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Recovery of high-valued products from styrene-based polymers through coprocessing: Experiments and mechanistic modeling

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Abstract

The recent emergence of pyrolysis as a viable resource recovery strategy has focused attention on understanding the complex chemistry underlying the decomposition processes. In this work, a quantitative link between measurable experimental changes and kinetics analysis was established to explain the behavior of styrene-based polymers alone and in binary mixtures during pyrolysis. Experiments with low molecular weight polystyrene and poly(α-methylstyrene) were carried out which showed that a higher selectivity to monomer was obtained for poly(α-methylstyrene) than for polystyrene. The binary mixture experiments revealed that the reactivity of polystyrene was enhanced in the presence of poly(α-methylstyrene), and the selectivity to styrene monomer was increased. Overall, the experimental results suggest that coprocessing is a viable polymer resource recovery strategy when the addition of an appropriate co-reactant is used to tailor the product distribution. Furthermore, novel polymer structures may be designed to promote degradation to high-valued products. The experimental results were interpreted using a detailed mechanistic model which described the reactions of α-methylstyrene and styrene trimers and was generated using software for automated model construction to describe 901 species using over 4000 reactions. By exploiting the capability to label the model reactants, a quantitative link between polymers and their mimics was established and probed the impact of the kinetic coupling between different polymers. © 1998 Elsevier Science B.V.

Keywords: Polymer resource recovery; Polystyrene degradation; Mechanistic modeling; Kinetic coupling

1. Introduction

The growing abundance of municipal solid waste has heightened the awareness within the public sector and the scientific community of its detrimental environmental impact. Polymeric materials are one of the most intractable components of municipal waste and as a result, have spawned considerable legislative and scientific activity aimed at recovering high-valued products from polymeric waste [1–3]. Industrialized nations are imposing rigid laws on the amount of plastic waste that must be recovered before rapidly approaching cut-off dates. Programs for the conversion of plastics to fuels, initiated during the 1970s and 1980s when the oil crisis caused producers to turn to alternative fuel sources, are being revived with encouraging results. However, burgeoning environmental concerns and economic limitations are driving the exploration of new strategies for viable plastics resource recovery.

Pyrolytic processing of mixed plastic waste, in which the polymer feedstock is heated in the absence

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of oxygen, has received considerable attention in recent years [4–7]. It has been shown to be an economical means of obtaining high-valued fuels and chemicals and is projected to grow 10-fold in the next decade [8]. The desirability of pyrolysis as a resource recovery process depends primarily on the relative selectivity to the desired products, which in turn depends on the feed composition, processing conditions and the presence of additives or contaminants. However, the complexity of the set of reactions occurring can obscure the relationships among these critical variables. Furthermore, the suppression of volatile degradation products and the influence of additives can catalyze specific degradation pathways, and their effect is not well understood [1]. The number of experiments required to probe these complex relationships among feedstock composition, processing conditions and additives is prohibitive. Therefore, a set of kinetics-based tools which could simultaneously account for the interaction among feedstock components, effect of processing conditions and the presence of additives would provide useful guidance for process optimization. Furthermore, valuable information as to why particular structural features direct decomposition along reaction pathways favorable to high-valued products would be obtained.

The database amassed from extensive experimental studies of polymer degradation at high temperatures provides general qualitative rules that guide the development of our set of kinetics-based predictive tools. In general, the tendency of a polymer toward particular degradation products can be attributed to three factors [9]:

- Strength of bonds in the polymer backbone.
- Presence of tertiary hydrogens.
- Relative strength of substituent bonds.

In some cases, a simple examination of the structure of the polymer allows quantitative prediction of the formation of certain products. For many single component polymers, and particularly for polymeric blends and multicomponent mixtures, examination of the structural features alone will not provide enough information to predict the weighted contribution of these qualitative rules. Therefore, the goal of this work was to interpret the experimental behavior of a single component and a mixed polymer pyrolysis system and to consolidate this information using quantitative kinetics-based modeling. In order to simultaneously take into account the intrinsic factors contributing to overall reactivity, mechanistic modeling, in which the transitions among active centers are explicitly accounted for, was carried out.

The experimental and modeling studies focused on styrene-based polymers, specifically polystyrene (PS) and poly(α-methylstyrene) (PAMS). Styrene-based polymers comprise an important class of commodity plastics present in mixed plastic waste in large volume. Production of monomer from polystyrene also provides a clear target for resource recovery efforts, since styrene requires a multistep synthesis for its production [10]. Furthermore, polystyrene and poly(α-methylstyrene) provide an excellent contrast between their structure/reactivity relationships. Poly(α-methylstyrene), which differs from polystyrene only by the presence of methyl substituents α- to the pendant phenyl groups and therefore does not possess any tertiary hydrogens, has been shown to form almost exclusively monomer at high temperatures [9,11,12]. The repeat units for PS and PAMS are shown in Fig. 1.

The present work sought a quantitative link between the measurable experimental changes and quantitative kinetics analysis that could explain the behavior of styrene-based polymers alone and in binary mixtures during pyrolysis. Experiments with low molecular weight polystyrene and poly(α-methylstyrene) synthesized in our laboratory were carried out, and an analytical protocol was developed to examine the full molecular weight range of products. The experimental results were interpreted through mechanistic models developed to describe the reactions of polystyrene and poly(α-methylstyrene) alone and in binary mixtures to simulate a mixed plastic waste. This allowed the impact of the kinetic coupling between different polymers to be probed and potential strate-

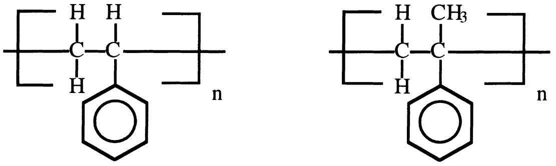


Fig. 1. Repeat units of polystyrene and poly(α-methylstyrene) polymers.

gies for resource recovery of mixed plastic waste to high-valued products to be evaluated.

2. Experimental

2.1. Preparation of polymeric reactants

2.1.1. Monomer

α-Methylstyrene (Aldrich) was treated to remove 4-tert-butyl catechol, added as an inhibitor, and trace amounts of water before use. Approximately 4 g aluminum oxide (Aldrich) and 2 g calcium hydride (CaH, Aldrich) were added to 100 ml α-methylstyrene, resulting in a gray suspension which was stirred for over 4 h, after which the CaH and the aluminum oxide were removed by filtering. Approximately 2 ml dibutyl magnesium were added to the monomer to eliminate any traces of water or other impurities. The monomer was then collected by repeated vacuum distillations. Styrene (Aldrich) was treated similarly; inhibitor remover and CaH were added and subsequently removed by filtering. Approximately 40 ml of styrene and 1 ml of dibutyl magnesium were injected into the distillation flask with stirring, and the styrene was vacuum distilled at room temperature and condensed at −10°C. Both monomers were stored at −15°C before use.

2.1.2. Solvent purification

Tetrahydrofuran (THF, HPLC grade, Aldrich) was placed in a two-necked flask purged with nitrogen, and 2 g sodium turnings were quickly added. The THF was refluxed with cool water for 3 h. Approximately 2.5 g of benzophenone were added to the solvent flask, resulting in a dark blue mixture, and the mixture was refluxed for an additional 15 min. A similar protocol was used to purify toluene. However, the distillation was carried out at 110°C in a nitrogen atmosphere for six days. 24 h prior to the polymerization, 2 ml of 1.3 M sec-butyl lithium (Aldrich) were added to the solvent to scavenge any trace impurities.

2.1.3. Polymerization

The polymerization of α-methylstyrene was carried out according to the procedure outlined by Fujimoto et al. [13]. Approximately 250 ml of distilled THF were collected in a two-necked flask used as the polymerization reactor which was placed in a water bath at 40°C. After allowing the solvent to equilibrate to this temperature for 15 min, 10.0 ml (0.0770 mol) of α-methylstyrene and 9.8 ml of 1.6 M *n*-butyl lithium in hexanes (Aldrich) were injected quickly into the reactor. After 30 min in the water bath, after which any last trace of impurities was scavenged, the reactor was placed in a dry ice/acetone bath (−78°C) with stirring for 160 min. The polymerization was terminated by injecting excess methanol into the reactor, followed by opening the reactor to air. The polymerization of styrene was carried out in toluene using 11.0 ml (0.0962 mol) of styrene and 1.85 ml (0.00240 mol) of sec-butyl lithium. After 60 min of stirring at room temperature, the polymerization was terminated by methanol injection.

To remove any unreacted monomer, the poly(α-methylstyrene) was dissolved in a minimum amount of methylene chloride, precipitated in excess methanol, allowed to settle, and decanted. After two additional washings, the polymer was allowed to dry in air, and then dried to completeness in a vacuum oven at room temperature. Similarly, the polystyrene was washed three times with methylene chloride and methanol and dried to completeness in a vacuum oven at 110°C.

3. Pyrolysis

The batch pyrolysis experiments were carried out by reacting approximately 20 mg of either polystyrene or poly(α-methylstyrene) in 2 ml gold band ampoules (Wheaton). For the binary mixture reactions of polystyrene and poly(α-methylstyrene), approximately 10 mg of each polymer were used. The ampoule was purged with argon and flame sealed. The ampoule and its contents were weighed both before and after the pyrolysis to ensure there was no leakage during reaction. The polymers were pyrolyzed for reaction times ranging from 1 to 300 min in an isothermal, fluidized sandbath at 350°C. After removal from the sandbath, the ampoules were cooled to room temperature. The reactants were initially liquid at the reaction temperature, and gaseous products were evolved during the course of the reaction, resulting in a two-phase system. The maximum pressure achieved was less than 5 atm for all reaction times studied.

4. Product analysis

The reaction products of each pyrolysis experiment were dissolved in 2.0 ml of toluene. In order to analyze the full molecular weight range of products observed from the polymer pyrolyses, three complementary analytical techniques were used: gel permeation chromatography (GPC), gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS). GPC was used to monitor the temporal evolution of the molecular weight distribution. In order to obtain more detailed identification and quantification of the low molecular weight products which could be analyzed by GC and GC–MS, the effluent of the GPC was passed through a fraction collector. The three analytical techniques are linked as shown in Fig. 2 and are described in more detail below.

The molecular weight distribution of the pyrolysis products was characterized using GPC (Waters) equipped with a differential refractometer and three Styragel 5 μm particle columns (7.8×300 mm, HR 1, 2 and 4). The flow rate was 1 ml min^{-1}, and operation was carried out isothermally at 35°C. A 100 μl aliquot of each sample solution was injected into the GPC using toluene as the mobile phase. The molecular weight distribution was characterized by the number average molecular weight (M_n) and the weight average molecular weight (M_w) obtained by calibrating against narrow polystyrene standards (Scientific Polymer Products). To determine the molecular weight of poly(α-methylstyrene) samples, the Mark–Houwink parameters summarized in Table 1 were applied [14]. The characteristics of the polymers as synthesized are also tabulated in Table 1.

Table 1
Mark–Houwink parameters and characterization of styrene-based polymers

Polymer	$K\times10^3$ (ml g^{-1})	a	M_n (g mol^{-1})	M_w (g mol^{-1})
Polystyrene	12.6	0.71	5160	5850
Poly(α-methylstyrene)	10.8	0.71	2330	2750

To allow low molecular weight products, including toluene, to be analyzed, the mobile phase was changed to dichloromethane, and the effluent of the GPC was passed through a fraction collector. By taking into account the calculated delay time from the refractometer to the fraction collector, it was determined that the fraction collected contained compounds with molecular weights ranging from 0 to 500 g mol^{-1}. Known amounts of diphenyl (Aldrich), ranging from 15 to 30 g, were added to the collected fractions for use as an external standard in subsequent GC analyses. Approximately 1–2 ml of this solution was transferred to a vial for product quantification.

2 μl of the fractionated product solution was analyzed using a Hewlett-Packard (HP) 5890 Series II Plus GC with a HP-5MS 5% phenyl methyl siloxane capillary column (30.0 m×250 μm×0.25 μm nominal) to quantify the low molecular weight products. Response factors were determined using diphenyl as an external standard. In order to identify the low molecular weight products, 1 ml of the fraction col-

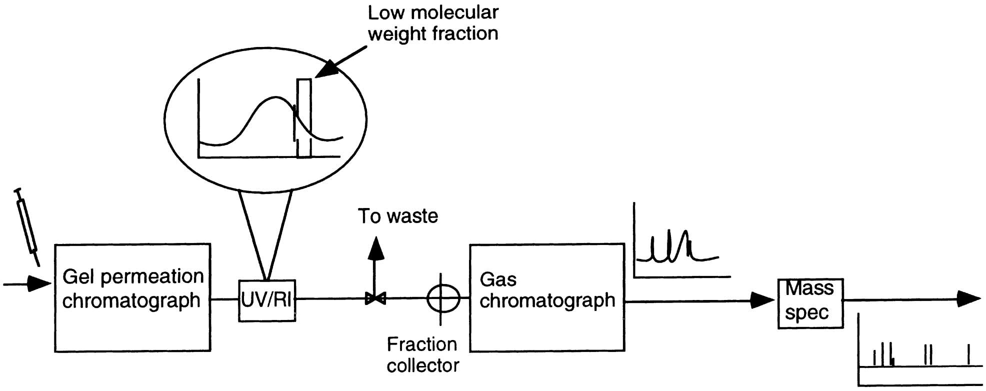


Fig. 2. Analytical protocol consisting of gel permeation chromatography linked through a fraction collector to GC and GC/MS to analyze low molecular weight products.

lected from the GPC was injected into a HP 6890 Series GC equipped with a mass selective detector (GC–MS) and the same column as used for GC analysis.

5. Experimental results and discussion

The degradation of the polymers was measured by the temporal variations observed in the molecular weight distributions and the formation of low molecular weight products. The evolution of the molecular weight distributions of both polymers was captured in terms of the number average molecular weight (M_n) and the weight average molecular weight (M_w) which are plotted as a function of reaction time in Fig. 3 and 4, respectively, where the curves have only been drawn to emphasize the trends. The thermal degradation of polystyrene proceeds more slowly than that of poly(α-methylstyrene). The molecular weight of poly(α-methylstyrene) achieved a minimum value after only 10 min of reaction time; the M_n of polystyrene continues to decrease until approximately 100 min. This was clearly observed in the chromatograms (not shown) in which the peak attributed to the PAMS polymer as synthesized completely disappeared after 60 min, while the PS polymer signature was still present. The evolution of the molecular weight distributions in the binary mixtures is not shown since it was not possible to deconvolute the contributions of the individual polymers to the observed molecular weight changes.

Combined GPC and GC/GC–MS analyses provided information about the relative product yields and selectivities of low molecular weight products from PS and PAMS pyrolysis. The selectivity to monomer was higher in the case of PAMS than for PS. The chromatograms revealed a large isolated peak identified as α-methylstyrene monomer, while the styrene monomer peak was smaller and in close proximity to other small molecule peaks. Collection of these low molecular weight fractions and subsequent GC–MS analysis revealed the formation of styrene, ethylbenzene, toluene, 1,3-diphenylpropane, 1,3-diphenylbutane and α-methylstyrene as major products from PS pyrolysis. Styrene was the product observed with the highest selectivity. The pyrolysis of poly(α-methylstyrene), in contrast, produced primarily α-methylstyrene with negligible amounts of other products.

The effect of the addition of a PAMS co-reactant on PS degradation kinetics was probed through examination of styrene production since this was the product

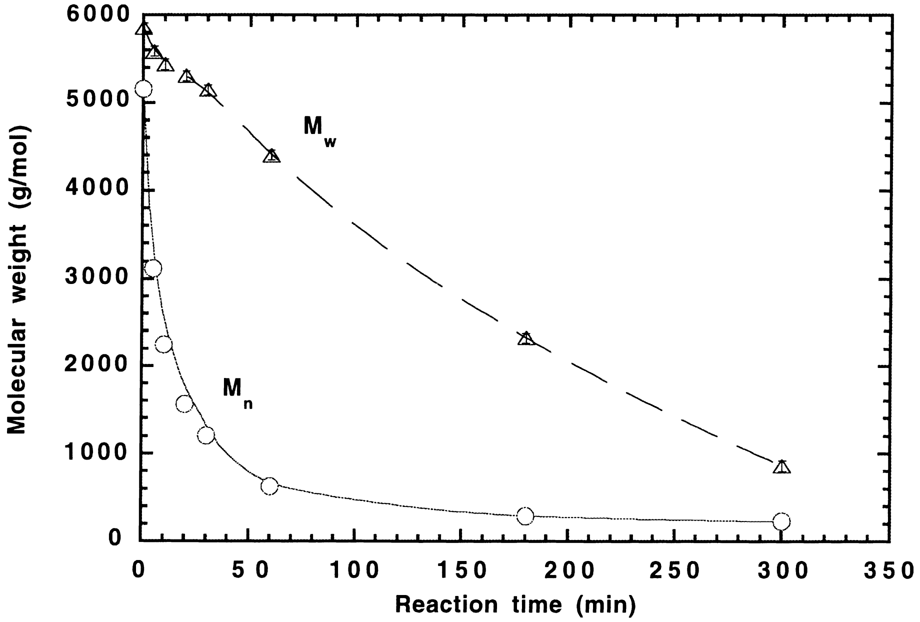


Fig. 3. Time evolution of the molecular weight of polystyrene during pyrolysis at 350°C.

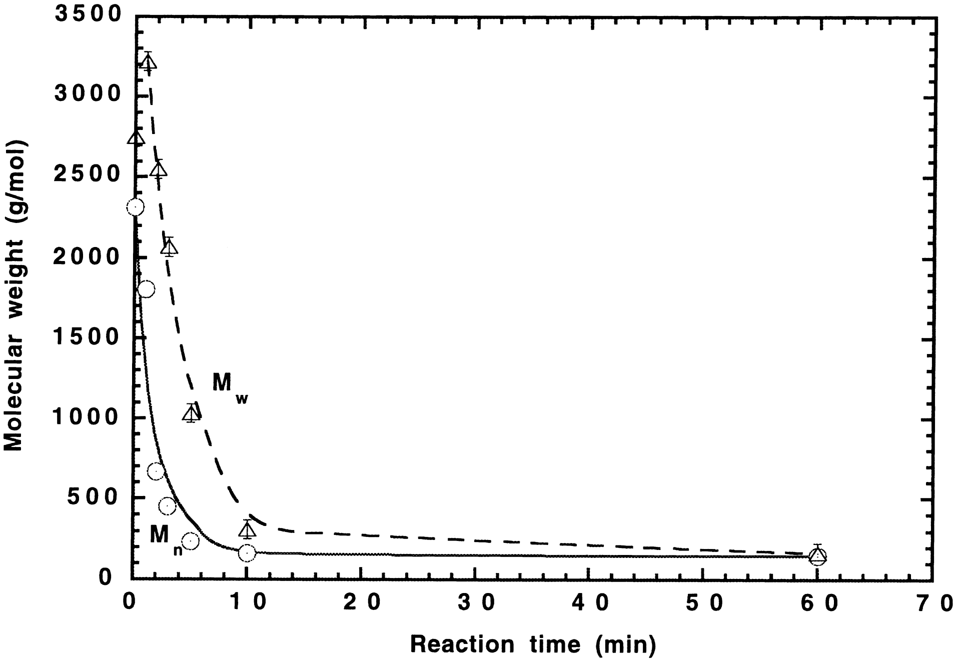


Fig. 4. Time evolution of the molecular weight of poly(α-methylstyrene) during pyrolysis at 350°C.

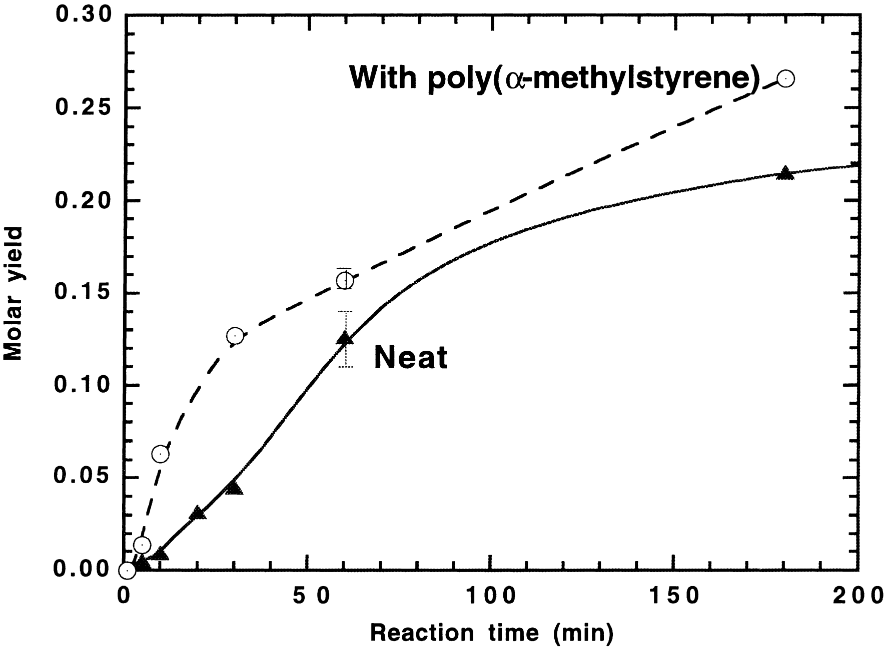


Fig. 5. Styrene production from polystyrene during pyrolysis at 350°C was enhanced in the presence of poly(α-methylstyrene).

observed with the highest selectivity, and an increase in styrene selectivity is a clear target of resource recovery efforts. A comparison of the yield of styrene monomer from PS when PAMS is present to that obtained from neat pyrolysis is shown in Fig. 5 where the curves are provided to accentuate the trends in the data. The yield of styrene is increased at a particular reaction time when poly(α-methylstyrene) is co-reacted compared to neat pyrolysis. In contrast, the formation of α-methylstyrene from poly(α-methylstyrene) was not significantly affected in the presence of polystyrene, as the rate of evolution for the single component and binary pyrolyses differed by only a factor of 1.2. This is consistent with the results of Richards and Salter [15] who examined the reaction of higher molecular weight poly(α-methylstyrene) samples.

Overall, the experimental results suggest that coprocessing is a viable polymer resource recovery strategy. Although poly(α-methylstyrene) is not found in significant quantities in mixed plastic waste, the results do suggest that the product distribution from pyrolysis of high volume plastics may be tailored through the addition of an appropriate co-reactant. The single component results are also noteworthy since a high selectivity to monomer is obtained for PAMS while PS, which is similar in structure, affords monomer with significantly lower selectivity. These results also suggest that novel polymer structures may be designed to promote degradation to high-valued products during pyrolysis if the combined factors affecting decomposition are quantified. We therefore sought to consolidate the experimental results obtained herein through mechanistic modeling to provide quantitative insight about the underlying controlling chemistry.

6. Mechanistic interpretation: substituent and backbone contributions to reactivity

Qualitatively, the tendency of a polymer toward particular degradation products can be attributed to three factors: (1) strength of bonds in the polymer backbone; (2) presence of tertiary hydrogens; and (3) relative strength of substituent bonds. The strength of the bonds in the polymer backbone has been quantified by the ceiling temperature, T_c, the temperature at which the free energy of polymerization is equal to zero [16]. Although the ceiling temperature is a useful measure of backbone reactivity, calculation of the ceiling temperature alone is insufficient to predict the overall tendency of a polymer to form a monomer. For many polymers with high ceiling temperatures, the elevated temperatures necessary to favor the decomposition reactions result in other reactions, such as chain transfer via hydrogen abstraction. For example, polyethylene, which has a ceiling temperature equal to 950 K but has abstractable hydrogens, affords only 2% monomer by weight under high vacuum conditions [9]. In contrast, high selectivities to monomer can still be achieved for polymers with high T_c values if they possess certain structural features. For example, poly(tetrafluoroethylene), which has no abstractable hydrogens attached to the polymer backbone and very strong carbon–fluorine bonds, affords 95% monomer under typical pyrolysis conditions. Notable exceptions to these rules include such important polymers as poly(isobutylene) and poly(trifluorostyrene) which afford uncharacteristically low yields of monomer. Prediction of the ceiling temperature alone would also fail for complex mixtures of polymers in which the presence of a substituent on one polymer may cause the usually high monomer yields from a second polymer to diminish. A comprehensive, quantitative assessment of the decomposition of polymers to high-valued products requires simultaneous prediction of all key measures of reactivity and therefore requires more fundamental understanding of the controlling underlying chemistry.

The experimental product spectra for styrene-based polymer decomposition obtained in this work and in the presence of a polyethylene co-reactant [17] suggested that the competition between β-scission and chain transfer is a key determinant of product formation. The capability for chain transfer depends on both the number of abstractable atoms and the ease with which they can be abstracted. The number is directly related to the polymer structure; the ease is a function of the relative stabilities of the reactant and product radicals of the transfer reaction and thus, the strengths of the bond broken and formed. Explicit and simultaneous accounting of each of these factors would provide an accurate prediction of the products afforded from a single component polymer, multicomponent mixtures, and polymeric blends alike.

Mechanistic kinetic modeling provides an ideal framework through which these factors could be taken into account. The reactivity of an active center is a function of its own structure and therefore is insensitive to the identity of the reactant from which it came. Thus, directly accounting for the interactions among active centers facilitates the description of interactions among feedstocks. Therefore, a detailed mechanistic modeling study was carried out to determine the combined role of backbone substituents and backbone reactivity in directing degradation of styrene-based polymers.

The challenge to mechanistic modeling is the complexity that explicitly accounts for the active intermediates demands. Each species in the reacting mixture corresponds to a single differential equation comprised of a term for each reaction in which the particular species is involved in order to account for the temporal changes in concentration. For reacting mixtures of multicomponent polymeric feedstocks, this implies a model size that can surpass hardware limitations. Even more formidable is the actual construction of such a model, since each reaction and its relationship to the species' differential equations must be tallied. The number of potential molecules and intermediates from a complex polymeric feedstock undergoing degradation prohibits manual construction of the corresponding model.

Therefore, tools for automated mechanism generation developed by Broadbelt et al. [18–20] were exploited. The required inputs are the structure of the reactants, the rules by which the reactant and product species react, and the parameters of a structure/property kinetic correlation. The algorithm transforms this information into reactant/product relationships, i.e., the reaction mechanism, species properties, rate constants, and the governing species' balance equations. Solution of the generated mechanistic model provides the temporal variations of species' concentrations and critically, the selectivity to monomer and other high-valued products.

7. Model development

The controlling thermal chemistry of PS and PAMS pyrolysis at elevated temperatures was summarized in terms of typical free radical reaction families. The free radical reactions considered were bond fission, hydrogen abstraction, β-scission, radical addition and termination via radical recombination. Although additional reaction types could be easily incorporated within the current approach, this set of reactions included the dominant reaction types at the temperatures of interest, accounted for the reaction products observed and allowed straightforward interpretation of the differences between PS and PAMS reactivity. Note that the reverse of each reaction type was included and therefore, each reaction in the mechanism is reversible. The reactions are summarized in terms of the reaction matrices used for automated mechanism generation in Table 2.

Incorporation of these free radical elementary step reactions in a model of polymer degradation requires specification of the rate parameters. In this modeling study, information was sought not only about the controlling reaction pathways but also quantitative values of the intrinsic kinetic parameters. Representation of the chemistry in terms of five free radical reaction families afforded a compact set of parameters. The kinetics within each family were captured in terms of a frequency factor and the parameters of a linear free energy relationship, which relates the activation energy to the value of an appropriate reactivity index. The rate constant, k_{ij}, has the form shown in the following equation, where i denotes the reaction family and j denotes the specific reaction,

$$k_{ij} = A_i \exp\left(\frac{-(E_{0,j} + \alpha_i \cdot RI_j)}{RT}\right). \tag{1}$$

Following the Polanyi logic [21], the heat of reaction was chosen as the reactivity index to describe the free radical pyrolysis reactions. The values of the heats of reaction for the model compound reactions were provided by the mechanism generator directly through on-the-fly calculation of heat of formation values performed using one of the two methods. The primary method accessed the structures and properties database from the National Institute of Standards [22,23]. Data are either extracted as experimental values tabulated from literature sources or estimated using the group additivity method parametrized by Benson [24]. Since the species which are included in the model are revealed as the mechanism is generated, it is possible that the database will fail to contain sufficient infor-

Table 2
Reaction matrix representations and kinetic parameters for five free radical reaction families incorporated into models for polystyrene and poly(α-methylstyrene) pyrolysis (optimized parameters are shown in italics)

		Parameters		
Reaction Type	Reaction Matrix	A/s^{-1} or l mol^{-1} s^{-1}	E$_o$/ kcal mol^{-1}	α
Bond fission	$\begin{array}{l} R_1 \\ R_2 \end{array} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$	*$(3.5 \pm 1.9) \times 10^{15}$*	0.0	1.0
Hydrogen abstraction	$\begin{array}{l} H \\ C \\ R\bullet \end{array} \begin{bmatrix} 0 & -1 & 1 \\ -1 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix}$	*$(1.5 \pm 0.9) \times 10^{8}$*	*12.8 ± 0.5*	0.5
β-scission	$\begin{array}{l} C\bullet \\ R_\alpha \\ R_\beta \end{array} \begin{bmatrix} -1 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 1 \end{bmatrix}$	1.0 x 10^{13}	*12.9 ± 1.6*	0.5
Radical addition	$\begin{array}{l} R_\alpha \\ R_\beta \\ R\bullet \end{array} \begin{bmatrix} 0 & -1 & 1 \\ -1 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix}$	3.2 x 10^{7}	*12.9 ± 1.6*	0.5
Radical recombination	$\begin{array}{l} R_1\bullet \\ R_2\bullet \end{array} \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}$	1.0 x 10^{9}	0.0	0.0

mation to allow a value of the heat of formation to be calculated. To provide flexibility, computational quantum chemistry was used to estimate the heat of formation when the database failed to return a value. MOPAC with the PM3 parameter set was used as the semiempirical computational chemistry package [25]. Accessing MOPAC required two-dimensional to three-dimensional conversion of the species graphs to provide an initial geometry for subsequent optimization. This conversion was accomplished by developing an interface between the mechanism generator and the translation package, Converter [26].

Specification of the 15 parameters, i.e, A_i, $E_{0,i}$ and α_i for each of the five reaction families, was facilitated by invoking a number of reasonable assumptions and relationships required for thermodynamic consistency. All bond fission reactions proceeded with activation energies equal to their heat of reaction. Thus, $E_{0,\mathrm{bond\ fission}}$ was set equal to 0 and $\alpha_{\mathrm{bond\ fission}}$ equal to 1. Thermodynamically, this is equivalent to assuming zero activation energy for radical recombination. Thus, $E_{0,\mathrm{radical\ recombination}}=0$ and $\alpha_{\mathrm{radical\ recombination}}=0$ which are reasonable assumptions for a wide range of hydrocarbon species [24]. The parameters for the reaction pair, β-scission/radical addition, were also constrained thermodynamically. The α parameters for hydrogen abstraction and the reaction pair β-scission/radical addition were set equal to 0.5 [27]. After the application of these assumptions, it was necessary to specify only the remaining seven parameters. The frequency factors for β-scission, radical addition and radical recombination were set equal to representative values obtained from the literature [24]. The remaining four parameters, $A_{\mathrm{bond\ fission}}$, $A_{\mathrm{hydrogen\ abstraction}}$, $E_{0,\mathrm{hydrogen\ abstraction}}$ and $E_{0,\beta\text{-scission/addition}}$, were optimized to capture the experimental data for neat polystyrene pyrolysis only. Therefore, the model results for poly(α-methylstyrene) and the binary mixture were pure predictions. The final set of parameters used is summarized in Table 2 with the four optimized parameters shown in italics.

In order to comply with hardware limitations and to construct a comprehensive yet manageable reaction mechanism, suitable model compound reactants were chosen. As a compromise between the number of product species, and thus model size, and an accurate representation of the polymeric backbone, a hydrogen-terminated trimer of each monomer was used as a polymeric mimic. These reactants are illustrated in Fig. 6.

In order to describe the behavior of a polymeric reactant more accurately using model compound reactants, analysis of the modeling results focused on the reactivity of the central monomer unit of the trimer. Isolating the reactivity of the central carbons from the reactions of the "end groups" provided a more accurate assessment of monomer selectivity, since in a polymer chain, the reactivity of the end groups is only a minor component of the overall decomposition observed. Therefore, the concept of labeling used routinely in kinetics experiments was incorporated into the modeling software. The approach involved labeling the eight carbons belonging to the central monomer unit, i.e., two backbone aliphatic and six aromatic carbons, such that products evolved containing one of these eight carbons were easily distinguished. The letter "X" was used to represent labeled carbon atoms, a convenient letter since it is unique from all atomic symbols of elements in the periodic table. Since determination of species' uniqueness relies on a lexicographical comparison of string codes representing the molecules, the mechanism generator distinguished among molecules with the same structure but differing in their labeled carbon constitution. However, the calculated species property, i.e., heat of formation, was insensitive to the labeled atoms. Using this approach, the reaction pathways involving the central monomer unit were tracked by the presence of labeled atoms in the products.

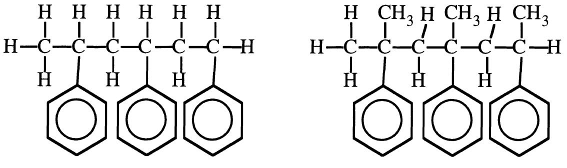


Fig. 6. Trimers of styrene and α-methylstyrene used as mimics of polystyrene and poly(α-methylstyrene).

Model construction focused on the development of a mechanism to describe the reaction of the PS and PAMS binary mixture since the single component PS and PAMS models were limiting cases of the binary model obtained by setting the initial concentration of one of the reactants equal to zero. The binary mixture model described the interaction of 901 species through 4110 reactions. The models were solved on a Silicon Graphics Indy R4400SC 150 MHz processor with 64 MB of RAM. Model generation allowed for formation of primary products and required a maximum of 30 min of CPU time. The experimental conditions used in this study were provided as input for model solution. The initial reactant loadings were 0.31 M for polystyrene, 0.26 M for poly(α-methylstyrene), and 0.16 and 0.13 M for polystyrene and poly(α-methylstyrene), respectively, in the binary mixture. These values were calculated based on the reactant loadings, the reaction volume, the known molecular weights of the polymers and a scale factor which maintained a constant number of styrene units between the trimeric model systems and the polymeric reactants. The reaction temperature was 350°C.

8. Model results

8.1. Relative energetics

Although the primary value of a mechanistic model is its ability to calculate quantitative yields and selectivities and enhance understanding of the controlling chemistry through model solution, valuable information may be obtained from a simple examination of the relative energetics of competing reactions within the same reaction family. Special attention was paid to assessing the relative rates of reaction for an individual reaction type as a function of reactant structure. In particular, the relative energetics for hydrogen abstraction reactions were examined since the presence of abstractable hydrogens along the polystyrene backbone is one potential key to the differences observed for monomer yield from PS and PAMS degradation.

The activation energies for abstraction of hydrogen from PS at the different sites along the polymer backbone by a representative radical derived from PS are summarized in Fig. 7. Overall, the lowest activation energies were observed for abstraction of hydrogen from backbone carbons with an aromatic substituent due to the ability of the aromatic ring to stabilize electron density at a benzylic carbon [24]. An average difference in activation energy of 5.9 kcal mol^{-1} for abstraction of hydrogen from the two different types of backbone carbon atoms was observed. This translates into a factor of 120 difference in rate at 350°C. It is clear from these quantitative results that the hydrogen atoms attached at benzylic positions along the polymeric chain dominate polystyrene hydrogen abstraction chemistry during decomposition.

8.2. Major reaction pathways

The ability of the PS and PAMS single component mechanisms to capture the experimental data was validated through comparison of the selectivities of the major reaction products. Furthermore, examination of the major products and identification of the reaction pathways leading to their formation provide an enhanced understanding of the structure/reactivity relationships dominating the decomposition chemistry during pyrolysis. This comparison is also a critical first step in extending and applying the modeling approach to mixed plastic waste.

The major products formed from reaction of PS trimer over the range of temperatures studied are summarized in Table 3. An aromatic ring balance reveals that these products account for greater than

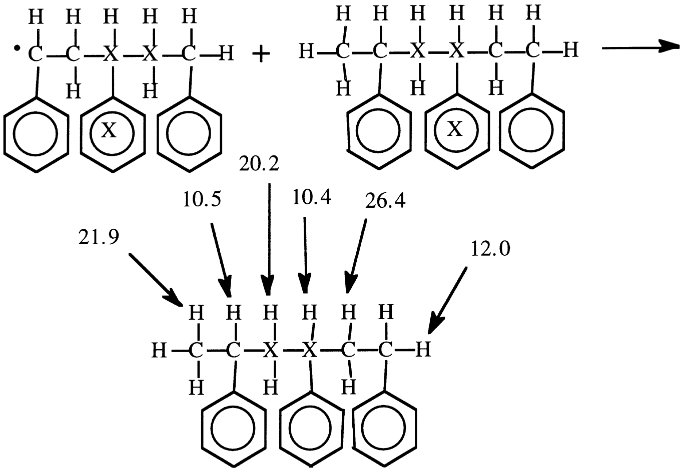
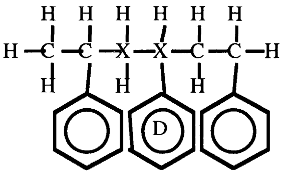
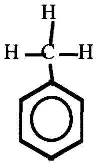
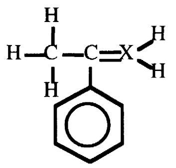
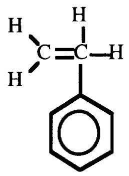
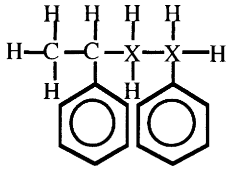
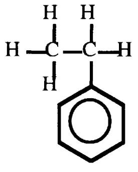
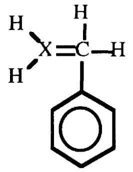
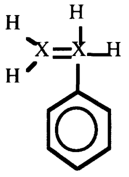
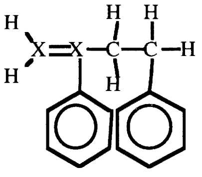


Fig. 7. Relative energetics of abstractable hydrogens on the styrene trimer backbone in kcal mol^{-1} based on calculated heats of reaction and the application of the kinetic parameters in Table 2. X represents a labeled carbon atom.

Table 3
Major products predicted from reaction of labeled polystyrene trimer at a temperature of 350°C (X represents a labeled carbon atom)

Reactant	Major Products	
		
		
		
		

93% of all reaction products over all reaction times and temperatures studied. Note that both products with saturated and unsaturated main carbon chains were observed, representing a competition between hydrogen abstraction and β-scission reaction pathways, and that the product spectrum described by the model, with the exception of 1,3-diphenylpropane, is identical to the major low molecular weight products observed from PS pyrolysis experiments.

The major products can be rationalized in terms of competing free radical pyrolysis cycles comprised of hydrogen abstraction from the energetically favorable benzylic positions and subsequent β-scission reactions. The major reaction pathways leading to the major products shown in Table 3 are summarized in Fig. 8. Only unimolecular decomposition reactions involving β carbon–carbon bond cleavage are illustrated with their corresponding activation

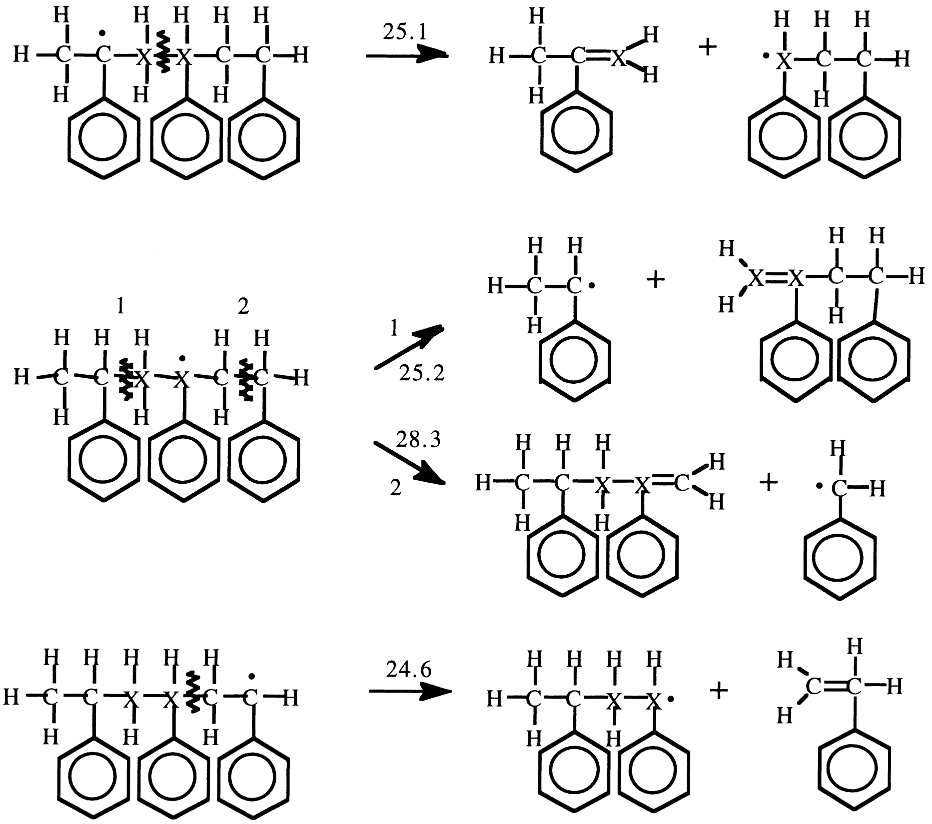


Fig. 8. Major products from styrene trimer decomposition are rationalized in terms of competing free radical pyrolysis cycles. X represents a labeled carbon atom.

energies since carbon–hydrogen β-scission was 13.7 kcal mol^{-1} higher in energy on average.

The product spectrum predicted for the pyrolysis of poly(α-methylstyrene) at a temperature of 350°C was also consistent with the experimental results reported herein and in the literature [9,11,28–30]. The three major products pictured in Table 4 were predicted from the model: α-methylstyrene with all labeled carbon atoms, unlabeled α-methylstyrene and cumene. An aromatic ring balance revealed that these three products accounted for greater than 97% of the ring-containing products. Note that α-methylstyrene with a combination of labeled and unlabeled carbon atoms was not observed in significant yield.

Interpretation of the model results allows the formation of the major products, which are both predicted and observed experimentally, to be rationalized in terms of the simple free radical mechanism depicted in Fig. 9. Radicals formed via bond fission abstract hydrogen from the single benzylic hydrogen, affording a tertiary radical. This hydrogen abstraction step is more energetically favorable by 10.3 kcal mol^{-1} than competing abstraction pathways. Although this is similar to the propagation step observed for polystyrene decomposition, the presence of a single tertiary hydrogen results in essentially exclusive formation of the PAMS-derived radical shown in Fig. 9. It must be noted, however, that this tertiary hydrogen would only be present as a hydrogen-terminated end group in a PAMS polymer chain.

The tertiary α-methylstyrene trimer radical next undergoes unimolecular decomposition via β-scission, cleaving the carbon–carbon bond of the backbone, evolving one molecule of α-methylstyrene monomer.

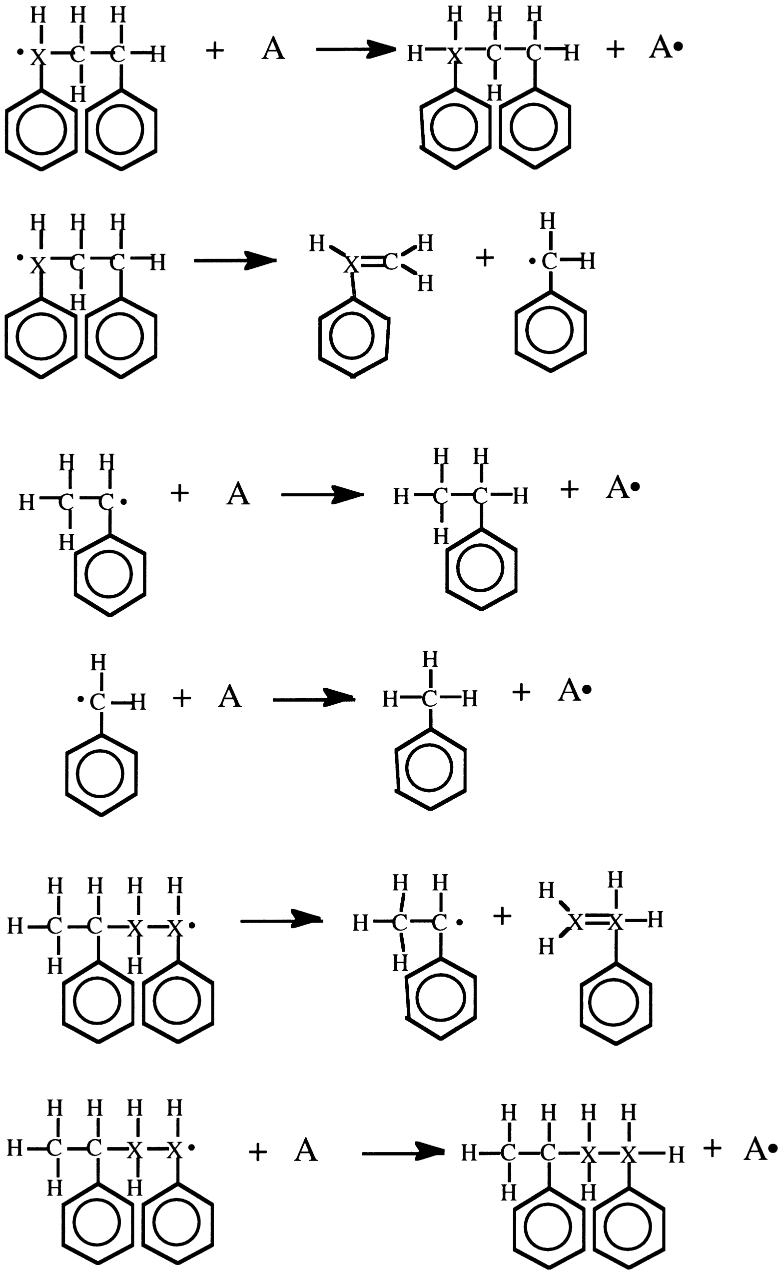
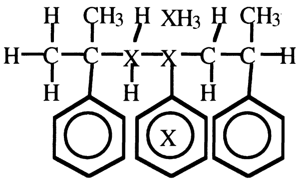
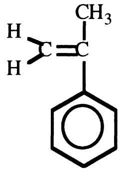
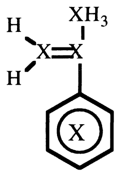
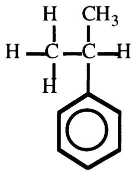


Fig. 8. (Continued)

An alternative β-scission reaction pathway affording a highly reactive hydrogen radical proceeds at a rate 2.9×10^5 more slowly than backbone cleavage at 350°C. This backbone cleavage is also rapid compared to the analogous decomposition observed for PS. The 2.1 kcal mol^{-1} lower activation energy corresponds to a factor of 5 rate enhancement at 350°C when the kinetic parameters of Table 2 are used and is consis-

Table 4
Model solution predicted the formation of three major products from reaction of labeled poly(α-methylstyrene) trimer at a temperature of 350°C (X represents a labeled carbon atom)

Reactant	Major Products	
		
		

tent with the faster overall disappearance kinetics observed for poly(α-methylstyrene) revealed by comparing Figs. 3 and 4.

The radical formed as a product of the first β-scission reaction has two reaction paths available to it: unimolecular decomposition and hydrogen abstraction. The rate of β-scission is approximately two orders of magnitude faster than hydrogen abstraction when a substrate concentration equal to the initial reactant concentration of 0.26 M is assumed. In contrast, decomposition of the analogous PS-derived radical via β-scission proceeded at a rate one order of magnitude faster than hydrogen abstraction.

The final step is a hydrogen abstraction reaction resulting in the formation of cumene. Formation of α-methylstyrene via β-scission would require an energetically unfavorable cleavage of a carbon–hydrogen bond. The high selectivity to cumene, approximately 1.0, is an artifact of the model since it was necessary to terminate the model trimer in a reasonable way, and a methyl group was selected. In contrast, formation of cumene from poly(α-methylstyrene) polymer would be due only to reaction at a chain end if the polymer were methyl-terminated, and therefore, would have negligible selectivity for polymers with molecular weights greater than 10^3 such as the PAMS sample studied herein.

8.3. *Product selectivities and yields*

The model results were also evaluated by comparing the calculated (PS) and predicted (PAMS and binary) product yields and selectivities to those observed experimentally. The product formed with the highest selectivity from solution of the model of PS pyrolysis was styrene monomer, which was the same result obtained from the experiment. The temporal variations of the evolution of styrene from the polymer experiments were also reproduced by the model well by calculating the ratio of the moles of styrene monomer formed with the aromatic ring labeled to the moles of labeled aromatic rings in the initial reactant charge. It was clear from this agreement that labeling of the model reactant permits

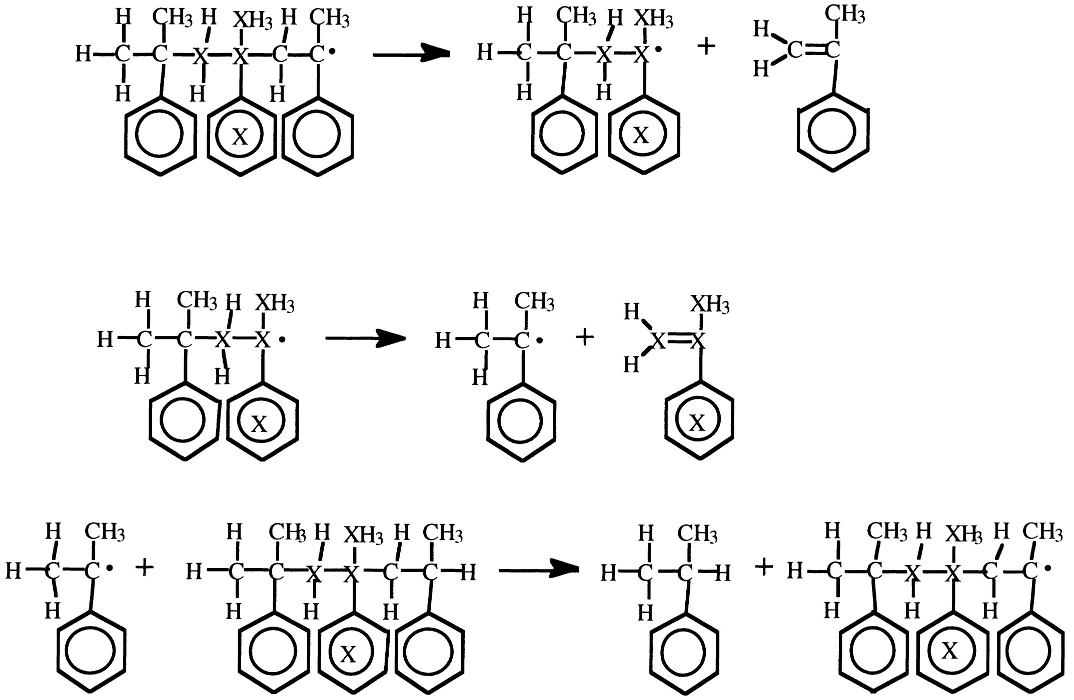


Fig. 9. The high selectivity of monomer from α-methylstyrene trimer decomposition is rationalized in terms of a single highly selective free radical pyrolysis cycle. X represents a labeled carbon atom.

this ratio to directly capture the probability that a given backbone unit will appear as styrene monomer without having to describe the chemistry of hundreds of individual polymeric segments explicitly. The model results and the experimental data for the evolution of styrene monomer as a function of reaction time are shown in Fig. 10.

The competition between hydrogen abstraction and β-scission reactions was directly assessed by calculating the ratio of the moles of styrene with all carbon atoms labeled to the moles of labeled 1,3-diphenylbutane. As depicted in the reaction pathways of Fig. 8, these two products are formed via a common intermediate and thus, their relative yields are a direct measure of the competing propagation reactions the intermediate can undergo. The molar ratio of styrene and 1,3-diphenylbutane was essentially constant at 4.6, in good agreement with the experimental values which averaged 5.0 over 0–180 min of reaction time.

Similar agreement between the experimental data and the model predictions was obtained for PAMS pyrolysis. The mechanistic model for PAMS pyrolysis predicted that the product formed with the highest selectivity was also monomer; a value of essentially 1.0 was achieved at all reactant conversions. The lack of easily abstractable hydrogens and the low energy barrier for decomposition via β-scission of an average of 24 kcal mol^{-1} leads to the "unzipping" observed for PAMS and the high yields of monomer obtained.

8.4. Polystyrene/poly(α-methylstyrene) coprocessing

The abundance of mixed plastic waste motivated examination of the pyrolysis of multicomponent mixtures to provide a more accurate assessment of pyrolysis as a resource recovery process. This would not only enable prediction of the effect of kinetic coupling during polymer coprocessing, but also provide guidance for process optimization through manipulation of the feedstock composition. In order to measure the effect of coprocessing in a well controlled environment through comparison with reactions of single components and assess the impact on conversion

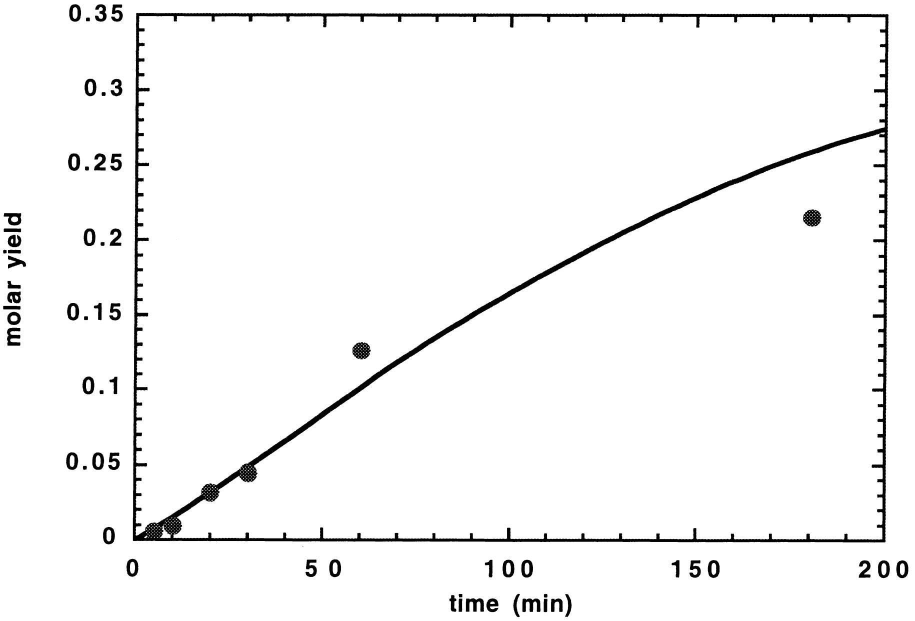


Fig. 10. The experimental yield of styrene monomer from experiments with polystyrene is in quantitative agreement with prediction of styrene monomer yield from reaction of the model trimer ((●) experimental data, and (———) model prediction).

and selectivity to monomers, the model predictions of the reactant disappearance and the evolution of labeled monomers were monitored.

The conversions of the single components alone and in the binary mixture are shown in the plots of Fig. 11(a) and (b) for PS and PAMS, respectively. Clearly, the addition of PAMS enhances the disappearance of PS, which is consistent with the enhancement in the rate of styrene production observed experimentally. Direct quantitative comparison of these results is not possible, however, since the molecular weights of the initial reactants are vastly different, and conversion cannot be directly calculated for the polymeric reactants. This is also consistent with the development by LaMarca et al. [31] in which it was shown that the effect of added initiation, in this case due to the weaker bonds in the PAMS trimer backbone, will always increase the rate for the case of ideal termination. The rate of PAMS disappearance decreases by a factor of 1.7. Therefore, both the experimental and the model results suggest that the addition of an easily degradable polymer with its own well-controlled decomposition pathways provides rate enhancement for a more intractable component during resource recovery through pyrolysis.

The model results also predicted that the presence of PAMS had a beneficial effect on the yield of styrene monomer as measured by the molar ratio of labeled styrene monomer to the moles of labeled aromatic rings converted. For example, at a conversion of 0.60 at 350°C, the selectivity was increased by a factor of 2.7 with the addition of PAMS. The increased selectivity to monomer formed via β-scission pathways is accompanied by a decrease in selectivity to 1,3-diphenylbutane, the hydrogen abstraction product observed with the highest selectivity. The molar ratio of styrene monomer to 1,3-diphenylbutane increased from a value of 4.6 to a value of 6.8. At the reactant loading reported herein, this is most easily rationalized in terms of the diminished pool of easily abstractable hydrogens with the addition of PAMS; specifically, PS trimer has two tertiary hydrogens, whereas PAMS only possesses one. However, experiments and modeling performed using 20 mg of polystyrene with 10 mg of poly(α-methylstyrene) added also resulted in an increased selectivity to styrene as compared to

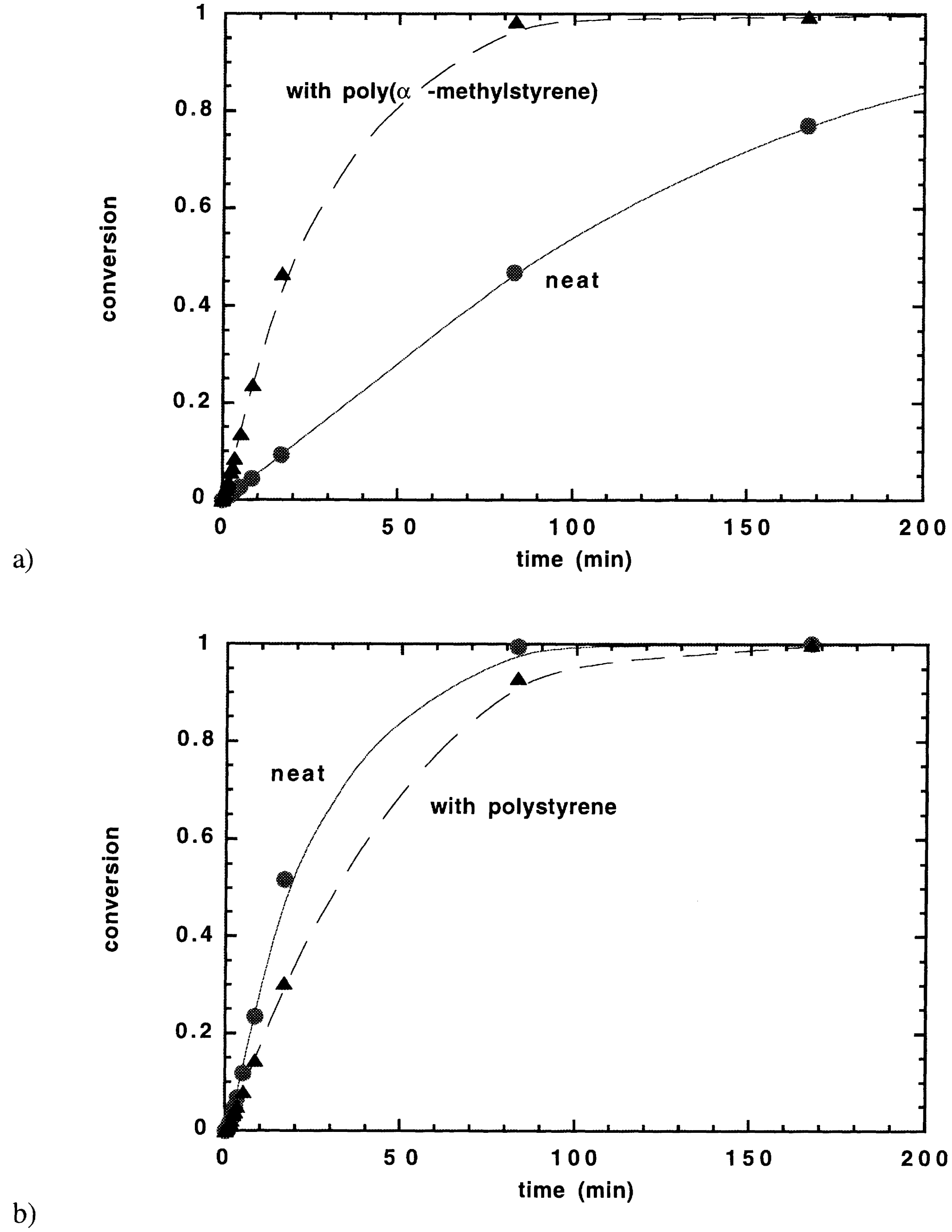


Fig. 11. Coprocessing of polystyrene and poly(α-methylstyrene) trimers resulted in (a) significant rate enhancement of polystyrene disappearance, and (b) slight rate retardation of poly(α-methylstyrene) disappearance.

neat pyrolysis. Therefore, the observed behavior is not solely a physical effect but is due in part to a chemical promotion effect.

The modeling study also examined the dependence of the enhancement in the styrene to 1,3-diphenylbutane selectivity on temperature. The selectivity to monomer was affected most dramatically at lower temperatures, where the hydrogen abstraction pathway is competitive. The difference is masked at higher temperatures because of the dominance of high activation energy β-scission reactions. However, the maximum monomer yield obtained was not significantly increased with the addition of PAMS as compared to the reaction of PS alone.

9. Conclusions

Overall, the experimental results suggest that coprocessing is a viable polymer resource recovery strategy. The reactivity of polystyrene was enhanced in the presence of poly(α-methylstyrene), and the yield of styrene monomer was increased as compared to reaction of neat polystyrene at a concentration of 0.31 M when poly(α-methylstyrene) was added at a concentration of 0.13–0.16 M and 0.31 M loadings of polystyrene. Although poly(α-methylstyrene) is not found in significant quantities in mixed plastic waste, the results do suggest that the product distribution from pyrolysis of high volume plastics may be tailored through the addition of an appropriate co-reactant. The single component results are also noteworthy since a high selectivity to monomer is obtained for PAMS while PS, which is similar in structure, affords monomer with significantly lower selectivity. These results may be used to suggest novel polymer structures which are designed to promote degradation to high-valued products during pyrolysis.

In order to understand the complex chemistry underlying the experimental results, a detailed mechanistic model was developed to describe the decomposition of single components and multicomponent mixtures of styrene-based polymers during pyrolysis. A model describing the reactions of α-methylstyrene and styrene trimer, individually and in a binary mixture, was generated using software for automated model construction and described 901 species using over 4000 reactions. Comparison of the reaction energetics calculated as the model was constructed identified the benzylic hydrogens as the key sites of hydrogen abstraction for both reactants and revealed a factor of 10^4 difference in abstraction rate. The model results were in good quantitative agreement with the experimental results, revealing that the rate of decomposition of α-methylstyrene trimer was a factor of 5 faster than that of styrene trimer. The faster disappearance kinetics were attributed to the energetically favorable sequential cleavages of backbone bonds via β-scission. The selectivity to α-methylstyrene monomer was approximately 1.0, in agreement with the experimental observations, while the selectivity to styrene monomer obtained was 0.65. The addition of an equal weight of α-methylstyrene trimer as a co-reactant enhanced the rate of styrene decomposition and resulted in an increased selectivity to styrene monomer.

Acknowledgements

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