# THERMOLYSIS OF MIXTURES OF POLYETHYLENE AND POLYSTYRENE

by

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# ABSTRACT

Thermolysis of mixtures of linear low density polyethylene, LLDPE, and polystyrene, PS, was investigated. Mixtures having various polyethylene/polystyrene ratios were reacted in a stirred, batch reactor under a nitrogen atmosphere at moderate temperatures, ranging between 350 and 420°C. The major products collected included a volatile product, which was a liquid at room temperature, and a wax-like residue. The liquid products were consistently found to contain over 90 percent styrene and toluene with the yield of styrene decreasing as the percentage of polyethylene in the mixture increased. Two fractions were identified in the residue: a high molecular weight polyethylene fraction and a lower molecular weight polystyrene fraction. A significant increase in the solubility of the residue in organic solvents at room temperature was observed as the polystyrene content was raised. The residue became completely soluble in chloroform at a 60/40 ratio of polyethylene/polystyrene. The effect of temperature on the degradation of a selected mixture was also investigated. At temperatures below 390°C, the volatile/residue ratio was independent of the reaction temperature. Above 390°C, the styrene and total liquid product yields increased with increasing temperature, while the yield of residue decreased.

# RESUME

L'étude porte sur la thermolyse de mélanges de polyéthylène linéaire basse densité, PELBD, et de polystyrène, PS. Des mélanges présentant divers pourcentages de polyéthylène et de polystyrène réagissent dans un réacteur discontinu agité sous une atmosphère d'azote à des températures modérées allant de 350 à 420°C. Un des composés majoritaires obtenus est un produit volatile, liquide à température ambiante, l'autre est semblable à une cire. Les composés liquides sont composés de plus de 90% de styrène et de toluène. Le pourcentage de styrène décroît lorsque le pourcentage de polyéthylène dans le mélange initial augmente. Deux composants ont été identifiés dans le résidu: du polyéthylène de haut poids moléculaire et du polystyrène de faible poids moléculaire. La solubilité du résidu dans les solvants organiques à température ambiante augmente de façon significative lorsque le pourcentage de polystyrène augmente. Le residu est complètement soluble dans le chloroforme pour un rapport 60/40 de polyéthylène/polystyrène. L'effet de la température sur la dégradation d'un mélange donné à également été étudié. Pour des températures inférieures à 390°C, le rapport volatile/résidu est indépendant de la température de réaction. Au-dessus de 390°C, les rendements en styrène et en composés liquides augmentent lorsque la température augmente, alors que le rendement en résidu diminue.

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# 1.0 INTRODUCTION

## 1.1 Status of the Solid Waste Crisis

The disposal of municipal solid waste (MSW) has become an environmental issue of growing concern [1-9]. The United States alone produces approximately 320 billion lbs. of MSW per year. This is equivalent to 3.5 lbs./day, per capita, which is almost twice the amount of trash per person generated in Europe and Japan [5]. The total production of MSW in North America is expected to increase by 20 percent by the turn of the century [7].

### 1.1.1 Plastics Role in Municipal Solid Waste

The largest components of MSW are paper, paper products and yard wastes. Together, they account for over 50 percent of the total by weight. The other components are food wastes (9%), textile products (9%), metals (9%), glass (8%) and lastly, plastics (7%) [3]. However, the above data may be misleading. In studies sponsored by the Society of Plastics Industry (SPI), it was determined that discarded plastics represent close to 20 percent of MSW on a volume basis [2,13]. This is due to the high volume to weight ratio of polymeric materials. Consequently, a given weight of discarded plastics will take up more space and create a greater volume of waste than a comparable weight of steel, rubble or newsprint. Volume considerations are important since landfill requirements are related more to total volume than to total weight. In addition, many plastics have "flex" memories and tend to resist landfill compaction.

### 1.2 A Solid Waste Solution

A panacea for the solid waste crisis does not exist. However, in response to the growing volume of waste and in order to address environmental concerns, the U.S. Environmental Protection Agency has proposed an integrated solid waste management plan which utilizes current technology. The scheme involves a blend of the following hierarchy of disposal methods: source reduction, recycling, thermal reduction by incineration and landfilling.

### 1.2.1 A Plastic Waste Solution

The management of plastic waste follows a scheme similar to the proposed EPA hierarchy for solid waste management, as shown below.

**i. Source Reduction**

**ii. Material Reuse**

**iii. Recycling**
   **material recycling**
   **chemical recycling**

**iv. Incineration**

**v. Landfilling**

The plan, proposed by the EPA, emphasizes source reduction, material reuse and recycling while reducing the dependence on landfilling and incineration.

Source reduction is any measure which reduces the volume of plastic waste produced. This is accomplished through material efficiency, i.e., reducing the quantity of plastic material used in packaging a particular item. Material reuse refers to utilizing a product repetitively without any processing modifications. Recycling generally involves the collection of waste plastic materials for reprocessing into new products. At present, source reduction and material reuse, where applicable, can be easily achieved with existing technologies. However, recycling poses a greater problem. The infrastructure necessary for large scale recycling is only just being developed.

Incineration is recommended for waste volume reduction and energy recovery. The majority of polymers burn cleanly and have comparable heating value to that of heating oils. The drawback is that incineration is often considered undesirable due to emission concerns. The cost of building modern waste-to-energy incinerators is also becoming prohibitive.

Currently, the lowest cost alternative for plastic disposal is landfilling. However, this method is not favored since landfill space is limited and concerns exist regarding site safety and groundwater contamination from leachate. The landfilling of plastic does not provide an economic return from the potential energy value inherent in plastics.

### 1.2.2 Degradable Plastics

The high visibility of plastic trash when discarded in the environment and the potential threat that discarded plastics pose to the environment and wildlife heightened public criticism on the extensive use of plastics. As a consequence, the plastics industry has been called to account for the entire waste crisis [16]. Legislators initially responded with a flurry of anti-plastics regulations and by mandating the use of degradable resins, such as bio- and photodegradable resins, in many packaging applications. Degradable resins are appropriate in some uses, such as six-pack ring containers, but research effort should focus on more viable approaches to plastic waste management, such as recycling [10]. Degradable plastics are not compatible with recycling programs. Moreover, in many cases, degradable resins which might be inevitably bound for a landfill will not decompose to a significant extent. Many concerns and questions about degradable resins still need to be addressed. For example, what are the long term consequences of degraded polymer residues accumulating in the soil ?, What is the time scale required to achieve degradation ? At what extent of decomposition is a plastic material considered "degraded" ?

### 1.2.3 Plastics Recycling

During the 1990's, the amount of recycled plastics is expected to increase at an annual rate of 16% [12]. So far, the growth in plastics recycling has been motivated mainly by legislation and government regulations. The cost of virgin commodity resins is currently too low to make recycling economically attractive. However, as the costs of common waste disposal techniques, such as landfilling and incineration, continue to rise, the economics of plastics recycling will become increasingly more attractive. At the same time, more legislation requiring recycling will be enacted. A typical case is the Resource Conservation and Recovery Act (RCRA), proposed in the United States Congress, which stipulates that plastics packaging must contain at least 25 percent post consumer resin by 1995 and 50 percent by 2001 [4]. The penalty for noncompliance would be $75,000 per day. Thus, there would be both economic incentive and regulatory pressure to develop the recycling infrastructure and recycling technologies.

Plastics recycling may be divided into the following four types. These are in decreasing order of residual value recovery: primary, secondary, tertiary and quaternary recycling.

Primary recycling, which has long been in effect in the plastics industry, is the most economical form of recycling. It refers to on site industrial recycling where waste plastic is fed back into the system as feedstock. Secondary recycling refers to the popular concept where plastics waste is collected and processed into new products. New products from secondary recycling are generally of a lesser value due to contamination problems and because the properties of the materials are generally degraded by repetitive reprocessing and exposure to heat treatment. In tertiary or chemical recycling, the waste polymeric material is degraded by mechanical, thermal and/or chemical action to yield valuable low molecular weight products and monomers. Quaternary recycling is the recovery of energy from plastics through incineration.

Table 1.2.3 shows data regarding plastics recycled in 1988 and projections for plastics recycling in the United States in 1998. In 1988, one billion lbs. of plastics waste were recycled (3% of total volume consumed). This is projected to increase to 4.8 billion lbs. by 1998 (8% of total volume consumed). Even with these increases in plastics reclamation, the rate of plastics recycling still lags far behind the recycling rates of aluminum at 30% and paper at 20% [8]. The greatest recycling potential can be seen to lie with the polyolefins which are most commonly used in packaging applications. Packaging products are considered non-durable, with useful lifetimes of less than 3 years. Therefore, they represent a major portion of the plastics waste stream.

The focus of this research is on the chemical recycling

**Table 1.2.3. U.S. recycled plastics by type in millions of lbs. [12]**

| TYPE | 1988 | 1998 |
|---|---|---|
| polyolefins | 756 | 2945 |
| PET | 119 | 524 |
| PVC | 75 | 620 |
| nylon | 60 | 107 |
| styrenics | 85 | 485 |
| eng.polymers | 1 | 165 |
| TOTAL | 1096 | 4846 |

of mixtures of polyethylene and polystyrene. According to Table 1.2.3, polyolefins and polystyrene represented 77% of recycled plastics in 1988 and are expected to represent 71% of the plastics recycling stream in 1998. Since collection and segregation of plastics incurs the highest capital costs in a recycling program, the recycling of mixtures is of significant interest. Furthermore, the study of the degradation of such mixtures could provide insight regarding the possibilities of interactions between polymers during degradation that might enhance recycling potential and economics.

## 2.0 BACKGROUND

### 2.1 Polymer Degradation

Polymer degradation is a process which typically involves the breaking down of long, high molecular weight chains to shorter, lower molecular weight molecules. The decomposition of a polymer can occur by the application of heat, mechanical forces or through chemical action. The presence of oxygen can enhance degradation due to the production of additional unstable radicals. The degradation of polymeric materials inevitably results in alteration of the physical properties of the polymer. Traditionally, the primary concern of degradation research was to maintain polymer stability while avoiding or minimizing the effects of degradation. In recent years, chemical recycling technologies, such as thermolysis, have provided a new and different incentive for research on degradation. These technologies employ degradation reactions in order to convert waste polymers into higher value chemical products.

### 2.2 Thermolysis

Thermolysis occurs when there is sufficient thermal energy to overcome bond dissociation energies and cause bond scissions [67]. The scissions can occur randomly or at weak points along the polymer chain. When bond cleavages occur at chain ends, the polymer is said to depolymerize. Chain scissions may occur along the chain causing a rapid decrease in molecular weight but very little monomer is formed. On the other hand, rapid depolymerization proceeds via an unzipping reaction where successive monomer units are taken off from the chain ends. Here, the reaction must proceed for a long time to achieve an appreciable decrease in molecular weight but high yields of monomer are readily obtained. Depolymerization is frequently observed with vinyl polymers [18].

The decomposition of different polymers follows different reaction patterns. The main schemes in polymer thermolysis are [19]:

1. decomposition into the monomer [poly(methyl methacrylate), PMMA and poly(tetrafluoroethylene), PTFE].
2. fragmentation of the principle chains into smaller chains of varying length [polyethylene, PE and polypropylene, PP]
3. decomposition according to a combination of both schemes 1 & 2 [polystyrene, PS and polyisobutylene PIB].
4. elimination of simple components leaving a charred residue [poly(vinyl chloride), PVC, yields hydrochloric acid, HCl and poly(vinyl acetate), PVAc, yields acetate, HAc].
5. elimination of side-chains followed by cross-linking

It can be seen that the thermolysis products from PS and PE will be quite different. When degraded alone, PS will produce relatively high yields of monomer and lesser amounts of dimer, trimer and other oligomers. On the other hand, PE will only produce fragmented chains of substantially lowered molecular weight but little or no monomer is evolved.

Polyethylene and polystyrene are low cost commodity thermoplastics. Both are addition polymers and degrade by a free radical chain process. The main reaction steps are initiation, propagation, chain transfer and termination. Competitive elementary and side reactions with high activation energies may also occur.

Thermolysis is initiated by carbon-carbon bond scissions which can occur at weak points, chain ends or randomly. The two competing reactions for decomposition are propagation and transfer. Mechanisms which are dominated by the propagation step will exhibit high monomer yields. The transfer reaction does not directly promote depolymerization but simply shifts radical location. This may involve intermolecular or intramolecular hydrogen abstraction. The reaction ceases when two radicals are mutually destroyed, either by coupling or by disproportionation.

### 2.2.1 Polyethylene

The thermolysis of polyethylene is initiated by random scission. The route to degradation products is governed by molecular transfer, producing low monomer yields, and disproportionation reactions, which lead to alkane and alkene formation [21,22]. The main degradation mechanism for PE is shown in Figure 2.1.1 [20,23].

Following this mechanism, the decomposition of PE results in the formation of three main product fractions: a solid residue resembling PE, a wax-like fraction which is volatile only at the reaction temperature and a volatile fraction containing low molecular weight gases or liquids [21,22,24,34-37]. The yields of these fractions are dependent on the reaction temperature. The volatiles and waxes are mainly n-alkanes containing a modest amount of unsaturation [36]. In addition, small amounts of branched hydrocarbons, aromatics and isomers may be formed [38].

Since the thermolysis of PE is dominated by molecular transfer, a small amount of volatiles will be produced in comparison to the thermolysis of polymers where scission is the favored reaction step. This also means that the volatiles will contain a negligible amount of monomer.

The degree of backbone branching is also an important factor for the conversion of PE [24]. Branching provides weak points due to the lower bond dissociation energy of any beta carbon-carbon bond. Therefore a high degree of backbone branching will promote chain scission and aid the degradation process. The most common commercial polyethylenes, listed in increasing order of branch frequency, are linear low density polyethylene (LLDPE), high density polyethylene (HDPE) and low

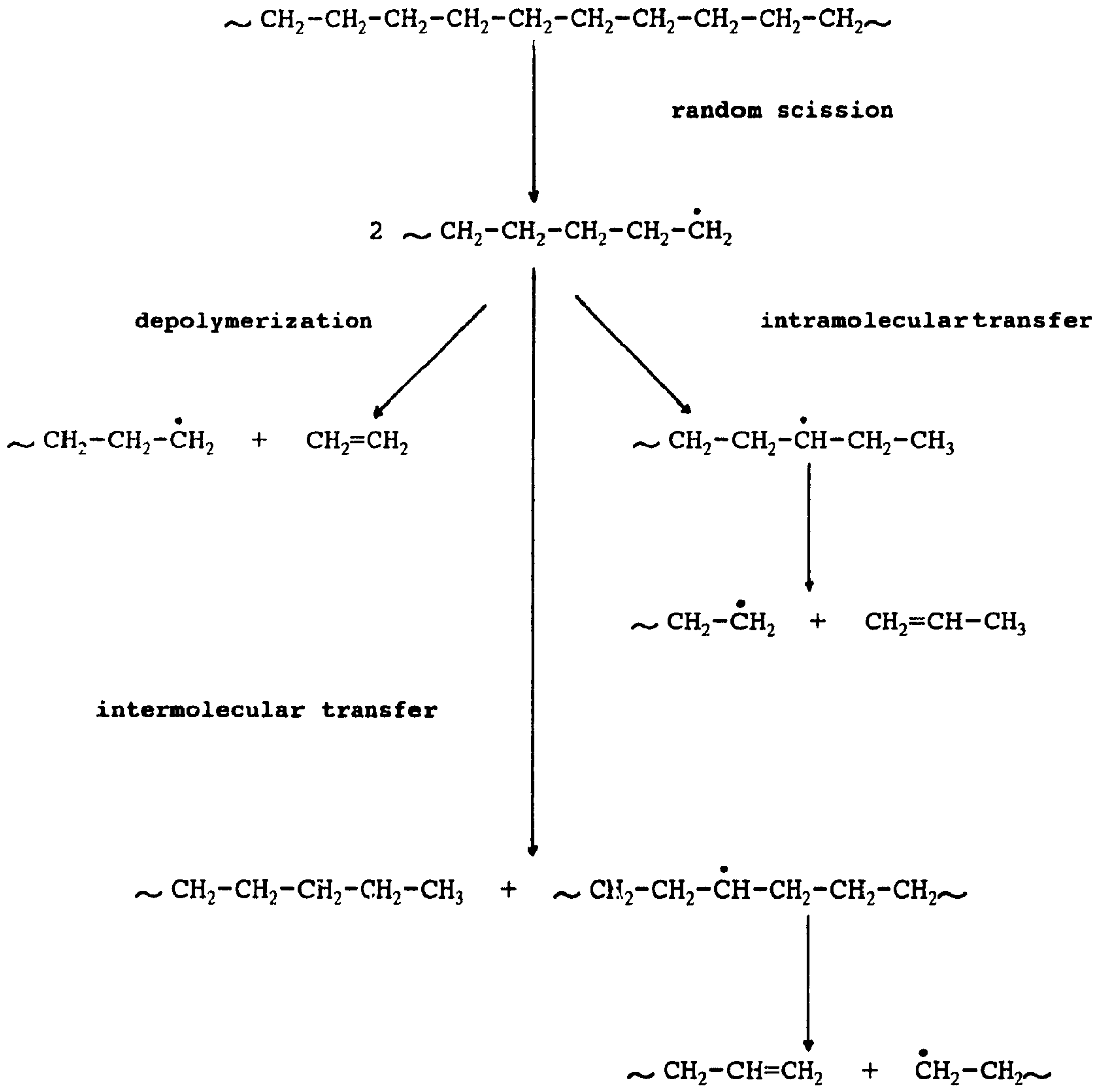


**Figure 2.2.1. Thermolysis of Polyethylene**

density polyethylene (LDPE). Based on this criterion, LLDPE has the greatest stability. The degree of branching will affect the degradation process and the initial temperature for decomposition, but the degradation products formed will be the same.

### 2.2.2 Polystyrene

Many studies have been performed examining the thermolysis mechanism of polystyrene [27,32,39-52]. As mentioned above, this is a radical chain process involving initiation, propagation, transfer and termination.

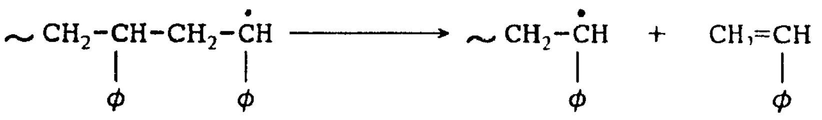
Decomposition is initiated by a carbon-carbon bond scission which occurs at weak points, chain ends or randomly. The weak points are structural irregularities which may include chain branches, double bonds, internal unsaturations or head to head linkages [53].

The most frequent reaction step during degradation is propagation which occurs by ß - scission. The ß - scission mechanism is depicted in Figure 2.2.2. This either involves a chain end radical causing depolymerization to produce styrene monomer or an internal radical resulting in the formation of a weak chain end.

The other competing reaction step is transfer which involves intramolecular (back biting) or intermolecular hydrogen abstraction with an available radical resulting in a saturated bond and a new internal radical. The decomposition process terminates either by coupling between radicals or a disproportionation reaction. The hydrogen abstraction process is depicted in Figure 2.2.3.

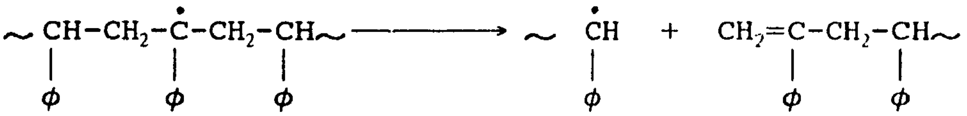
The temperature at which the initial thermal degradation begins depends on the polymer structure. In an inert atmosphere, polystyrene begins to degrade at 280°C resulting in a decrease in molecular weight but no volatiles are evolved. Above 300°C, volatile products, consisting of styrene monomer, dimer, trimer and smaller quantities of toluene, $\alpha$-methyl styrene and other fragments, begin to evolve [53].

**Chain end radical**



$$\sim CH_2-\underset{\phi}{\underset{|}{CH}}-CH_2-\underset{\phi}{\underset{|}{\dot{C}H}} \longrightarrow \sim CH_2-\underset{\phi}{\underset{|}{\dot{C}H}} + CH_2=\underset{\phi}{\underset{|}{CH}}$$

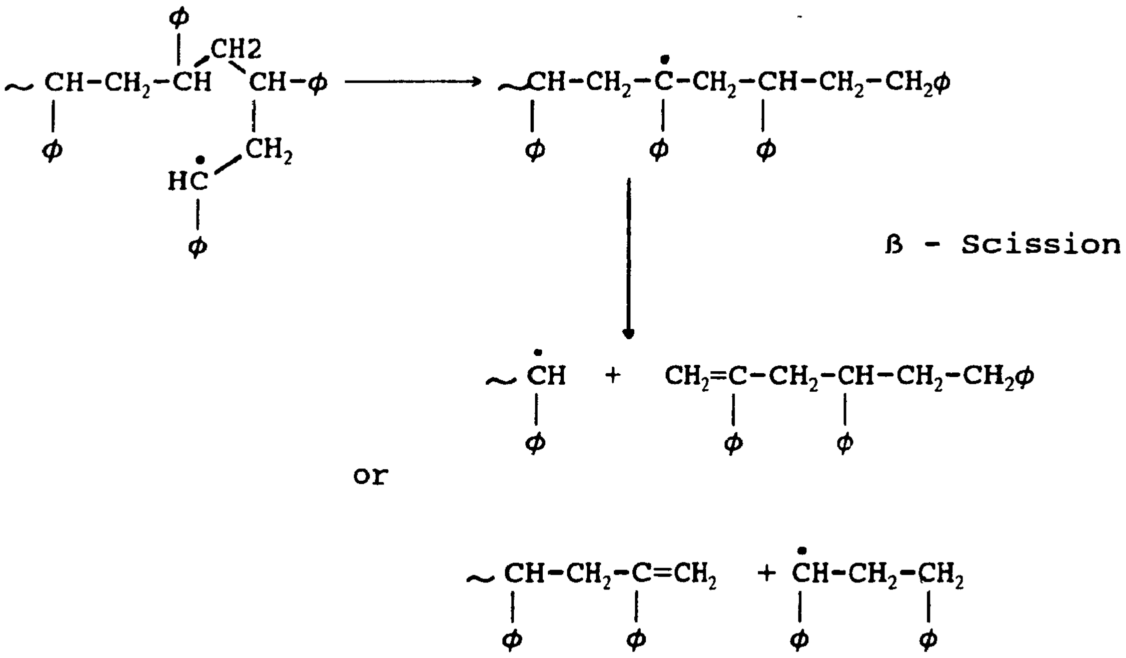
**Internal radical**



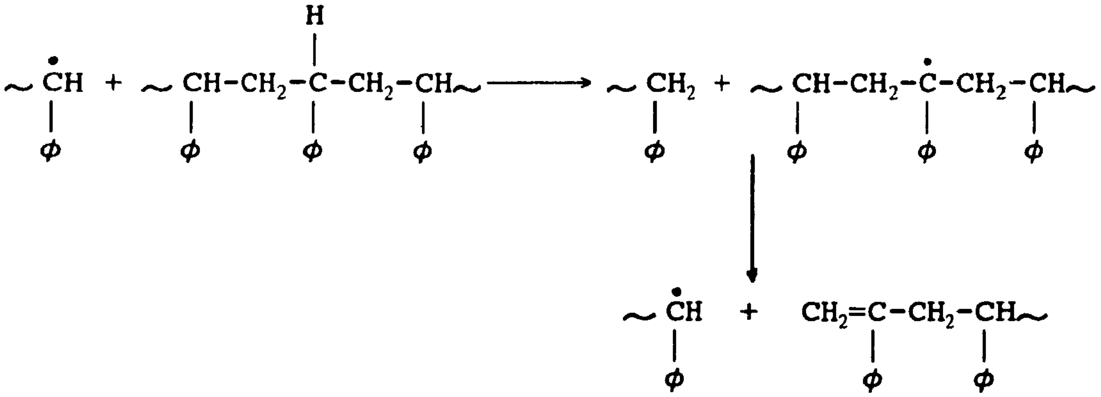
$$\sim CH-CH_2-\underset{\phi}{\underset{|}{\dot{C}}}-CH_2-\underset{\phi}{\underset{|}{CH}}\sim \longrightarrow \sim \underset{\phi}{\underset{|}{\dot{C}H}} + CH_2=\underset{\phi}{\underset{|}{C}}-CH_2-\underset{\phi}{\underset{|}{CH}}\sim$$

Figure 2.2.2. ß - Scission Mechanism

**Intramolecular (back-biting)**



**Intermolecular**



$$\sim \underset{\phi}{\dot{C}H} + \sim \underset{\phi}{CH}-CH_2-\underset{\phi}{\overset{H}{C}}-CH_2-\underset{\phi}{CH}\sim \longrightarrow \sim \underset{\phi}{CH_2} + \sim \underset{\phi}{CH}-CH_2-\underset{\phi}{\dot{C}}-CH_2-\underset{\phi}{CH}\sim$$

$$\downarrow$$

$$\sim \underset{\phi}{\dot{C}H} + CH_2=\underset{\phi}{C}-CH_2-\underset{\phi}{CH}\sim$$

Figure 2.2.3. Hydrogen Abstraction

### 2.2.3 Polymer Mixtures

Only limited literature is available on the thermolysis of polymer mixtures. Most previous research has focused on the methods of polymer degradation and dealt with analyzing the decomposition of pure polymeric materials. Such research provides useful insight into the thermolysis mechanisms of the individual polymers and can be applied to develop chemical recycling technologies. However, the purity of post-consumer plastics waste cannot be guaranteed. Economic incentive exists to degrade polymers together due to the high costs incurred during polymer separation. It is, therfore, justified and advantageous to pursue research that will focus on the effect that mixtures or blends of various polymers have on the degradation process. Generally, research in this field has been limited to studies of blend degradation during intensive processing and extrusion or by pyrolysis.

In a study performed by Roy at al. [54], mixtures of polyethylene and polystyrene were pyrolysed at various conditions in order to provide background on the pyrolytic behavior of wastes. Roy selected the high commodity polymers polyethylene and polystyrene since they represent a large percentage of the current plastics waste and are likely to be found intermingled when discarded as municipal solid waste. In the study, the effect of temperature, pressure and reaction atmosphere on the production of gases and carbonaceous residues from various polyethylene/polystyrene mixtures was analyzed. The experiments were performed at temperatures ranging from 300 to 900°C, at atmospheric or reduced pressures and either in an inert nitrogen or carbon monoxide atmosphere. Results were compared with similar experiments by Menzel on single polymers [55]. It was observed that when the pyrolysing temperature was attained by gradual heating, and when pyrolysis occurred at pressures in excess of 200 torr, the polymers behaved as if each component was present alone. There was no evidence of polymer interaction. Under the above conditions, the known mechanisms for pyrolysis of the individual polymers can be applied to the behavior of mixtures. Interactions between the polymers, or among the pyrolysis by-products, were observed when pyrolysis occurred at pressures less than 20 torr. However, no mechanism for the interactions was suggested.

The products obtained during pyrolysis were found to be dependent on the rates of attaining the pyrolysing temperature. It was observed that more rapid rates favored the production of carbon-rich solid residues for possible use as carbon blacks. As a closing remark, it was suggested that further investigation and a more detailed understanding of pyrolytic processes in polymer mixtures was needed. This would permit optimization of operating conditions to produce the optimum balance of useful value added products.

Investigation of the thermolysis of polymer mixtures was studied by Dodson and McNeill [56]. The objective was to study the possibility of interactions between a polymer or its degradation products and a second polymer in the same environment, as is the case of polymer blends or graft copolymers. Reference was made to previous research which found that in blends the presence of degrading poly-α-methylstyrene [57] or poly(oxyethylene glycol) [58] caused polystyrene to degrade more rapidly. On the other hand, thermal degradation of blends of polystyrene and poly(methyl methacrylate) showed no evidence of polymer interaction [59]. These references indicate the uniqueness of each polymer mixture and that the thermolysis mechanism is highly dependent on the polymers under investigation.

Dodson and McNeill analyzed films containing both polystyrene and poly(vinyl chloride) which were degraded and examined by thermal volatilization analysis (TVA) and thermogravimetry (TG). These techniques allow the determination of the number of stages and mode of breakdown, a quantitative measure of the weight loss in any stage, the threshold temperatures and temperatures of maximum weight loss. A weakness in these methods is that they do not provide any direct information about the degradation products since there is no method to collect the degradation products. TVA curves only indicate volatile products of degradation under vacuum at room temperature.

Sample blends were reacted in a dynamic nitrogen atmosphere at a heating rate of 10°C/min. Weight loss curves for the individual polymers were obtained and a theoretical curve which would be expected for a 1:1 mixture was constructed. This was then compared with the experimental curve for the mixed film. In this case, the curves did not coincide, indicating that some interaction was taking place between the polymers. The interaction resulted in a more rapid decrease in the molecular weight of the polystyrene due to the presence of poly(vinyl chloride). Despite the apparent polymer interactions, the final degradation products were the same as when the polymers were degraded individually, indicating that only the rate of decomposition was affected. It was also observed that no chlorine grafting or incorporation was noted on the PS in experiments where 36 Cl-labelled PVC was used.

McNeill et al. [60] also investigated the interaction between polymers in blends of polystyrene and polybutadiene using the same experimental techniques. Again, polymer interaction affected the rate of decomposition but not the products obtained. Polybutadiene degraded first and the volatile products resulting from the decomposition of the polybutadiene, such as 4-vinyl cyclohexene, were believed to diffuse into the PS phase of the blend and act as radical inhibitors, thereby reducing the degradation rate of the PS.

Similar results were obtained by Jamieson and McNeill [61] for blends of poly(vinyl acetate) and polystyrene. In this case, TVA analysis revealed that the presence of polystyrene has no affect on the behavior of poly(vinyl acetate). Styrene production was retarded in the mixture, compared to the expected yield for pure polystyrene. The retardation is believed to be due to interference with intermolecular transfer in polystyrene.

Murata and Akimoto [62,63] examined two and three component blends of equal amounts of polyethylene, polypropylene and polystyrene in a continuous flow reactor at temperatures between 400 and 425°C. The resulting products were analyzed by differential thermogravimetry. Kinetic analysis showed that the degradation rates of these blends were the mean of the degradation rates of the individual components. Blending did not have an effect on the degradation products, since the degradation products corresponded to the sum of the products of the individual polymers. It was also shown that polymer interaction affected only the decomposition rate and not the types of products collected. The effect on the decomposition rate was interpreted to be due to reduced intermolecular radical transfer. Intramolecular radical tansfer was not affected.

## 3.0 OBJECTIVES

This project is part of a larger effort in the polymer laboratories of the Department of Chemical Engineering at McGill University to investigate the feasibility of utilizing chemical recycling for the upgrading of post-consumer plastics waste. The general objective is to achieve thermo-chemical conversion of plastics waste into chemical products or fuel at moderate temperatures (below 500°C). The desirable products would be monomers or intermediate chemicals/fuels that are solid or liquid at room temperature. Both segregated individual plastics or mixed waste plastics are considered. The effort attempts to carry out experimental and kinetic studies to evaluate the feasibility of chemical recycling of key components in the M.S.W. plastics waste stream and to elucidate the mechanisms involved in the thermo-chemical conversion of these materials.

The scope of this Master's research project is to investigate the thermo-chemical conversion of mixtures of polyethylene and polystyrene and the feasibility of chemical recycling of these mixtures. The specific objectives of the research are listed below:

1. to carry out experiments for the thermo-chemical conversion of mixtures polyethylene and polystyrene under various moderate temperature conditions.

2. to characterize the chemical composition and molecular weight distributions of the reaction products by using the appropriate analytical techniques, and

3. To investigate the effect of varying the composition ratio and the temperature on the reaction products and the relevant reaction mechanisms.

## 4.0 MATERIALS AND METHODS

### 4.1 Materials

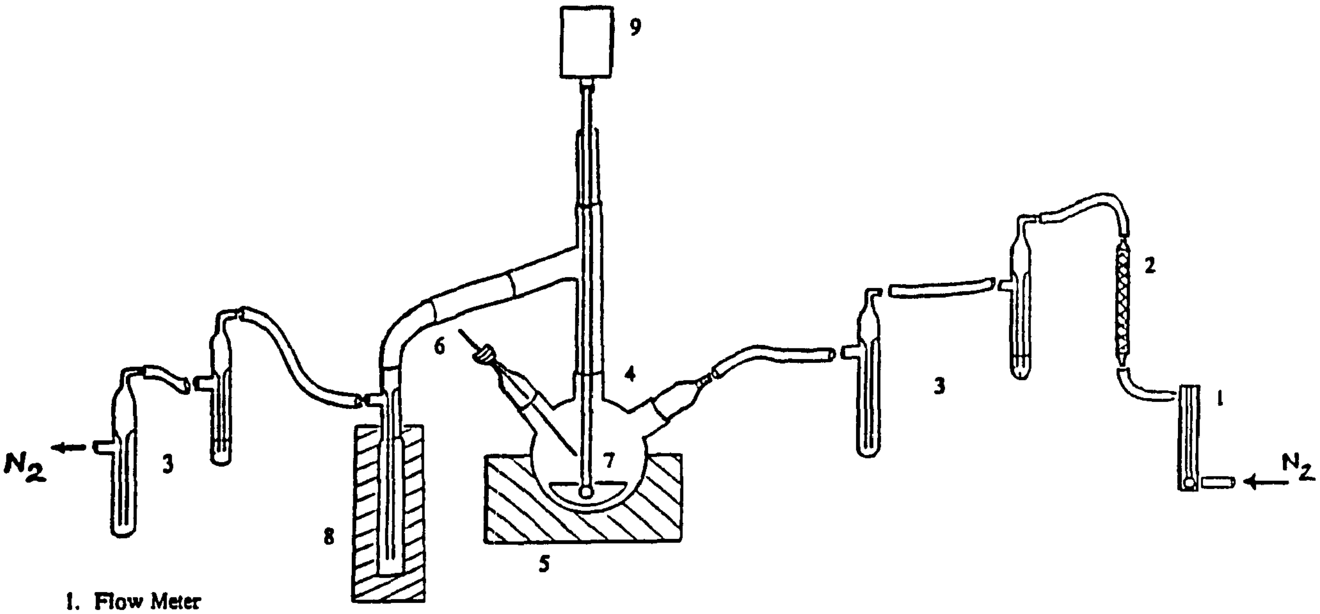
The polymers investigated in this research were powdered resins of linear low density polyethylene (LLDPE), hereafter referred to as PE, and polystyrene (PS). The polyethylene (type SCLAIR 8111) was supplied by Du Pont Canada Ltd. The number average molecular weight ($M_n$) was $1.7x10^4$, with a polydispersity ($M_w/M_n$) of 2.97. The molecular weight distribution of SCLAIR 8111 is shown in Appendix A. The polystyrene (STYRON 688), produced by free radical polymerization, was supplied by Dow Chemical Canada Inc. The number average molecular weight and polydispersity index were $1.38x10^5$ and 2.6, respectively.

### 4.2 Experimental Apparatus

A schematic diagram of the apparatus is shown in Figure 4.2.1. All the parts are Pyrex glass supplied by LaSalle Scientific in Montreal. The connections are 24/40 ground glass.

### 4.2.1 Experimental Procedure

Sample mixtures weighing 4 grams were prepared to obtain the following compositions: 80PE/20PS, 60PE/40PS, 40PE/60PS and 20PE/80PS (w/w). The samples were mixed in a 100 mL, 3-necked round bottom flask equipped with a stirring bar/paddle



1. Flow Meter
2. Dessicator
3. Bubblers
4. Reaction Flask
5. Heating Mantle
6. Thermocouple
7. Stirring Rod/Paddle
8. Cold Trap
9. Motor

**Figure 4.2.1. Schematic diagram of experimental apparatus**

arrangement. The motor for the stirrer, type RZR1 rated at 70 W, was supplied by Caframo. The stirring speed was adjusted through a variable transformer from Staco Energy Products Co. The reaction flask was heated with a Glas-Col mantle rated at 230 W, with a maximum attainable temperature of 650°C. The mantle was controlled with an Omega Engineering Inc. temperature controller connected to a J-type thermocouple. This thermocouple was placed between the reaction flask and the heating mantle. An additional J-type thermocouple connected to an Omega digital display was used to determine the melt temperature at three minute intervals during each experiment. The use of two thermocouples was necessary because continuous measurement of the melt temperature was not possible since thermocouple placement for melt temperature readings impeded the motion of the paddle mixer. It was observed that the temperature difference between the mantle and the polymer melt was approximately 100°C. The temperature range investigated during experiments was 350-420°C.

A typical heating profile from an experimental run is shown in Figure 4.2.2. It can be seen that a 15 to 20 minute heat-up time is necessary to bring the system to the reaction temperature. In this case, the reaction temperature was 395°C. An average standard deviation of 4°C in the reaction temperature was observed for all experiments. The reaction time, which refers to the length of the experiment after attaining the desired reaction temperature, investigated was

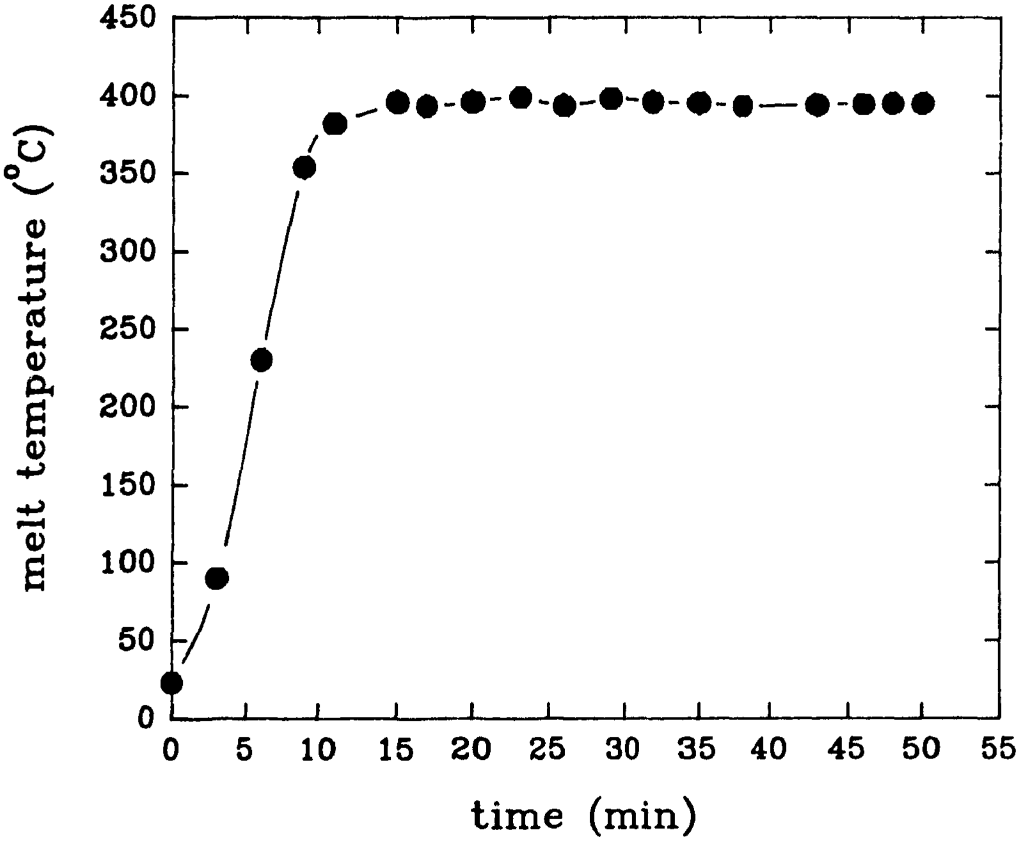


Figure 4.2.2. Typical temperature profile

consistently 30 minutes.

During experimental runs, high purity nitrogen was passed through the apparatus at a steady rate. The system was purged prior to every experiment for 15 minutes to remove any traces of oxygen. This would prevent the occurrence of thermo-oxidative degradation during the reaction. During the purging, the samples were also vigorously stirred to ensure a homogeneous polymer mixture. The individual parts of the apparatus were weighed prior to and after each run for mass balance calculations. The degraded products were collected as two main fractions: a wax-like residue which remained in the reactor flask and a volatile fraction which was liquid at room temperature. The condensable volatiles were collected in a cold trap immersed in an ice bath. An ice bath was used instead of liquid nitrogen in order to avoid the possible condensation of oxygen in the system. Both fractions were recovered and stored in a freezer under nitrogen for future analysis.

## 4.3 Analytical Methods

### 4.3.1 Gas Chromatography

The volatile fraction from the degraded polymer samples was characterized with a Hewlett Packard 5890A Gas Chromatograph fitted with a Flame Ionization Detector. The column used was selected for its ability to separate small hydrocarbons and aromatic compounds. The operating conditions are recorded in Table 4.3.1.

Samples from the volatile fraction were injected to determine the component distributions and concentrations. The peak areas calculated by the GC Integrator were considered to be directly proportional to the concentration of each respective component in the injected sample. This was justified by injecting standard test mixtures with known concentrations to determine correction factors for each component. It was observed that the error was less than 5% (1.0±0.05).

The components of interest were identified by injecting standards and comparing their retention times with those of the degraded product. By this method, it was possible to account for over 90% of the components in the degraded samples. A typical GC chromatogram for the mixture 60PE/40PS, degraded at 395°C, is shown in Figure 4.3.1.

It was determined by experiment that the results obtained from the GC column for aromatic concentrations were identical with results obtained on the column (5.0% SP-1200/1.75% Bentone 34, 100/120 mesh) used by Marc [33].

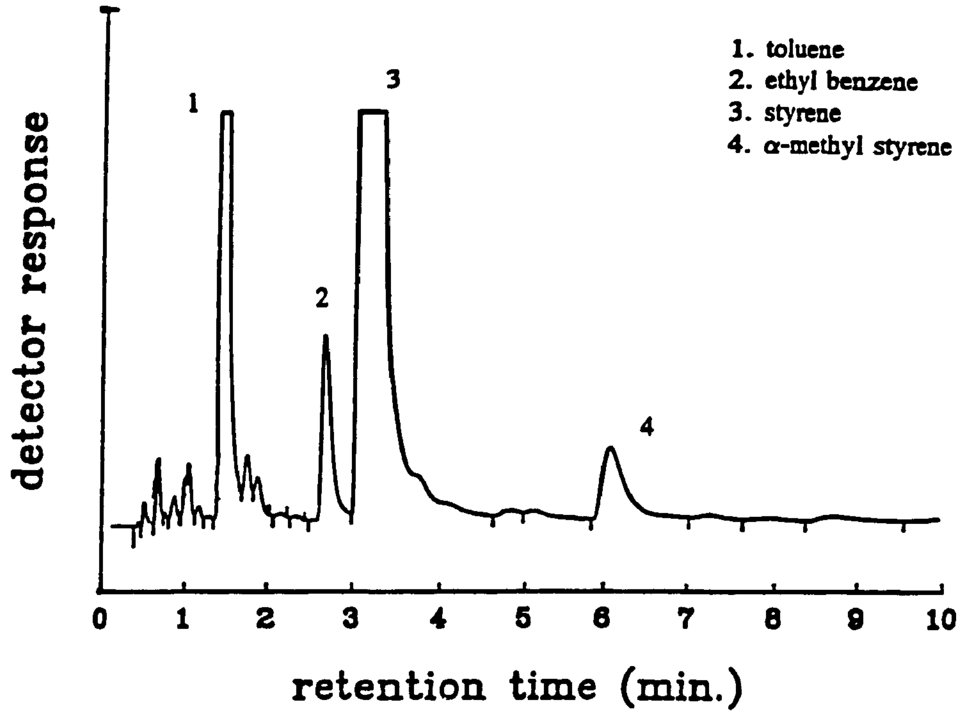


Figure 4.3.1. Typical GC chromatogram of volatile fraction. 60PE/40PS at T=395°C.

### 4.3.2 Gel Permeation Chromatography

The molecular weights and the molecular weight distributions (MWD) of the residue were determined by gel permeation chromatography (GPC), a technique of size exclusion chromatography. Residue samples were dissolved in toluene at 80°C and then filtered using a 2.0 micron cup filter. PS standards were used for column calibration. The calibration curve and molecular weight chromatograms for each mixture are shown in Appendix B. The GPC analysis was performed by American Polymer Standards in Mentor, Ohio. A summary of conditions employed in GPC analysis is given in Table 4.3.2.

### 4.3.3 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) was performed using a Perkin Elmer 1020 Series TGA 7 Thermal Analysis System to determine the weight loss and the rate of weight loss (first derivative) of the polymer mixtures as a function of time. A typical TGA curve for a polymer mixture is shown in Figure 4.3.2. In this experiment, the weight loss from the mixture 60PE/40PS was measured at 395°C for 70 minutes. This included a 15 minute heat-up time. It was observed that the maximum rate of weight loss was reached after around 25 minutes and the rate approached zero for times longer than 50 minutes. Similar trends were observed for the other mixture ratios and the control experiments of pure PE and pure PS. Based on the above, a reaction time of 30 minutes was selected and deemed

**Table 4.3.1. Gas Chromatograph Conditions**

| | |
|---|---|
| Chromatograph | Hewlett-Packard 5890A |
| Detector | Flame Ionization |
| Column | 6'x1/8" stainless steel |
| Packing | 3% OV-101 on chromasorb W HP 100/120 mesh |
| Column temperature | 60°C |
| Injector temperature | 275°C |
| Detector temperature | 300°C |
| Helium flow | 30mL/min |
| Hydrogen flow | 30mL/min |
| Air flow | 300mL/min |
| Sample size | 0.05μL |

**Table 4.3.2. Gel Permeation Chromatograph Conditions**

| | |
|---|---|
| Columns | AM Gel 2x500A + 100A |
| Detector | M-150-C (64/25) |
| Solvent | toluene |
| Temperature | 80°C |
| Flow rate | 1.0 mL/min |
| Injection volume | 150μL |
| Data Module | IBM/AT GPC-PRO 3.13 Viscotek |
| Type of Calibration | Series of PS Standards |

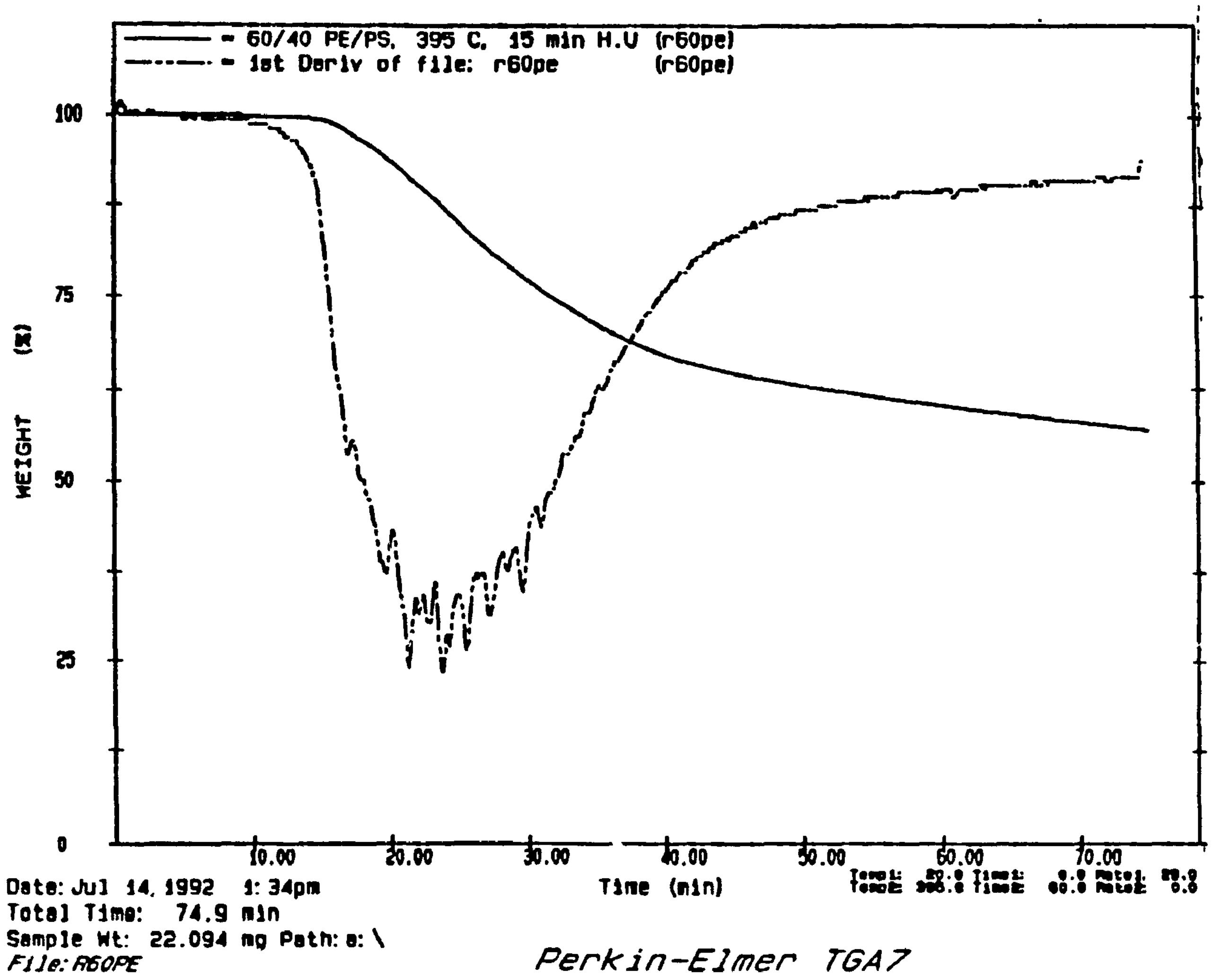


Figure 4.3.2. TGA curve for 60PE/40PS (T=395°C)

satisfactory for all degradation experiments. Appendix C contains the experimental TGA curves for each mixture at 395°C.

### 4.3.4 Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) is a suitable technique for determining the proportions of aromatic, vinylic and aliphatic protons in a sample. All samples for analysis were dissolved in deuterated chloroform at room temperature. For this study, NMR was used to determine the ratio between aromatic and alkyl protons in the solid residue product. This ratio was then used for comparison to determine the accuracy of calculations based on GC and GPC results. The NMR analysis was performed in the Department of Chemistry at McGill University using a Varian XL-300 NMR Spectrometer.

# 5.0 RESULTS

## 5.1 Mass Balances

### 5.1.1 Overall Mass Balance

Mass balance calculations were performed in an effort to determine the typical losses from the system. This was accomplished by weighing each piece of glassware of the experimental apparatus prior to and after each experiment. System losses averaged 8% of the initial charge (weight of polyethylene/ polystyrene mixture) with a standard deviation of 3%.

Mass balance calculations for the production of volatiles for all experiments, carried out at different temperatures, are illustrated in Figure 5.1.1. This graph depicts the production of volatiles in grams versus the amount of weight loss from the reaction vessel. Ideally, a given weight loss from the residue or solid phase would produce an equivalent amount of liquid products. However, the experimental values are seen to fall below the line for an ideal mass balance. The vertical deviation from the line represents the losses in the system. Figure 5.1.2 shows that the magnitude of the system losses is constant and does not increase with an increase in the weight of the volatile fraction, as might be expected.

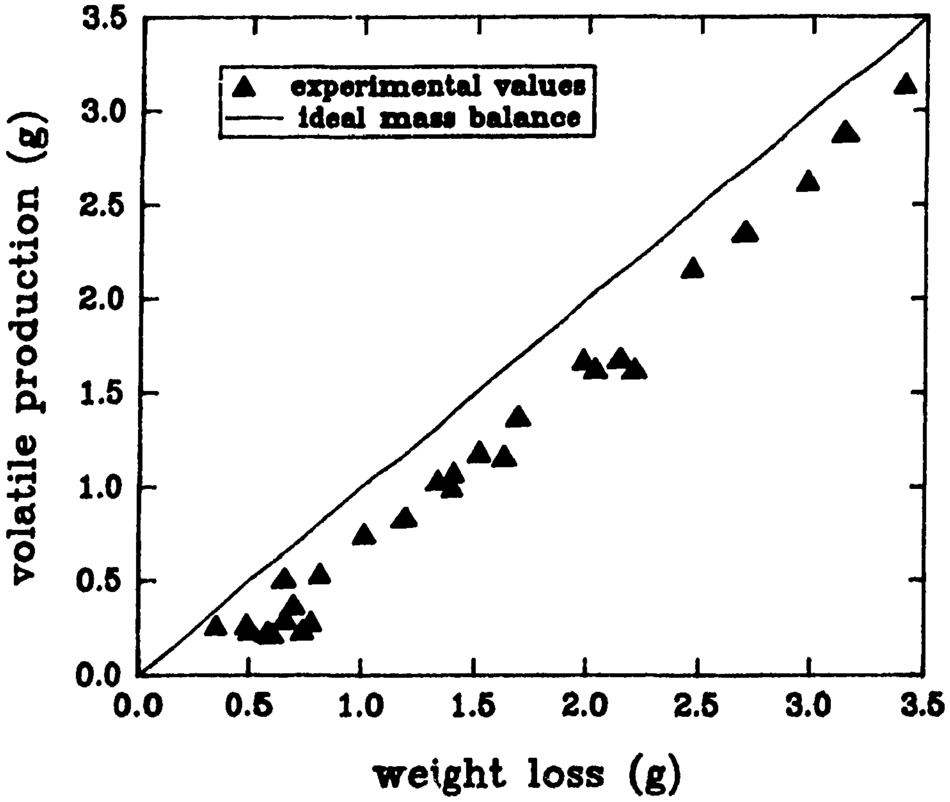


Figure 5.1.1. Volatile production versus residue weight loss for all experiments.

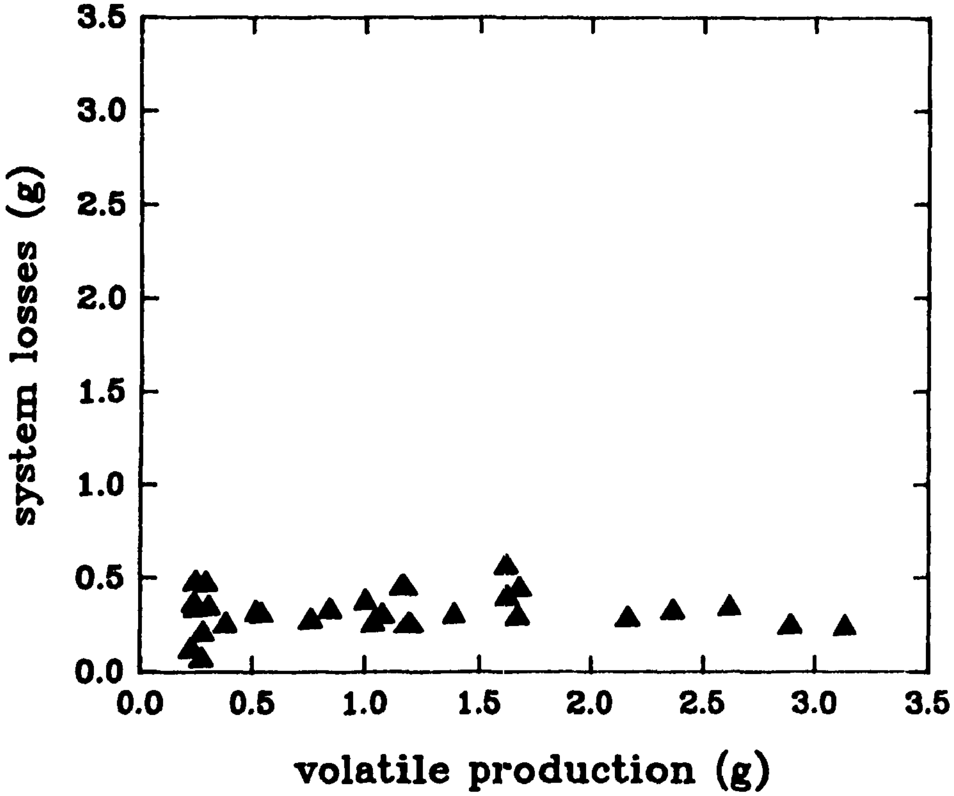


Figure 5.1.2. System losses versus volatile production for all experiments:

### 5.1.2 Product Mass Balance

A mass balance for the mixture 60PE/40PS was performed to evaluate the extent of conversion of the inital sample mixture to final products. The precision of the various analytical techniques was compared based on data from NMR, GC and GPC. The objective was to determine the ratio between aromatic and aliphatic products remaining in the residue fraction using the results from the different analytical methods.

A NMR spectrum for the residue fraction of the mixture 60PE/40PS is shown in Figure 5.1.3. It can be estimated from this that the ratio of aromatics to aliphatics is 7.21 / (3.62+71.12) or 0.096.

From GPC data, Figure 5.2.5, which provides the breakdown of weight percent and molecular weight of each component in a sample, it was calculated that there were 0.523 mols of aromatics present in the residue, assuming a basis of 250 grams (100g PE, 150g PS) of initial mixture. GC data revealed that 97%, or 5.17 mols, of the initial charge of alkyl hydrocarbons remained in the residue. Therefore, GPC and GC data suggest that the ratio of aromatic to aliphatic products is 0.523 / 5.17 or 0.101. These results are within 5% of the estimate obtained by NMR. Therefore, the results of the various techniques appear to be consistent.

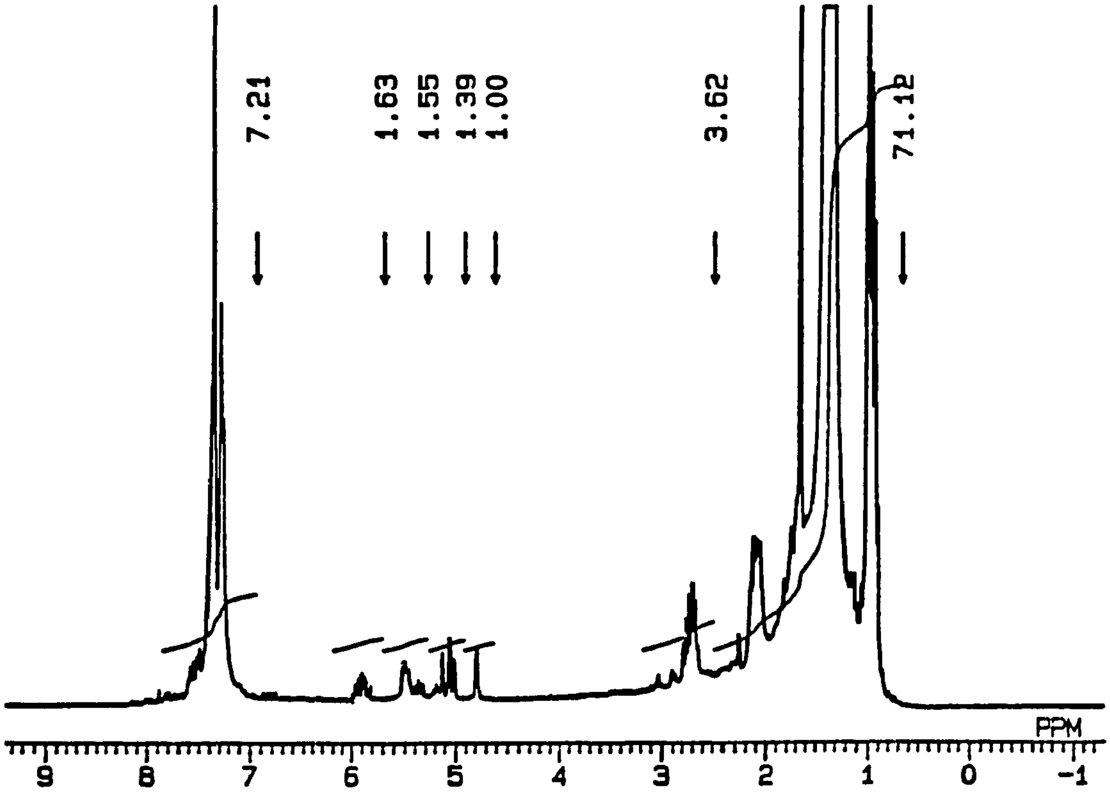


Figure 5.1.3. NMR spectra of residue fraction for 60PE/40PS mixture at T=395°C.

## 5.2 Thermolysis Products

Thermolysis experiments resulted in the production of two product fractions: a low boiling volatile fraction and a high boiling wax-like residue. The low boiling fraction, which is volatile at the reaction temperature, was condensed and collected in the cold trap. The high boiling fraction, non-volatile at the reaction temperature, remained in the reactor flask. The yields (percent of initial mixture weight) of the residue and volatile fractions for different mixture ratios for experiments at 395 and 420°C are shown in Figures 5.2.1 and 5.2.2, respectively. The results at both temperatures exhibited similar patterns.

In the absence of interactions between PE and PS, the degradation products, volatiles and residue, would follow the straight lines shown in Figures 5.2.1 and 5.2.2. However, the experimental data suggest that there is significant interaction between the two polymers, as indicated by a positive deviation from the straight line for the residue and a negative deviation for the volatiles. Thus, the interactions tend to increase the residue and lower the volatiles in comparison with the levels that would be obtained in the absence of interactions.

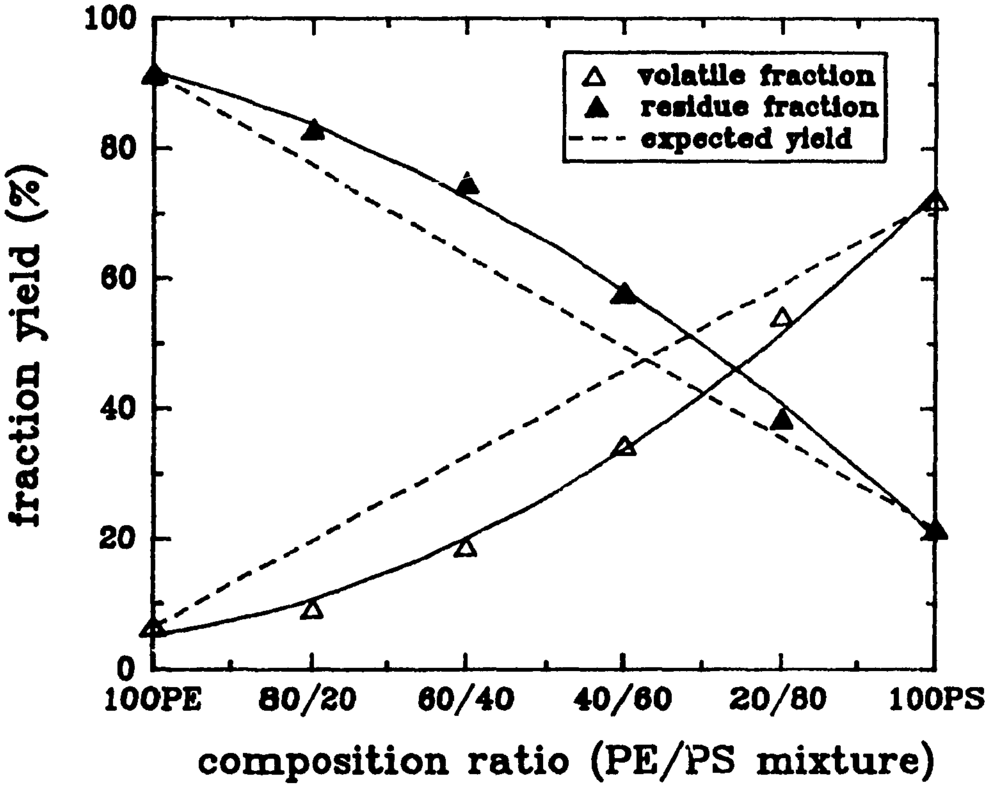


Figure 5.2.1. Fraction yields for varying composition ratios at T=395°C.

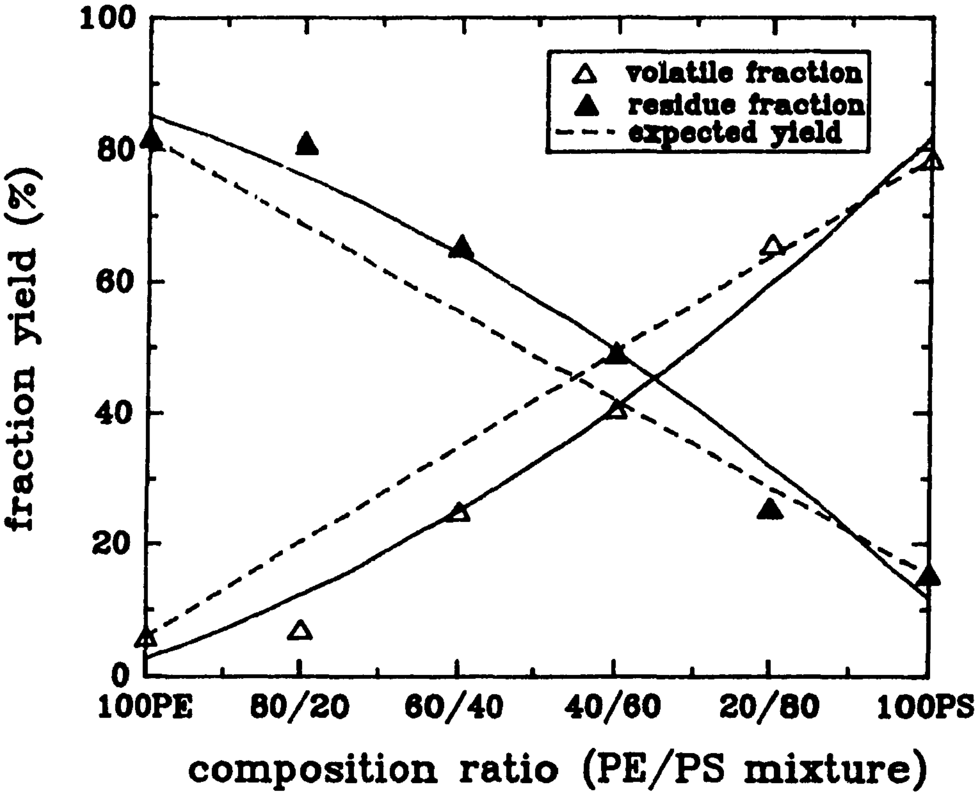


Figure 5.2.2. Fraction yields for varying composition ratios at T=420°C.

### 5.2.1 Volatile Fraction

Gas chromatography (GC) was used to characterize the volatile fraction. The compositions of the volatile fractions obtained for the mixture ratios investigated at 395 and 420°C are summarized in Tables 5.2.1 and 5.2.2, respectively. The shaded data refer to products which were identified by comparison with retention times of standards.

The tables include results for the control experiments of pure PE and PS at 420°C and for pure PS at 395°C. The degradation of pure PE at 395°C did not produce a volatile fraction in a sufficient quantity for GC analysis. For pure PS, at both temperatures, it was possible to identifty over 99% of the components present in the volatile fraction. The fraction of components identified decreases as PE concentration increases because of the increasing diversity of products being formed. As a result, it became more difficult to identify the possible products. This can be seen for pure PE at 420°C where only 25% of the components by weight were identified.

The volatile fraction is found to comprise a number of aromatic compounds produced by the degradation of PS. These were identified, in decreasing order of prevalence, as: styrene, toluene, α-methyl styrene, ethyl benzene, benzene and iso-propyl benzene. Styrene and toluene consistently accounted for over 90% of the total volatiles produced. The per cent styrene in the volatile fraction decreases while the

## Table 5.2.1. GC Results. Composition of volatile fraction for varing mixture ratios at T=395 C.

| | | component percent | | | | |
|---|---|---|---|---|---|---|
| RT (min) | compound | 100 PS | 20PE / 80PS | 40PE / 60PS | 60PE / 40PS | 80PE / 20PS |
| 0.48 | | 0.003 | | 0.008 | 0.004 | 0.001 |
| 0.56 | pentane | | 0.005 | 0.051 | 0.137 | 0.023 |
| 0.72 | hexane | | 0.030 | 0.151 | 0.548 | 0.130 |
| 0.82 | | | | | 0.101 | 0.031 |
| 0.94 | benzene | 0.119 | 0.132 | 0.221 | 0.385 | 0.122 |
| 1.09 | iso-octane | | 0.039 | 0.142 | 0.520 | 0.383 |
| 1.14 | heptane | | 0.030 | 0.139 | 0.477 | 0.350 |
| 1.28 | | | 0.011 | 0.066 | 0.226 | 0.170 |
| 1.41 | | | 0.003 | 0.037 | 0.121 | 0.109 |
| 1.58 | toluene | 8.232 | 11.524 | 20.108 | 31.142 | 33.391 |
| 1.92 | | | 0.015 | 0.056 | 0.314 | 0.649 |
| 2.05 | | | | 0.040 | 0.233 | 0.509 |
| 2.32 | | | | | 0.026 | 0.063 |
| 2.51 | | | | 0.004 | 0.024 | 0.068 |
| 2.88 | ethyl benzene | 1.836 | 2.041 | 1.975 | 2.434 | 3.701 |
| 3.47 | styrene | 84.366 | 83.732 | 74.751 | 61.895 | 56.170 |
| 4.09 | | | | | | 1.403 |
| 4.42 | iso-propyl benzene | 0.090 | 0.036 | | | |
| 5.29 | | 0.109 | 0.084 | 0.298 | 0.129 | 0.133 |
| 5.60 | | | | | 0.161 | 0.300 |
| 6.66 | methyl styrene | 5.144 | 2.249 | 1.847 | 0.932 | 1.592 |
| 7.99 | | | | | 0.083 | 0.387 |
| 8 68 | | | | | 0.042 | 0.221 |
| 9.57 | | 0.089 | 0.059 | 0.097 | 0.059 | 0.090 |
| 10.75 | | 0.011 | 0 01 | 0.01 | 0.005 | |
| Percent of products identified | | 99.788 | 99 818 | 99.384 | 98.472 | 95.866 |

## Table 5.2.2. GC Results. Composition of volatile fraction for varying mixture ratios at T = 420 C.

| | | component percent | | | | | |
|---|---|---|---|---|---|---|---|
| RT (min) | compound | 100 PS | 20PE/80PS | 40PE/60PS | 60PE/40PS | 80PE/20PS | 100 PE |
| 0.48 | | 0.004 | 0.006 | 0.019 | 0.012 | | 0.053 |
| 0.56 | pentane | | 0.038 | 0.137 | 0.184 | 0.017 | 0.612 |
| 0.65 | | | | | 0.020 | 0.002 | |
| 0.72 | hexane | | 0.118 | 0.408 | 0.697 | 0.704 | 4.994 |
| 0.82 | | | 0.014 | 0.059 | 0.129 | 0.099 | 0.968 |
| 0.90 | | | | | | | 1.436 |
| 0.94 | benzene | 0.074 | 0.150 | 0.282 | 0.429 | 0.424 | |
| 0.96 | | | | | | | 0.590 |
| 1.09 | iso-octane | | 0.102 | 0.336 | 0.687 | 2.800 | 9.341 |
| 1.14 | heptane | | 0.098 | 0.296 | 0.655 | 2.710 | 10.331 |
| 1.28 | | | 0.027 | 0.101 | 0.313 | 1.129 | 4.637 |
| 1.41 | | | 0.009 | 0.031 | 0.193 | 0.284 | 2.400 |
| 1.52 | | | | | | | 2.583 |
| 1.58 | toluene | 4.682 | 10.478 | 18.128 | 27.481 | 50.522 | |
| 1.65 | | | | | | | 6.385 |
| 1.92 | | | 0.057 | 0.272 | 0.578 | 2.981 | 13.883 |
| 2.05 | | | 0.040 | 0.222 | 0.499 | 2.117 | 12.222 |
| 2.32 | | | 0.007 | 0.037 | 0.061 | 0.201 | 2.866 |
| 2.50 | | | 0.007 | 0.031 | 0.056 | 0.109 | 2.420 |
| 2.72 | | | | | | | 1.235 |
| 2.88 | ethyl benzene | 0.661 | 2.016 | 3.193 | 3.369 | 1.095 | |
| 2.90 | | | | | | | 0.560 |
| 3.11 | | | | | | | 2.030 |
| 3.31 | | | | | | | 0.947 |
| 3.39 | | | | | | | 1.474 |
| 3.47 | styrene | 90.582 | 82.114 | 74.689 | 61.510 | 34.278 | |
| 3.77 | | | | | | | 5.389 |
| 4.13 | | | | | 0.717 | | 5.716 |
| 4.42 | iso-propyl benzene | | 0.125 | 0.040 | 0.367 | | |
| 5.30 | | 0.067 | 0.139 | 0.090 | 0.127 | | |
| 5.60 | | | 0.101 | 0.061 | 0.173 | | 0.496 |
| 6.66 | methyl styrene | 3.825 | 4.098 | 1.392 | 1.410 | 0.401 | |
| 6.87 | | | | | | | 0.424 |
| 7.99 | | | 0.019 | 0.068 | 0.144 | 0.127 | 3.283 |
| 8.68 | | | 0.015 | 0.032 | 0.080 | | 2.725 |
| 9.57 | | 0.092 | 0.189 | 0.067 | 0.095 | | |
| Percent of products identified | | 99.837 | 99.370 | 98.910 | 96.803 | 92.951 | 25.278 |

concentration of toluene increases with increasing PE content. Furthermore, with increasing PE content, the volatile fraction was found to contain increasing quantities of short hydrocarbon compounds. Some of these were identified as pentane, hexane, iso-octane and heptane. These hydrocarbons did not account for more than 5% of the liquid products. Hydrocarbons longer than C9 were not observed. The composition of the volatile fraction for the control of pure PE at 395°C was not obtained due to the small amount of volatiles evolved. However, it can be seen that, with the addition of 20% PS (80PE/20PS), measurable quantities of a number of small alkanes are evolved. This is also observed at 420°C.

The yields of aromatic products, based on the mole per cent of the initial PS concentration, are shown in Table 5.2.3. The styrene, toluene and total aromatic yields are plotted in Figures 5.2.3 and 5.2.4. It is important to note in these figures that the scales of the ordinate axes have changed. The scale represents the molar yield based only on the initial PS in the mixture, not the mass of the entire mixture. With this in mind, the yield of liquid aromatic products is seen to decrease with increasing PE content. This is again evidence that a polymer interaction is occurring during degradation. The PE appears to inhibit the production of liquid PS compounds and to keep these products in the residue fraction. Styrene yields of 60% at 395°C and

## Table 5.2.3. Aromatic yields (molar % of initial PS) for varying composition ratios

| mixture | T ( C) | styrene | toluene | benzene | ethyl benzene | methyl styrene | iso-propyl benzene | total aromatic |
|---|---|---|---|---|---|---|---|---|
| 100PS | 395 | 60.85 | 6.71 | 0.12 | 1.30 | 3.27 | 0.06 | 72.31 |
| 20PE/80PS | 395 | 56.74 | 8.83 | 0.12 | 1.36 | 1.34 | 0.02 | 68.42 |
| 40PE/60PS | 395 | 42.83 | 13.02 | 0.17 | 1.11 | 0.93 | 0.00 | 58.07 |
| 60PE/40PS | 395 | 28.96 | 16.47 | 0.24 | 1.12 | 0.38 | 0.00 | 47.18 |
| 80PE/20PS | 395 | 25.99 | 17.46 | 0.08 | 0.17 | 0.65 | 0.00 | 45.85 |
| | | | | | | | | |
| 100PS | 420 | 71.05 | 4.15 | 0.08 | 0.51 | 2.65 | 0.00 | 78.44 |
| 20PE/80PS | 420 | 67.39 | 9.72 | 0.17 | 1.62 | 2.96 | 0.09 | 81.96 |
| 40PE/60PS | 420 | 50.67 | 13.90 | 0.26 | 2.13 | 0.83 | 0.02 | 67.82 |
| 60PE/40PS | 420 | 38.42 | 19.41 | 0.36 | 2.06 | 0.78 | 0.20 | 61.23 |
| 80PE/20PS | 420 | 12.06 | 20.09 | 0.20 | 0.38 | 0.12 | 0.00 | 32.84 |

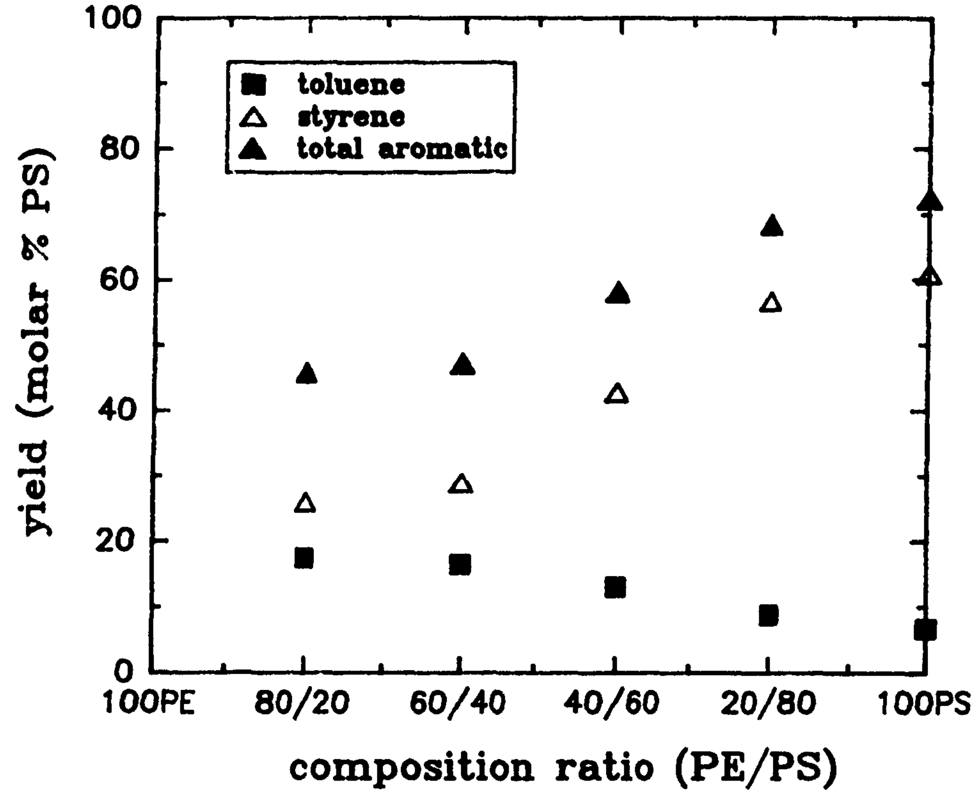


Figure 5.2.3. Effect of mixture composition on aromatic yields at T=395°C.

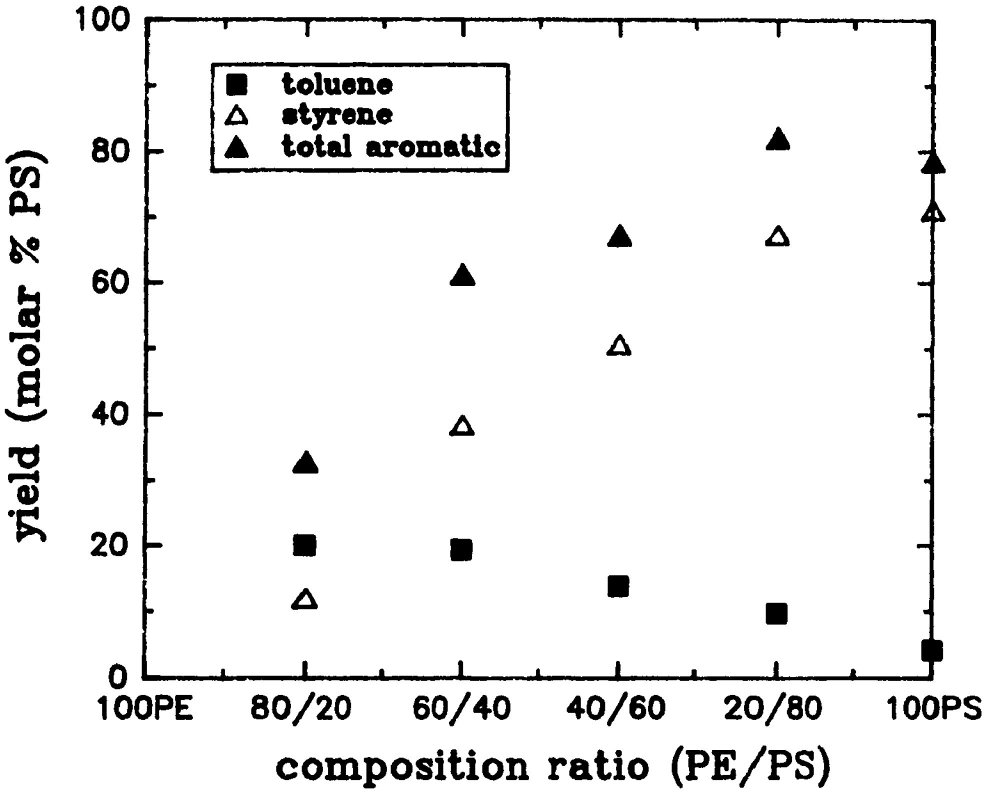


Figure 5.2.4. Effect of mixture composition on aromatic yields at T=420°C.

70% at 420°C are observed for pure degraded PS. This is consistent with literature data [25-33]. This yield also decreases with increasing PE content. At 395°C, only a 7% decrease in the styrene yield is observed with the addition of 20% PE to the degradation mixture. The styrene yield decreases by more than half from pure PS to the value obtained for a 80PE/20PS mixture. Although the production of liquid aromatics is decreasing, the presence of PS appears to enhance the evolution of small hydrocarbons. This can be seen in Tables 5.2.1 and 5.2.2. At 395°C, 100PE does not produce a sufficient volatile fraction for analysis, but with the addition of 20% PS it is then possible to collect a diversity of alkanes in the volatiles. These are all lower than C9, which could be easily separated and recovered.

### 5.2.2 Residue Fraction

The molecular weight distribution, MWD, for the residue fractions produced at 395°C is shown in Figure 5.2.5. The most obvious feature is that the MWD is bi-modal. It consists of a low molecular weight PS portion and a high molecular weight PE portion. As shown below, the polydispersity increases with increasing PE content.

| **Mixture** | $M_w/M_n$ |
|---|---|
| Pure PS | 1.7 |
| 20PE/80PS | 5.6 |
| 40PE/60PS | 8.2 |
| 60PE/40PS | 10.5 |
| 80PE/20PS | 17.1 |

Actual values for number or weight average molecular weights are meaningless with these high polydispersities. However, the peak molecular weights reveal trends. The MWD for PS alone is seen to contain peaks at molecular weights around 200 and 300 representing dimer and trimer, respectively. The tailing off of this line depicts other oligomers in lesser amounts. The other residue fractions also have a low molecular weight peak at 200 for styrene dimer but have reduced amounts of higher oligomers.

The relative size and the peak molecular weight of the high molecular weight portion increases with PE content. For

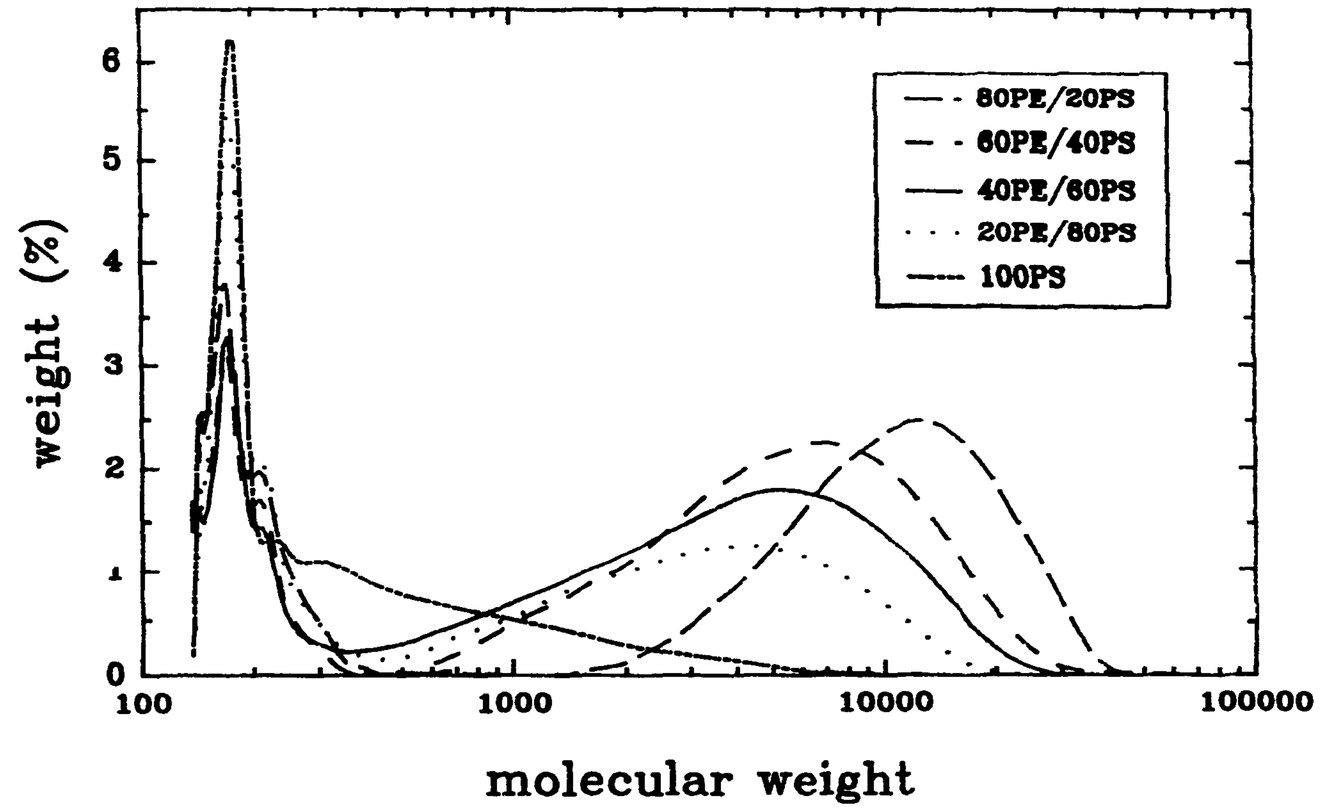


Figure 5.2.5. Molecular weight distribution of residue fractions for experiments at T=395°C.

the mixture 80PE/20PS, the peak molecular weight is 12,000. This value is only slightly lower than the value of 17,000 measured for the number average molecular weight of the original PE sample before degradation.

### 5.3 Residue Solubility

Although the MWD displays a high molecular weight PE fraction, solubility experiments have determined that the residue fraction is remarkably tractable. The percent of the residue that is soluble in chloroform at room temperature is shown in Figure 5.3.1. It shows the dramatic increase in the solubility of the residue fraction. The residue from the control experiment of 100PE is highly intractable with only 15% solubility. Upon the addition of 20% PS, the solubility has increased to 45%. For the mixture 60PE/40PS, the residue has become 100% soluble even though the residue contains a polymer portion with molecular weights as high as 30,000.

### 5.4 Temperature Effects

#### 5.4.1 Fraction Yields

The effect of temperature on the yields of the volatile and residue fractions is shown in Figure 5.4.1. These results are for the mixture 60PE/40PS. Similar trends would be expected with the other mixtures.

It is observed that between 350 and 390°C the production of either volatiles or solid residue remains constant and is

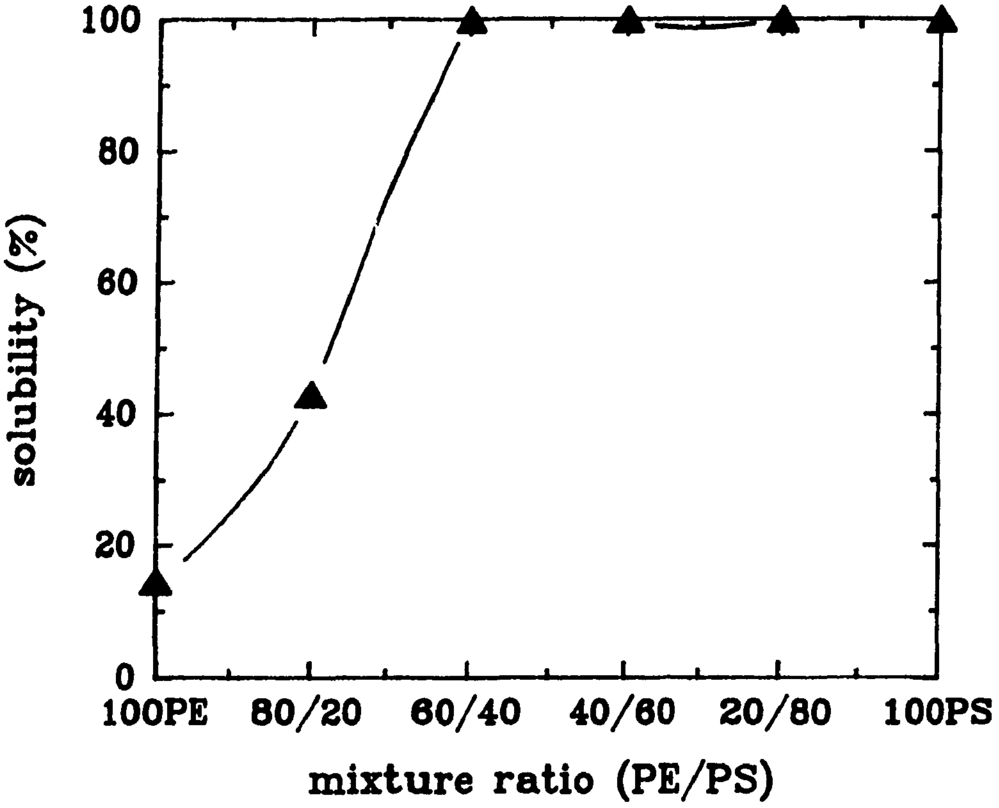


Figure 5.3.1. Effect of mixture composition on solubility of residue fraction in $CHCl_3$ for experiments at T=395.

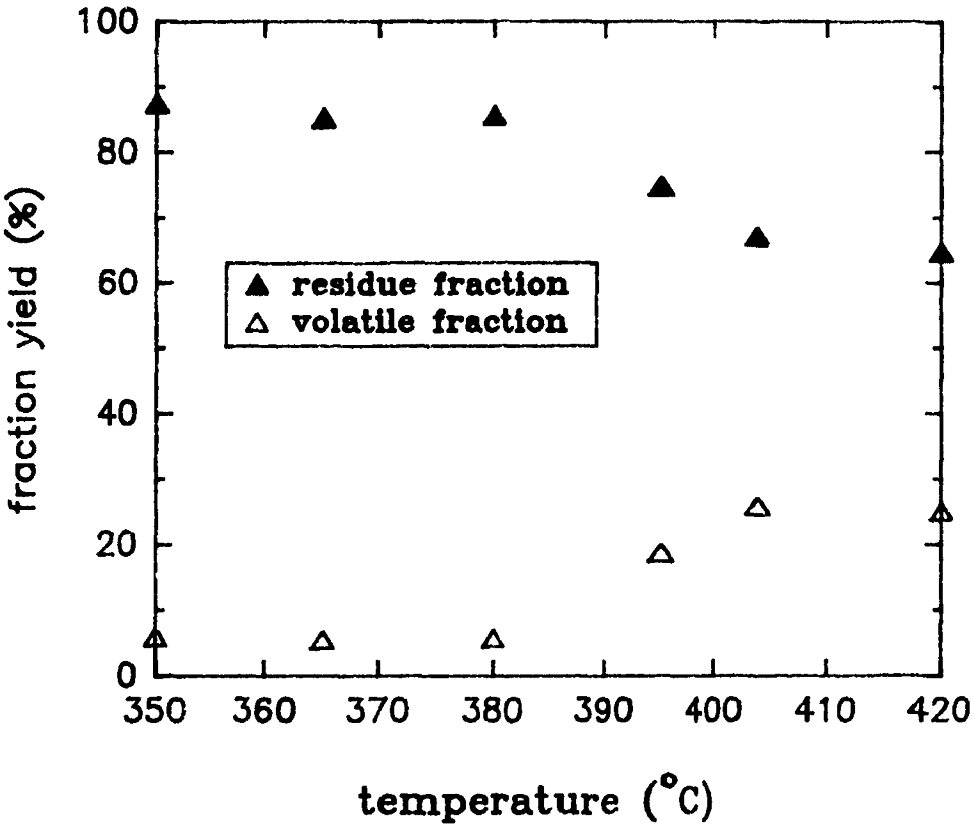


Figure 5.4.1. Effect of temperature on yields of the volatile and residue fraction for the mixture 60PE/40PS.

independent of the actual temperature. Above 390°C, a temperature dependence is noted. The yield of the volatile fraction increases, and the residue decreases with increasing temperature.

### 5.4.2 Aromatic Products

Figure 5.4.2 depicts the effect of temperature on the yields of styrene, toluene and total aromatic products. Again, the yields are constant until approximately 390°C where a significant increase is observed. This observation is related to the increase in volatile production with temperature shown in Figure 5.4.1.

### 5.4.3 Solubility

The effect of temperature on the solubility of the residue fraction for the mixture 60PE/40PS is shown in Figure 5.4.3. The residue solubility is seen to increase with temperature until 100% solubility is attained at 395°C. As expected, the residue remains soluble at higher temperatures.

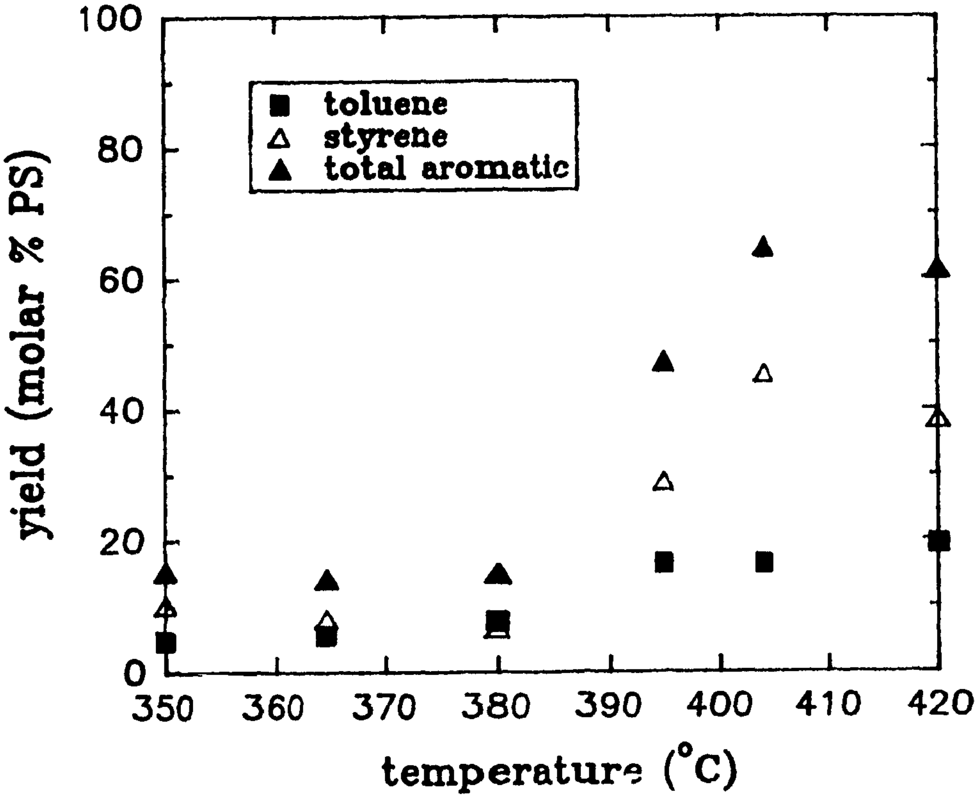


Figure 5.4.2. Effect of temperature on aromatic yields for the mixture 60PE/40PS.

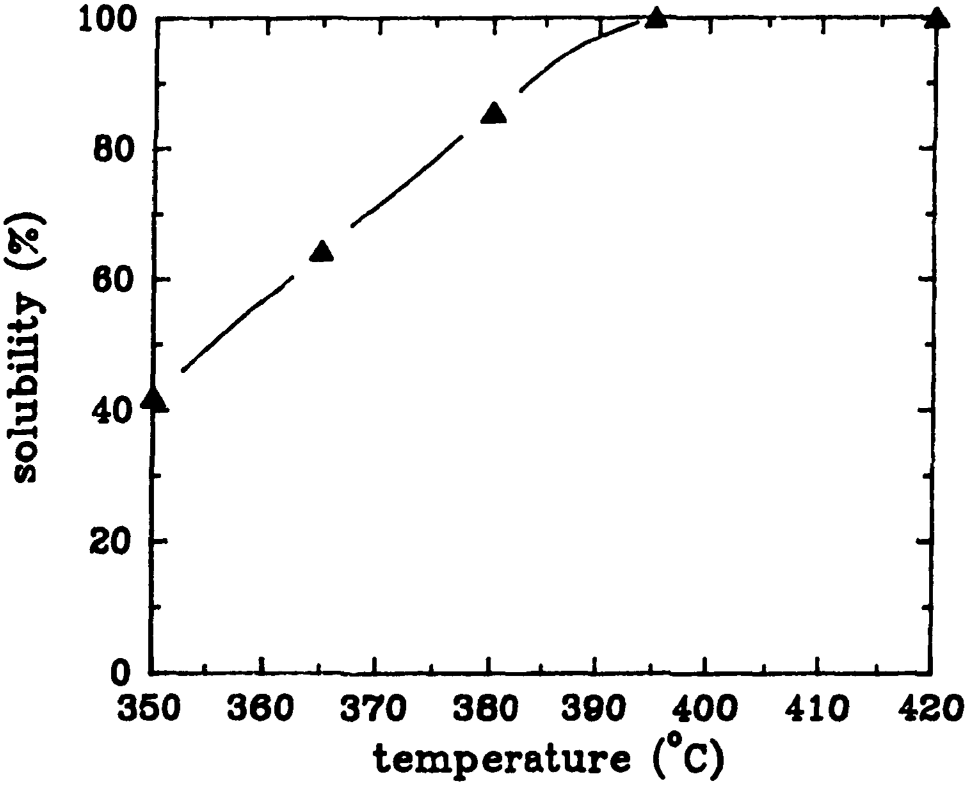


Figure 5.4.3. Effect of temperature on residue solubility for the mixture 60PE/40PS.

# 6.0 DISCUSSION

## 6.1 System Mass Balance

The results of the overall system mass balance for every experiment were presented in Figures 5.1.1 and 5.1.2. This included experiments at temperatures ranging between 350°C and 420°C. It was revealed that system losses were evident in every experiment and normally represented 8% of the initial mass. The losses maintained a constant mass and did not increase with an increase in volatile production or temperature. This can be explained if the losses are due to the apparatus design and the experimental procedure. For example, polymer accumulated on the stirring rod but, due to its shape, it was not possible to weigh the rod for mass balance calculations. This loss was a constant value, independent of the reaction temperature.

## 6.2 Formation of Products

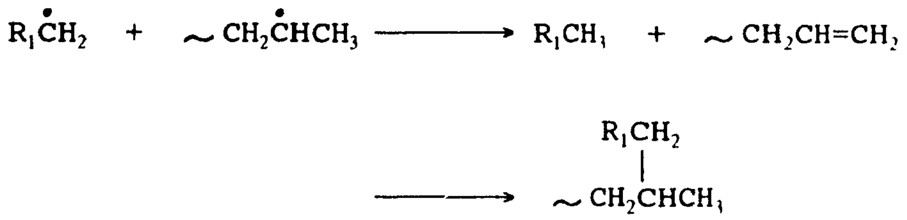
It has been shown that the decomposition of polyethylene, polystyrene and mixtures of these polymers produces two fractions: a volatile fraction which condensed to a mixture of liquid products at room temperature and a solid, wax-like residue. The fraction yields and the composition of each fraction are dependent on the mixture ratio and the reaction temperature, as shown in Figures 5.2.1, 5.2.2 and 5.4.1. The liquid products formed were similar to the product mix that would be expected by combining the volatile products obtained from the degradation of the individual polymers. Previous researchers have reported similar results [54-63]. Most studies on blend degradation have shown that only the decomposition rate is affected by polymer interactions but not the final degradation products.

### 6.2.1 Liquid Products

Polymer interactions affected the yields of liquid products. A decrease in the volatile fraction yield was observed in Figures 5.2.1 and 5.2.2. A summary of the liquid products obtained from the decomposition of PE and PS was presented in Tables 5.2.1 and 5.2.2. The formation of small alkanes by the decomposition of PE is not unusual, and the mechanism for production involves simple cleavages of the macromolecule. The thermolysis mechanism for PE was presented in Figure 2.2.1. The alkanes which were identified were pentane, hexane, iso-octane and heptane. Since over 99% of the possible aromatic products formed were identified, it is assumed that the remaining unidentifiable components are alkenes, iso-alkanes or iso-alkenes. A number of degradation schemes might explain the production of these compounds.

The first scheme depicts a termination between a chain end radical and an internal radical which may react by disproportionation or coupling [44].

**Scheme 1**



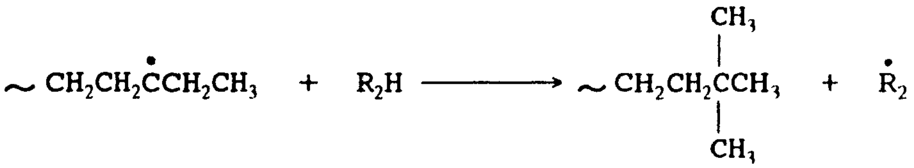
$$R_1\dot{C}H_2 + \sim CH_2\dot{C}HCH_3 \longrightarrow R_1CH_3 + \sim CH_2CH{=}CH_2$$

$$\longrightarrow \sim CH_2\overset{R_1CH_2}{\overset{|}{C}}HCH_3$$

Disproportionation and coupling both produce straight and branched hydrocarbons.

Branched alkanes can also be produced by an isomerization reaction, depicted in scheme 2 [38].

**Scheme 2**



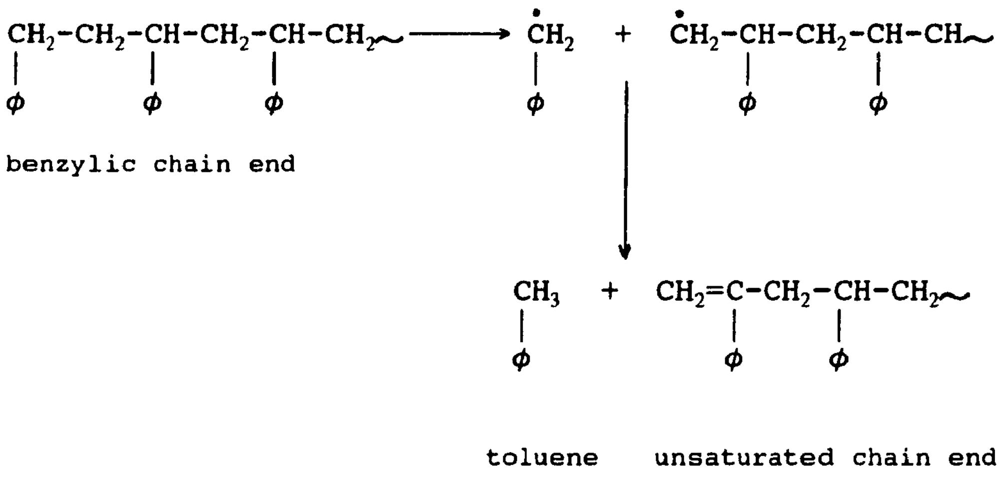
$$\sim CH_2CH_2\dot{C}CH_2CH_3 + R_2H \longrightarrow \sim CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_3 + \dot{R}_2$$

Branched hydrocarbons are less volatile than straight chains and will remain in the reactor flask unless additional chain scissions occur near the branch points reducing the overall size of the molecule. Again, alkanes or alkenes larger than C9 were not observed in the volatile fraction, and did not exceed 5% of the total liquid production.

The liquid products produced by the decomposition of PS were identified as styrene, toluene, α-methyl styrene, ethyl benzene, benzene and iso-propyl benzene. Styrene and toluene were the most significant products. The mechanism for styrene formation was shown in Figure 2.2.2. The mechanisms for the formation of the other aromatic products are shown in the following schemes. Iso-propyl benzene can be produced by scheme similar to the isomerization reaction shown for the alkanes.

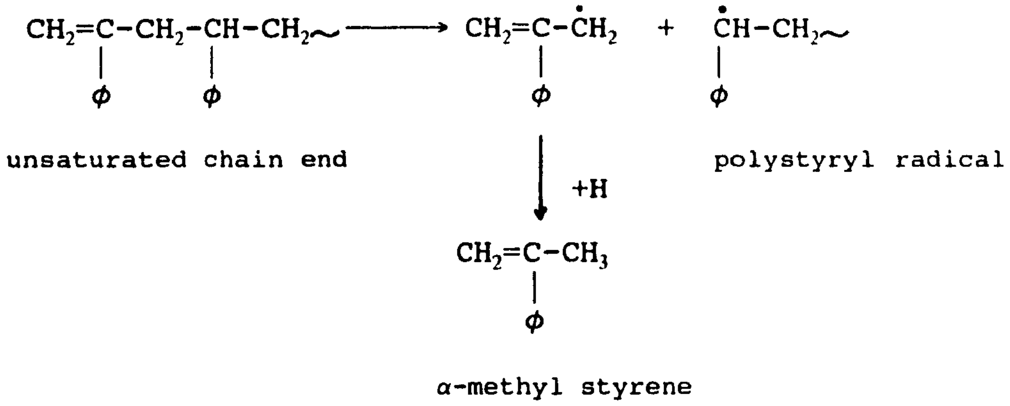
The mechanism for toluene formation is depicted in Scheme 3. It involves a C-C scission near a chain end, producing two radicals, followed by disproportionation [53].

**Scheme 3**



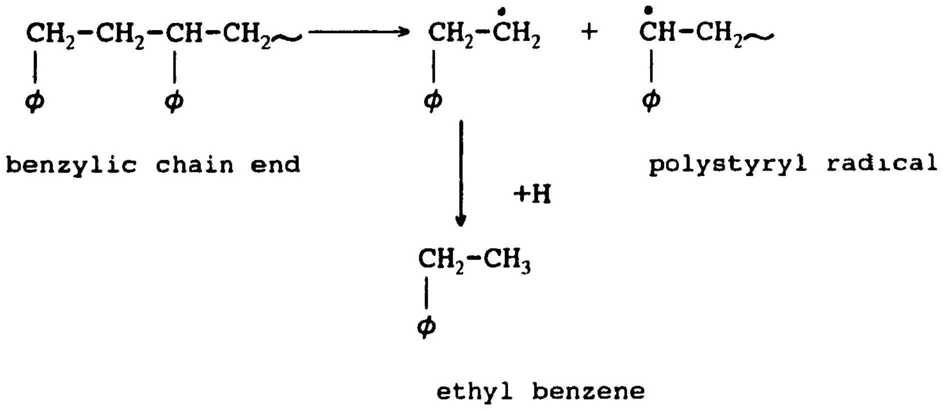
Scission near an unsaturated chain end will produce two radicals and if followed by hydrogen abstraction will produce α-methyl styrene and a polystyryl radical [53].

**Scheme 4**



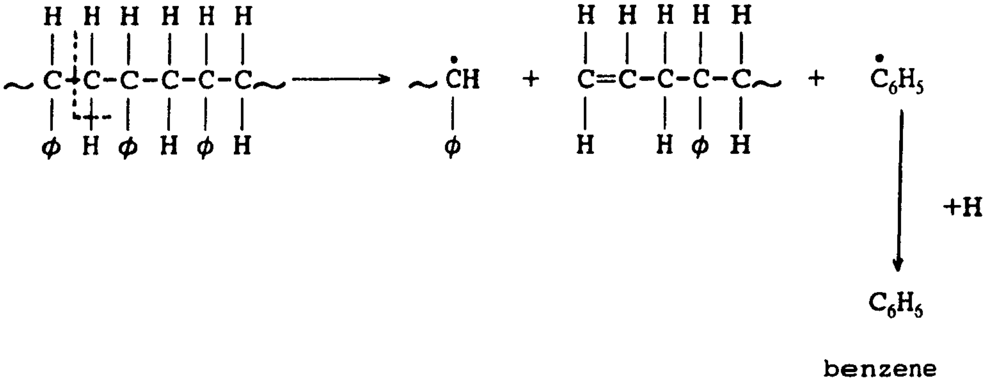
Ethyl benzene is produced in a similar manner to α-methyl styrene except the starting point is a benzylic chain end as shown in Scheme 5.

**Scheme 5**



Scheme 6 shows a mechanism for the formation of benzene. A phenyl group is split off as a free radical causing a scission in the backbone of the chain. The free radical then abstracts hydrogen to form benzene.

**Scheme 6**



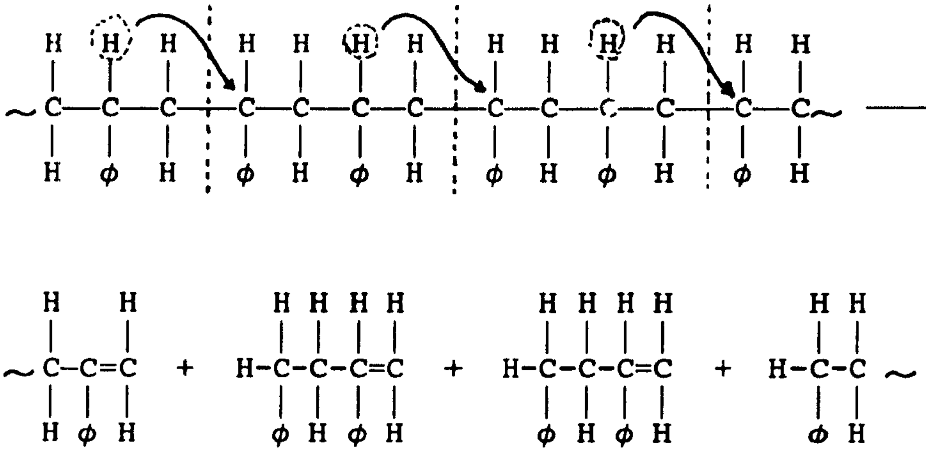
It was observed in Figures 5.2.3 and 5.2.4 that the overall yield of liquid aromatic products decreased with increasing PE content. This effect may be explained by two factors. Firstly, an increase in PE concentration increases the extent of molecular transfer relative to the other degradation steps. This occurs at the expense of the propagation step. It should be recalled that, PE degradation is governed by molecular transfer and PS degradation is governed by propagation or $\beta$ - scission [21,22]. Secondly, as previously mentioned in the literature review [62,63], blending of polyethylene, polypropylene and polystyrene reduces the rate of intermolecular transfer during degradation while intramolecular transfer remains unaffected. The decrease in liquid aromatic yields is, therefore, believed to be due to a combination of these factors. A decrease in propagation, $\beta$ - scission, results in less scissions of the PS chains and when this is compounded with the reduction in the rate of intermolecular transfer, a significant decrease in the decomposition rate is expected. The lifetime of a radical will increase since intramolecular transfer is the only available mechanism, making molecular transfer the limiting step. Aromatic products will form, in high PE content mixtures, but at a greatly decelerated rate. Those which are formed, have to arise mostly from intramolecular transfer.

### 6.2.2 Solid Products

The residue yield, presented in Figures 5.2.1 and 5.2.2, was observed to be dependent on the component ratio of the polymer mixture. The increase in solid product yield with increasing PE content is related to the corresponding decrease in the liquid production yield. Based on GPC analysis, the MWD's for the residues were observed to be bi-modal, consisting of a low molecular weight PS portion and a high molecular weight PE portion. The PE portion increased with increasing PE content in the initial mixture and contained relatively undegraded polyethylene. The peak MW for the mixture 80PE/20PS was observed to be around 12,000. Normally, when PE is degraded individually, at these temperatures, much lower molecular weights are expected. Number average molecular weights on the order of 500 were observed by Lo [34] under similar conditions. In comparision with results by McNeill et al. [60], the relatively high MW of the PE may be due to the volatile products resulting from the decomposition of PS. These are believed to diffuse into the PE phase and act as radical inhibitors, thereby, reducing the degradation rate of the PE.

In the low molecular weight range of the residue fraction, peaks representing styrene dimer and trimer were identified. The mechanism proposed for dimer formation is shown below in Scheme 7.

**Scheme 7**



Similar reactions are involved for the formation of trimers and other PS oligomers.

## 6.3 Residue Solubility

Probably, the most noteworthy effect of the interaction between PE and PS is the surprising solubility of the residue fraction, as shown in Figure 5.3.1. A dramatic increase in solubility is observed despite the high molecular weight PE components in the residue. Normally, the degradation of PE produces a highly intractable wax-like residue. The exact reason for the solubility effect is not known. It is possible that a small amount of styrene has been incorporated into the PE portion. However, based on a mass balance calculation for the mixture 60PE/40PS, it was determined that all the initial PS could be accounted for as volatile products or in the low molecular weight portion of the residue as dimer, trimer or other oligomers. The mass balance closes to within less than 2% error. In this case, the solubility may not be a chemical effect. Rather, it may be a physical effect due to the presence of the low molecular weight portion. If the residue were fractionated into the low molecular weight PS portion and the high molecular weight PE portion, a more accurate determination of the observed solubility effect could be made. It is suggested that the initial mixture begin with 40% PS content. This would allow for 100% solubility of the residue and based on Figure 5.2.3, at 395°C, 50% of the initial PS input will still evolve as liquid aromatic products.

### 6.3 Temperature Effects

A set of experiments were conducted at different temperatures for the mixture 60PE/40PS to investigate the change in degradation products with temperature. It was observed that at temperatures below 390°C, the product yields were independent of temperature. Above 390°C, a temperature dependence was noted and high yields of liquid products were observed. Previous research by Lo [34] on the thermolysis of PE showed the same dramatic increase in product conversion at approximately 410°C under similar experimental conditions. On the other hand, such an increase in product conversion with temperature was not observed by Marc [33] for pure PS. It has been postulated by Schneider [65] and Holmström [66] that this phenomenon is characteristic of polyethylene degradation. Decomposition of the PE chain produces chain fragments of various lengths. However, if the temperature of formation is below the temperature of volatilization, the products will accumulate until the higher temperature is reached.

The observed temperature effect is probably specific to this system, since the degradation process is dependent on the composition of the polymer mixture. Based on the results of this research and the previous research by Lo, it is expected for this system that as PE content in the initial mixture increases, the temperature where this dramatic increase in product formation is observed will also increase.

## 7.0 CONCLUSIONS

Thermolysis of mixtures of polyethylene and polystyrene at moderate temperatures can yield useful products. The final products were collected as two fractions: a volatile fraction containing liquid products at room temperature and a wax-like residue. Interactions between the polymers were observed. These interactions affected the fraction yields, the decompostion rate and the chemical properties of the residue fraction. The liquid products were the same as expected when combining the individual polymers. The liquid products consisted mainly of styrene and toluene. High yields of liquid aromatic products were obtained when PS was mixed with PE but the aromatics decreased with increasing PE content.

The solid residue was also seen to contain two fractions: a low molecular weight fraction comprised of PS oligomers and a high molecular weight fraction which increased in size and peak molecular weight with increasing PE content. The polydispersity was also seen to increase with increasing PE content. Despite the high molecular weight of the residue, a dramatic increase in solubility in a common organic solvent at room temperature was noted with the addition of PS. It is recommended, for chemical recycling of PE/PS mixtures, that temperatures above 390°C be used. The use of a mixture containing 40% PS would maximize the production of useful products.

The results of this research can be applied to develop chemical recycling technologies to recover useful chemical products from waste polymer mixtures. Further research is necessary to fully characterize the solid residue. Fractionating the residue would allow for a direct determination of its composition and might provide an explanation of the observed solubility effect. In addition, the effect of catalysts, higher temperatures and a larger apparatus should also be investigated.

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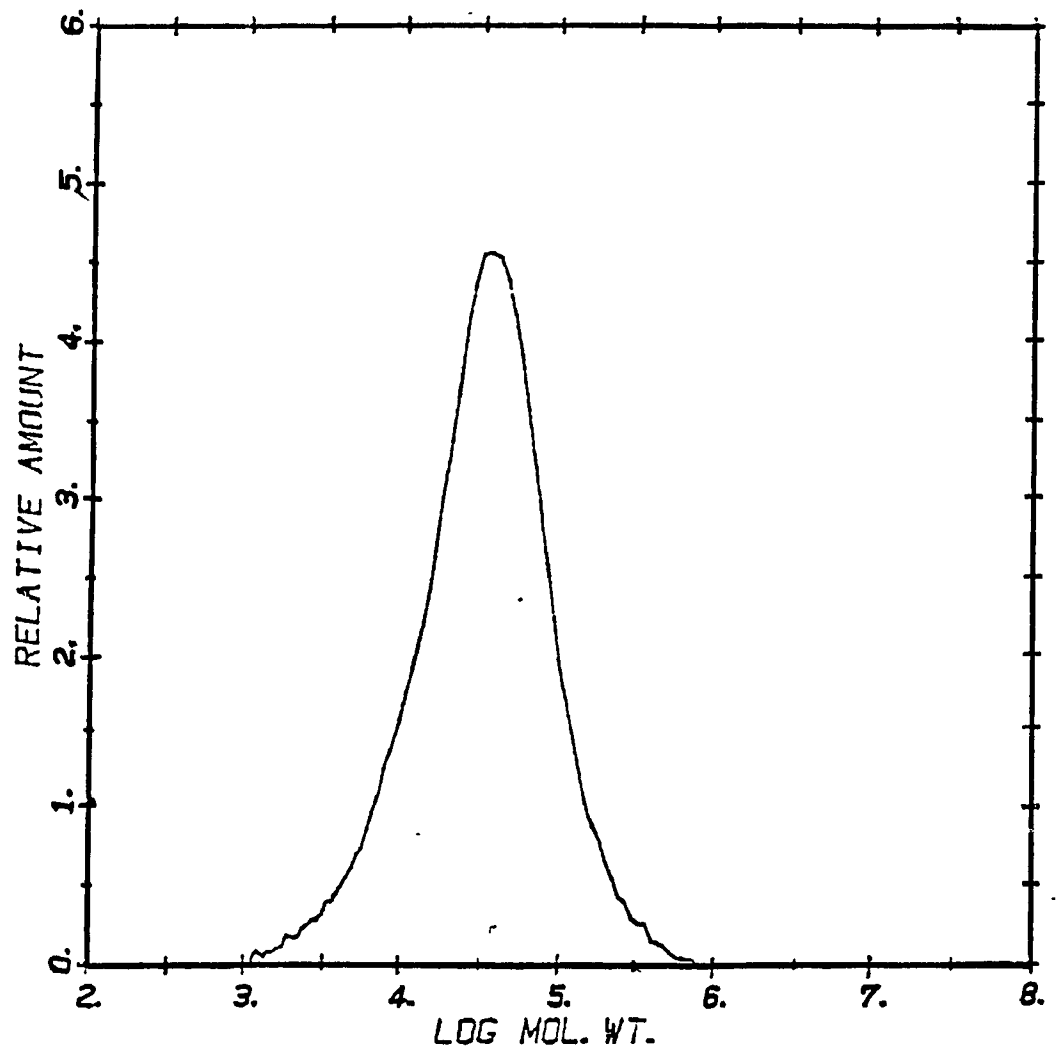
# **APPENDIX A:** MWD of LLDPE (SCLAIR 8111)

SEC REPORT #14104 G111\91083

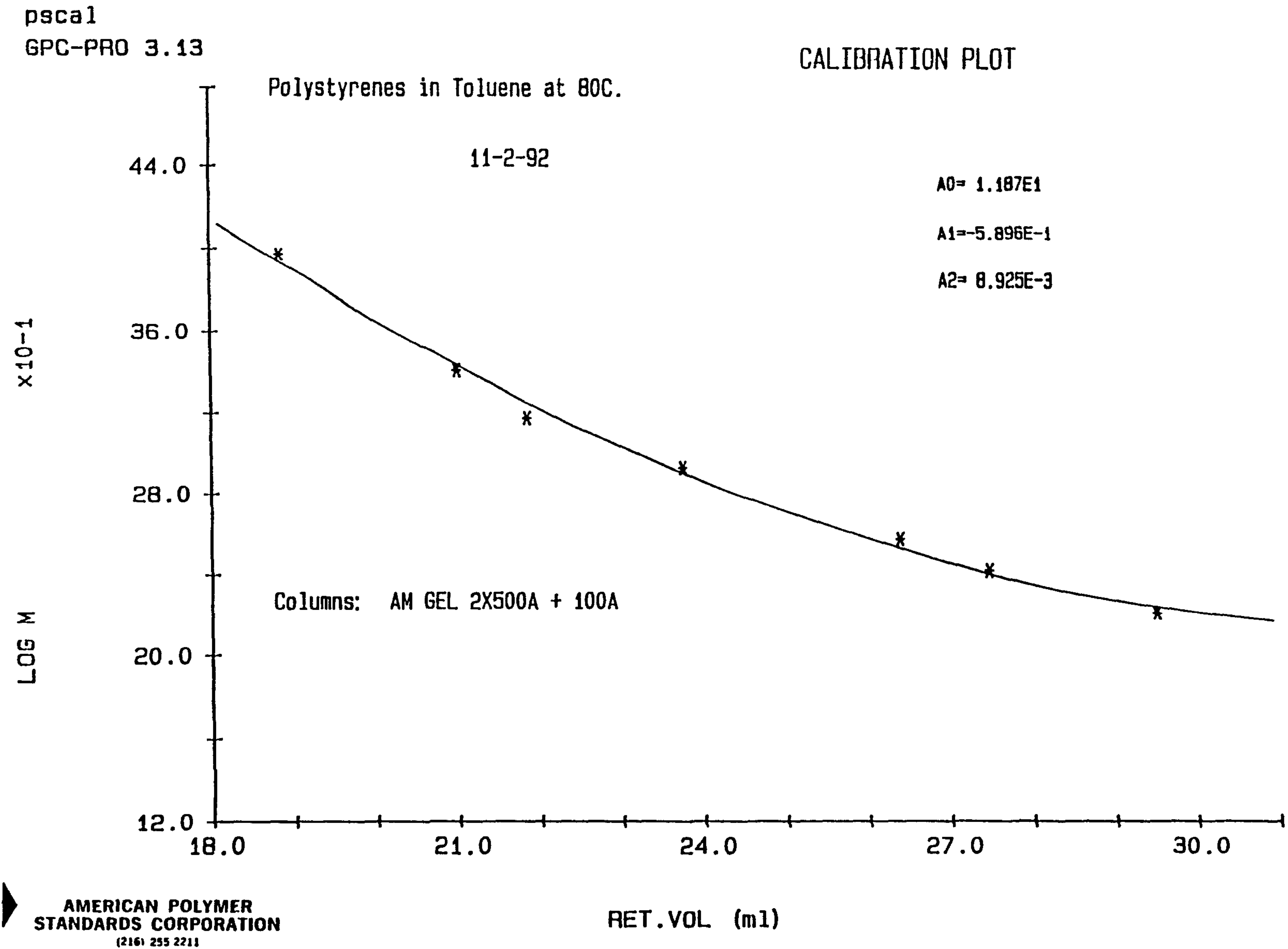


DATE: 09-NOV-89
BY: R. E. MURRAY

MN = 17310
MW = 51352
MZ = 129350
MZ+1 = 259465
MW/MN= 2.97
MZ/MW= 2.52
MZ+1/MZ= 2.01

| MOL WT | CUM WT% |
|---|---|
| 1000000 | 0. |
| 700000 | 0.03 |
| 500000 | 0.23 |
| 300000 | 1.3 |
| 100000 | 11.73 |
| 10000 | 66.3 |
| 5000 | 94.57 |
| 2000 | 99.3 |

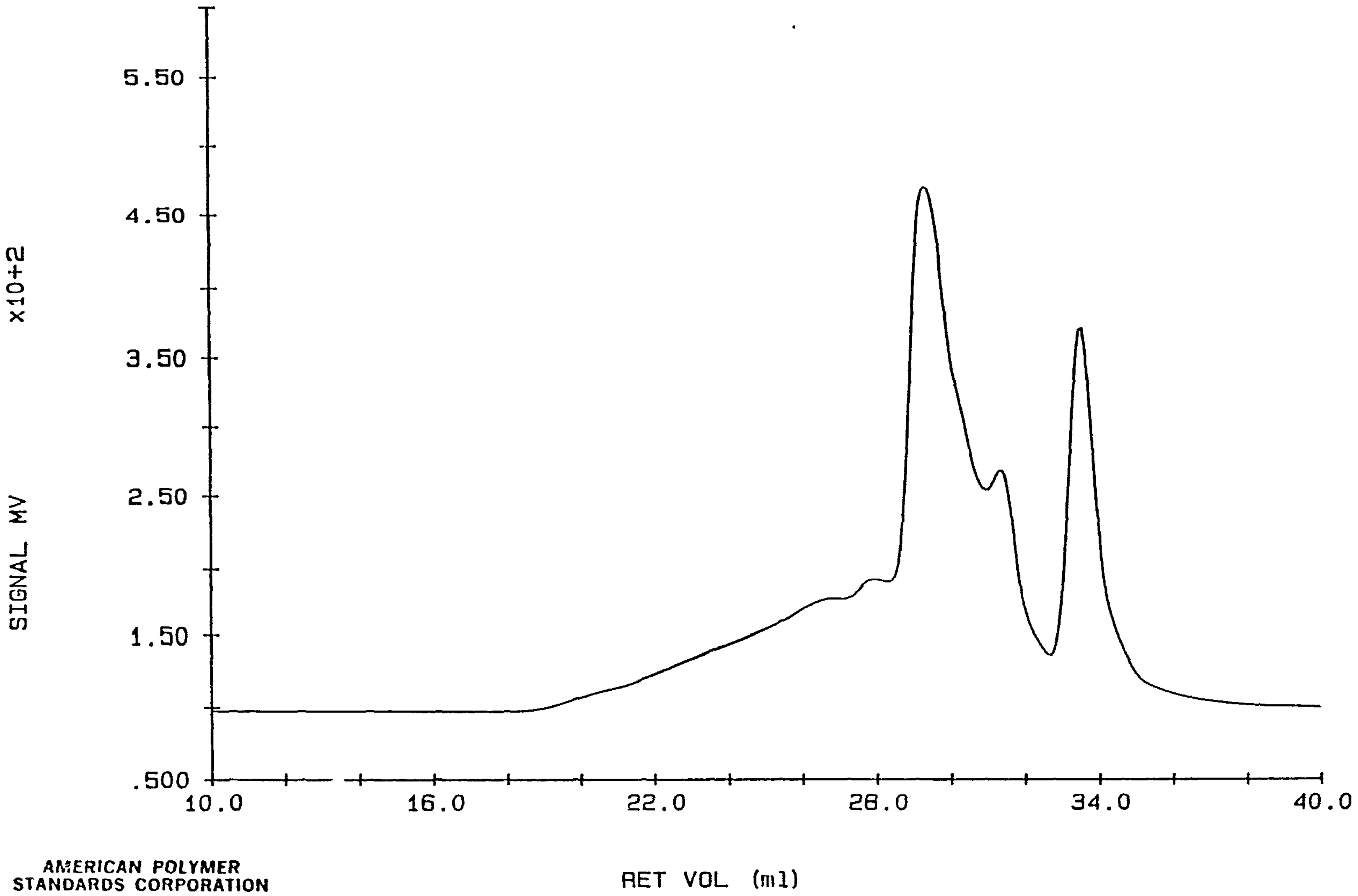
# **APPENDIX B:** GPC Chromatograms and calibration curve



**AMERICAN POLYMER STANDARDS CORPORATION**
(216) 255 2211
FAX (216) 255 8397

g5a-1 ENDED: 10/31/92 18: :
GPC-PRO 3.13 100%PS

dri CHROMATOGRAM



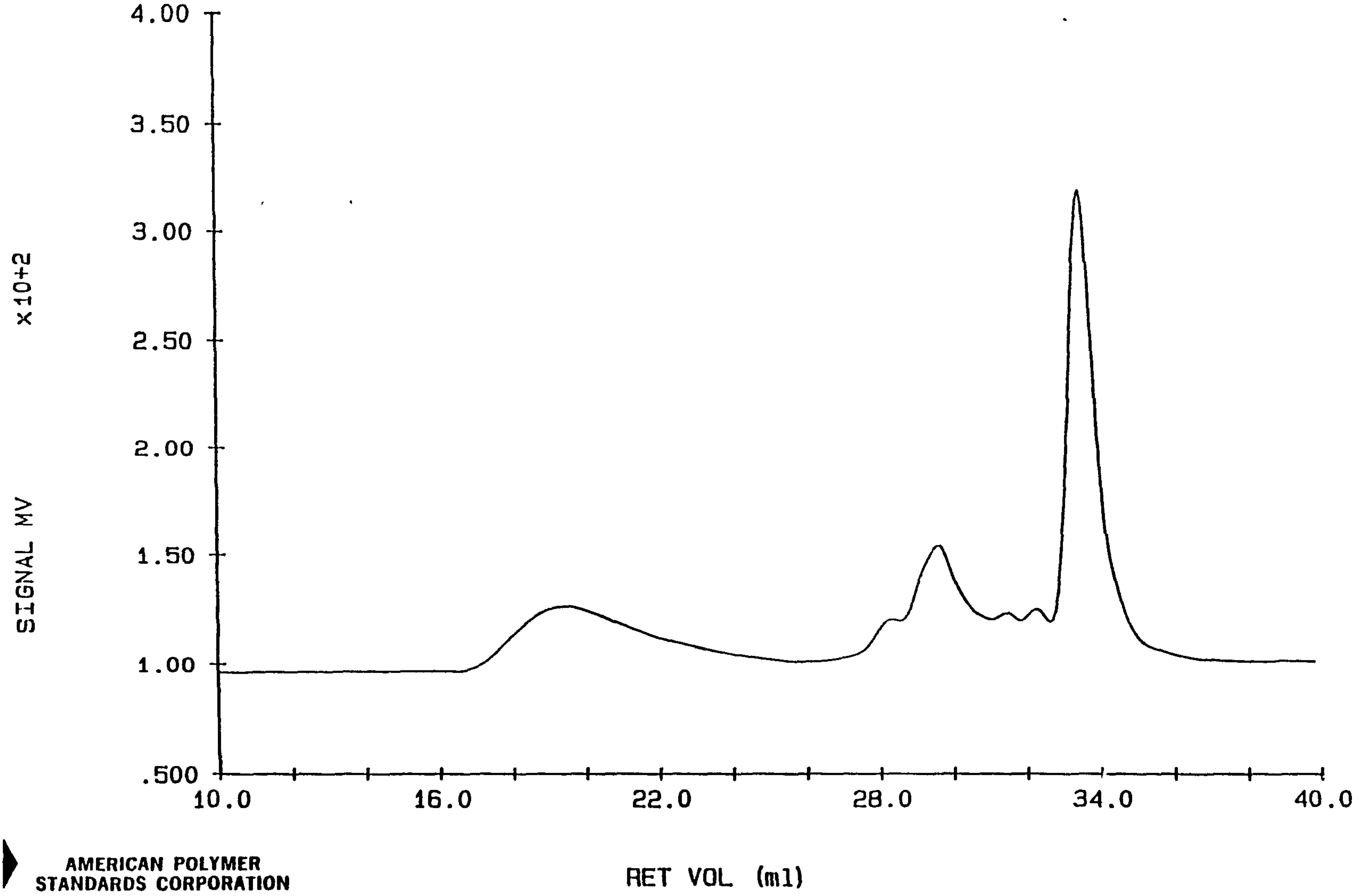
AMERICAN POLYMER
STANDARDS CORPORATION
(216) 255 2211
FAX (216) 255 8397

g4a-1
GPC-PRO 3.13

20PE/80PS

ENDED: 10/31/92 17:

dri CHROMATOGRAM



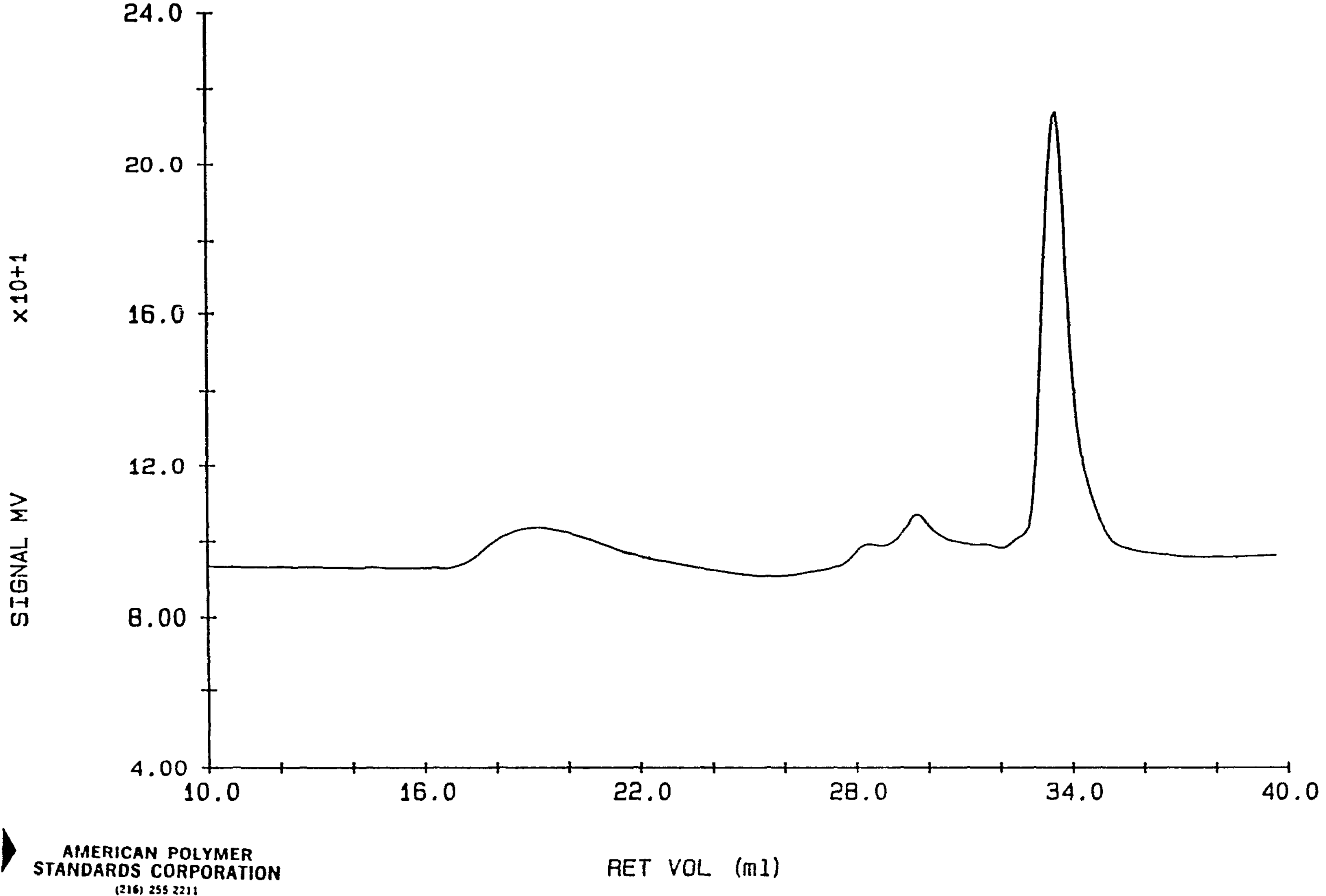
**AMERICAN POLYMER STANDARDS CORPORATION**
(216) 255 2211
FAX (216) 255 8397

g2a-2
GPC-PRO 3.13

40PE/60PS

ENDED: 10/31/92 15:

dri CHROMATOGRAM



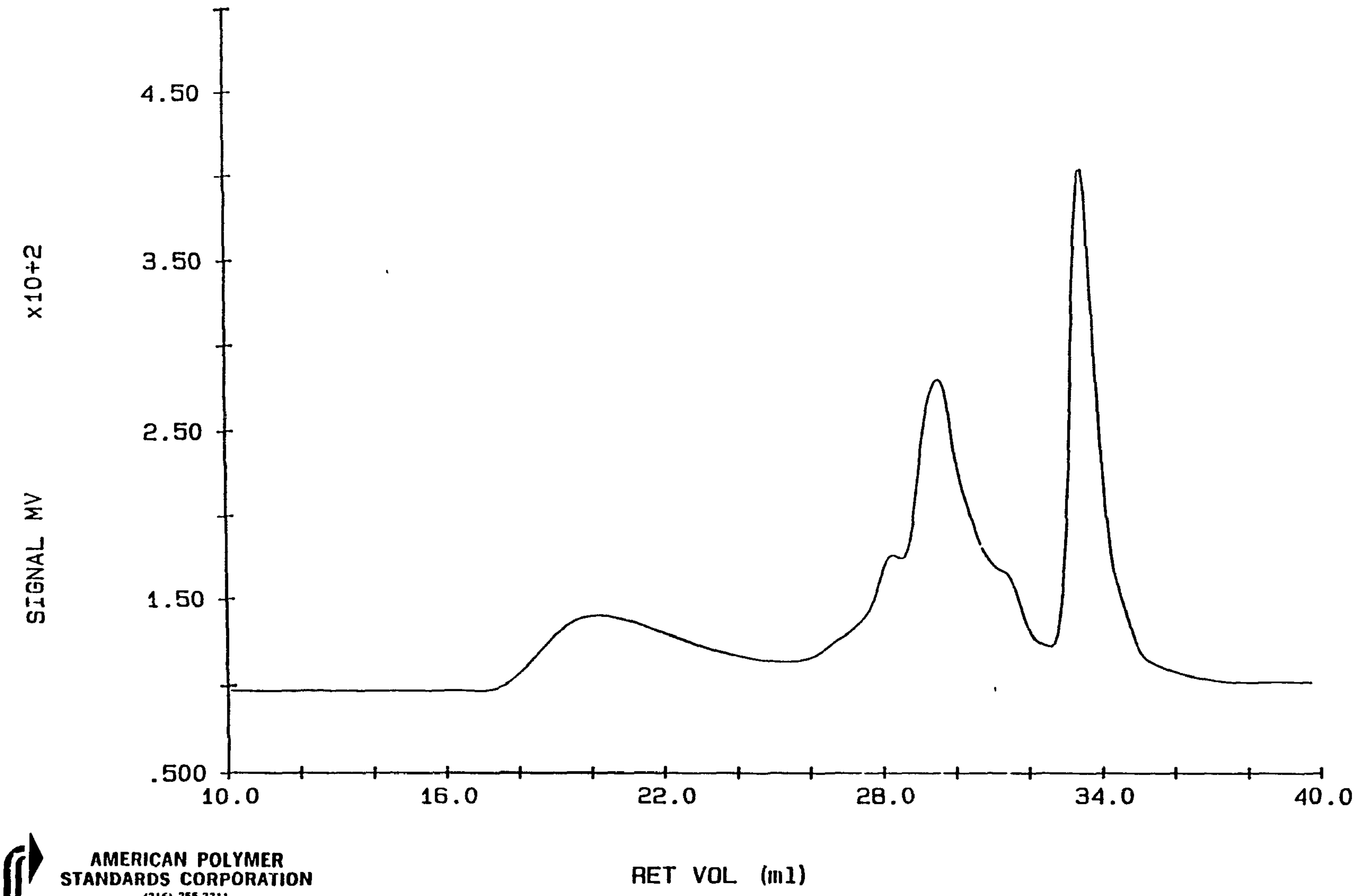
AMERICAN POLYMER
STANDARDS CORPORATION
(216) 255 2211
FAX (216) 255 8397

g3a-1
GPC-PRO 3.13

60PE/40PS

ENDED: 10/31/92 15:

dri CHROMATOGRAM



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(216) 255 2211
FAX (216) 255 8397

g1a-2
GPC-PRO 3.13

80PE/20PS

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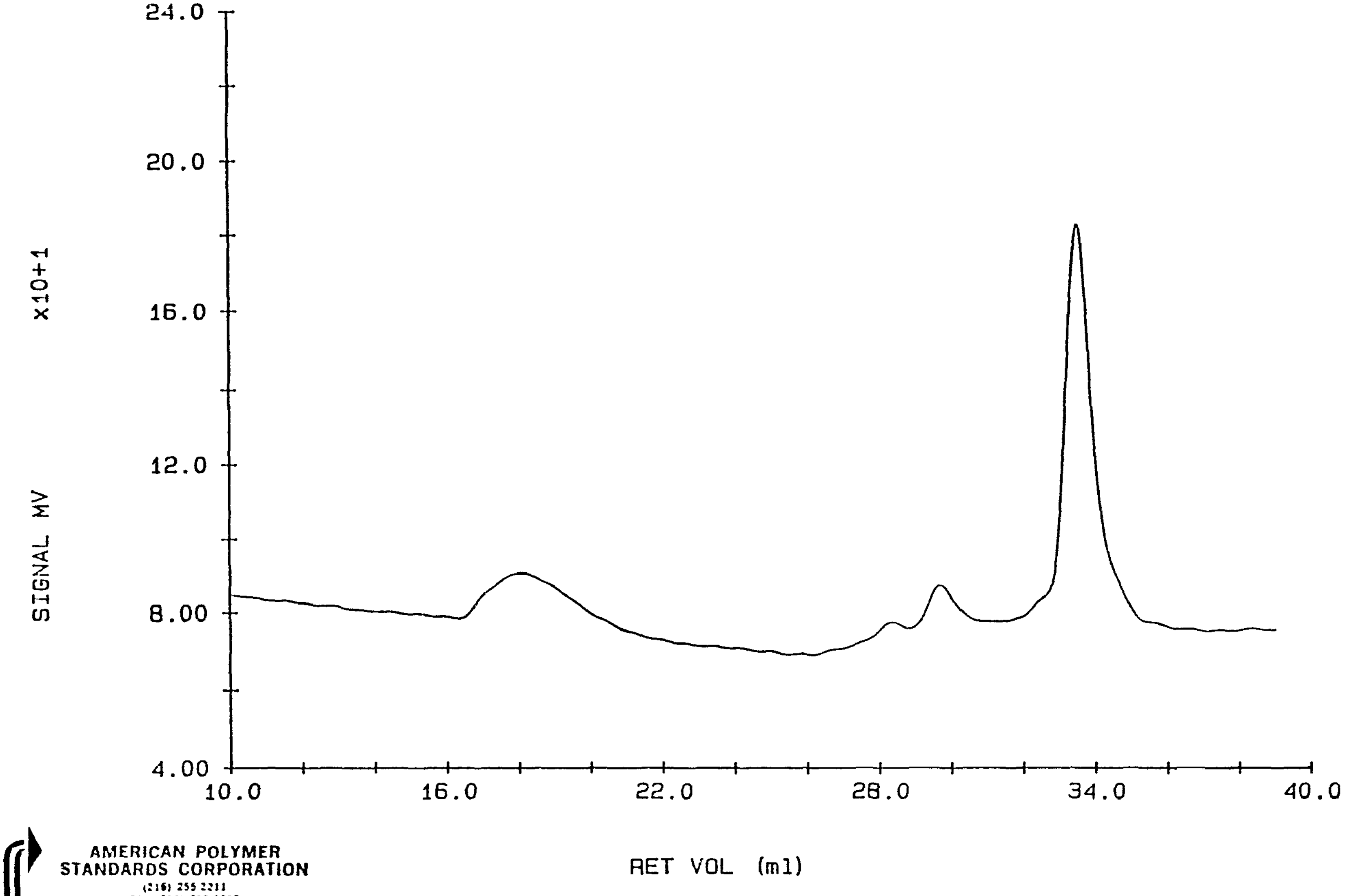

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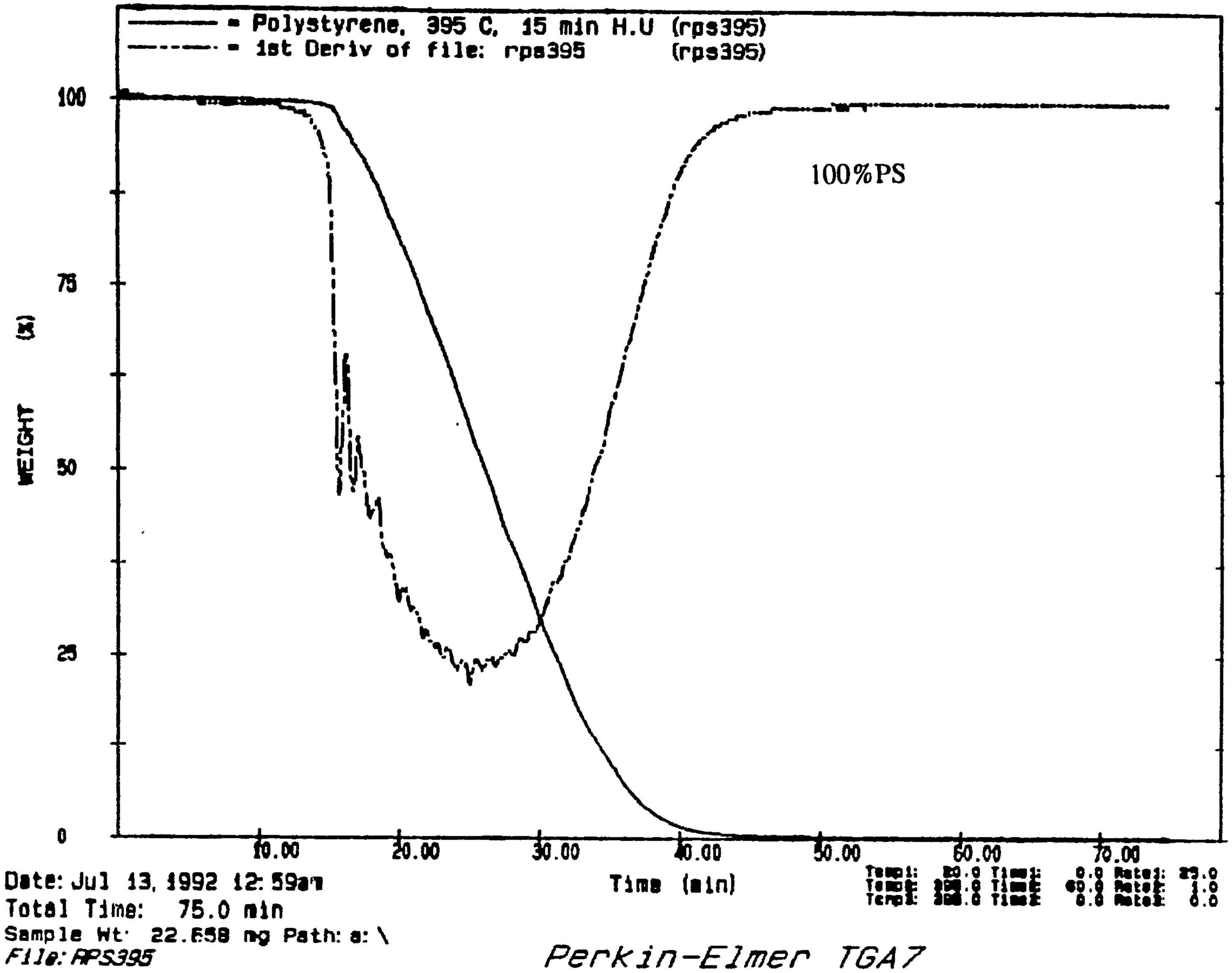
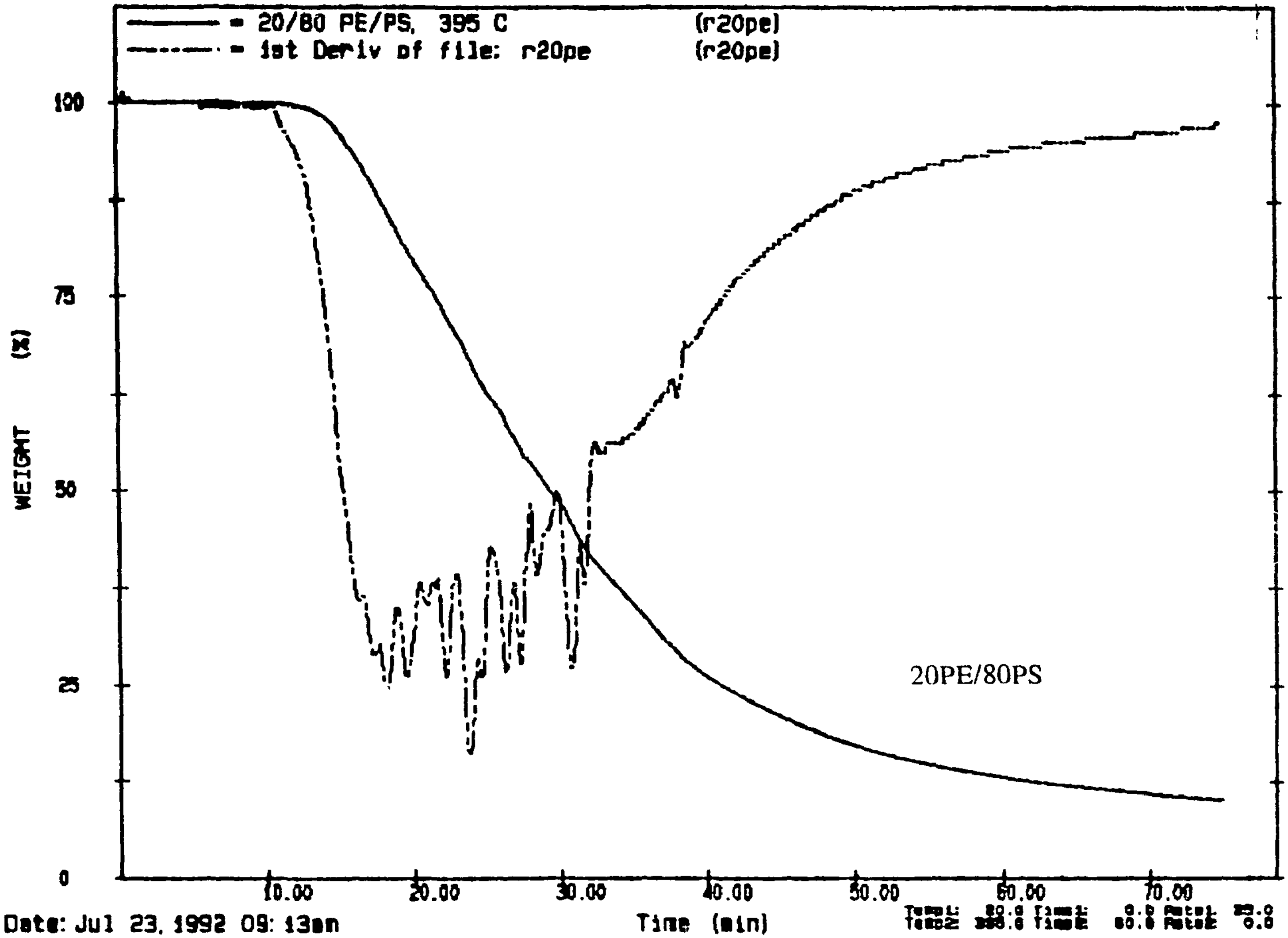
## **APPENDIX C:** TGA curves for all mixtures @ T=395°C


= Polystyrene, 395 C, 15 min H.U (rps395)
= 1st Deriv of file: rps395 (rps395)
100%PS
WEIGHT (%)
100
75
50
25
0
10.00
20.00
30.00
40.00
50.00
60.00
70.00
Time (min)
Temp1: [illegible].0 Time1: 0.0 Rate1: 25.0
Temp2: [illegible].0 Time2: 60.0 Rate2: 1.0
Temp3: [illegible].0 Time3: 0.0 Rate3: 0.0
Date: Jul 13, 1992 12:59am
Total Time: 75.0 min
Sample Wt: 22.658 mg Path: a:\
File: RPS395
Perkin-Elmer TGA7



Date: Jul 23, 1992 09:13am
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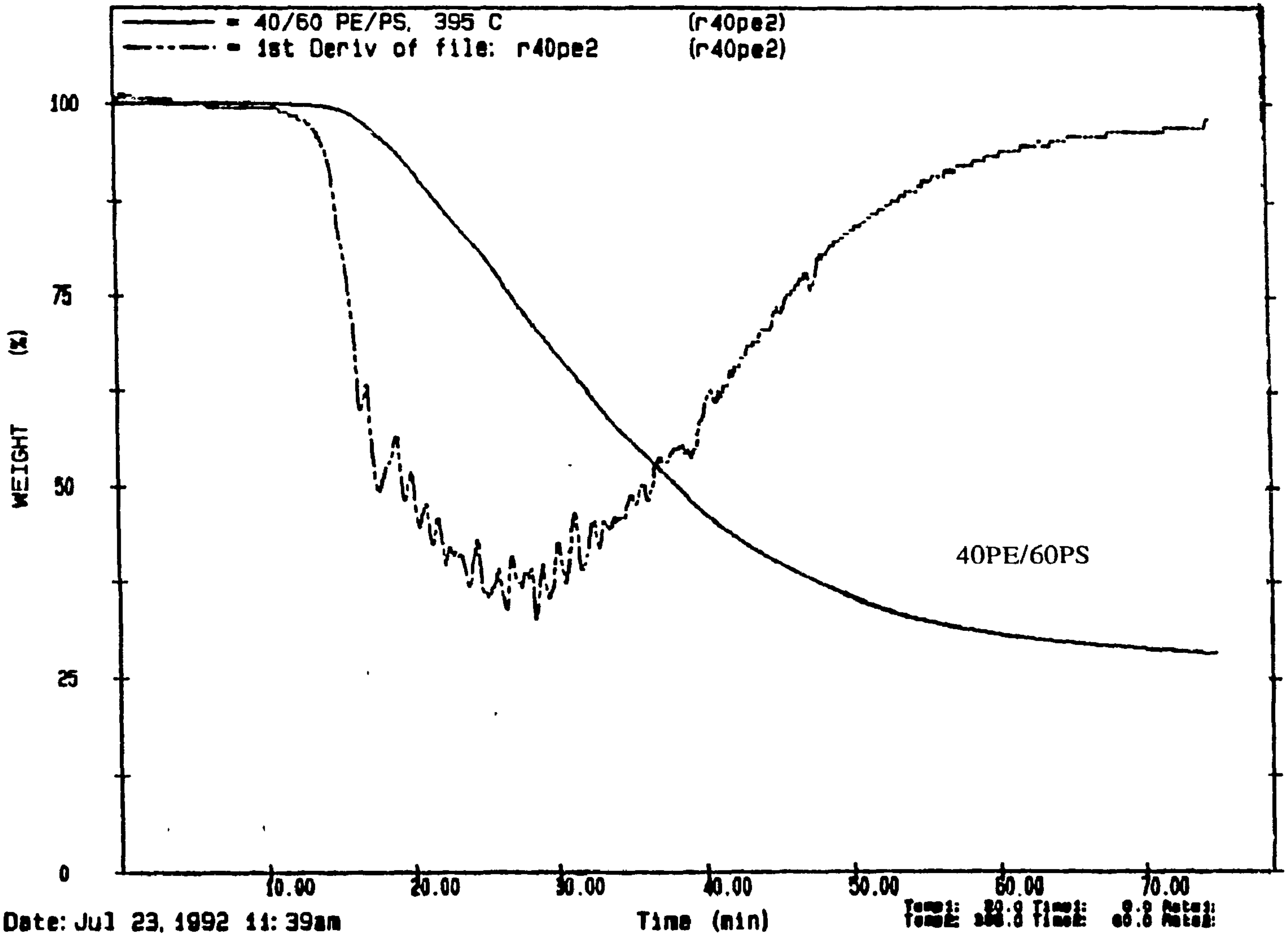
Sample Wt: 23.376 mg Path: a:\
*File: R20PE*

*Perkin-Elmer TGA7*



Date: Jul 23, 1992 11:39am
Total Time: 74.9 min
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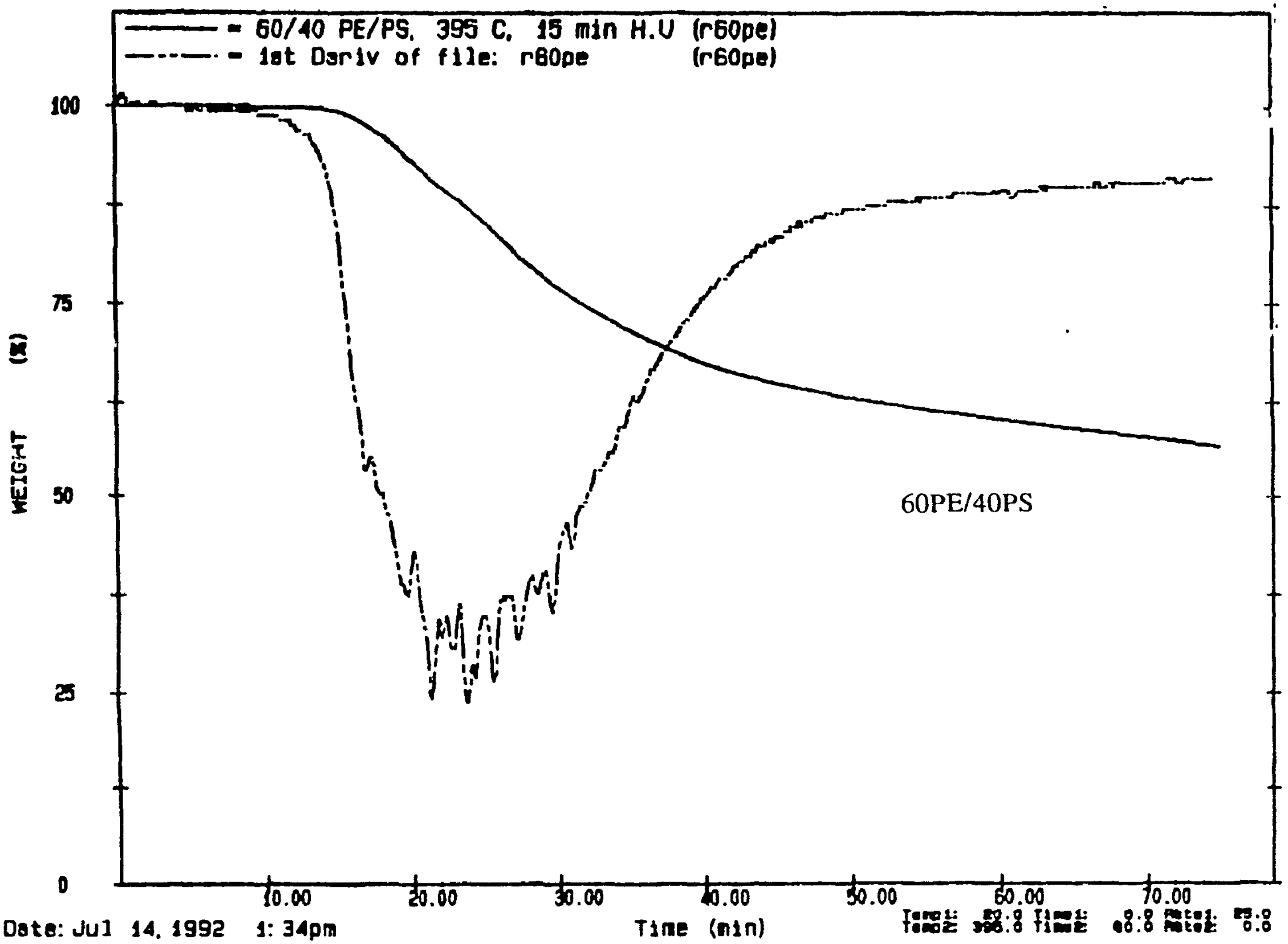
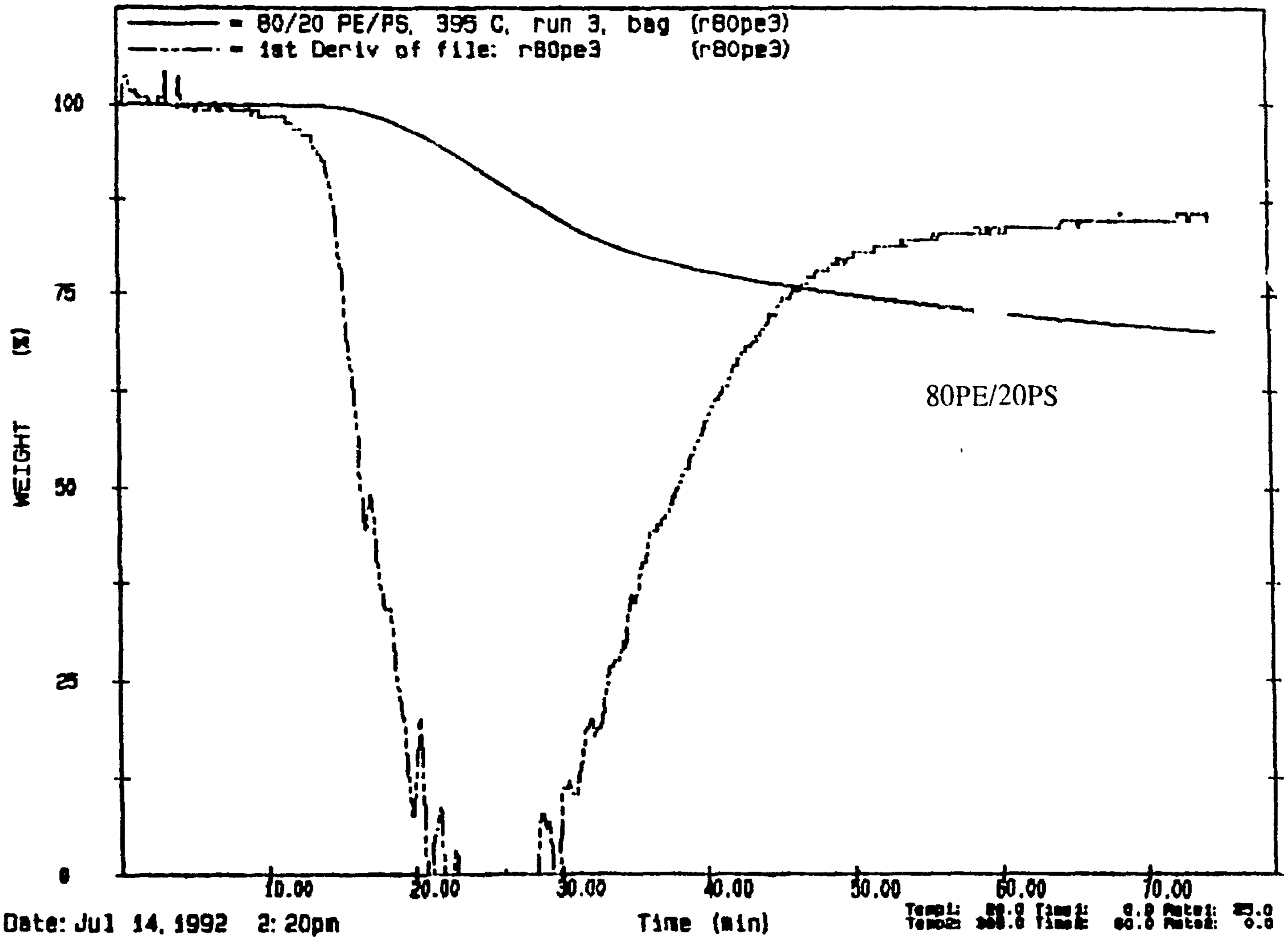
*File: R40PE2*

*Perkin-Elmer TGA7*



Date: Jul 14, 1992 1: 34pm
Total Time: 74.9 min
Sample Wt: 22.094 mg Path: a: \
*File: R60PE*

*Perkin-Elmer TGA7*



Date: Jul 14, 1992 2: 20pm
Total Time: 75.0 min
Sample Wt: 24.658 mg Path: a: \
*File: R80PE3*

*Perkin-Elmer TGA7*