

Thermolysis of Polyethylene/Polystyrene Mixtures

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SYNOPSIS

The thermolysis of 60/40 mixtures of polyethylene (PE) and polystyrene (PS) was investigated at temperatures below 440°C. Liquid yield from the mixture, 84.1%, was comparable to yields obtained with the individual polymers. The yields of styrene monomer, 57.1%, and α -olefins, 27.7%, increased over those obtained when the polymers were processed individually. A significant interaction was observed between the polymers in which the addition of PS enhanced the rate of thermolysis of PE. It is proposed that this enhancement was due to the abstraction of hydrogen from the PE fraction by polystyryl radicals. The result of this effect is to increase the rate of volatile production from the PE and increase the solubility of the residue in chloroform. The data also support a mechanism for dimer production other than the generally accepted 1,3 transfer. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Tertiary, or thermochemical, recycling of polymeric wastes has received growing attention in recent years. To date, the bulk of the research has focused on elucidating the mechanism of degradation for pure polymers.¹⁻⁹ Most waste streams, however, contain a mixture of polymers which are costly to segregate. In addition, polymer blends are increasingly being used to meet growing requirements for polymeric materials with diverse properties. It is very difficult to separate such blends into the constituent polymers. Therefore, it would be advantageous to recycle commingled and blended polymers.

Two polymers, polyethylene (PE) and polystyrene (PS), accounted for 34% and 8%, respectively, of the total resin sales in the United States in 1994. Furthermore, they represent the largest share of the polymers used in the packaging market. The major source of polymers found in municipal solid waste are from the packaging of consumer products. For this reason, mixtures of PE and PS were selected for this study.

To date, several studies have investigated the pyrolysis of PE/PS mixtures, at reaction temperatures

between 500°C and 790°C.¹⁰⁻¹⁶ These studies have reported conflicting results. Some studies indicate a significant interaction between the two polymers during degradation,^{12,13,16} while others have found no observable interaction.^{10,11} Pyrolysis is a high-energy process which generally yields gaseous products with very short chain lengths. To avoid these limitations, thermolysis was used in this study. Thermolysis is a milder process conducted at lower temperatures (<450°C). It has been reported to produce a high yield of liquid products.^{17,18}

Studies using electron spin resonance (ESR) spectroscopy have shown that polyethylene degrades by a free radical process.¹⁹ A complex mechanism has been postulated involving many possible steps, including random initiation, depropagation, intramolecular and intermolecular transfer followed by β -scission, and finally, termination by recombination or disproportionation.¹ This mechanism has been studied extensively, and subsequent work has shown that the major pathway for degradation is by random initiation, intermolecular transfer, and termination by disproportionation.²⁰

ESR spectroscopy has also indicated that PS degradation involves a free radical process.²¹ However, the mechanism for PS degradation is quite different from that for PE. The major mechanism for PS has been proposed to involve initiation, depropagation, and termination.^{4,22-24} Random initiation

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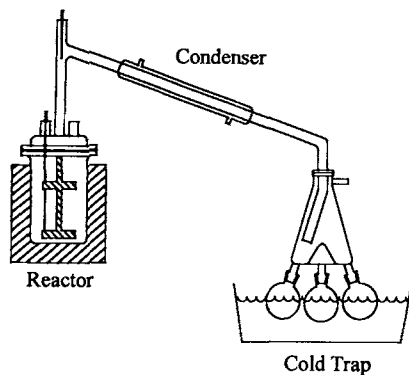


Figure 1 Thermolysis apparatus.

produces primary and secondary polystyryl radicals. Depropagation of both types of radicals, by β -scission, produces styrene monomer.⁶ This mechanism has been supported by experimental observations.²⁴ Intramolecular transfer plays an important role, but to a lesser extent than depropagation.²⁵ It has been suggested that dimer and trimer are produced by 1,3 and 1,5-transfer, respectively, followed by β -scission.²⁷ Subsequent work has shown that 1,3-transfer may not be the primary pathway of the production of dimers.²⁶

EXPERIMENTAL

Materials

The PS used in this study, STYRON 688, was supplied in both powder and pellet form by Dow Chemical Canada Inc. The number average molecular weight was 138,000 and the polydispersity was 2.6. For the PE, the linear low-density polyethylene SCLAIR 8111 was supplied in powder form by DuPont Canada Ltd. The number average molecular weight was 17,000 and the polydispersity was 2.97.

Thermolysis Apparatus

The reactor system used for the experiments (Fig. 1) was the same as previously described.¹⁷ Prior to the thermolysis experiments, a 175- or 200-g sample of polymer was added to the reactor and the oxygen was removed by purging with nitrogen gas. A continuous flow of nitrogen gas (5 mL/min) was maintained throughout the duration of the reaction. Volatile products were collected as a condensate at -20°C . The reaction system allowed for the sequential collection of condensate samples.

Product Characterization

Liquid samples were characterized by gas chromatography (Hewlett Packard 5890 Series II with a FID and a $30\text{ m} \times 0.53\text{ mm}$ DB1 capillary column by Chromatographic Specialists) and the retention times were compared with those of known standards. Higher molecular weight residue fractions were analyzed for functional groups using both $^1\text{H-NMR}$ (Varian XL-300 NMR spectrophotometer) and infrared spectroscopy (Nicolet Magna-IR System 550). The molecular weight of the residue fraction was determined by cryoscopy (Cryette WR, model 5009), using bromoform as the solvent. The solubility of the residue fraction in chloroform was determined by Soxhlet extraction.

RESULTS

The thermolysis of PE and PS generally resulted in the production of three major fractions: gas, liquid, and a residue. The gas fraction consisted of volatiles which were not condensable at -20°C . The largest fraction was volatile at the reaction temperature but was collected as a liquid condensate. The final fraction (residue) was the material that remained inside the reactor when the experiment was terminated. Overall yields of the liquid and residue fractions were determined gravimetrically and the yield of the gas fraction was determined by mass balance. Production of these three fractions from the thermolysis of PE, PS, and a 60/40 PE/PS mixture are presented in Table I.

The yields of liquid products generated with time for the thermolysis of PS and PE individually are presented in Figure 2. The production of liquid from the thermolysis of PE was not significant until approximately 40 min after the start of the experiment whereas the initial liquid production with PS occurred much earlier, after about 10 min. The pro-

Table I Overall Production

Thermolysis Fraction	Yield (Wt % of Initial Charge)		
	PS (391°C)	PE (440°C)	Mixture (438°C)
Gas	0.8	5.2	4.4
Liquid	84.9	70.2	84.1
Residue	14.3	24.5	11.4

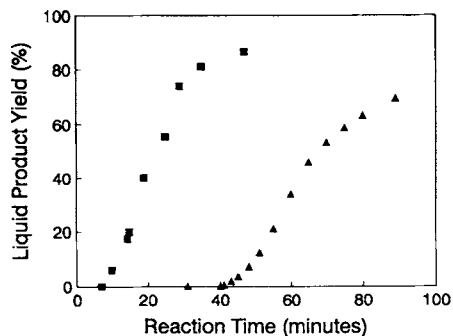


Figure 2 Overall yields of condensable products from the thermolysis of individual polymers: (■) PS alone at 395°C; (▲) PE alone at 440°C.

duction of liquid products from mixtures of PS and PE is presented in Figure 3. The products that were derived from the PS (aromatics) are plotted separately from the products that would be obtained from PE (aliphatics). The start of the evolution of the aliphatic products was shifted significantly when the PE was processed as a mixture.

The variation with time of the composition of the liquid product from the thermolysis of PS alone is presented in Figure 4. Using gas chromatography, and by injecting known standard compounds, 96.3 wt % of the products were identified. The variation in composition of the liquid fraction obtained from thermolysis of PE alone is presented in Figure 5. For the liquid fraction from PE, 77.3 wt % of the sample was shown to be alkenes and alkanes with a ratio of 0.88. The balance of the sample was considered to be branched aliphatics and α,ω -olefins. Fourier transform infrared (FTIR) and $^1\text{H-NMR}$ analyses indicated that there was no aromatic production during the thermolysis of the PE. The evolution of the aromatic and aliphatic compounds produced from the thermolysis of a 60/40 mixture of PS and PE is presented in Figures 6 and 7, respectively. Of the overall liquid produced during thermolysis, a total of 81.6 wt % was characterized. Significantly more toluene was produced when the polymers were processed as a mixture. For the mixture, the ratio of alkenes to alkanes increased to approximately 1 : 1. A summary of the total aromatic production from both PS and the mixture is given in Table II. The summary for the aliphatic production from both PE and the mixture is given in Table III.

The molecular weights of the residues obtained from the thermolysis of PS, PE, and a 60/40 mixture were 577, 518, and 368, respectively. The solubility of the residues in chloroform is given in Table IV.

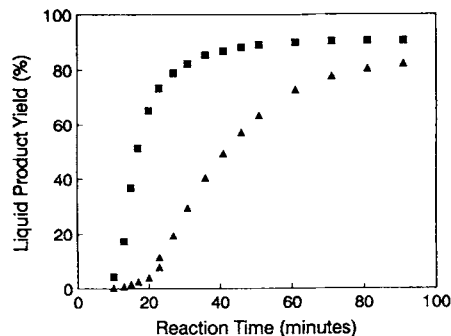


Figure 3 Overall yield of condensable products from the thermolysis of a 60/40 mixture of PE and PS at 440°C; (■) Aromatic products from PS; (▲) aliphatic products from PE.

DISCUSSION

Thermolysis of Mixtures

Yields of liquid from the thermolysis of mixtures of PS and PE were higher than from PE alone and approached those obtained when pure PS was thermolyzed. In every case, analysis of the liquid fractions showed that they consisted of compounds similar to those produced by thermolysis of the individual polymers. In previous work, the thermolysis of PS was shown to produce only aromatic compounds.¹⁷ Similarly, the thermolysis of PE, without a catalyst, at 440°C was shown to produce only aliphatic compounds.¹⁸ At the reaction conditions used in this study, 440°C and atmospheric pressure, a Diels-Alder reaction was considered unlikely. As expected, no aromatic compounds or Diels-Alder adducts were observed in any of the reaction products in this study from PE alone. Thus it was reasonable to assume that PE, when thermolyzed in a mixture with PS, would continue to produce similar

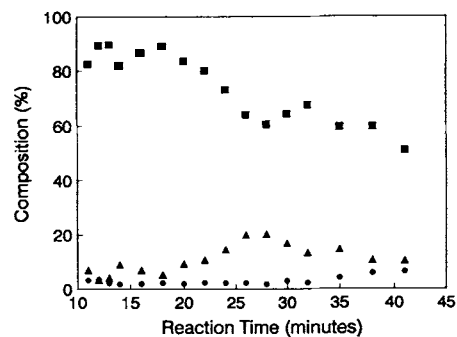


Figure 4 Evolution of various aromatic compounds in the condensable fraction from the thermolysis of PS at 395°C: (■) styrene; (●) toluene; (▲) dimer.

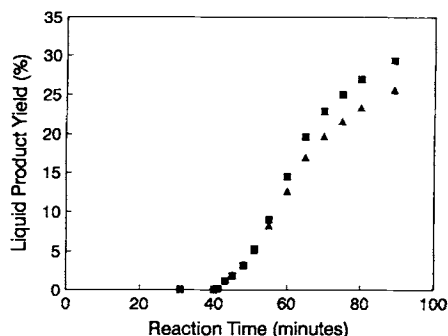


Figure 5 Variation of the composition of straight chain aliphatics in the condensable fraction from the thermolysis of PE at 440°C: (■) alkanes; (▲) alkenes.

products. Implicit in this argument is the assumption that the termination of radicals was by disproportionation and not by recombination. Since no phenyl-substituted aliphatics were observed in any of the liquid or residue samples, it can be concluded that there was no incorporation of aromatic groups from PS into the products from PE. Therefore, aliphatic products were generated from the PE fraction of the mixture and any aromatic products were generated from the PS fraction. Using this rationale, the thermolysis of both polymers in the mixture could then be followed separately.

Even though there were no hybrid products, there were significant consequences from processing the polymers as a mixture. When the aliphatic and aromatic components of the liquid products were examined separately, the aliphatic products were observed to evolve from the reactor much earlier than in the individual case. In fact, production of the aliphatics started at the same time as the aromatic products (Fig. 3). This is significant because the ali-

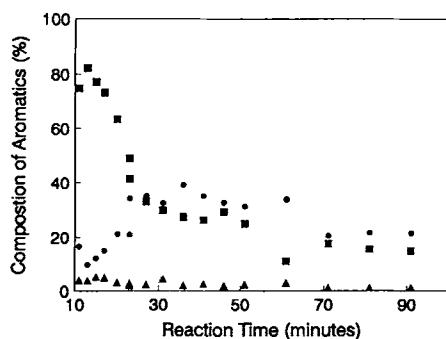


Figure 6 Evolution of various aromatic compounds in the condensable fraction from the thermolysis of a 60/40 mixture of PE and PS at 440°C: (■) styrene; (●) toluene; (▲) dimer.

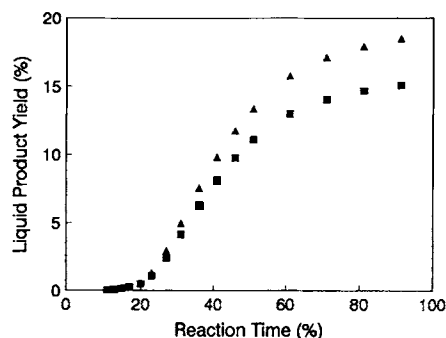


Figure 7 Variation of the composition of the aliphatic compounds in the condensable fraction from the thermolysis of a 60/40 mixture of PE and PS at 440°C: (■) alkanes; (▲) alkenes.

phatic products from PE, when processed alone, would start approximately 30 min later than the aromatics from PS (Fig. 2). A similar effect has been reported for mixtures of poly(α -methylstyrene) and PS.²⁷ In that study the addition of poly(α -methylstyrene) was beneficial to the degradation of the PS. Styrene monomer production was observed at 300°C for the mixtures, conditions at which monomer was not produced when PS was processed alone.²⁷

Further evidence of an interaction between the polymers in the mixture was that the residue remaining inside the reactor at the completion of the reaction was 100% soluble in chloroform (Table IV). This behavior is in sharp contrast to the residues produced when PE was processed alone. These residues became soluble only after extremely long reaction times. A possible explanation for this change was that the products from the PS fraction acted as

Table II Aromatic Yield

Compound	Yield (Wt % of Charge)	
	PS ^a	Mixture ^b
Benzene	0.05	1.0
Toluene	2.3	17.7
Ethyl Benzene	0.6	3.4
Styrene	54.8	57.1
1-Phenyl Propane	0.1	0.6
α -Methyl Styrene	2.9	3.8
1,3-Diphenyl Propane	2.4	2.9
Dimer	10.7	3.4
Trimer	0.8	0.8

^a Reaction temperature: 391°C.

^b Reaction temperature: 438°C.

Table III Aliphatic Yield

Chain Length	Yield (Wt % of Charge)			
	PE		Mixture	
	Alkene	Alkane	Alkene	Alkane
C ₅ -C ₉	7.77	6.52	7.55	8.13
C ₁₀	2.69	1.96	2.49	1.67
C ₁₁	2.18	2.06	2.03	1.79
C ₁₂	2.15	1.99	2.03	0.02
C ₁₃	1.86	1.85	1.95	2.1
C ₁₄	1.83	1.77	1.73	1.88
C ₁₅	1.54	1.74	1.64	1.46
C ₁₆	1.36	1.6	1.68	1.44
C ₁₇	1.16	1.54	1.6	.15
C ₁₈	0.98	1.38	1.33	1.51
C ₁₉	0.73	1.27	1.09	1.41
C ₂₀	.53	1.1	0.83	1.31
C ₂₁ -C ₂₅	.16	3.54	1.70	3.09
Total	24.92	28.32	27.65	25.96

a cosolvent. To test this theory, an experiment was conducted: the residues from experiments in which the polymers were processed individually were mixed and chloroform was added. The solubility of the PE fraction remained unchanged, thus ruling out a co-solvent effect.

Another possible explanation for the change in solubility of the residue is that free radicals from the PS abstracted hydrogen from the PE molecules. This would promote chain scission of the PE molecules, which would increase the rate of molecular weight reduction and thus increase the solubility of the residue. A similar effect was observed during the pyrolysis of binary mixtures of PS mixed with poly(methyl acrylate) and poly(butyl acrylate).²⁸ In that study, the rate of styrene monomer production was observed to increase when PS was processed with the acrylate polymers. Importantly, the nature of the interaction between mixtures of PS and poly(methyl acrylate) or poly(butyl acrylate) would be similar to PE and PS mixtures because each of the polymers degrades by a free radical mechanism. The interaction for PS and polyacrylates was proposed to be primarily by intermolecular transfer from the polyacrylate macroradicals to the PS molecules.²⁸ A similar interaction is proposed for PS and PE mixtures with the polystyryl radicals abstracting hydrogen from the PE molecules. This

would cause the rate of chain scission of the PE molecules to increase.

The site of hydrogen abstraction from the PE molecules is most probably random. This would result in a random scission of the PE chains, which would rapidly reduce the molecular weight of the polymer and increase the solubility of the resulting residue. In fact, both the solubility of the residue and the rate of degradation of the PE were observed to increase dramatically when processed in a mixture with PS (Table IV). These results are consistent with a similar effect which was observed for the pyrolysis of 1 : 1 mixtures of PS and PE at 500–700°C.^{12,13} In that study, the overall rate for the degradation of both PE and PS mixtures was also observed to increase.

Mechanism of Interaction

If the interaction of the polymers occurred via hydrogen abstraction from the PE molecules by polystyryl radicals, the effect should be reflected in the composition of the reaction products. Any transfer of hydrogen atoms from the PE fraction to the PS fraction should be reflected in the degree of unsaturation of the aliphatic products. For pure PE, the ratio of straight chain α -olefins to straight chain alkanes was approximately 0.88 with a yield of 24.9% *n*-alkenes and 28.32% *n*-alkanes (Fig. 5, Table III). When the polymers were thermolyzed as a mixture, the ratio increased to 1 : 1 with a 27.7% yield of *n*-alkenes with a corresponding decrease of *n*-alkanes to 25.96% (Fig. 7, Table III). The increase in alkene production from the mixture was most pronounced for alkenes of chain length greater than 12 carbons. The overall alkene production from the mixture was higher (27.65%) than from PE alone (24.92%). This increase in unsaturated products suggests that there was a net loss of hydrogen from

Table IV Residue Solubility

Reaction Time (min)	Solubility by Soxhlet Extraction (Wt %)		
	PS	PE	Mixture
30	100	—	84.5
35	100	15	96
42	100	—	99.5
60	100	—	100

Reaction temperature: 395°C.

the polyethylene fraction. A corresponding increase in net hydrogen should be reflected in the aromatic products. To test whether the polystyryl radicals were abstracting hydrogen atoms, a hydrogen balance was calculated for the products from pure PS and from a 60/40 mixture. The products from the mixture were found to have approximately 3% more hydrogen than those from PS alone. These data further support the hypothesis of an interaction between PS and PE *via* intermolecular hydrogen abstraction.

While the aromatic products from the thermolysis of PS and PE mixtures were similar to those produced from PS alone, their relative concentrations changed significantly (Table II). Any change in the product distribution should be explainable by examining the proposed mechanism for the degradation of PS. The mechanism for styrene production is proposed to be by depropagation or β -scission [Fig. 8, eq. (a)]. The presence of extra hydrogen supplied by the PE is not expected to significantly decrease the yield of products formed by intramolecular rearrangements and β -scission. If β -scission were blocked, a decrease in the styrene yield would be expected and a corresponding increase in the production of random degradation products such as dimer and trimer should be observed. This effect was not observed, as the yield of styrene monomer actually increased slightly to 57.1% for the mixed case when compared to 54.8% for PS alone. The effect of the PE on the rate of degradation of the PS could not be quantified because the reaction data were no longer consistent with first-order kinetics, as was observed with PS alone.

The mechanism for trimer production is proposed to be by 1,5-transfer of a secondary polystyryl radical followed by β -scission [Fig. 8, eq. (e)]. The effect of the polyethylene on trimer production should be similar to styrene production. In fact, this was observed as the trimer yield remained unchanged at 0.8% for both pure PS and for the mixtures.

It is commonly proposed that dimer is produced by 1,3 transfer followed by β -scission.^{2,7} It follows from the behavior of the trimer that the production of dimer should also not be affected by the addition of PE. However, this was not observed as the dimer yield decreased from 10.7% for pure PS to 3.4% for the mixed case. This decrease in dimer yield suggests that the main mechanism may not be by 1,3 transfer. An alternative mechanism for the production of styrene dimer by a more complex

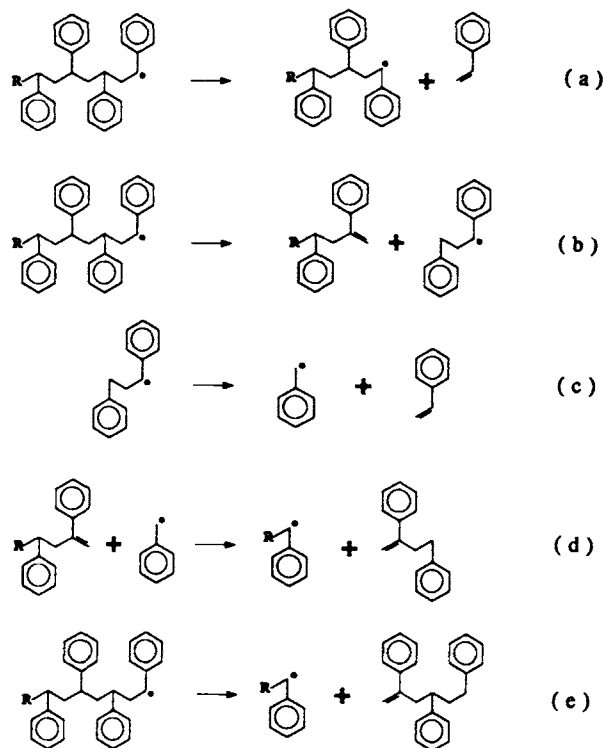


Figure 8 Mechanism of degradation for PS. Equation (a): depropagation of a polystyryl radical by β -scission to produce monomer. Equation (b): 1,5-transfer followed by β -scission to produce a 1,3-diphenyl-propyl radical. Equation (c): β -scission of a 1,3-diphenyl-propyl radical to produce a tolyl radical. Equation (d): reaction of PS with a tolyl radical to produce 2,4-diphenyl-1-butene. Equation (e): 1,5-transfer followed by β -scission to produce 2,4,6-triphenyl-1-hexene.

mechanism has been proposed involving several reactive intermediates.²⁹ According to this mechanism, dimer formation is also initiated by 1,5 transfer followed by β -scission. β -scission, however, produces a 1,3-diphenyl-propyl radical, not the trimer molecule [Fig. 8, eq. (b)]. This 1,3-diphenyl propyl radical then further degrades by β -scission to produce a tolyl radical and a styrene molecule [Fig. 8, eq. (c)]. Finally, the dimer molecule is produced when a tolyl radical combines with another suitable molecule. One possible mechanism is that the tolyl radical could combine with a vinyl group on a PS molecule to produce the dimer molecule [Fig. 8, eq. (d)].

With the addition of PE to the system, any of the radical intermediates (produced by intramolecular transfer reactions of the polystyryl radicals) could be stabilized by intermolecular hydrogen transfer. This is, in fact, observed with the yield of the in-

Table V Reaction Mechanism for PE/PS Mixtures

Polymer	Free Radical Initiation	Product Formation/ Molecular Weight Reduction	Radical Termination
Polystyrene (PS)	Random	Depropagation → monomer	Intermolecular hydrogen abstraction from both PS and PE
	Labile end groups	1,5-transfer → trimer 1,5-transfer → reactive intermediates → dimer Stabilization of intermediates by H abstraction from PS and PE molecules	Radical disproportionation
Polyethylene (PE)	Random	Intramolecular transfer	Intermolecular hydrogen abstraction from both PS and PE
	H abstraction by polystyryl radical followed by β -scission	Intermolecular H transfer from polyethylene	Radical disproportionation

intermediates (toluene and 1,3-diphenyl propane), which increase for the mixed case when compared with PS alone. Furthermore, any stabilization of the reactive intermediates should decrease the yield of the dimer. This effect was also observed, with the dimer yield decreasing from 10.7% to 3.4%. Thus these observations suggest that the main mechanism for the production of dimer is not by 1,3 transfer but by the more complex mechanism involving several reactive intermediates.

The data suggest that the overall interaction for the thermolysis is by free radicals abstracting the most convenient hydrogen, regardless of the polymeric species. A scheme summarizing the major mechanisms of interaction between PS and PE during thermolysis is presented in Table V. This mechanism is essentially the same as those for the individual polymers, only the intermolecular hydrogen transfer steps have been added.

CONCLUSION

The thermolysis of mixtures of PS and PE will be no more difficult than reacting the individual polymers. In fact, reacting the polymers as a mixture was shown to have a beneficial effect. The yields of styrene monomer and α -olefins were increased over those obtained when the polymers were processed individually. Notably, the yield of toluene increased significantly. Moreover, while residues from PE thermolysis were not soluble in chloroform, residues

from thermolysis of the mixtures were readily soluble.

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