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THERMAL STABILITY OF POLY(STYRENE) CONTAINING NO HEAD-TO-HEAD UNITS

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General purpose poly(styrene) prepared by conventional radical techniques contains a head-to-head unit as a consequence of polymerization termination by radical coupling. As has been previously demonstrated, thermal stress promotes homolysis of the bond linking the head-to-head components. The macroradicals generated depolymerize rapidly to generate styrene monomer. This decomposition during processing can lead to finished articles containing objectionable levels of styrene monomer, particularly for food packaging applications in which even low levels of monomer can promote objectionable taste and aroma. Polymer containing no head-to-head units should not be prone to this facile decomposition. In this instance, poly(styrene) has been prepared by nitroxyl-mediated polymerization of styrene monomer followed by reductive removal of nitroxyl end groups. Polymer prepared in this manner contains no head-to-head units and displays thermal stability much greater than that observed for conventional poly(styrene). A direct comparison of the stability for the two polymers is readily available by thermogravimetric techniques. A quantitative reflection of the difference in stability is available from the rate constants for the respective decomposition.

Keywords: *fully head-to-tail poly(styrene), mode of decomposition, poly(styrene) microstructure, poly(styrene) stability, thermal degradation*

Introduction

Poly(styrene) is a large volume, commodity polymer with a broad range of applications. Common uses include housing for electronic equipment, inexpensive housewares, toys and disposable packaging. Its relatively low cost, easy processability, and transparency make it ideal for packaging baked goods, pastries, and other similar food items. Under conditions of thermal processing poly(styrene) often undergoes some degradation. If styrene monomer is formed as a product of degradation finished articles with unacceptable taste and aroma characteristics may be produced. This unacceptable outcome could be avoided by use of a poly(styrene) that was less susceptible to thermal degradation. Most commercial poly(styrene) is produced by radical techniques and often contains a head-to-head unit as a consequence of polymerization termination by radical coupling. At relatively low temperature (280°C) the head-to-head unit may be cleaved thermally to generate macroradicals which rapidly expel styrene monomer [1]. If the polymer could be produced by means that would not incorporate a head-to-head unit it should display thermal stability considerably greater than commercial general purpose poly(styrene).

Experimental

Polymers

Mediated radical polymerization of styrene

A solution of 0.01 g (0.032 mmol) of 2,2’-azobis(4-methoxy-2,4-dimethylvaleronitrile), 0.017 g (0.11 mmol) of 2,2,6,6-tetramethylpiperidinyl-l-oxy radical (TEMPO), and 0.003 g (0.013 mmol) of camphorsulfonic acid in 13.65 g (131.25 mmol) of styrene monomer was placed in a Pyrex polymerization tube and degassed by a freeze-pump-thaw technique at least three times before the mixture was heated to 55–60°C (oil bath) for three hours to form the initiator. The temperature was elevated to 120°C and the solution was heated 6 h to effect polymerization. The tube was placed in cold water to quench the reaction. Polymer was precipitated by addition of a 10-fold volume of methanol and the polymer was collected by filtration at reduced pressure and repeatly dissolved in benzene and reprecipitated by addition of methanol. The polymer purified in this manner was collected and final traces of solvent were removed at reduced pressure (15 torr) and 50°C. Analysis of the polymer by ^{1}H NMR spectroscopy confirmed the presence of a TEMPO end group (absorption for the benzylic methylene proton alpha to the nitroxyl oxygen at δ 4.8–5.2). For repeated

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preparations monomer conversion determined gravimetrically was approximately 80%.

Reductive removal of the TEMPO end group in the polymer generated by mediated radical polymerization of styrene

Polymer from mediated radical polymerization of styrene (2.00 g) was dissolved in 50 mL of xylene, and a ten-fold (based on moles TEMPO end groups present) excess of 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added [2]. The mixture was heated to 140°C and maintained at that temperature for 6 h. Xylene was evaporated and the polymer was dissolved in acetone. The solution was poured into a ten-volume excess of methanol to precipitate the polymer. The dissolution/precipitation process was repeated at least twice. The polymer was collected and dried as described above. The absorbtion at δ 4.8–5.2 in the ^{1}H NMR spectrum of the starting polymer was absent in the spectrum of this material.

Conventional racial polymerization of styrene

Conventional polymerization of styrene was carried out as described above for mediated polymerization, 2,2’-azobis(4-methoxy-2,4-dimethylvaleronitrile was used as initiator at 60°C but with no TEMPO present.

Methods and instrumentation

Polymers were characterized by spectroscopic, thermal and chromatographic methods. Nuclear magnetic resonance spectra (^{1}H and ^{13}C) were obtained using solutions in deuterochloroform or toluene-d_8 containing tetramethylsilane (TMS) as an internal reference and 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. Polymer molecular masses were determined by size exclusion chromatography (SEC) using a Waters 150-CV instrument equipped with three mixed bed columns (Polymer Laboratories, Inc.) in series. Samples (1% by mass in THF) were filtered through a 45 μm nylon filter prior to injection. Tetrahydrofuran at 1 mL min^{-1} was used as eluant and narrow distribution poly(styrene) standards were used for calibration. The glass transition temperatures (T_g) of polymers were determined by differential scanning calorimetry (DSC) at a heating rate of 10°C min^{-1} using a Perkin Elmer PYRIS Diamond instrument. Sample masses were 6–10 mg in sealed aluminum pans. The sample compartment was subject to a constant purge of dry nitrogen at 50 mL min^{-1}. Calibration was accomplished using Perkin Elmer protocols. The thermal degradation characteristics of both conventional poly(styrene) and poly(styrene) containing no head-to-head units, i.e., fully head-to-tail polystyrene were examined by thermogravimetry using a TA Instruments model 2950 TG unit interfaced with the Thermal Analyst model 2100 control unit. The TG cell was swept with nitrogen at 50 mL min^{-1} during degradation runs.

The sample size was 5–10 mg in a platinum sample pan. For isothermal kinetic studies the temperature was rapidly ramped to a fixed temperature between 280 and 350°C and allowed to equilibrate three minutes before data acquisition was begun.

Results and discussion

It has previously been observed that poly(styrene) produced by conventional radical polymerization and containing one head-to-head unit per chain as a consequence of polymerization termination by radical coupling undergoes thermal degradation at relatively low temperature, 280°C [1]. At this temperature the polymer mainchain is cleaved at the head-to-head unit to generate macroradicals which unzip with the expulsion of styrene monomer. This sequence may occur during thermal processing of the polymer to lead to the production of finished articles containing unacceptably high levels of styrene monomer. This is particularly a problem in the production of food packaging in which even very low levels of styrene monomer may impart objectionable taste and aroma. It might be expected that poly(styrene) lacking a head-to-head unit, i.e., the fully head-to-tail polymer would display significantly greater thermal stability than that produced by conventional radical techniques. To generate such a polymer it is necessary to prepare poly(styrene) by a method that prohibits its polymerization termination by radical combination. Generally, there are three possibilities for generation of such a polymer: mediated radical polymerization; anionic polymerization; and metathesis polymerization. The demands of anionic polymerization [scrupiously clean monomer, absence of protic substances (e.g., moisture) and air] make it less amenable to routine use then is radical polymerization. Metathesis polymerization leads to the formation of lower molecular weight polymers than those obtained by radical polymerization and those customarily used in degradation studies [1, 3–6]. For these reasons mediated radical polymerization was selected as the method for the preparation of poly(styrene) containing no head-to-head units, i.e., a fully head-to-tail poly(styrene). A suitable initiator/mediator could be conveniently prepared in situ from the thermal decomposition of 2,2’-azobis(4-methoxy-2,4-dimethyl)valeronitrile [Wako V-70] in styrene

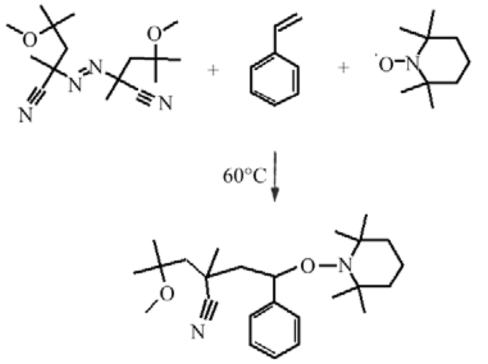

Fig. 1 Formation of an alkoxyamine initiatior/mediator from the thermal decomposition of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) in styrene monomer containing the stable nitroxyl radical, TEMPO

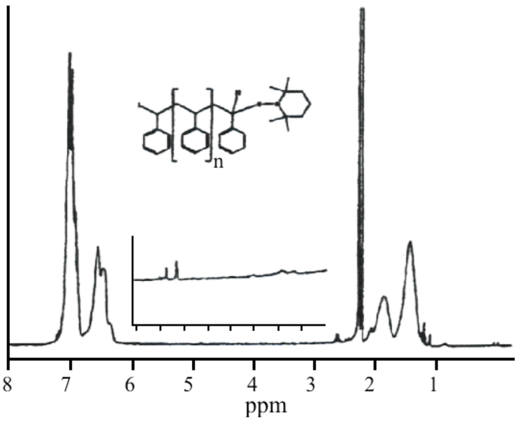

Fig. 2 ^{1}H NMR spectrum of poly(stryrene) containing no head-to-head units and a TEMPO chain end

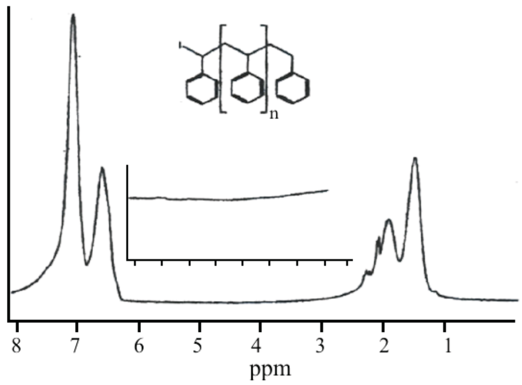

Fig. 3 ^{1}H NMR spectrum of poly(styrene) containing no head-to-head units after the removal of a TEMPO end group by a reductive technique

monomer containing the stable radical, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (Fig. 1). This process could readily be carried out at 60°C, a temperature well-below that required for the homolysis of the alkoxyamine C–O bond and below the temperature required for styrene dimmer formation and consequent thermal initiation of styrene polymerization. Mediated styrene polymerization was then carried out by simply increasing the temperature of the mixture to 120°C. It was found that the best results were obtained using a mole ratio of V-70 to TEMPO of 1:1.5 and 100 ppm of camphorsulfonic acid (CSA) in styrene monomer. The presence of CSA was necessary to promote non-radical decomposition of the styrene dimmer formed at polymerization temperature and, therefore, limit thermal polymerization.

The presence of the TEMPO end group in the initially-formed polymer was readily apparent from the ^{1}H NMR spectrum of the material. The absorption for the benzylic methine proton adjacent to the chain end is present at δ 4.5 well away from other absorption in the spectrum (Fig. 2). The remainder of the spectrum is very similar to that for poly(styrene) generated by other techniques [7, 8]. This signal is removed from the spectrum by heating a solution of the polymer in the presence of 2,6-di-*t*-butyl-4-methylphenol (BHT) indicating that the labile nitroxyl end group had been removed (Fig. 3).

The polymer generated in this way had M_w=75.966, M_n=56.104 and PDI=1.35 (SEC). For comparison polymer prepared under similar conditions with V-70 as initiator but in absence of TEMPO had M_w=115.112, M_n=65.852 and PDI=1.75.

The stability of these two materials, 1) the polymer containing no head-to-head units with the TEMPO chain ends removed reductively and 2) the polymer produced by conventional radical polymerization and presumably containing one head-to-head unit per chain, was examined using thermogravimetry. The temperature of the sample was rapidly brought to the desired set point, three minutes were allowed for the temperature to stabilize at the selected point, and mass loss at the temperature of interest as a function of time was monitored for at least two half-lives (usually longer). Degradation of the two polymers was examined at several temperatures between 280 and 350°C [4]. Kinetic plots ($-\ln[M]/[M_0]$ where M is the sample mass at any time t and M_0 is the mass at the time the first data point was recorded) *vs*. time for these polymers at 280°C are displayed in Fig. 4.

Data from the early portion of these plots are recast in Fig. 5. Early in the decomposition the process for the two polymers is similar.

However, the decomposition behavior for the polymers deviates very early in the process. The rate constants for initial decomposition obtained from the slope of the plots in Fig. 5 are $1.91\cdot10^{-5}$ s^{-1} for conventional poly(styrene) and $8.70\cdot10^{-6}$ for the fully head-to-tail poly(styrene). As may be seen from Fig. 4 the slope for the degradation of the fully head-to-tail polymer is constant over the entire range of decompo-

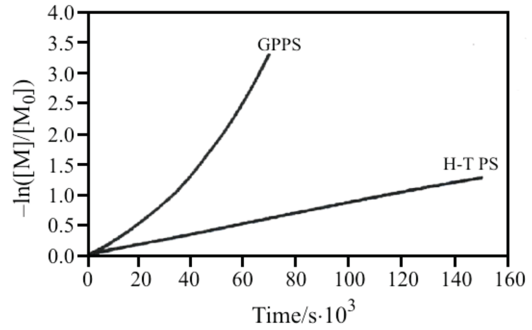

Fig. 4 Thermal degradation at 280°C of poly(styrene) containing no head-to-head units and poly(styrene) produced by contventional radical techniques

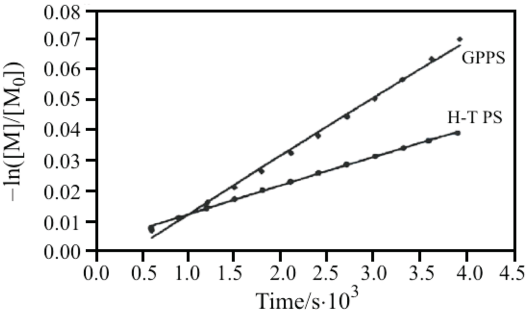

Fig. 5 Early portion of kinetic plots for the thermal degradation of fully head-to-tail poly(styrene) and general purpose poly(styrene) at 280°C

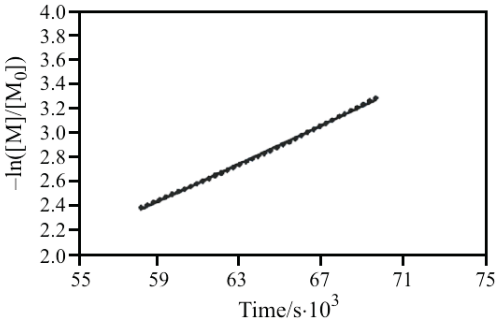

Fig. 6 Kinetic plot for the thermal degradation of conventional atactic head-to-tail poly(styrene) at 280°C at long reaction time

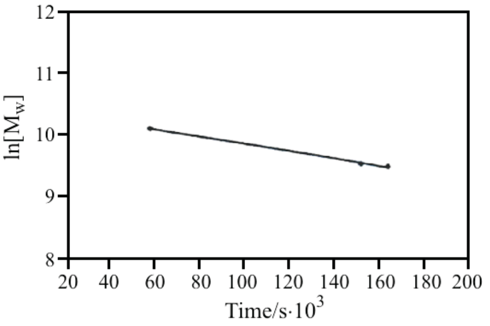

Fig. 7 Change in molecular weight of fully head-to-tail poly(styrene) as function of time at 280°C

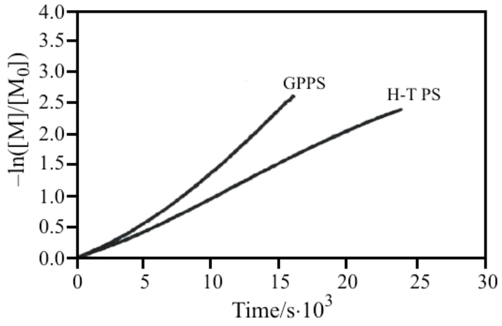

Fig. 8 Kinetic plots for termal degradation of poly(styrene) containing no head-to-head units and general purpose poly(styrene) at 320°C

sition. In contrast, the nature of the degradation of conventional poly(styrene) changes dramatically. A portion of the data for degradation of this polymer obtained at longer reaction time is reploted in Fig. 6. The slope of this plot yields a rate constant of $7.84\cdot10^{-5}$ s^{-1}. Clearly, two different processes are involved in the decomposition of the conventional polymer. As has been noted previously, the initial reaction involves mainchain cleavage at head-to-head units to produce macroradicals which then evolve monomer at a rate much greater than that for intitial chain cleavage [1]. The rate constant for mainchain scission at a head-to-head unit is $1.91\cdot10^{-5}$ s^{-1} while that for unzipping of the macroradicals generated is $7.84\cdot10^{-5}$ s^{-1}. On the other hand, degradation of the fully head-to-tail (no head-to-head units) polymer results from random mainchain cleavage with a rate constant of $8.70\cdot10^{-6}$ s^{-1}. Random chain scission is confirmed by a decrease in polymer molecular weight as a function of time (Fig. 7). At higher temperatures the decomposition behavior of both polymers is more complex.

Plots for degradation at 320°C are displayed in Fig. 8.

When the decomposition temperature was raised to 350°C, the degradation characteristics of both polymers were very similar to those at 320°C. However, the degradation of general purpose poly(styrene) was still much more rapid than that for the polymer containing no head-to-head units as shown in Fig. 9. At this temperature it is likely that several processes are occurring simultaneously, i.e., sufficient energy is available to bring about random chain scission in both polymers and structural differences are not as apparent as for degradation at lower temperatures.

Kinetic plots for degradation of the polymer containing no head-to-head units at various temperatures are collected in Fig. 10. The corresponding rate constants are collected in Table 1.

A plot of ln(*k*/*T*) *vs.* 1/*T*, where *T* is the Kelvin temperature and *k* is the corresponding rate constant, is shown below in Fig. 11. Using the slope of this line, $-\Delta H^{\ddagger}/R$, the enthalpy of activation for the thermal degradation for fully head-to-tail poly(styrene) may be determined as 43.0 kcal mol^{-1}.

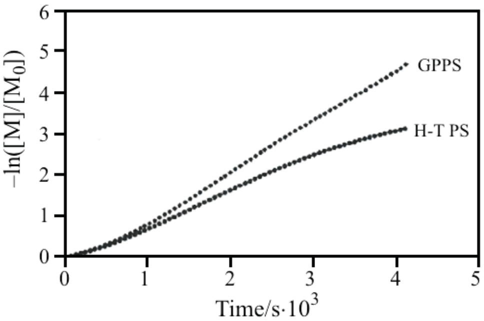

Fig. 9 Kinetic plots for thermal degradation of poly(styrene) containing no head-to-head units and general purpose poly(styrene) at 350°C

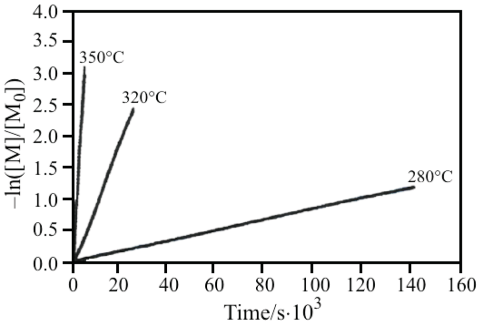

Fig. 10 First order kinetic plots for the thermal degradation of poly(styrene) containing no head-to-head units at several temperatures

Table 1 Rate constants for the thermal degradation of poly(styrene) containing no head-to-head units

Temperature/°C	$k\cdot 10^5$/s^{-1}
280	0.87
320	10.5
350	84.0

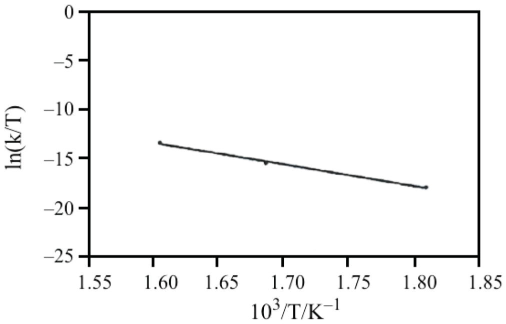

Fig. 11 Temperature dependence for the rate constants for the thermal degradation of poly(styrene) containing no head-to-head units

Conclusions

Based on the observations reported here as well as those previously described [1] it is apparent that the degradation of poly(styrene) produced by conventional radical polymerization, i.e., general purpose poly(styrene), at temperatures below 300°C is initiated by mainchain scission at a head-to-head unit present in the polymer as a consequence of polymerization termination by radical coupling. The macroradicals thus formed readily unzip to expel monomer so that the mass loss as a function of time is rapid. The rapid loss of mass is apparent from thermogravimetry and the identity of styrene monomer as the single entity being lost has been deomonstrated by evolved gas analysis [1]. In contrast, a fully head-to-tail poly(styrene) prepared by nitroxyl-mediated polymerization of styrene monomer followed by removal of the nitroxyl end groups by a reductive technique is much more thermally stable than the corresponding polymer prepared by conventional radical polymerization. Degradation corresponds to random mainchain scission to form oligomers as opposed to the expulsion of monomer as observed for the conventional polymer.

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