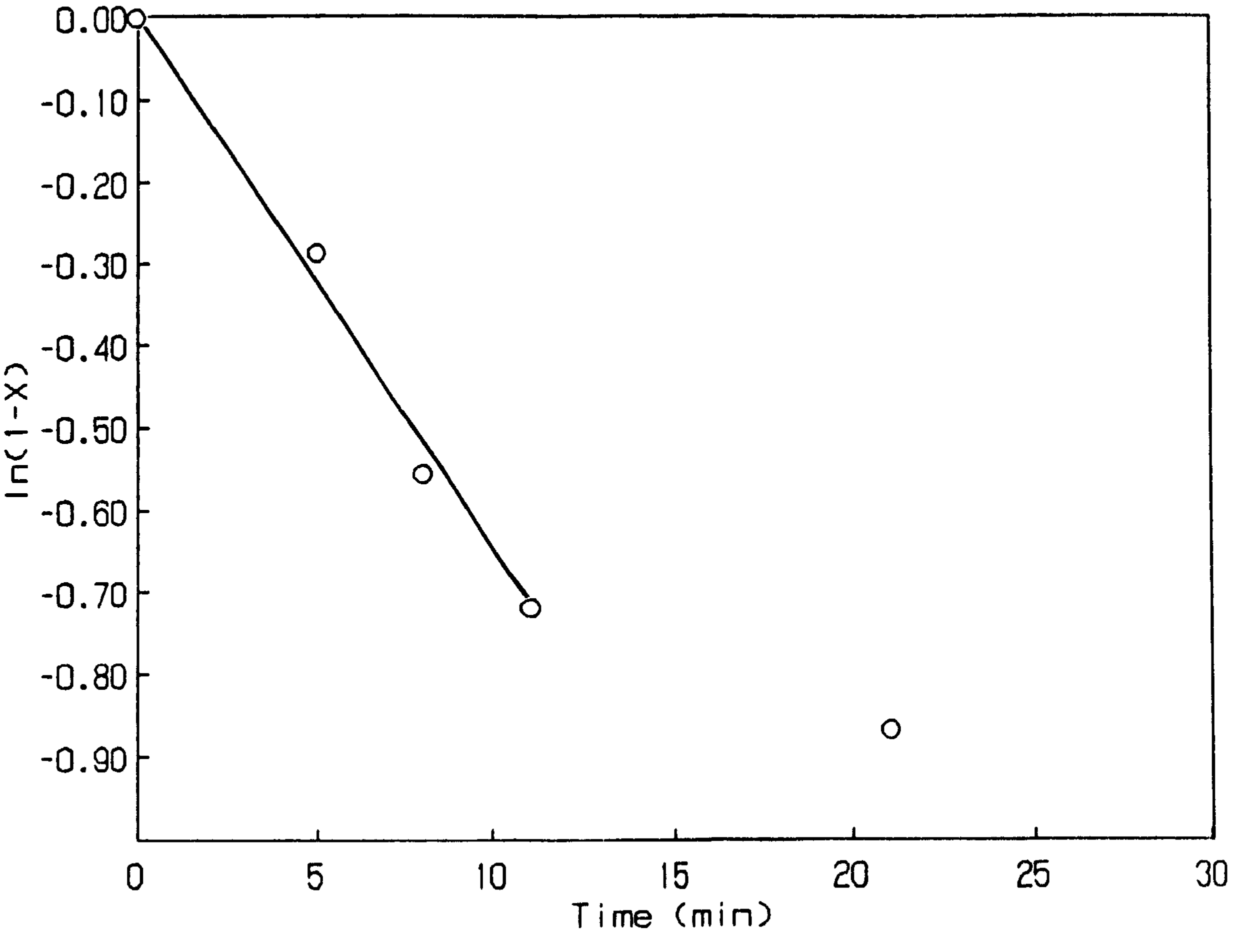


Figure 5.5.4 First order model, ln(1-X) versus time, T=395°C

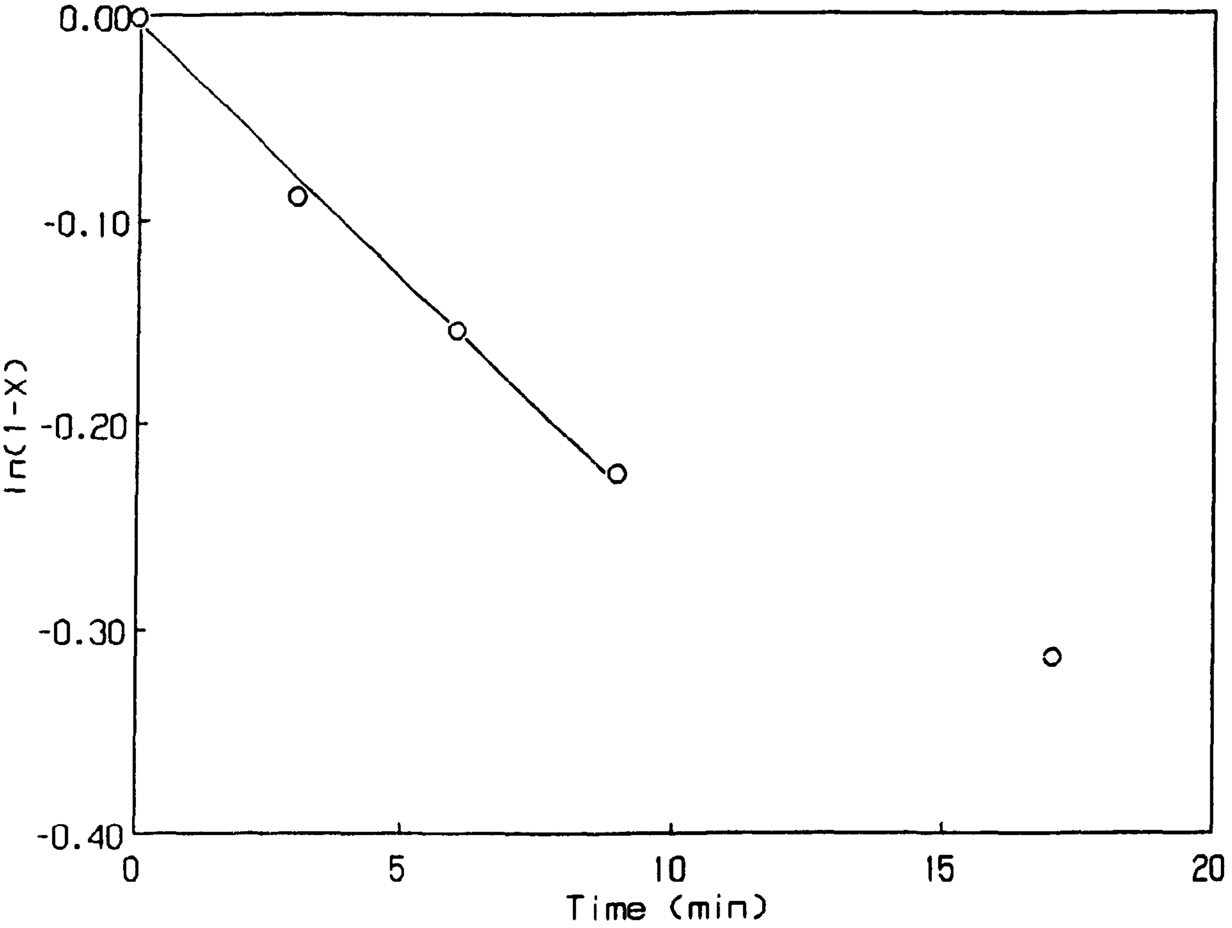


Figure 5.5.5 First order model, ln(1-X) versus time, T=392°C

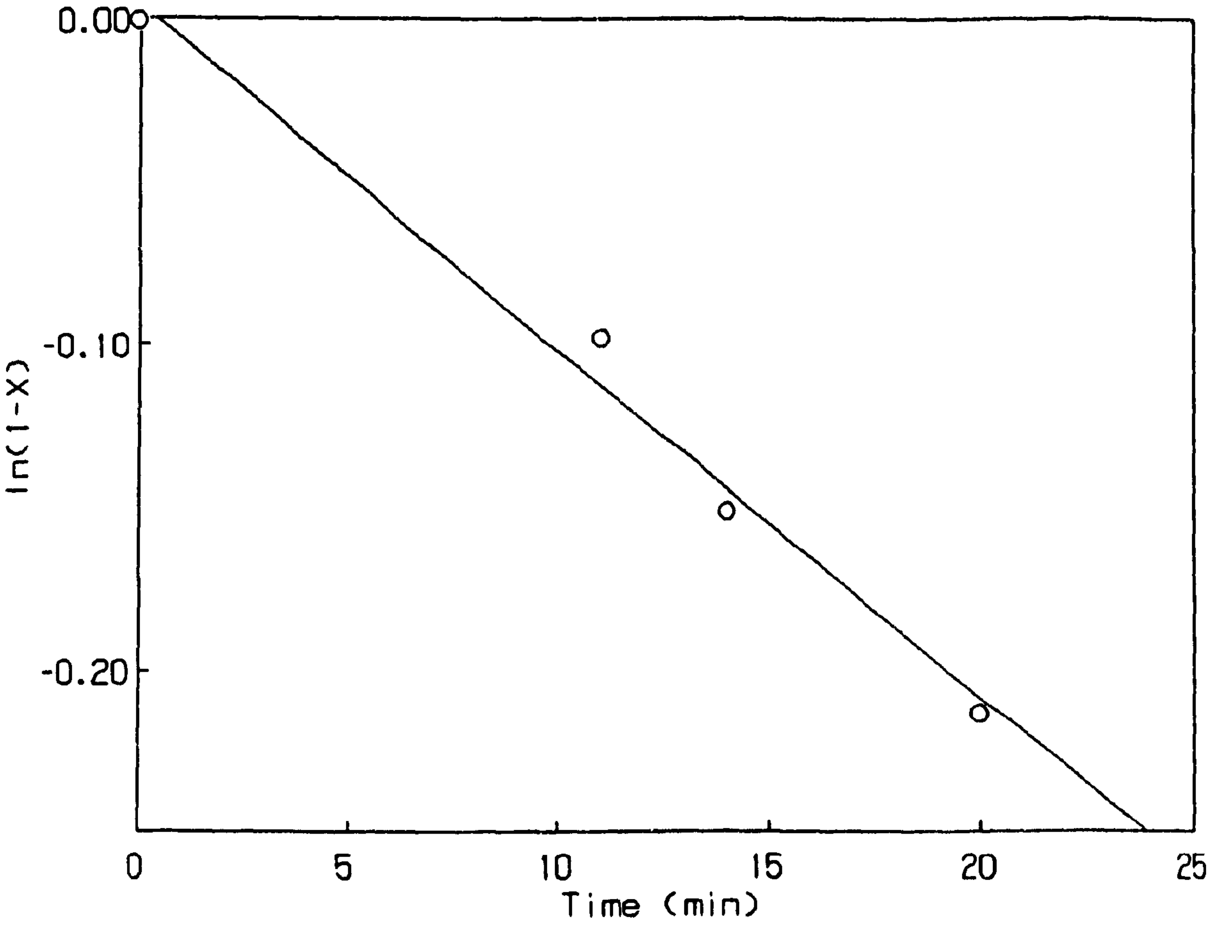


Figure 5.5.6 First order model, ln(1-X) versus time, T=383°C

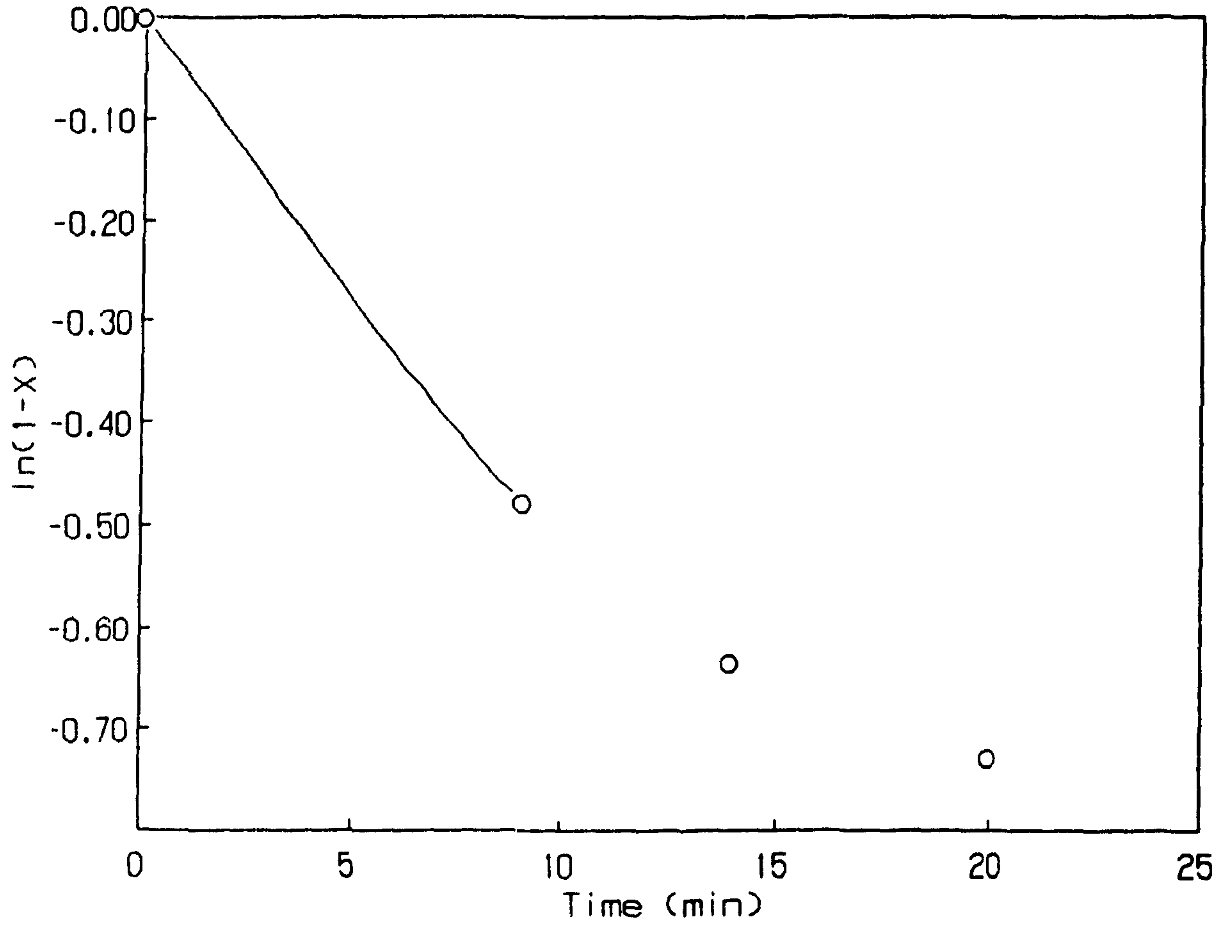


Figure 5.5.7 First order model, ln(1-X) versus time, T=376°C

The Arrhenius plot of lnk versus 1/T is given in Figure 5.5.8. The linear fit of the experimental data is quite good ($R^2=0.976$). The activation energy obtained is 181 kJ/mol (43.3 kcal/mol).

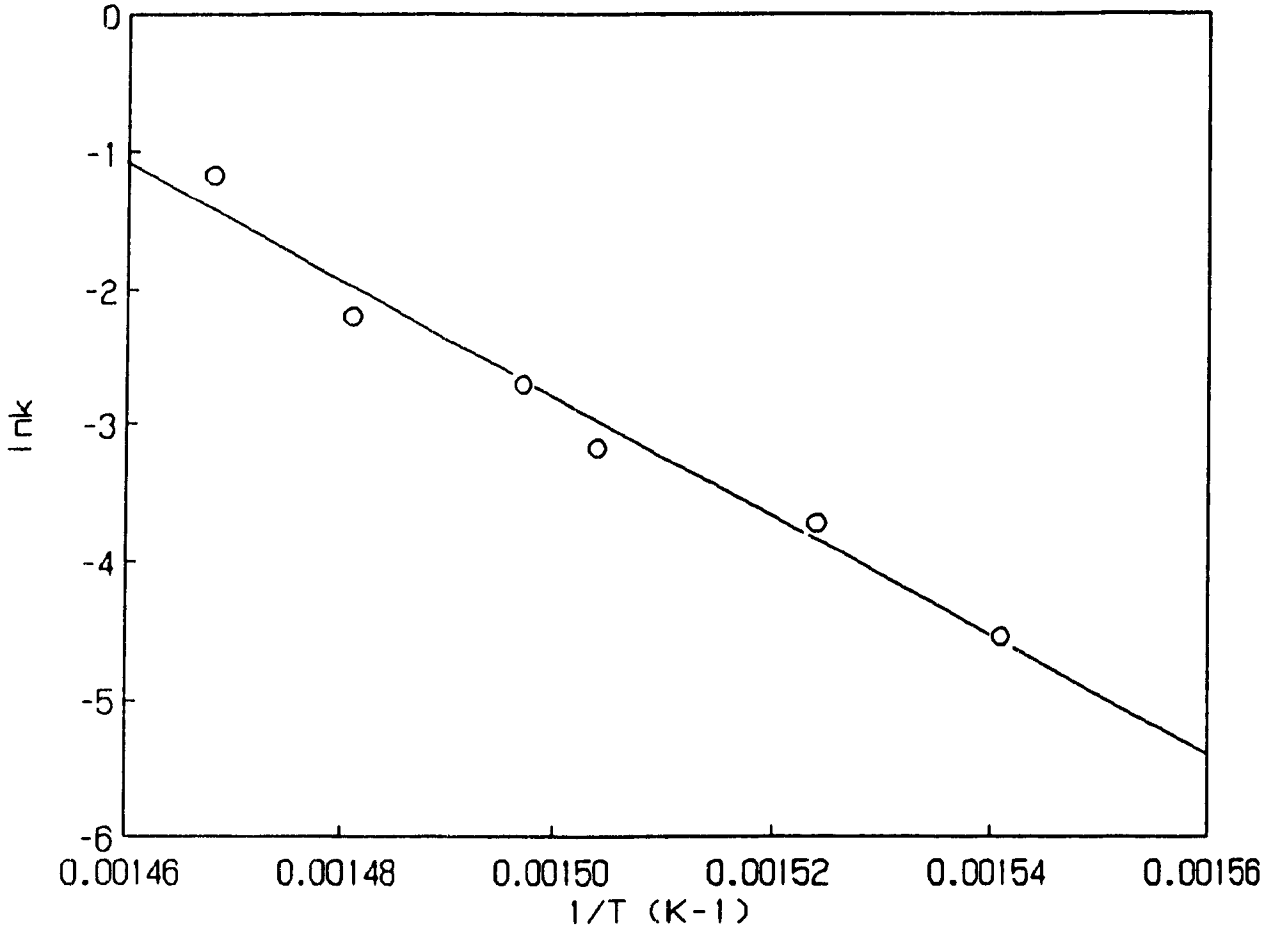


Figure 5.5.8 Arrhenius plot

6. DISCUSSION

6.1 Reproducibility

Complete conversion of the volatiles to liquid products with no losses in the apparatus would give the line illustrated in Figure 5.1.1. However, as can be seen in the figure, the mass balances did not reach this ideal. Due to the nature of the apparatus, not all of the liquid could be recovered (e.g., liquid stuck in the glass tubing and joints). However, the experimental data are linear and the losses are consistent between experiments. The experimental method utilized was reproducible.

6.2 Effect of Catalysts

The experiments performed with mixtures of polystyrene and catalysts were found to be no different from experiments with polystyrene alone, as can be seen in Figures 5.4.1 and 5.4.2, and in Table 5.1.1. The effect of the potential catalysts is negligible on the yields of styrene and residue. These results are in sharp contrast with other workers, who found that the catalysts improve polystyrene degradation. This is summarized in Table 6.2.1.

Our results without catalysts compare equally or are better than the results of Ide et al. [68] and much better than the results of Audisio et al. [64] in terms of the yield of styrene. This is probably due to differences in the experimental arrangement. The present study shows that the catalysts employed in this study do not contribute significantly to increasing the degradation rate of polystyrene or the yield of styrene.

Table 6.2.1 Comparison of Results for Catalytic and Thermal Degradation

Authors	Set-Up	Temp.(°C)	Time (hr)	Styrene Yield (%wt of PS)
Ide et al. [67]	N_2 atm. PS + active charcoal	300 350	2.4 2.4	49 43
Audisio et al. [63]	vacuum PS + silica-alumina PS + zeolite	350 550 350 550	1 1 1 1	1 4 3 28
This work	N_2 atm. PS alone	353 357 383 407	1 1 0.5 0.5	39 58 40 64

6.3 Effect of Starting Material

The styrene content of the volatile fraction obtained was slightly dependent upon the starting material, as seen in Figure 5.2.4. The mixtures of polystyrene and catalyst gave less styrene than polystyrene alone because the catalysts altered the chemistry of the degradation reaction. For example, the mixture of polystyrene and poly(α-methylstyrene) (PMS) resulted in a liquid containing less styrene but more α-methylstyrene due to the presence of PMS which depolymerizes to form α-methylstyrene.

However, there is no difference in the styrene content of the volatile fractions obtained when thermally degrading polystyrene waste or when using pure polystyrene. By comparing the results of experiments number 26 and 36 in Table 5.1.1, it can be seen that the results in terms of the yields of styrene and residue were the same for pure polystyrene and the polystyrene cup. The same conclusions can be made by examining Figures 5.4.1 and 5.4.2. Therefore, there is no difference when using consumer polystyrene or pure polystyrene as the starting material for our set-up. This is encouraging news in terms of future chemical recycling of polystyrene waste.

6.4 Styrene Content of Volatile Fraction

The composition of the volatile fraction did not change significantly in the temperature range investigated (330-410°C), as this range was quite small. This is in accordance with Madorsky et al. [48,49] as can be seen by their results in Table 2.3.3, namely a constant composition of the volatilized part. However, the composition of the volatile fraction itself is significantly different from the composition obtained by other workers [48,49,76,88,89] who have in addition identified styrene dimer and trimer in the volatile fraction in greater amounts than obtained here. Table 6.4.1 shows the styrene content in the volatile fraction obtained by different researchers.

It is not surprising that the styrene content in the volatile fractions obtained by different researchers vary since different conditions were employed. Different levels of pressure or vacuum were used thereby allowing more or less volatile intermediate products to leave the reaction mixture. Also, the temperatures were different. Even the sample sizes were not the same. Inside a large sample, diffusion of the degradation products is retarded and the products are thus subject to secondary reactions [18]. The extent of the reaction depends on many factors, for example, the initial reaction temperature, the rate of cooling of the products, the rate of flow of nitrogen, the geometry and thermal properties of the reaction vessels, etc.

Table 6.4.1 Styrene Content of Volatile Fraction Obtained by Different Researchers

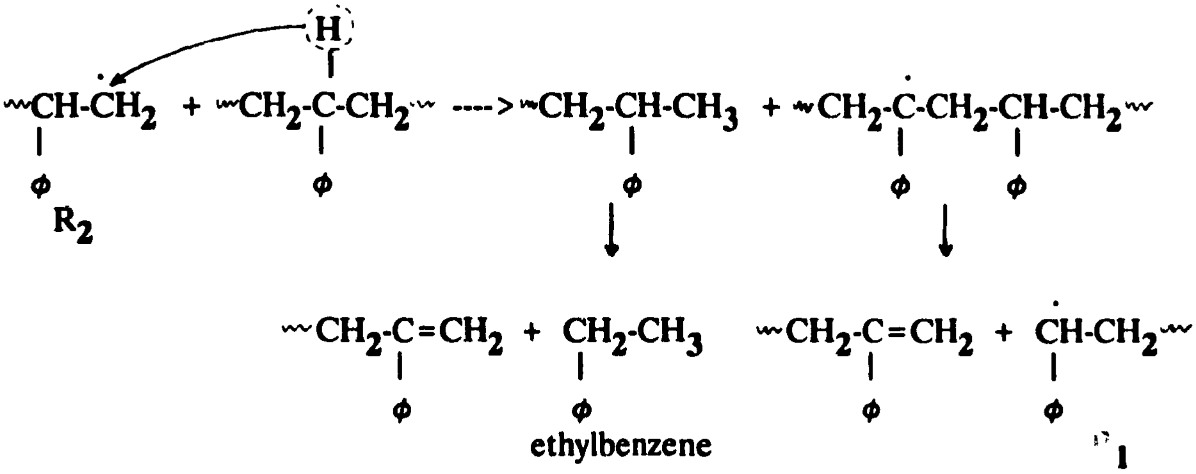
Authors	Set-Up	Temp. (°C)	Time (hr)	Styrene Content of Volatiles (wt.%)
Costa et al. [76]	N_2 atm.	348	40%volatilization	36
Madorsky et al. [47,48]	vacuum	336-375	0.5-4	41
Lehmann and Brauer [88]	He atm. flash pyrolysis	425 525 625	-----	64.3 67.5 74.4
Yamamoto et al. [69]	N_2 atm.	>310	5	70
Veron et al. [89]	N_2 atm. flash pyrolysis	650	-----	82.7
Lehrle et al. [38]	N_2 atm. flask pyrolysis	450-480	-----	100
This work	N_2 atm.	330-410	0.5-1	97

Lehrle et al. [38] obtained 100% styrene when they degraded polystyrene in the form of thin films using a heated filament at 450-480°C in a nitrogen atmosphere. They explained that some oligomers were possibly produced as primary products in the degradation of the thin films and that they may have decomposed during their residence in the hot primary reaction zone. This explanation can also apply to our results. The volatile fraction we obtained was almost pure styrene, which could easily be repolymerized back to polystyrene thereby closing the recycling loop.

The production of styrene can be accounted for by depolymerization, that is an unzipping mechanism whereby the monomer molecules are successively peeled off the chain ends until an entire polymer molecule has been converted to monomer. This mechanism was illustrated in the background section in Scheme 3.

6.5 Composition of Volatile Fraction with Time

The possible mechanisms for the observed products were presented in the background section. An additional mechanism showing how ethylbenzene is formed is shown below:



This is an intermolecular hydrogen transfer involving a methylene end group radical (R_2) and thus forming ethylbenzene, unsaturated chain ends, and a normal polystyryl radical (R_1).

To explain the changing composition of the volatile fraction with reaction time, namely, styrene and toluene content decreasing with time, and α-methylstyrene and ethylbenzene content increasing with time, the following is proposed: initially, depolymerization takes place, thus styrene is formed, but as the reaction proceeds, the side reactions start becoming increasingly important and thus increasing amounts of α-methylstyrene and ethylbenzene are produced. The amount of toluene decreases since there are decreasing amounts of benzylic chain ends but increasing amounts of unsaturated chain ends since many side reactions form unsaturated chain ends.

6.6 Styrene Yield

The yields of styrene reported here are comparable or higher than ones obtained by other workers. This is shown in Table 6.6.1. However, the results are dependent on the specific experimental conditions employed in the degradation. The yield of styrene increases with temperature which is in accordance with the results of other workers [48,52,54,74].

Table 6.6.1 Comparison of Styrene Yield Obtained by Different Researchers

					This Work[i] :	
Authors	Set-Up	Temp (°C)	Time (hr)	Styrene Yield (%wt of PS)	Styrene Yield (%wt of PS)	Temp (°C)
Madorsky and Straus [47]	vacuum	354 375	0.5 0.5	23 39	15 32	354 376
Straus and Madorsky [51]	vacuum	400	0.5	50	60	402
Costa et al. [76]	N_2 atm.	348	0.5	36	26	350
Costa et al. [30]	N_2 atm.	334	1	41	26	335
Scott et al. [77]	N_2 atm.	532	0.5	76	66	408
Carniti et al. [78]	vacuum	400	0.5	3	66	402

(i) reaction time = 0.5 hour

6.7 Molecular Weight Decrease

Our results involving the decrease in the molecular weight of the polystyrene and its residue as a function of degradation, are in fairly good agreement with Madorsky [18], Jellinek [43], and Malhotra et al. [53], as seen in Figure 6.1.1. Shown is the molecular weight decrease as a function of % volatilization. The molecular weight drops abruptly in the first 15% volatilization and afterwards the drop is more gradual. However, we were able to reduce the polystyrene molecular weight down further than other researchers [18,43,53].

Lehrle et al. [38] have shown that initiation of the depropagating chain reaction yielding monomer occurs both by random scission and at chain ends, therefore the molecular weight decreases at the same time as monomer is being produced. Hence, the reactions which are occurring involve a combination of random scission and chain end scission. So, initially the molecular weight decreases abruptly, but as the reaction proceeds, the decrease is more gradual because the production of unsaturated chain ends increases and therefore random scission becomes less important.

From Figure 5.3.2, it is seen that the high molecular weight components of the original PS have been converted to lower molecular weight products. This agrees with the data of other researchers [18,43,53]. This low molecular weight residue could possibly be used as a fuel source or perhaps as a substrate for microbial growth.

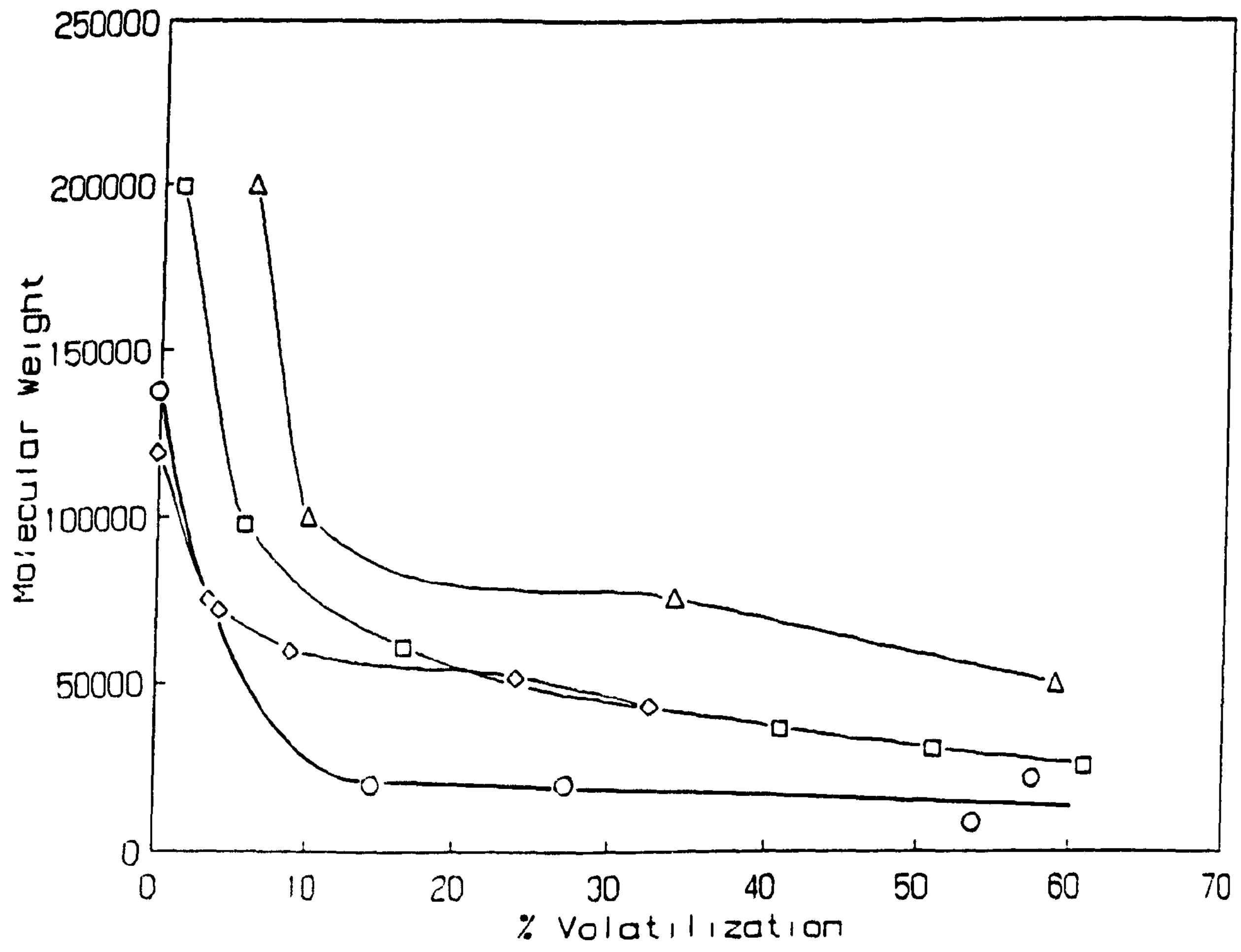


Figure 6.7.1 **Decrease in molecular weight of polystyrene as a function of %volatilization obtained by different researchers: △ Malhotra; □ Madorsky; ◇ Jellinek; ○ This work**

When the reaction temperature is increased, it is observed that the molecular weight of the PS residue decreases further, thereby indicating chain scissions are favoured at higher temperatures. This is in accordance with the results of Ide et al. [68] who worked in the 310-390°C temperature range and also found that with an increase in reaction temperature the molecular weight of the degraded polystyrene tended to decrease.

6.8 Kinetic Interpretation

As shown in Figures 5.5.2 to 5.5.7, the initiation reaction fits a first order model. The essential points of the kinetics of polystyrene thermal degradation are summarized below:

A first order rate equation for the evolution of volatile product is:

$$dn/dt = k(n_o-n) \qquad \ldots(1)$$

where n = number of styrene units in the volatile product
m_o = original number of styrene units in the sample
k = first order rate constant, min^{-1}

Integration of equation(1) gives:

$$n = n_o(1-e^{-kt}) \qquad \ldots(2)$$

and $n, n_o \alpha m, m_o$

where m = mass of the styrene
m_o = initial mass of the polystyrene

Therefore, rearrangement of equation(2) gives:

$$\ln(1-m/m_o) = -kt \qquad \ldots(3)$$

or

$$\ln(1\text{-}X) = -kt \qquad \ldots(4)$$

where X = fractional conversion m/m_o at time t

A linear plot of ln(1-X) versus time at the beginning of the reaction confirms that the system displays first order kinetics for the initiation reaction. The slope obtained is equal to k. lnk versus 1/T is plotted to obtain the activation energy by the Arrhenius equation (rate α $e^{-E/RT}$).

The activation energy we obtained, 181 kJ/mol, is comparable to literature values as can be seen by examining Table 2.3.7. Most depolymerization activation energies are between 84 and 272 kJ/mol [90]. They show much variation because the values depend on a number of factors, such as, purity of the initial polymer, method of preparation, molecular weight, heating rate, conversion and mechanism applied to the polymer degradation and hence the method of treating the data.

7. CONCLUSIONS

The main conclusions which can be made about this investigation into the thermo-chemical recovery of styrene from polystyrene waste are as follows:

1. Using our set-up, polystyrene can be thermally treated in order to produce styrene monomer, dimer, and trimer.

2. High conversions of polystyrene to styrene (up to 70% styrene yield) can be obtained at relatively moderate conditions (330-410°C, nitrogen atmosphere).

3. The use of catalysts is not necessary for the thermal degradation of polystyrene, that is, the additives tested did not affect the yields of styrene and residue obtained. We obtained higher styrene yields by thermally degrading polystyrene alone compared to results of experiments by other workers who used catalysts.

4. The initial rate of thermal degradation of polystyrene was found to fit a first order model. The activation energy obtained was 181 kJ/mol, which is in accordance with literature values.

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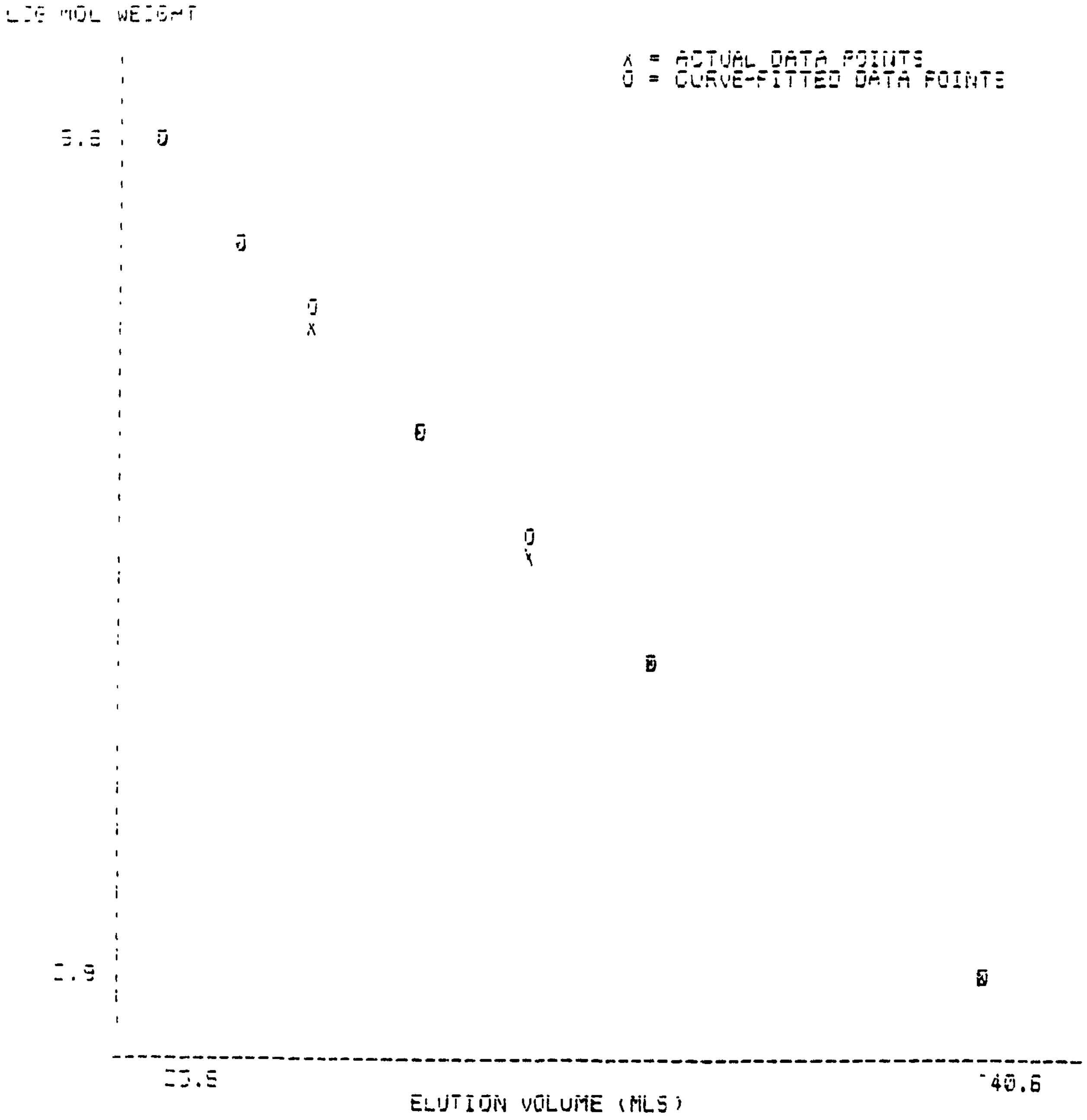
APPENDIX: GPC CALIBRATION CURVES

CALIBRATION CURVE

Y = (7.5603) + (-0.3314)*(X) + (0.0234)*(X^2) + (-0.0002)*(X^3)

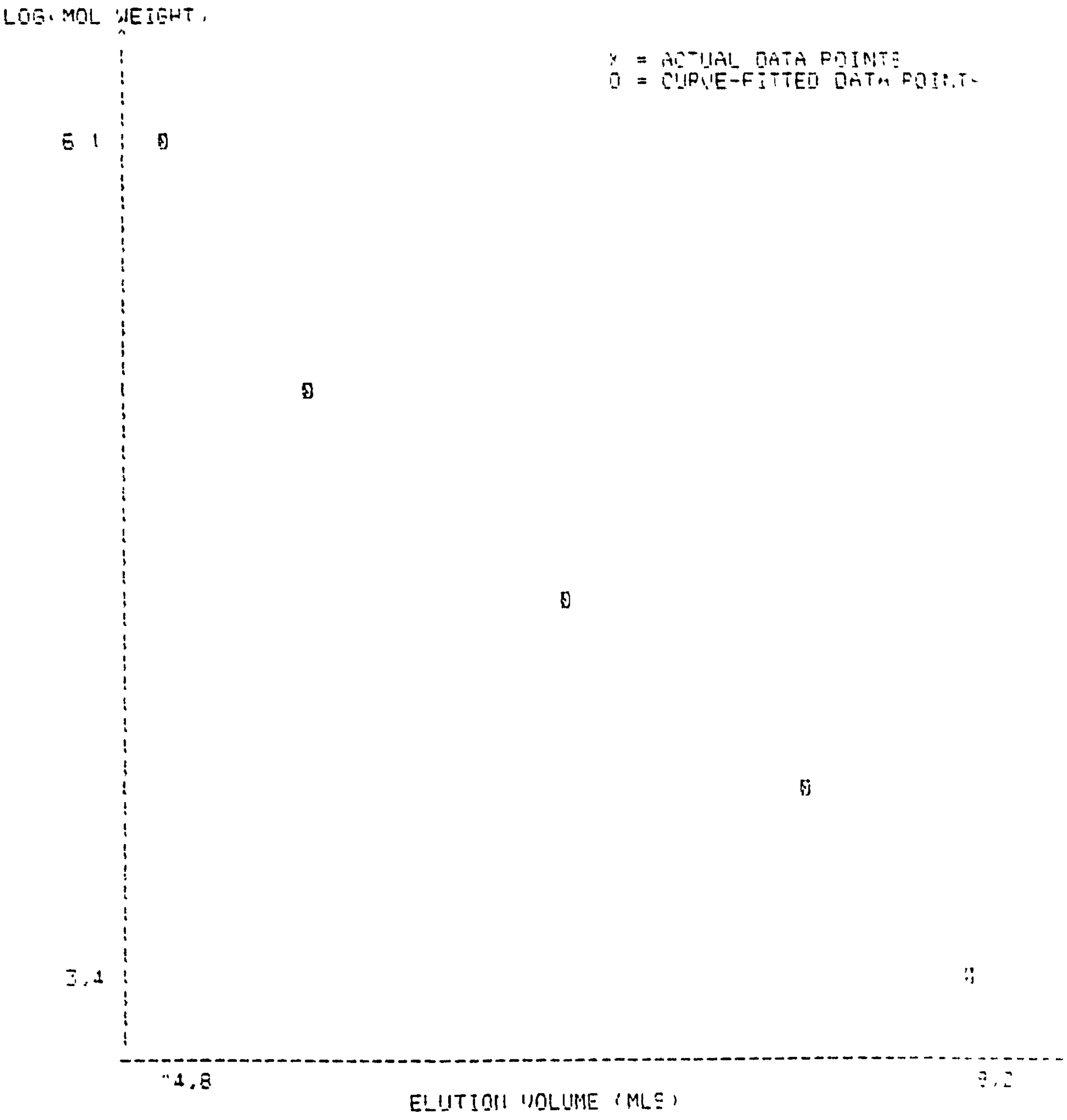


VERTICALLY: EACH ':' REPRESENTS 0.0662 UNITS
HORIZONTALLY: EACH '-' REPRESENTS 0.2853 UNITS

CALIBRATION COMPLETE

```
CALIBRATION CURVE
-----------------

Y = 24.9893 + (-7.7406 (X) + (1.0159)*(X^2) + (-0.0469)*(X^3
```



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VERTICALLY:  EACH '!' REPRESENTS 0.0666 UNITS
HORIZONTALLY:  EACH '-' REPRESENTS 0.0736 UNITS

CALIBRATION COMPLETE
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