Assessment of the thermal degradation characteristics of isomeric poly(styrene)s using TG, TG/MS and TG/GC/MS

Bob A. Howell[*], Yumin Cui, Duane B. Priddy

Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859, USA

Abstract

Atactic poly(styrene) is thermally less stable than would be expected for a purely head-to-tail polymer. To determine whether or not head-to-head units in the polymer might be responsible for this instability the degradation of both a typical atactic head-to-tail poly(styrene) and the corresponding fully head-to-head polymer has been examined using several thermal techniques—all involving thermogravimetry as a basic component. At low temperatures, e.g., 280 °C, the initial degradation is identical for the two polymers. However, while the degradation for the head-to-head polymer is well-behaved over long periods of time that for the head-to-tail polymer undergoes change relatively early in the reaction period. Further, the nature of the volatile fragments produced by degradation at 280 °C is strikingly different for the two polymers. The volume of volatiles formed is much smaller for the head-to-head polymer than for the head-to-tail polymer. Volatile products from decomposition of the head-to-head polymer reflect cleavage of the polymer main chain at head-to-head linkages while decomposition of the head-to-tail polymer smoothly generates *only styrene monomer*. At higher temperatures, 320 and 350 °C, degradation of the head-to-head polymer is still well-behaved while that for the head-to-tail polymer becomes much more complex. It can be concluded that degradation of the head-to-head polymer reflects scission of head-to-head linkages over a wide range of temperature. In contrast, the nature of the degradation of the head-to-tail polymer is strongly temperature dependent. At low temperatures (<300 °C) the initial degradation event is clearly scission of head-to-head linkages present as a consequence of polymerization termination by radical coupling. The macroradicals thus formed undergo unzipping to evolve styrene monomer. At higher temperatures, the degradation is more complex and involves random chain scission and subsequent transformations as well as head-to-head scission.
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1. Introduction

Poly(styrene) is a large volume, commodity polymer with a broad range of uses. Many of these are in food packaging applications. For these uses the level of monomer in the finished product must be very low.

* Corresponding author. Tel.: +1-517-774-3582;
fax: +1-517-774-3883.
E-mail address: bob.a.howell@cmich.edu (B.A. Howell).

Styrene monomer has a low taste and odor threshold and the presence of even trace amounts in a food item will detract from its overall attractiveness. The processing of poly(styrene) for the formulation of packaging materials invariably involves some thermal treatment. It has long been known that poly(styrene) undergoes thermal degradation at relatively modest temperatures [1]. A detailed understanding of the degradation process would clearly be useful in developing optimum conditions for processing of the

polymer. The degradation of poly(styrene) has been variously studied over the past several decades but no definitive results have previously been obtained. An early study in which volatile evolution and molecular weight changes during decomposition were monitored provided considerable insight [2,3]. On the basis of molecular weight changes with time of heating, it was concluded that an initial rapid drop in chain length is due to scission at a number of weak points distributed randomly along the polymer chains. However, the idea of random degradation was rejected for a number of reasons. First, a plot of (molecular weight)$^{-1}$ versus time, which should be linear for a simple random degradation, showed rapid departure from linearity, suggesting that the initial rate at which bonds are broken is not sustained. Second, the molecular weight distributions of degraded material were narrower than a random degradation would generate. Third, more monomer was produced than would be expected for random chain scission and fourth, the energy of activation was lower than anticipated. It was suggested that the initial high rate of volatilization is due to depropagation initiated at unstable chain ends produced by scission of weak links. Head-to-head linkages which might be more prone to scission than the typical head-to-tail links are introduced into the polymer main chain by polymerization termination by radical coupling. The suggestion that the degradation of poly(styrene) is initiated at head-to-head links gained some support from the observation that the degradation of similar polymer produced by anionic techniques (no termination by coupling) is apparently the result of random chain scission [4]. A plot of (molecular weight)$^{-1}$ versus time for the degradation of this polymer is linear. Other studies have provided mixed results and have led to the suggestion that, under some conditions, processes other than chain scission, e.g., hydrogen atom transfer, make important contributions to the degradation [5–11]. The inconsistency in results arose from a number of factors including different temperatures (often high) utilized for decomposition, decomposition carried out in the presence or absence of oxygen, differences in the thermal history of the polymer samples used, and a lack of uniformity with respect to the methods of preparation/purification of the polymers subjected to degradation. In an attempt to bring some clarity to the situation, the wholly head-to-head polymer was synthesized and

its thermal degradation behavior compared to that of conventional nominally head-to-tail polymer [12,13]. Unfortunately, the degradation of the polymers was carried out at high temperatures (>300 °C) at which any differences in behavior would be minimized and not be reflective of processes occurring during polymer processing. Under the conditions employed for the degradation, the rates of degradation for the two polymers were comparable—the head-to-tail polymer was actually somewhat more stable than the head-to-head polymer. The products of degradation were also different for the two polymers. Degradation of the head-to-tail polymer afforded a much more complex product mixture than that obtained from the head-to-head polymer. Because of the way the assessment of stability was carried out, this comparison was less definitive and less useful than intended.

The goal of the work reported herein was to prepare well-defined samples of both head-to-head and atactic head-to-tail poly(styrene) and to assess the thermal stability of both polymers at modest temperatures using thermogravimetry and evolved gas analysis to provide clarification of the mode of degradation of conventional poly(styrene).

2. Experimental

2.1. Methods and instrumentation

Polymers were characterized by spectroscopic, thermal and chromatographic methods. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained in deuterochloroform using a General Electric QE-300 spectrometer. Infrared spectra were obtained using solid solutions (1%) in anhydrous potassium bromide (as pellets) or thin films between sodium chloride discs using a model 560 Nicolet MAGN-IR spectrophotometer. Ultraviolet spectra of the polymers were obtained using dilute solutions in THF and a CARY 1 UV-Vis spectrophotometer. The scanned wavelength ranged from 200 to 400 nm. Molecular weights of the polymers were routinely determined by size exclusion chromatography (SEC) using solutions in THF, miscrostyrogel columns, and linear poly(styrene) calibration. For branching studies, solutions were prepared at a concentration of 1 mg/ml in THF and filtered through a 0.2 μm PTFE filter. The injection vol-

ume was 50 ml. THF was used as eluant at 1 ml/min. Separation was accomplished with three mixed bed columns (Polymer Laboratories) in series. For detection a Viscotek model H-502 differential viscometer was used in series with a Waters 2410 differential refractive index detector. Columns and detectors were held at 35 °C. Narrow distribution poly(styrene) standards were used to generate the universal calibration curve. Polystyrene 1683, a broad, linear poly(styrene) standard was used to verify system performance. The glass transition temperatures (T_g) of polymers were determined using differential scanning calorimetry (DSC) at a heating rate of 10 °C/min, using a TA Instruments Inc. Thermal Analyst model 2100 system equipped with a model 2910 MDSC cell. The sample compartment was subject to a constant purge of dry nitrogen at 50 ml/min. The thermal degradation characteristics of head-to-head poly(styrene) and head-to-tail poly(styrene) were examined by thermogravimetry using a TA instruments model 2950 TGA unit interfaced with the TA Instruments Inc. Thermal Analyst model 2100 control unit. The TGA cell was swept with nitrogen at 50 ml/min during degradation runs. The sample size was approximately 5–10 mg in a platinum sample pan. The temperature was ramped at a rate of 2 or 10 °C/min. For isothermal kinetic studies the temperature was held at a specific temperature between 280 and 350 °C. Mass loss was recorded as a function of time. Evolved gas analysis was accomplished using a Thermo Cahn TG-2131 microbalance in conjunction with a Thermo Finnigan TRACE GC/MS instrument. Approximately, 2 mg of sample contained in platinum sample pan was placed in the furnace. The furnace compartment was purged with helium at a flow rate of 50 ml/min for 20 min prior to analysis. The temperature of the furnace was ramped from 25 °C to the set point (280, 320, 350 °C) at 10 °C/min and held at the set temperature for 60 min. For the thermogravimetry/mass spectrometry (TG/MS) analysis, the TG transfer line was maintained at 250 °C in the GC oven. The mass spectrometer was operated in the electron impact mode using 70 eV electrons for ionization. The detector was maintained at 400 V. During the TG/MS experiment, a portion of the volatiles were collected in a cryotrap which was maintained at −100 °C. After the TG/MS experiment was complete, the GC oven was cooled to ambient temperature and analysis of the mixture of volatiles in

the cryotrap initiated. The column used was a Restek Corporation RTX-5MS of 15 m length and 0.25 mm internal diameter with a film thickness of 0.25 µm. The temperature program used was 40 °C for 2 min and then 40–330 °C at 10 °C/min. Programmed flow was used for the helium carrier gas. The flow was maintained at 4.5 ml/min for the first 4.5 min to maximize the amount of analyte pushed onto the column from the cryotrap. After that, the flow was reduced to 1.5 ml/min for the remainder of the analysis.

## 2.2. Polymers

2.2.1. Head-to-head poly(styrene)

Poly(2,3-diphenyl-1,3-butadiene). 2,3-Diphenyl-1, 3-butadiene was polymerized in a sealed polymerization tube using freshly crystallized AIBN as initiator in benzene solution (8.04 mmol/l). A 50 ml polymerization tube with a two-way stopcock was charged with AIBN solution (4 ml, 0.032 mmol of AIBN) and 4.8 g (23.3 mmol) of 2,3-diphenyl-1,3-butadiene. The polymerization tube was warmed at 55 °C to afford a homogeneous solution which was degassed at 3 Torr using the freeze–thaw technique (five repetitions), and sealed under nitrogen. The polymerization was carried out by placing the tube in a constant temperature bath at 60 °C. After 86 h, the tube was opened and the solid polymer was dissolved in 200 ml of benzene. The solution was added dropwise into 2000 ml of methanol to precipitate the polymer. The polymer was collected by filtration and dried at 40 °C (0.1 Torr) overnight. The ^{1}H NMR spectrum of the polymer contains absorptions at $\delta = 2.06$ (4H, methylene protons) and $\delta = 6.89$ (10H, aromatic protons). This spectrum contains no absorption in the olefinic region indicating that the polymer did not contain pendant vinyl groups, i.e., the polymerization occurred in 1,4-fashion. The ^{13}C NMR spectrum contains sets of absorptions corresponding to the polymer of *cis* and *trans* configuration at the double bond of the main chain at $\delta = 34.2$ and 32.4, 126.0 and 125.4, 128.3 and 127.2, 129.8 and 129.6, 137.9 and 137.5, and 142.6 and 141.9. The ratio of *cis* to *trans* absorptions by electronic integration is 53:47. This is very close to 1:1 and suggests that there is no great preference for one stereoisomeric arrangement over the other. The UV spectrum (THF) contains maximum absorption at 252 nm ($\varepsilon_{max} = 4.3 \times 10^3$ l/mol cm).

Hydrogenation of poly(2,3-diphenyl-1,3-butadiene). Into a dry, three-necked, round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser bearing a gas-inlet tube and a three-way stopcock was placed poly(2,3-diphenyl-1,3-butadiene), 1.0 g (4.9 mmol), under a flow of dry nitrogen. Dry THF (100 ml) and dry ethanol (5.7 ml, 98 mmol) were added through the three-way stopcock by means of a hypodermic syringe. Potassium metal 3.7 g (0.095 g-atom) was added portionwise as the reaction mixture was stirred magnetically under dry nitrogen. The solution became cloudy as potassium ethoxide formed. After 24 h the reaction was stopped by adding 20 ml of ethanol to destroy excess potassium. The solution was dropped into 600 ml of methanol to precipitate the polymer, which was collected by filtration and dried at 25 °C and 20 Torr overnight. The recovery was 0.92 g (92%). The degree of hydrogenation was 84% as determined using UV spectroscopy. The hydrogenation procedure was repeated twice to obtain the completely hydrogenated product, head-to-head poly(styrene). The polymer was repeatedly (4×) dissolved in toluene and precipitated by the addition of methanol to remove any residue from the reduction and then dried at 40 °C and 0.1 Torr for 24 h. T_g for the polymer determined by DSC was 104 °C. Analysis by SEC indicated that it was an unbranched polymer with $M_W = 1.4 \times 10^5$, $M_n = 4.9 \times 10^4$ and

$M_W/M_n = 2.86$. The proton NMR spectrum of the polymer contains absorptions at $\delta = 0.95$ (2H, methylene protons), $\delta = 2.11$ (1H, methine protons) and $\delta = 6.85$ (5H, aromatic protons). The ^{13}C NMR spectrum contains a multiplicity of absorptions due to the presence of polymer of both *erythro* and *threo* configuration. The chemical shifts are 31.0, 51.0, 126.1 and 125.4, 127.2 and 127.1, 129.0 and 128.7, and 143.9 and 142.8. The UV spectrum (THF) contains a maximum absorption at 252 nm with $\varepsilon_{max} = 67$ l/mol cm.

2.2.2. Head-to-tail poly(styrene)

Atactic head-to-tail poly(styrene) was prepared by AIBN initiated radical polymerization of styrene in benzene. A polymerization tube with two-way stockcock was charged with inhibitor-free, dry styrene (7.9 g, 76 mmol) and AIBN (33 mg, 0.20 mmol) in 6 ml of benzene. The tube was cooled in a liquid nitrogen bath and degassed at 3 Torr. The degassing (freeze–thaw) procedure was repeated three times. The polymerization was carried out by placing the tube in a constant temperature bath at 60 °C for 96 h. The polymer was precipitated by the addition of methanol, collected, and subjected to the same reduction procedure as used for the conversion of poly(2,3-diphenyl-1,3-butadiene) to head-to-tail poly(styrene)—this was to assure that the histories of the two polymers were as nearly the same as possible.
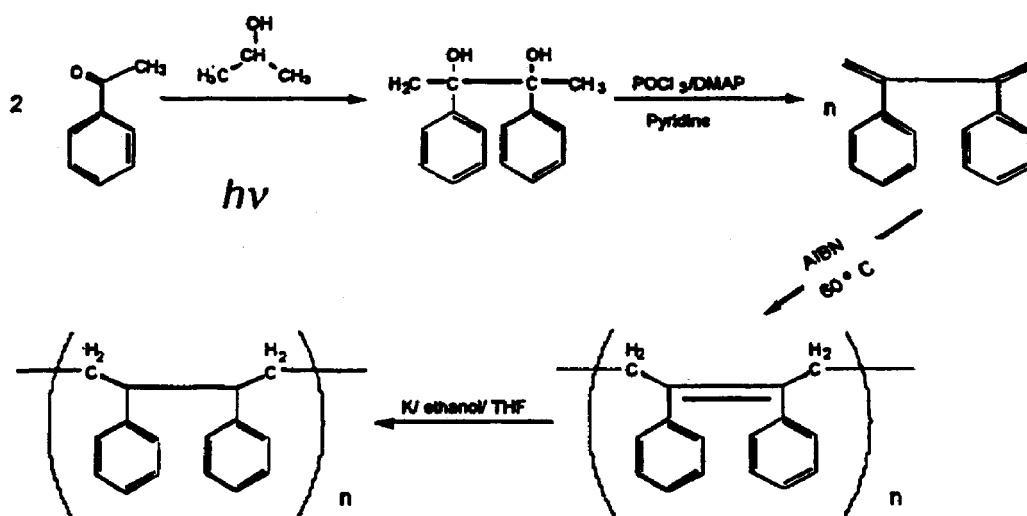
Scheme 1. Synthesis route to head-to-head poly(styrene).

The polymer was purified by repeated dissolution in toluene and precipitation with methanol and dried at $40\,^\circ$C and 0.1 Torr for 24 h. T_g determined by DSC was $108\,^\circ$C. SEC analysis provided the following parameters: $M_W = 1.8 \times 10^5$, $M_n = 5.7 \times 10^4$, $M_W/M_n = 3.16$. The ^{1}H NMR spectrum contains absorptions at $\delta = 1.42$ (4H, methylene protons), $\delta = 1.83$ (2H, methine protons), and $\delta = 6.58$–7.00 (10H, aromatic protons).

3. Results and discussion

The thermal degradation of poly(styrene) has long been of interest and has complicated processing of the polymer by thermal techniques [1]. Despite this, the degradation process is not yet fully understood. It has been clearly established that monomer is evolved and that polymer molecular weight decreases during degradation [2,3]. Further, it has often been suggested that degradation is probably initiated at head-to-head units within the polymer mainchain. However, even this has not been established with certainty [12]. In an attempt to bring some clarity of understanding to the degradation process two polymers, the fully head-to-head poly(styrene) and atactic head-to-tail poly(styrene), have been prepared and subjected to degradation under controlled conditions

at modest temperatures (similar to those that might be utilized for the processing of poly(styrene)). Conventional head-to-tail poly(styrene) could readily be prepared by radical polymerization in benzene solution using AIBN as initiator. The head-to-head polymer was prepared less directly using a procedure similar to that previously reported as outlined in Scheme 1. Photoreduction of acetophenone generated 2,3-diphenyl-2,3-butanediol which could be dehydrated most efficiently by treatment with phosphoryl chloride/pyridine, to produce monomeric 2,3-diphenyl-1,3-butadiene. Polymerization in benzene solution using AIBN as initiator afforded poly(2,3-diphenyl-1,3-butadiene). That the monomer had undergone 1,4-polymerization was evidenced by the absence, in either the infrared or proton NMR spectrum of the polymer, of absorption for the terminal olefinic methylene group that would have been formed if 1,2-polymerization had occurred to a substantial extent. Head-to-head poly(styrene) was obtained by hydrogenation of poly(2,3-diphenyl-1,3-butadiene) with potassium and ethanol in dry THF as solvent. The reduction process had to be repeated several times (at least three) to achieve full reduction. To exclude any differences in preparation processes for the two polymers, the head-to-tail polymer was subjected to the potassium reduction procedure. The two polymers were purified by the same dissolution/precipitation
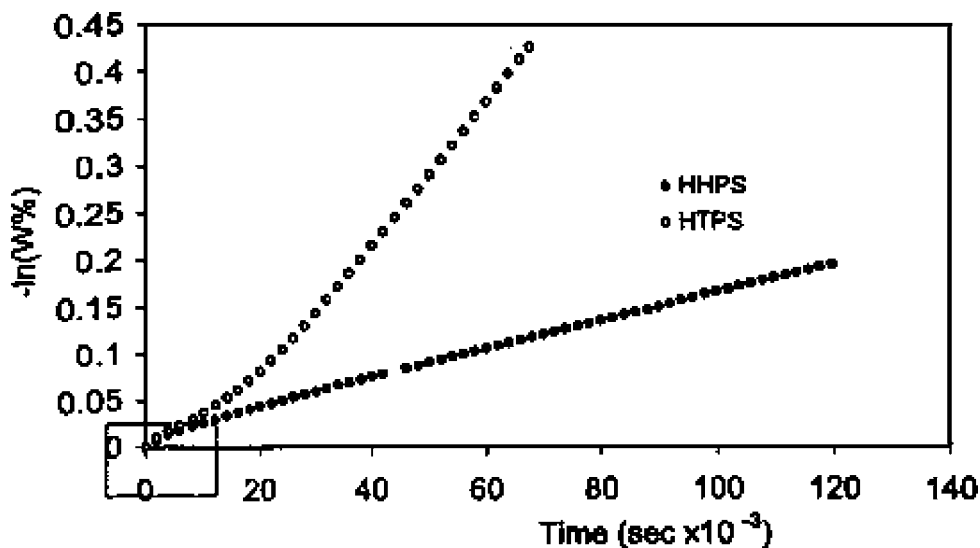

Fig. 1. Kinetic plots for thermal degradation of head-to-head poly(styrene) and head-to-tail poly(styrene) at $280\,^\circ$C.

Table 1
Molecular weights and polydispersities for head-to-head poly(styrene) and atactic head-to-tail poly(styrene)

Polymer	M_W	M_n	M_W/M_n
Head-to-head poly(styrene)	1.4×10^5	4.9×10^4	2.86
Head-to-tail poly(styrene)	1.8×10^5	5.7×10^4	3.16

process and then isolated and dried in the same way. Molecular weight data for the two polymers are presented in Table 1.

The thermal degradation characteristics of the two polymers over a range of temperatures, 280–350 °C, were compared using thermogravimetry. Kinetic plots ($-\ln W\%$ versus time) for the degradation of both head-to-head and head-to-tail poly(styrene) are dis-

played in Fig. 1. As may be noted, at the outset these plots are essentially identical for the two polymers (see inset and Fig. 2). The rate constants determined from the slopes of the plots in Fig. 2 are $3.49 \times 10^{-6}\,\mathrm{s}^{-1}$ for head-to-head poly(styrene) and $4.15 \times 10^{-6}\,\mathrm{s}^{-1}$ for head-to-tail poly(styrene). While these numbers are not identical they are quite similar and suggest that the initial degradation process is the same for the two polymers. Degradation of head-to-head poly(styrene) is well-behaved over the entire range of degradation and presumably reflects mainchain cleavage between head-to-head units. The same is apparently the case for head-to-tail poly(styrene) degradation during the initial stages of decomposition. However, the number of head-to-head units in the head-to-tail poly(styrene) is not greater than about one per chain, assuming that
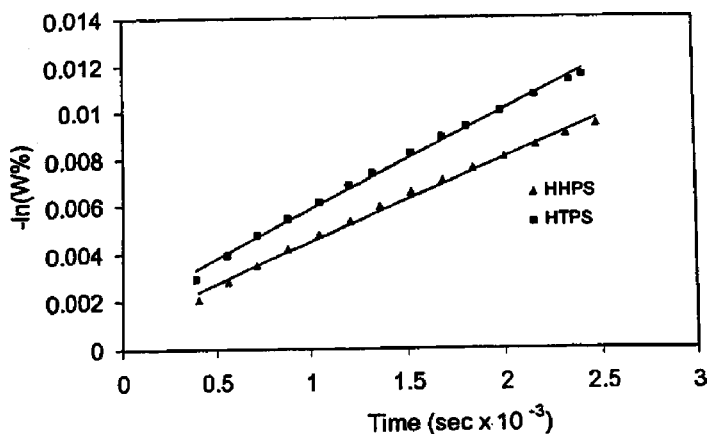

Fig. 2. Early portion of kinetic plots for the thermal degradation of head-to-head poly(styrene) and head-to-tail poly(styrene) at 280 °C.
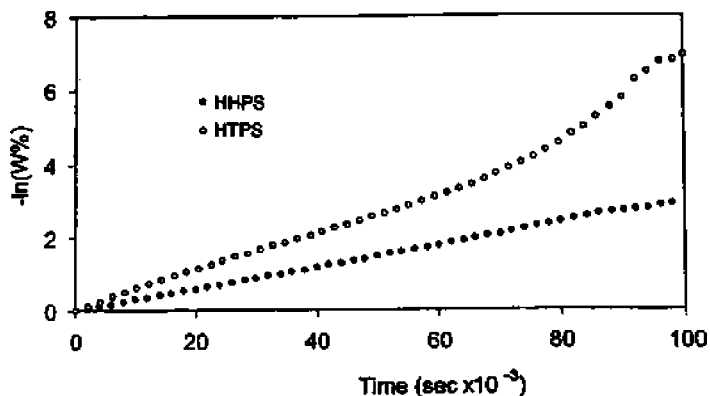

Fig. 3. Kinetic plots of thermal degradation of head-to-head poly(styrene) and head-to-tail poly(styrene) at 320 °C.
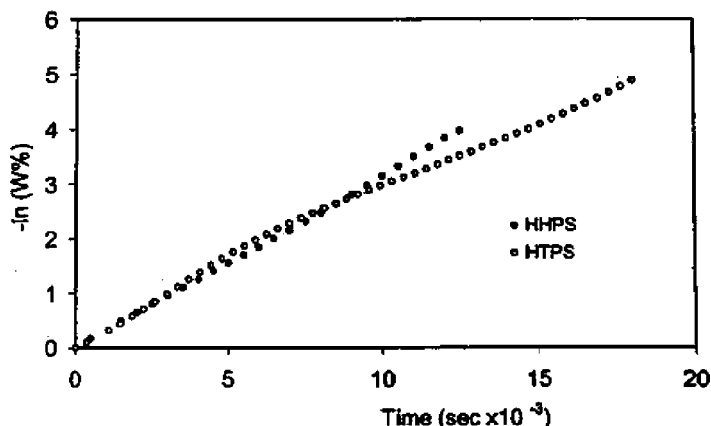
Fig. 4. Kinetic plots for thermal degradation of head-to-head poly(styrene) and head-to-tail poly(styrene) at 350 °C.

termination of polymerization occurs exclusively, or nearly exclusively, by radical coupling. After these units are removed degradation of head-to-tail polymer is much more rapid than that for the head-to-head polymer. The degradation for the head-to-tail polymer is well-behaved at this temperature and probably reflects chain unzipping to generate styrene monomer (see Fig. 1).

When degradation of the two polymers is carried out at 320 °C, the kinetic plots deviate earlier indicating that random events for decomposition of the head-to-tail polymer begin to occur at this temperature. This is illustrated in Fig. 3.

When the decomposition temperature is raised to 350 °C (Fig. 4), the degradation characteristics of the head-to-head polymer remains well-behaved. The degradation of the head-to-tail polymer is more complex and is probably reflective of several different processes occurring simultaneously.

The degradation of head-to-head poly(styrene) is well-behaved at all temperatures utilized. The degradation is clearly first-order over a range of temperatures for which the reaction was examined. This is illustrated in Fig. 5. The rate constants for degradation at the various temperatures are shown in Table 2. A plot of $\ln(k/T)$ versus $1/T$, where T is
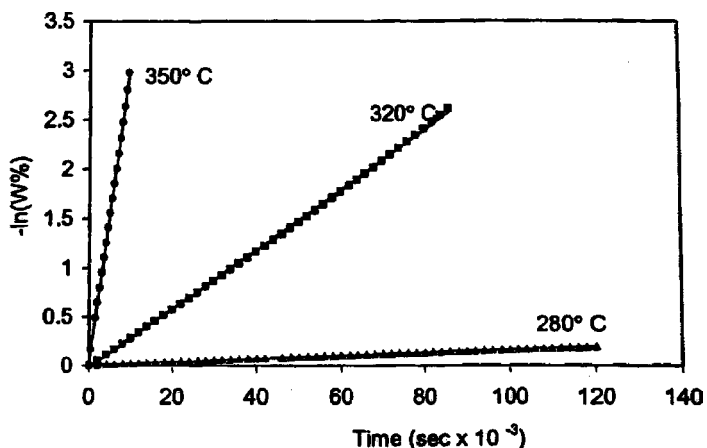

Fig. 5. First-order kinetic plots for the thermal degradation of head-to-head poly(styrene) at several temperatures.

Table 2
Rate constants for the thermal degradation of head-to-head poly(styrene)

Temperature (°C)	$k \times 10^5$ (s^{-1})
280	0.153
320	3.02
350	30.9

the Kelvin temperature and k is the corresponding rate constant, is shown in Fig. 6. Using the slope of this line, $(-\Delta H^{\neq}/R)$, the enthalpy of activation of 50.5 kcal/mol for this process may be obtained.

At 280 °C the degradation of head-to-tail poly(styrene) is well-behaved beyond the initial decomposition (see Fig. 1). A portion of the data contained in Fig. 1 is replotted in Fig. 7. The slope of this plot yields a rate constant of 7.52×10^{-6} s^{-1}. If what is occurring here is chain unzipping to generate styrene monomer and it is uncomplicated competing processes, this provides a good reflection the facility of that process. It might be noted that this value is only marginally greater than that (4.15×10^{-6} s^{-1}) attributed to the cleavage of head-to-head linkages in this polymer. However, the one is largely complete before the other begins (see Fig. 1).

Based on all the foregoing, it is possible to suggest that the initial event in the thermal degradation of head-to-tail poly(styrene) is the cleavage of head-to-head linkages largely present in the polymer as a consequence of polymerization termination by combi-
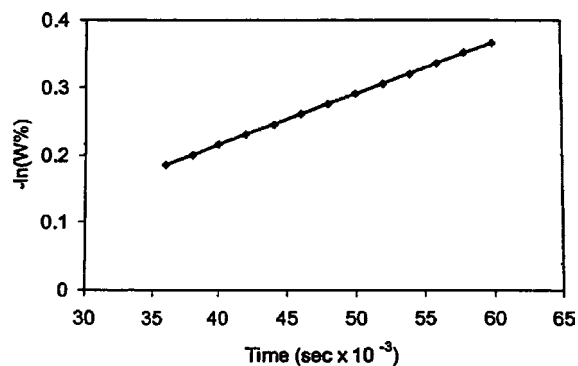

Fig. 7. Kinetic plot for the thermal degradation of atactic head-to-tail poly(styrene) at 280 °C and long reaction time.

nation of propagating species. This early stage degradation is very similar to that observed for head-to-head poly(styrene) over the entire range of degradation. After all the head-to-head units are removed, more complex degradation occurs. At low temperature, i.e., 280 °C, the predominant process would seem to be chain unzipping to form monomer. At higher temperature (>300 °C), degradation probably involves significant random chain scission.

Evolved gas analysis for the degrading polymers was conducted by TG/MS and thermogravimetry/gas chromatography/mass spectrometry (TG/GC/MS). In the first case, samples were held at 280 °C for 80 min with any volatile fragments formed being carried by the helium purge gas to a mass selective detector tuned
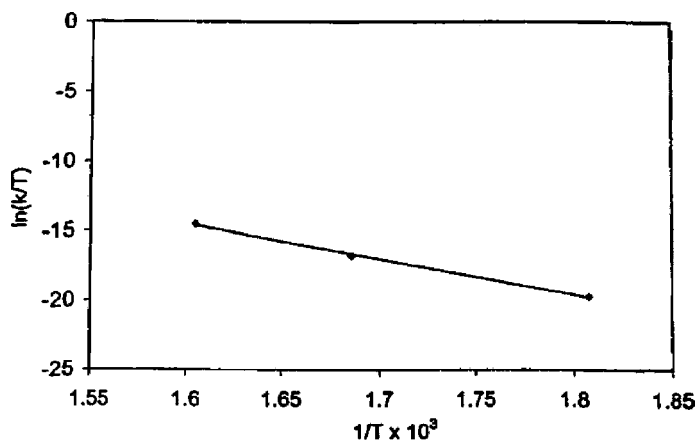

Fig. 6. Temperature dependence for the rate constants for the thermal degradation of head-to-head poly(styrene).
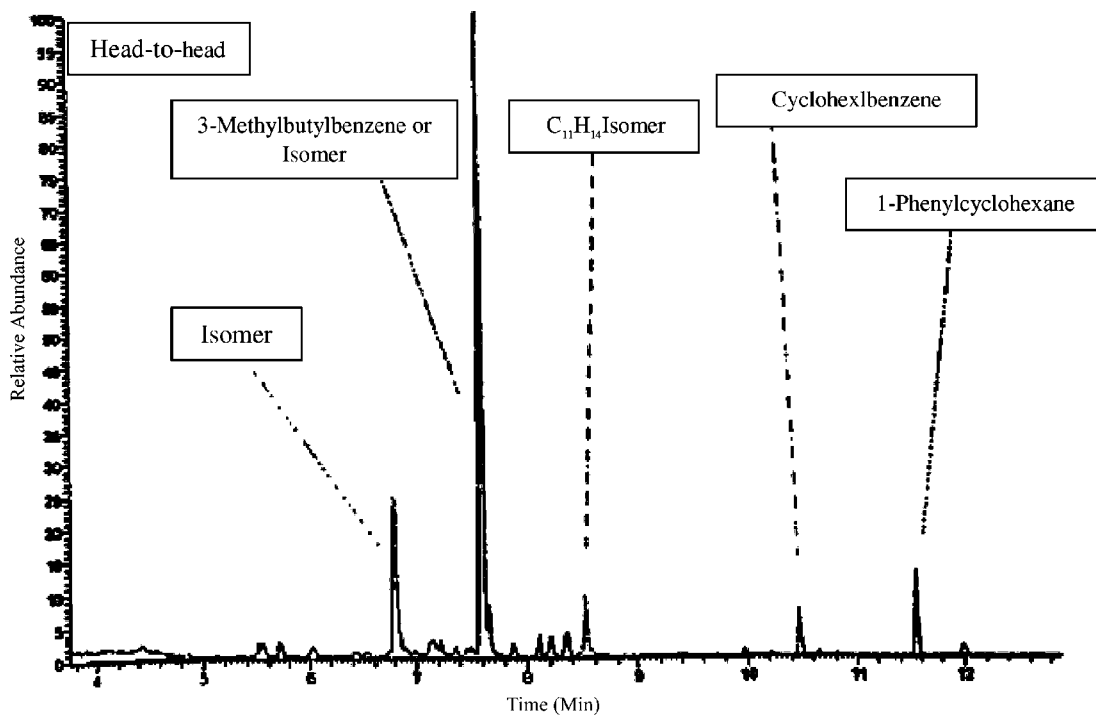
Fig. 8. Evolved-gas chromatogram (TG/GC/MS) for initial degradation of head-to-head poly(styrene) at 280 °C.
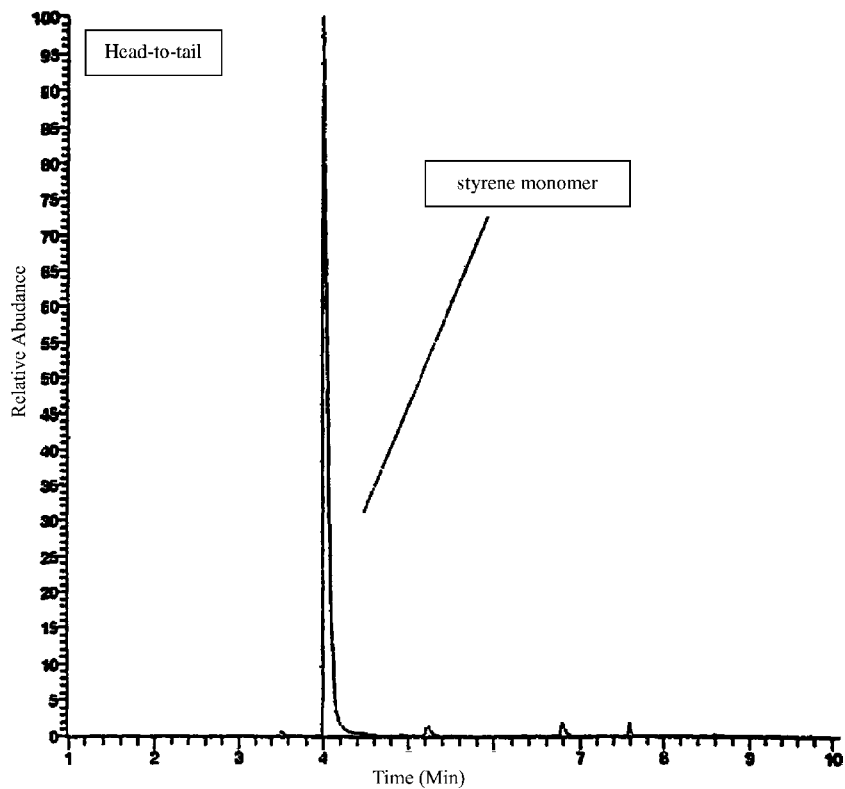

Fig. 9. Evolved-gas chromatogram (TG/GC/MS) for initial degradation of atactic head-to-tail poly(styrene) at 280 °C.

to m/e 104 (styrene monomer). For the head-to-head polymer no signal was detected nor was any measurable weight loss noted, i.e., the polymer was relatively mass stable at 280 °C over the course of the experiment (it should be noted that the time at 280 °C for this experiment was much shorter that previously utilized for thermogravimetry at 280 °C). In contrast, the head-to-tail polymer lost 7.7% of its initial mass.

The TG/GC/MS experiments were even more revealing. The experiments were identical to those described above except that the volatiles formed from degradation of the polymer were carried onto the GC column prior to the mass selective detector. Again, the head-to-head sample lost very little mass at 280 °C for 80 min. However, evolution of some volatile fragments, albeit in very small amounts, was detected. The chromatogram of evolved gases from the degradation of the head-to-head polymer is shown in Fig. 8. It might be noted that the mixture of volatile products contains few components and no styrene monomer.

The major component of the mixture is a $C_{11}H_{16}$ isomer tentatively identified as 3-methylbutylbenzene. All other components are present at very low level.

Again, the behavior of the head-to-tail polymer stands in sharp contrast to that of the head-to-head polymer. The TG/GC/MS chromatogram is shown in Fig. 9. The *only* volatile compound formed from initial degradation of head-to-tail poly(styrene) at 280 °C is *styrene monomer*.

For comparison, both chromatograms are shown in Fig. 10. It is clear in this comparison that while degradation of head-to-tail poly(styrene) occurs when the polymer is subjected to 280 °C for even a short time and that styrene monomer is evolved, the head-to-head polymer is relatively mass stable at this temperature and no styrene monomer is evolved.

The results of the evolved gas analysis are fully consistent with those generated by thermogravimetry. They suggest that the thermal degradation of head-to-tail poly(styrene), particularly at low temperature
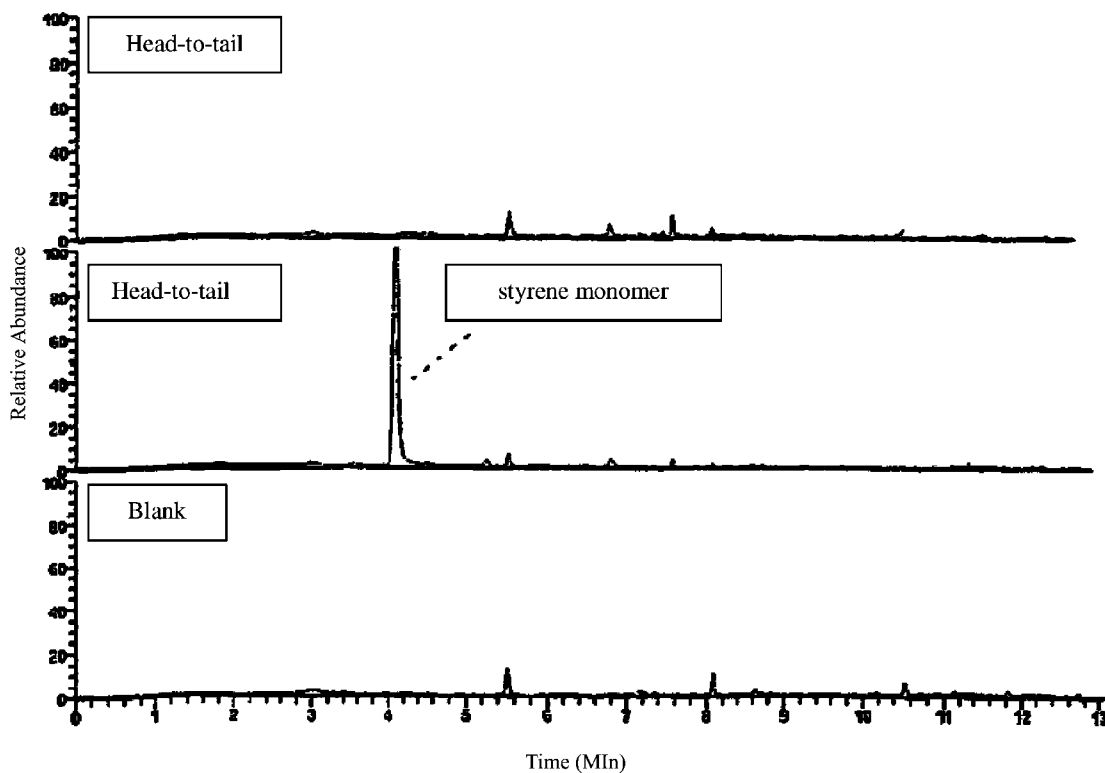

Fig. 10. Evolved-gas chromatogram (TG/GC/MS) for initial degradation of poly(styrene)s at 280 °C.

(<300 °C), is initiated at head-to-head linkages present in the polymer as a consequence of polymerization termination by radical coupling. The macroradicals formed then undergo sequential unzipping to evolve styrene monomer.

4. Conclusions

The thermal degradation of both head-to-head and conventional atactic head-to-tail poly(styrene) has been assessed using thermal techniques—conventional thermogravimetry and evolved gas analysis. The degradation of the head-to-head polymer is well-behaved over a wide range of temperatures and reflects scission of head-to-head linkages. This process occurs with an activation enthalpy of 50.5 kcal/mol. In contrast, the nature of the degradation of the head-to-tail polymer is strongly temperature dependent. At low temperature (<300 °C) the initial degradation event is clearly scission of head-to-head linkages. The macroradicals thus formed undergo unzipping to evolve styrene monomer. At 280 °C, both processes are first-order with rate constants of 4.15×10^{-6} and 7.52×10^{-6} s^{-1}, respectively. At higher temperatures, the degradation is more complex and involves random chain scission and subsequent transformations as well as head-to-head scission.

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