Thermal Degradation of Poly(1-butene sulfone)

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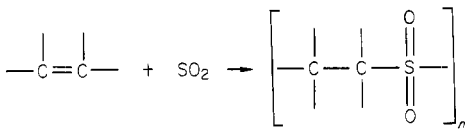
ABSTRACT: The kinetics of the thermal degradation of poly(1-butene sulfone) (PBS) were studied over the temperature range 100–240 °C. Above 200 °C the kinetics were first order with respect to sample weight with an activation energy of ~48 kcal/mol. Below 200 °C the kinetics were complex with an activation energy of ~12–14 kcal/mol. The onset of thermal decomposition was at 135 °C. The mechanism of the high-temperature decomposition was attributed to random chain scission followed by rapid chain depropagation. The low activation energy of the low-temperature decomposition is suggestive of a diffusion-controlled process. Initiation of the low-temperature decomposition was attributed to the presence of random weak links in the chain. These could be removed by an isothermal treatment, and subsequent analysis only showed the high-temperature decomposition mechanism.

Introduction

The reaction of sulfur dioxide with an olefin or other double-bond-containing compound to form a polysulfone is well-known and may be represented by the equation



Polysulfones have been formed from a wide variety of olefins but they all suffer from the common defect of poor thermal stability. Indeed, it is their lack of thermal stability that has been one of the major reasons preventing commercial utilization of the resins since the softening point of the polymers is higher than the temperature of decomposition.[1]

We have been studying the processing variables of poly(1-butene sulfone) (PBS), which is used as a positive resist in electron beam lithography. Prebaking the resist after spin coating on a suitable substrate is necesssary to remove excess solvent from the solid film, relieve strain in the film, and promote better adhesion to the substrate. Preferably, the prebake temperature should be above the glass transition temperature, T_g, of the polymer. The heat distortion temperature of PBS at a tensile stress of 60 psi has been reported to be 89 °C[2] and the T_g should lie several degrees above this temperature.

However, the majority of thermal degradation studies on polysulfones have been done at temperatures above the polymer melt temperature, PMT. (This is the temperature at which the polymer melts and leaves a trail of polymer when moved across a hot metal bar.[3]) The PMT is reported to be 160 °C for PBS, 20 °C above the onset of decomposition.[4] Above this temperature, the major products of degradation as determined by pyrolysis/gas chromatography/mass spectrometry are reported to be mainly olefin and sulfur dioxide.[5-7] The question arises as to the nature and extent of degradation in the intermediate temperature range, viz., T_g to PMT. Obviously, this will be important as far as selecting a prebake temperature is concerned in view of the marked dependence of sensitivity on molecular weight and distribution.[8] Any substantial reduction in molecular weight due to thermal degradation during prebaking would serve to reduce the electron sensitivity of the resist.

Very little quantitative information on the thermal degradation of PBS exists, especially in the range 100–160 °C. Dainton and Ivin[9] found that PBS was thermally unstable above 130 °C, liberating gaseous products that contained about 50% sulfur dioxide. This is in contrast to the differential scanning calorimetry results of Brown and O'Donnell,[10] who reported that PBS did not start to decompose until 215 °C. Dainton and Ivin found that at 70 °C, the specific viscosity of a solution of PBS in chloroform decreased but without weight loss. They suggested therefore that predominantly random chain scission occurs at 70 °C and decomposition mainly to olefin and sulfur dioxide (which they attributed to depolymerization) occurs at 130 °C. However, no quantitative data were reported. Crouch and Wicklatz[2] studied the degradation of PBS in the range 160–190 °C but they presented no data beyond 3 h at a given temperature. Hill and Caldwell[4] reported that PBS lost 30% weight after 3 h at 190 °C. More recently, Kiran et al.[6] reported on the application of pyrolysis/gas chromatography/mass spectrometry to the degradation of several poly(olefin sulfones). They also published complementary TGA and DTA results at a heating rate of 20 °C/min that indicated that these materials, notably polysulfones from butene, pentene, and hexene, underwent a two-step degradation process, the initial degradation occurring in the temperature range 100–200 °C and the major degradation taking place at higher temperatures. Bowmer and O'Donnell[11] also investigated the thermal decomposition of several poly(olefin sulfones) at 150 and 200 °C. Their measurements of volatile product yields indicated that most of the poly(olefin sulfones) studied underwent depolymerization to give olefin and sulfur dioxide in comparable yields. While this was approximately true for PBS at 200 °C, results at 150 °C showed a much greater proportion of olefin than sulfur dioxide and appear to be in contrast with the results of Dainton and Ivin.

The present work was undertaken to obtain further information on the nature of the degradation of PBS over the temperature range 100–250 °C.

Experimental Section

PBS was prepared by polymerization of an equimolar mixture of 1-butene (Philips, research grade) and sulfur dioxide (Matheson, anhydrous). The polymerization was initiated by 0.1% azobis(isobutyronitrile) at 35 °C. Following polymerization, the polymer was dissolved in acetone, precipitated into an excess volume of methanol, and dried under a vacuum at 40 °C for 24 h. It was then ground and passed through a 360-mesh sieve. The viscosity-average molecular weight, as determined by dilute solution viscosity with methyl ethyl ketone as a solvent, was calculated from the expression[12]

$$[\eta] = 0.026 M_v^{0.55}$$

and was found to be 3.0×10^6.

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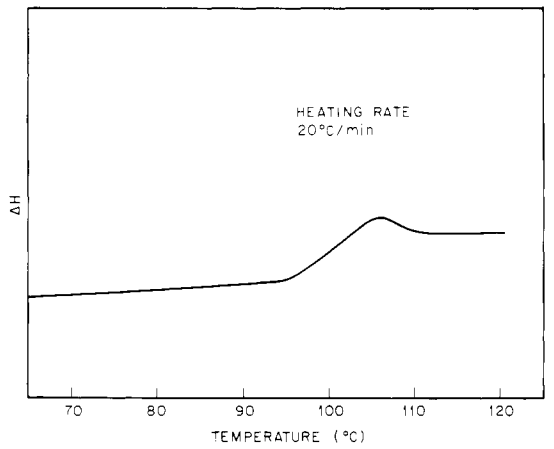


Figure 1. DSC thermogram of PBS.

Dynamic thermal properties were measured on a Perkin-Elmer differential scanning calorimeteter (DSC) and a Mettler Model TG-1 thermogravimetric analyzer (TGA). The Mettler instrument has the capability for simultaneous measurement of differential thermal analysis (DTA) and differential TGA. It was also used to investigate the isothermal weight loss on samples of weight ~10 mg.

Samples for subsequent molecular weight analysis were obtained from isothermal runs on ~1-g samples. For these experiments, the powdered polymer was spread evenly over the flat floor of a glass reaction vessel. The system was evacuated and then lowered into an oil bath that was maintained at the required temperature, and samples were withdrawn at varying time intervals. The sample was continually evacuated during the degradation.

Results and Discussion

The glass transition temperature was determined by differential scanning calorimetry (DSC). A typical DSC trace, with a heating rate of 20 °C/min, is shown in Figure 1. T_g was taken as the temperature at which the slope of the base line commences to deviate, giving a value of 95 °C. This is somewhat above the reported heat distortion temperature of 88 °C,[2] as expected, and well above the value of 64 °C reported by Gipstein et al.[13]

On further increasing the temperature, there was the onset of an endothermic peak at 135 °C. This correlates with the onset of thermal degradation as evidenced in Figure 2, which shows the results of a simultaneous TGA/DTA run using the Mettler thermobalance at a heating rate of 10 °C/min. There was no weight loss up to 135 °C, above which the sample started to lose weight at an increasing rate. These results confirm the observations of Dainton and Ivin but contradict the results of Brown and O'Donnell.[10] Observation of the DTA, TGA, and DTGA curves above the decomposition temperature indicates that PBS undergoes a two-step degradation process, the initial degradation occurring in the temperature range 135–240 °C and the major degradation taking place at higher temperatures. A similar two-stage decomposition for PBS was observed by Kiran and co-workers.[6]

Observation of the sample both inside the cup during a TGA run and also during heating on the stage of an optical microscope at a heating rate of 10 °C/min showed that over the temperature range 200–230 °C, the melt viscosity of the polymer decreased to a point where individual particles agglomerated. The gases liberated during the decomposition reaction caused the agglomerated mass to bubble and increase in volume. At higher temperatures, the viscosity was low enough to allow escape of the gases without any distortion of the polymer melt. This raises the possibility that the two-step nature of the degradation

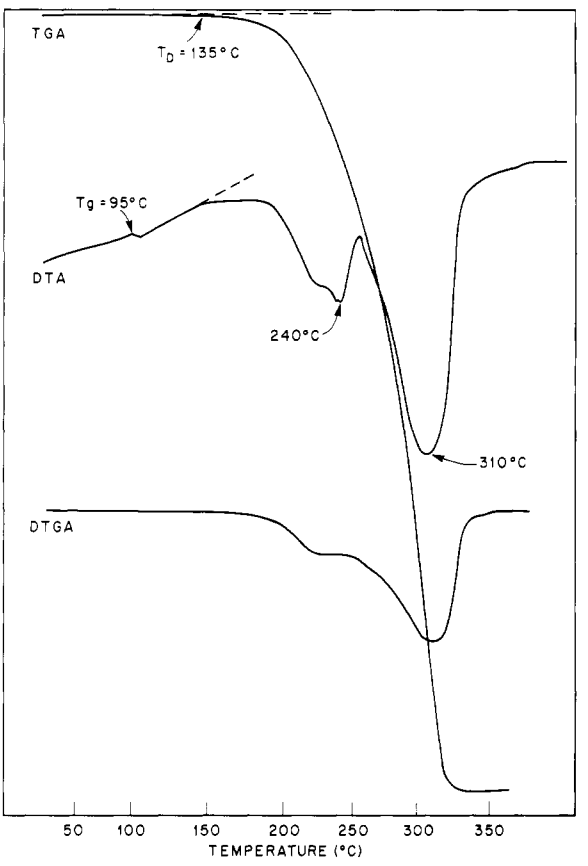


Figure 2. Simultaneous TGA, DTA, and DTGA thermograms for PBS obtained at a heating rate of 10 °C/min.

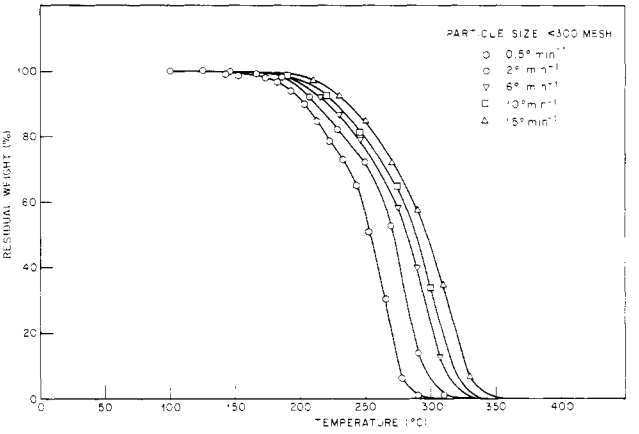


Figure 3. Effect of particle size on the decomposition of PBS.

may be a result of physical effects associated with this transformation rather than a mechanism change. In order to check whether physical characteristics of the sample, viz., particle size, are important, a series of TGA analyses was done on samples with particle size varying from 50 mesh (0.0117 in.) to <300 mesh (0.0018 in.). The results are shown in Figure 3 and indicate no significant effect of particle size. All subsequent measurements were made on samples <300 mesh at a heating rate of 10 °C/min.

In order to gain further insight into the degradation mechanism, weight loss was studied isothermally at several temperatures over the range 120–240 °C. These results are shown in Figure 4. These curves clearly demonstrate the apparent change in mechanism beween low-temperature (<200 °C) and high-temperature (>200 °C) degradation. Above about 200 °C, the reaction was first order as may be seen in Figure 5, which shows a plot of logarithm of the residual weight as a function of time. Good linear

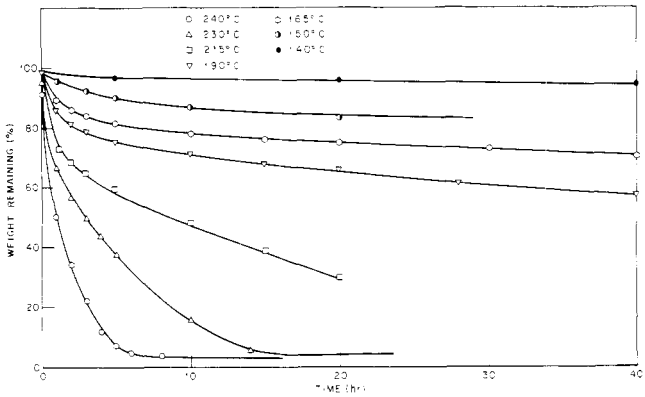


Figure 4. Isothermal weight loss of PBS as a function of temperature.

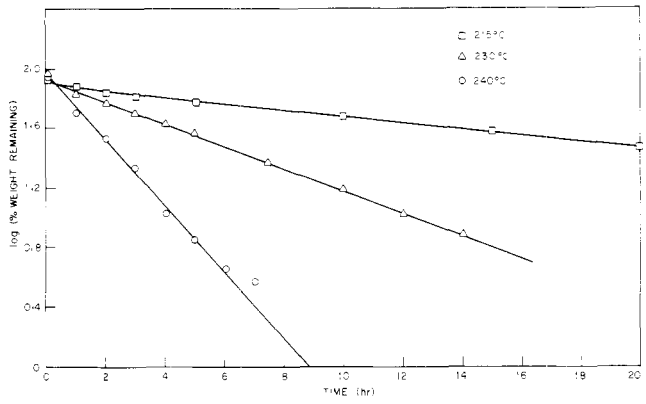


Figure 5. First-order plots of decomposition in "high-temperature" mode calculated from Figure 4.

plots were obtained from which the rate constant, k, could be calculated at each temperature. The activation energy of the process obtained by plotting the logarithm of the rate constant against the inverse of the absolute temperature (Figure 6) was found to be 46.8 ± 1.21 kcal/mol. This is somewhat higher than the activation energy for the degradation of poly(propylene sulfone), which was reported by Naylor and Anderson to be 32 kcal/mol.[14] They also reported that the degradation was first order. First-order kinetics are consistent with a random degradation mechanism and are shown by several polymers that decompose with monomer as the principal product, e.g., poly(tetrafluoroethylene).[15] Various kinetic schemes[16,17] have been devised based on random initiation followed by depropagation and bimolecular termination and result in expressions for the rate of weight loss such as

$$-\frac{dW}{dt} = k_d\left[\frac{2k_i m}{\rho k_t}\right]^{1/2} W \qquad (1)$$

where k_d, k_i, and k_t are rate constants for depropagation, initiation, and termination, respectively; m is the monomer molecular weight, ρ the density, and W the weight remaining at time t. From this equation, the overall activation energy may be expressed in terms of the activation energies for the various steps in the mechanism:

$$E_{tot} = E_d + \tfrac{1}{2}E_i - \tfrac{1}{2}E_t \qquad (2)$$

where E_d, E_i, and E_t are the activation energies for depropagation, initiation, and termination, respectively. The degradation reaction may be written as

poly(1-butene sulfone)(condensed) → butene(g) + SO_2(g)

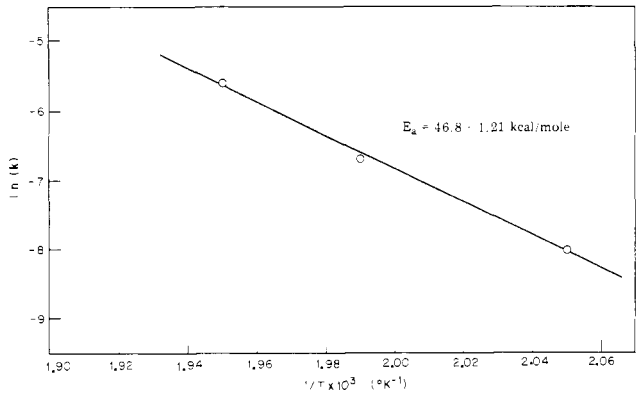


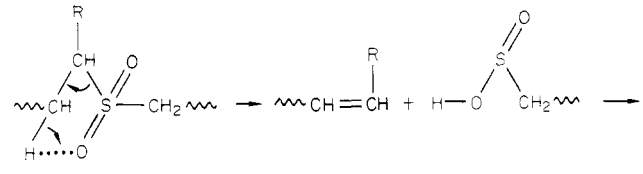
Figure 6. Arrhenius plot of ln k vs. $1/T$.

for which the activation energy for depropagation may be expressed as $E_d = E_p - \Delta H_{gc}$. E_p is the energy of activation for propagation and ΔH_{gc} is the heat of polymerization for formation of polymer in the condensed state from gaseous monomer. ΔH_{gc} is readily calculated at 25 °C from the standard heats of formation of PBS and the gaseous monomers. Using $\Delta H_f°$(PBS) = −101.47 kcal/mol,[18] $\Delta H_f°$(butene(g)) = −0.03 kcal/mol,[19] and $\Delta H_f°(SO_2(g))$ = −70.95 kcal/mol,[19] we calculate $\Delta H_{gc}°$ at 25 °C to be −30.5 kcal/mol. This value is in excellent agreement with that calculated from the expression derived by Brown and O'Donnell,[20] which was $\Delta H_{gc}° = \Delta H_{lc} - \Delta H_{vap}° - \Delta H_{mix}$. Taking average values of heat capacities for PBS ($\bar{C}_p$ = 44.4 (cal/deg)/mol),[21] butene ($\bar{C}_p$ = 25.7 (cal/deg)/mol),[19] and SO_2 ($\bar{C}_p$ = 10.3 (cal/deg)/mol)[19] over the temperature range 25–225 °C, we calculate the value of ΔH_{gc} at 225 °C to be −28.8 kcal/mol. ($\bar{C}_p$ at 225 °C for PBS was obtained by extrapolation of Dainton et al's data above 25 °C;[21] such an extrapolation does not take account of the effect of T_g on C_p but the overall error should be relatively small). Taking a value of 5 kcal/mol for E_p,[22] we obtain a value of 33.8 kcal/mol for E_d. Substituting into eq 2 gives

$$E_i - E_t = 26 \text{ kcal/mol} \qquad (3)$$

There is uncertainty in the literature concerning the activation energy for termination by combination of polymeric radicals in a viscous medium. Like PBS, poly(methyl methacrylate) (PMMA) undergoes extensive depropagation at elevated temperatures, degradation being initiated both at the chain ends and at random. Grassie and MacCallum[23] have shown that the energetic results for PMMA degradation quoted by various authors are self-consistent when the correct thermodynamic parameters are used, from which they obtained a value of 37 kcal/mol for E_t, indicating a diffusion-controlled process for termination. If we assume a similar diffusion-controlled termination in PBS degradation, then from eq 3 we obtain a value of 63 kcal/mol for E_i.

The mechanism of polysulfone degradation has been the subject of considerable debate. Naylor and Anderson[14] found that the decomposition rates of poly(olefin sulfones) increased as the number of hydrogen atoms attached to the carbon atom positioned β to the sulfone linkages increased and suggested a possible β elimination as the initial step as shown below:



H• + SO_2 + •CH_2 ~ → depropagation

A similar mechanism was also invoked by Wellisch et al.[24] in their studies of the thermal decomposition of poly(methylene sulfones). The activation energy for initiation would be considerably lower than 63 kcal/mol, which would require E_t to be somewhat lower than 37 kcal/mol. Grassie and Melville[25] took E_t to be zero in their studies of PMMA degradation in the temperature range 270–300 °C. This is contrary to the results of Jellinek and Luh,[26] who derived a value of E_t of 31.9 kcal/mol for PMMA degradation above 300 °C. The bulk of evidence appears to favor termination being a diffusion-controlled reaction in the molten state with values of E_t greater than at least 20 kcal/mol.

An alternative initiation mechanism involves the simple homolytic scission of the carbon–sulfur bond. It is interesting to note that the value of E_i calculated from the overall activation energy of the degradation reaction and a value of 37 kcal/mol for E_t is of similar magnitude to the dissociation energy of the C–S bond. This would suggest that initiation at temperatures above 200 °C occurs predominantly by random scission of the C–S bonds. However, the value of E_t is too tenuous to permit an absolute assignment of mechanism and additional work on the effect of polymer chain length on the overall activation energy is planned to provide independent evidence of the magnitude of E_i.

Referring again to Figure 4, one can see that below 200 °C there is significant deviation from first-order kinetics, with the rate rapidly decreasing and becoming essentially invariant after several hours. This cannot be due to repolymerization of the monomer as it diffuses through the film because of ceiling temperature considerations (the equilibrium pressure at 140 °C is calculated to be $>10^4$ atm using the data of Brown and O'Donnell;[20] a buildup in pressure of this magnitude is clearly untenable, particularly since the samples were continuously evacuated during degradation). This effect was also observed by Bowmer and O'Donnel,[11] who reported that the rate of degradation of PBS decreased greatly after 2 h at 150 °C. The activation energy calculated with either the initial rates of degradation or the steady-state values determined from the slope of the linear portion of the curves is extremely low, being on the order of 12–14 kcal/mol. Naylor and Anderson[14] also observed a sharp drop in activation energy for the degradation of poly(propylene sulfone) below 200 °C. Crouch and Wicklatz[2] showed plots of the extent of decomposition of PBS as a function of time up to 3 h over the temperature range 160–190 °C. Taking the slopes of their rate curves at the 0.25-h point as an average measure of the initial rate, one obtains an activation energy of ~15 kcal/mol, in good agreement with the present work. These values are in the range to be expected for diffusion of a molecule like SO_2 through a polymer matrix.

It is difficult to see how normal main-chain scission can be the primary mode of degradation since cleavage of a chain at these temperatures would result in extensive unzipping and the production of a large amount of monomer. This is certainly true of radiolytic degradation of PBS at 140 °C[27] and while it is recognized that thermal degradation involves low energies and should be less extensive than radiolytic degradation, one would not expect the degradation rate to decrease as rapidly as it does.

We therefore suggest that degradation takes place in this range by a mechanism that does not create radicals in the main chain. A similar postulate was made by Dainton and Ivin[9] to explain degradation without weight loss in these systems. Apparently, only small amounts of gaseous product are liberated, which diffuse out through the polymer. The results of Bowmer and O'Donnell on PBS degradation at 150 °C are interesting in this regard in that the volatile product yield after 30 min at 150 °C showed approximately 3 times more olefin produced than sulfur dioxide whereas radiolysis produces approximately equimolar proportions.[28] Further work is planned to investigate the degradation products as a function of temperature to try to clarify this picture.

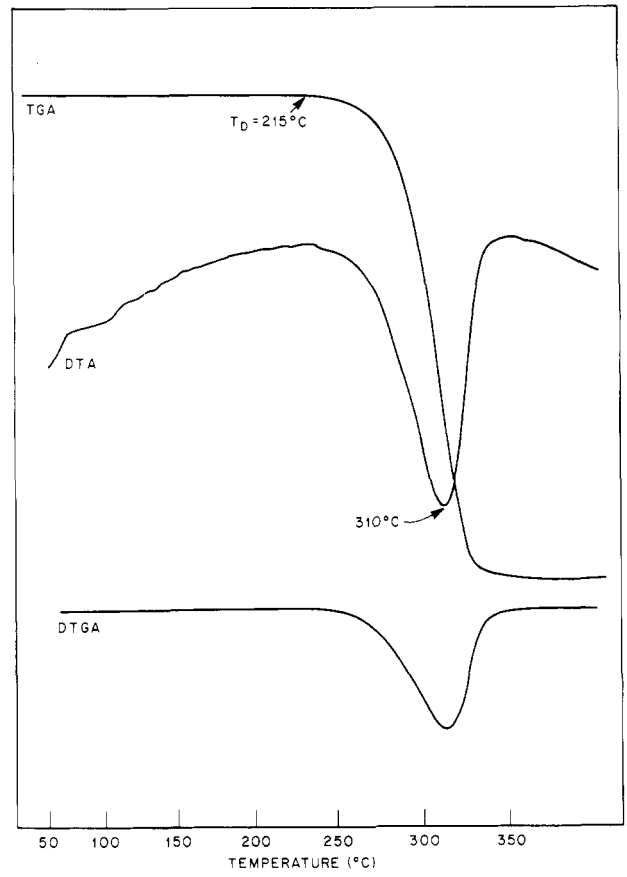


Figure 7. Simultaneous TGA, DTA, and DTGA thermograms for PBS after prior annealing at 140 °C for 72 h.

One possibility is that degradation in the low-temperature range takes place at weak links located randomly in the chain. If so, it might be expected that they could be removed during isothermal heating anywhere within the low-temperature range and that on a subsequent TGA run, only the high-temperature decomposition should be evident. Figure 7 shows the results from a TGA run on a sample that had been heated isothermally for 72 h at 140 °C. The weight loss during the isothermal period was only 5% yet the low-temperature decomposition mechanism is entirely absent. Under these conditions, the new decomposition temperature is 215 °C and it is interesting to note that this coincides with the temperature quoted by Brown and O'Donnell[10] for the onset of degradation.

The kinetic parameters of the high-temperature degradation can be obtained from a single TGA thermogram. In particular, the difference differential method of Freeman and Carrol[29,30] has been widely used to determine the order and activation energy of the degradation. The rate of degradation (R_d) may be written as follows:

$$R_d = -\frac{dW}{dt} = kW^n = \frac{A}{HR}e^{-E_d/RT}W^n \qquad (4)$$

where k is the rate constant, A the preexponential factor, HR the heating rate, W the weight remaining, E_d the ac-

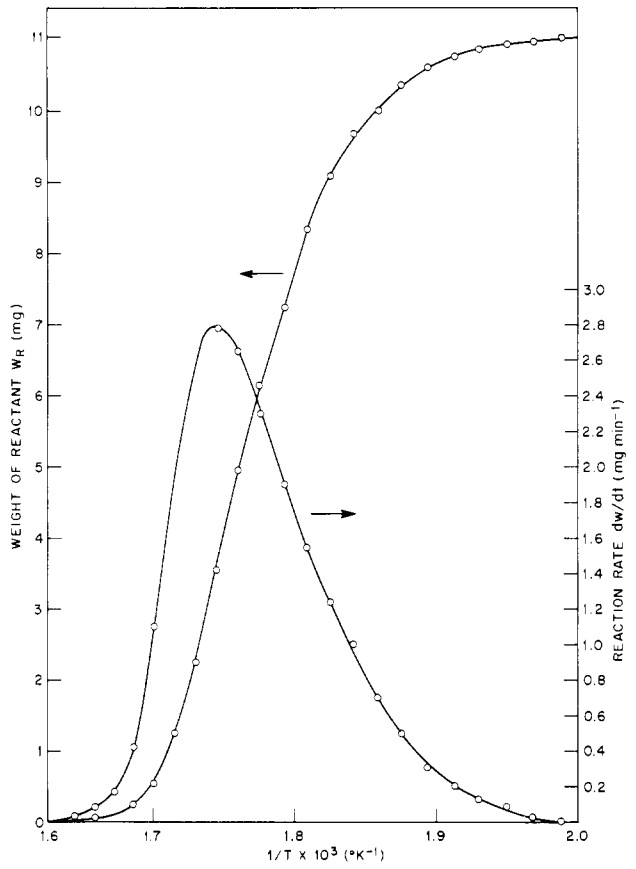


Figure 8. Plots of weight remaining and rate of weight loss as a function of $1/T$ calculated from Figure 7.

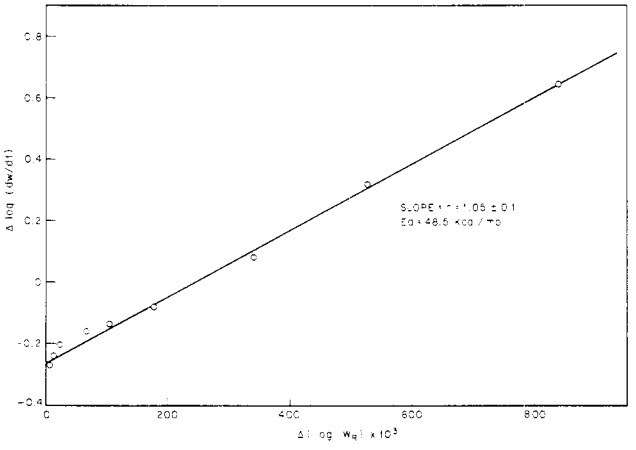


Figure 9. Kinetics of thermal decomposition plotted according to the method of Freeman and Carrol.

tivation energy, n the order of the reaction, R the gas constant, and T the absolute temperature. When eq 4 is applied at two different temperatures and the resultant expressions subtracted from one another, eq 5 is obtained:

$$\Delta(\log R_d) = n[\Delta(\log W)] - [E_d/2.303R]\Delta(1/T) \quad (5)$$

W and dW/dt are plotted against $1/T$ in Figure 8, from which the necessary ordinates of R_d and W at constant $\Delta(1/T)$ can be obtained. As can be seen in Figure 9, a plot of $\Delta(\log R_d)$ vs. $\Delta(\log W)$ at constant $\Delta(1/T)$ is linear with a slope n of 1.05. The activation energy calculated from the intercept is 48.5 kcal/mol and is in good agreement with the value determined from the isothermal study. Our suggestion that the low-temperature degradation takes place randomly at weak links within the chain is further

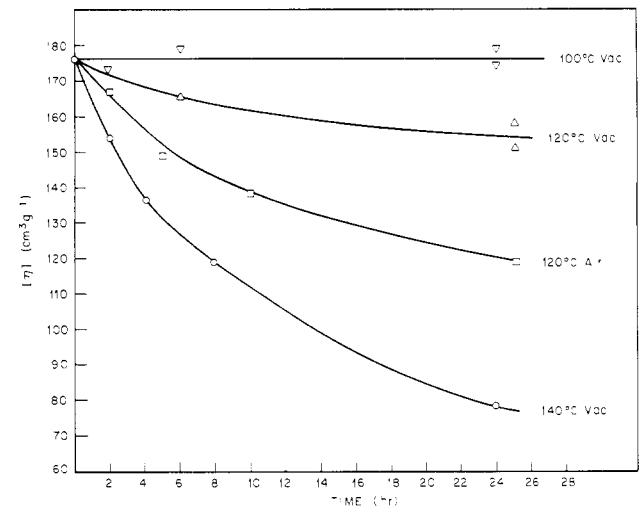


Figure 10. Variation of intrinsic viscosity with time as a function of temperature.

substantiated by the results of Figure 10, which shows the effect of temperature on the intrinsic viscosity. At 140 °C there is a rapid drop in intrinsic viscosity even though the weight loss is very small. If the initiation site were at the end of a chain, no such drop would be observed.

Conclusions

PBS shows a two-step degradation mechanism, the initial degradation occurring in the temperature range 130–200 °C and the major degradation taking place at higher temperatures. Isothermal TGA and DTA studies coupled with the temperature dependence of molecular weight indicate minimal degradation occurs at temperatures below 120 °C over reasonable time periods. This temperature thus defines the upper prebake temperature for PBS when used as a resist.

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Specific Volumes of Styrene–Butadiene Block Copolymers. 2. Effect of Solvent Sorption on Density Measurements

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ABSTRACT: The slight deviations from additivity in the specific volumes of butadiene–styrene block copolymers previously reported are now shown to be smaller than the previous values when corrections are made for the extent of swelling of the samples due to sorption by the sample of the water–2-propanol in the density gradient column.

In our previous paper[1] it was shown that specific volumes of block copolymers of butadiene and styrene calculated from density measurements in a density gradient column almost exactly followed the linear additivity law

$$v_t = x_A v_A + (1 - x_A) v_B \quad (1)$$

where v_t is the specific volume of the block copolymer, v_A and v_B are the specific volumes of the styrene and butadiene homopolymers, and x_A is the weight fraction of the styrene segments. The slight deviations from additivity, whose maximum amounted to 0.0027 $cm^3\ g^{-1}$ at 25 °C for the 61.2 wt % styrene sample, were interpreted as resulting from a lower density in the thin interfacial layers between the butadiene and styrene blocks. At that time no correction was made for a possible swelling of the polymer samples due to sorption of either water or 2-propanol while in the density gradient column.

This paper will include a brief discussion of new swelling measurements as well as of the kinetics of the sorption process and data for the sorption as a function of the 2-propanol concentration in the density gradient column.

Experimental Section

Materials. The pure polybutadiene (PB) and pure polystyrene (PS) came from General Tire and Rubber Co. as in the previous paper. Kraton 1101, kindly donated by Shell Development Co., contained 30 wt % styrene and 70 wt % butadiene segments and Kraton 1102 28 wt % styrene and 72 wt % butadiene. The microstructure of the pure PB was 38% *cis*-1,4-butadiene, 54% *trans*-1,4-butadiene, and 8% vinyl. Its weight-average molecular weight was 225×10^3 and its intrinsic viscosity, $[\eta]$, 2.32 dL/g as measured in benzene at 25 °C. The microstructure[2] of the butadiene segments in the Kraton samples was very similar to that of the pure PB, namely, 41% *cis*-1,4-butadiene, 49% *trans*-1,4-butadiene, 2% 1,2-butadiene, and 8% vinyl. The PS was the same as that used previously.

The Kraton samples were repurified by dissolving them in toluene and reprecipitating in methanol. The precipitated polymer was then washed with methanol and dried at 80 °C for more than 2 h to constant weight in a vacuum oven. Slabs were made of the purified Kraton 1101 and 1102 by heating samples in vacuo at 120 °C between glass plates held apart by a thin spacer but with a lead weight on the top glass plate so as to squeeze out excess polymer. The thickness of the slabs was about 60 mils. The slabs of PS were transparent, indicating the absence of cavities, and the block copolymers were only slightly turbid.

Sorption. To determine the extent of sorption of the water and 2-propanol, the liquids of the density gradient column, previously weighed samples of the polymers were suspended over the water–2-propanol solution in Erlenmeyer flasks kept in a constant temperature bath at 25 °C. Eight days in the vapor phase was sufficient to reach sorption equilibrium as determined by weighing in a weighing bottle. The sorption studies were carried out with a mixture of water and 2-propanol containing 35 wt % 2-propanol. This mixture has a density of about 0.9375 g cm^{-3} at 25 °C, which is within the range of the block copolymers studied here. As shown below the weight of vapors sorbed by Kraton 1101 does not change very much over the range of solvent composition from 10 to 40 mol % 2-propanol, or from 27.3 to 69 wt %. Desorption was followed by merely measuring the decrease in weight of the sample on exposure to air.

Swelling. To measure the swelling we projected an image of a small piece of solid polymer on a long piece of chart paper affixed to a wall. The polymer image or shadow was produced by putting the piece of polymer in a 35-mm Kodak Ektagraphic slide projector, Model E-2. A brass frame, the size of a 35-mm slide, with two hook-shaped brass rods in the middle of the opening was constructed. The small rod-shaped polymer sample could be laid on the brass hooks and its shadow then projected on the chart paper about 20 feet away. The brass frame was inserted into the projector in the slot where the 35-mm slides are normally inserted. Thus the position was reproducible and the lens of the projector could be moved until the brass holder was in focus. The polymer sample could then be laid on the hooks and the length of the shadow quickly measured before the sorbed vapors had time to evaporate to any significant extent. The size of the image was about 130 cm long, resulting in a magnification of the 1.5-cm-long sample about 85-fold. Actually, in practice it turned out that the length measurements were more reproducible than the weight measurements. After the length of the polymer saturated with the vapors was measured, the sample was dried in a vacuum oven at 70 °C for 2 h, at which time the measured length became the same as that before the sorption.

To estimate the changes in density from the length changes it is necessary to assume that the swelling occurs isotropically so that the ratio of volume after swelling, v_a, to volume before swelling, v_b, can be set equal to l_a^3/l_b^3, the cube of the ratio of length after swelling to that before. In a partial test of this assumption a square piece of polymer was cut from the slabs mentioned above and the swelling measured along both the length and width axes. No difference in the l_a^3/l_b^3 ratios greater than the experimental uncertainties could be detected; see Table II. However, it was not possible with our equipment to measure accurately the thickness of the sample, so we can only state

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