Thermal and Oxidative Degradation of Poly(methyl methacrylate): Weight Loss

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ABSTRACT: The effects of gas-phase oxygen on the weight loss of poly(methyl methacrylate) (PMMA) were studied by comparing weight loss behavior of PMMA degraded in nitrogen with that of PMMA degraded in air. Thermogravimetry (TG) and isothermal heating experiments were conducted to obtain kinetic constants for the degradation of PMMA. The results show that there are two distinct effects of oxygen on the weight loss of PMMA; one is an increase in PMMA stability at low temperatures and the other is a destabilization of PMMA at high temperatures by enhanced random scission. There are two reaction stages for the weight loss from PMMA degraded in nitrogen and four reaction stages for PMMA degraded in air. These four reaction stages are, however, caused mainly by impurities in the sample. The effects of purification of the commercial PMMA on the weight loss are small for samples degraded in nitrogen, but they are significant for samples degraded in air.

Introduction

In our previous study,[1] changes in the molecular weight of PMMA degraded in nitrogen and in air were studied in order to clarify the degradation mechanism and to obtain degradation kinetic constants of PMMA. These results are essential for the development of theoretical models to predict the gasification rates of PMMA exposed in various fire environments. Measurements of the molecular weight showed that the number-average degree of polymerization of PMMA degraded in air decreased more rapidly than that of PMMA degraded in nitrogen. The activation energy for the random chain scission is about 4 times lower for PMMA degraded in air than that for PMMA degraded in nitrogen.

The weight loss from PMMA is the final result of a complex degradation process consisting of chain initiation reactions, depropagation reactions, termination reactions, and transport of the decomposition products through softened PMMA from the inside of the sample to the outside.[1] Hence, global kinetic constants determined from the weight loss of the sample and our previous data obtained from molecular weight measurements are combined to clarify the degradation mechanism of PMMA.

From previous studies[2-4] of weight loss it has been inferred that there are two types of chain initiation reactions for PMMA degraded in a vacuum. One is chain-end initiation, due to double-bond-terminated polymer chains, and the other is initiation at random positions by chain scission. There are few reported studies of the effects of gas-phase oxygen on weight loss from PMMA. Reported results are not consistent with each other. An early Russian study[5] reported that degradation of PMMA was observed in air at 200 °C but not in nitrogen. Another study[6] reported that oxygen has a strong inhibiting effect on the degradation of PMMA powders but accelerates the degradation of block specimens; apparently, gas-phase oxygen displays a dual character in degradation. A recent study[7] indicated that there are no effects of gas-phase oxygen on the weight loss of PMMA as seen by TG. On the other hand, our study[8] showed that the rates of weight loss from bulk PMMA specimens heated by external thermal radiation increased substantially with an increase in gas-phase oxygen concentration. Futhermore, our measurements of molecular weight show that the activation energy for the random scission of polymer chains is about 4 times lower for PMMA degraded in air than that for PMMA degraded in nitrogen.[1] This result indicates that one should expect strong effects of oxygen on the weight loss of PMMA, because the rate of chain initiation by random scission controls the rate of weight loss for PMMA.[1] Thus, the literature is ambiguous about whether there are effects of gas-phase oxygen on the weight loss of PMMA. The objective of this paper is to clarify this ambiguity.

In this study, the weight loss of PMMA degrading in nitrogen and in air was measured by TG at various heating rates and also by isothermal heating experiments at various temperatures. The effects of oxygen on weight loss were ascertained and values of global kinetic constants for degradation reactions of PMMA were determined.

Experimental Section

The PMMA material used in this study was commercial Plexiglas G (Rohm and Haas, Inc.);[28] this material is commonly used for studies of ignition and flame spread. According to the manufacturer, the material contains about 0.1% of a parting agent, 0.5–0.7% of monomer, and a small quantity of an ultraviolet absorber. It was polymerized by free radical initiation. Therefore, it is expected that initially some polymer chains are terminated with a double bond. The number-average molecular weight of the material is 402 000.[1] The samples were disk-shaped, about 5.5 mm in diameter and about 200 μm thick, and were milled from a commercially available sheet originally 900 μm thick. The weight of the sample disks ranged from 5.3 to 6.1 mg.

The weight loss from the sample was measured by TG and isothermal heating by using a Mettler TA2000 thermoanalyzer. A prebaked thin aluminum cell without a lid was used as the sample container for both TG and the isothermal heating experiments. For the isothermal heating experiments, the samples were initially heated at the maximum programmed heating rate (nominally 200 °C/min) from room temperature to a selected temperature and then held at this temperature. The fluctuation of the temperature around the selected temperature was within 1 °C. Despite use of the maximum programmed heating rate, the actual heating rate was much lower. The actual heating time to the selected temperatures in the range 217–375 °C used in this study took 6–7 min, which was necessary to avoid any overshooting of the temperature above the specified value. Time zero for the isothermal heating experiments was taken as the instant when the temperature reached the selected value.

The experiments were conducted with two different atmospheres, air and nitrogen. For air, two flow rates of about 25 and 90 mL/min were respectively introduced into the furnace through the top and the bottom and were discharged through an outlet on the side of the furnace. Before nitrogen was substituted for air, the furnace and the TG system dead volume were subjected to two repeated cycles of evacuation and filling with nitrogen to

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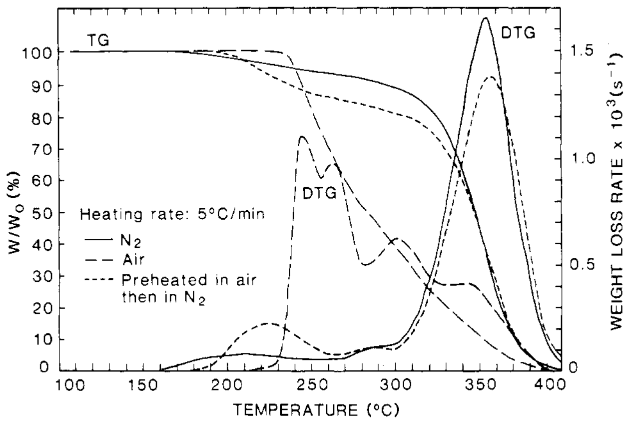

Figure 1. TG and DTG curves of PMMA degraded in nitrogen and in air.

atmospheric pressure. The oxygen concentration in the furnace was less than 0.05%. The sample was then heated in a nitrogen flow of about 90 mL/min which was introduced from the bottom of the furnace.

The weight of the sample, its temperature, and the time were simultaneously recorded by a computer. At first, a base-line experiment with the empty cell was conducted, and then a sample experiment was repeated for each TG and isothermal heating experiment. The actual weight of the sample was calculated from the difference between the sample experiment and the base-line experiment. This procedure removed the artificial change in the weight caused by buoyancy generated by heating the furnace.

Results

Thermogravimetry. Effects of Gas-Phase Oxygen. Typical results for TG and derivative thermogravimetry (DTG) on PMMA degraded in nitrogen and in air are shown in Figure 1. The DTG results were obtained by taking the time derivative, $d(W/W_0)/dt$, of the ratio of the sample weight, W, to the initial sample weight, W_0. The DTG curve for the sample degraded in nitrogen indicates two main reaction stages occur during the degradation. The first reaction stage appears around 160 °C and ends around 300 °C. The first reaction stage can be divided into two steps: one is a small deviation from the base line in the range 160–240 °C; the other is a small peak around 290 °C. The second main reaction stage appears from about 300 to 400 °C. This DTG curve for the sample degraded in nitrogen agrees well with the thermal volatilization analysis (TVA) curve reported by McNeil[9] for PMMA prepared by free radical polymerization. However, his other two curves with PMMA prepared by anionic polymerization did not have a peak around 290 °C. Anionically polymerized PMMA does not have the unsaturated double bond at one end of the polymer chain. He concluded that the second small peak of the first reaction stage was caused by end initiation from the unstable ends and that the second main reaction stage was caused by unzipping initiated by random scission. The initial small peak of the first reaction stage, between 160 and 240 °C in Figure 1, was also observed in his TVA curves of PMMA prepared by both polymerization processes. McNeil did not describe the cause of this peak. Impurities in our commercial sample caused this peak in our experiment. As discussed in a later part of this paper, purified PMMA did not show any significant weight loss at these low temperatures.

The TG curve for PMMA degraded in air shows a very rapid weight loss starting around 230 °C and its DTG curve shows four consecutive peaks, indicating a complex oxidation process. Comparison of TG and DTG curves of PMMA degraded in air with those of PMMA degraded in nitrogen shows that gas-phase oxygen increased the PMMA stability by causing a 50 °C increase in temperature for initiation of the weight loss. However, above 230 °C, gas-phase oxygen destabilizes the sample significantly, as shown in Figure 1. Since the thermal oxidative degradation of PMMA is initiated by random scission,[1,5] the destabilization of PMMA by gas-phase oxygen is due to a significant oxidative enhancement of random scission compared with thermally initiated random scission. The stabilization of the early stage of PMMA degradation by oxygen might be due to the suppression of the end initiation process as a result of some oxygen-induced modification of the unsaturated double bond at one end of the polymer chain or scavenging of polymeric carbon-centered radicals by oxygen at these low temperatures. These dual roles of gas-phase oxygen in the weight loss process of PMMA, and stabilizing role in the first stage of degradation at low temperatures and a destabilizing role in the second stage of the degradation at high temperatures, might explain the conflicts among the previous studies. The effects of gas-phase oxygen on PMMA weight loss depend on the temperature range used in the study.

In order to obtain further information on the effects of gas-phase oxygen on PMMA weight loss, a sample was preheated to 200 °C with a heating rate of 1 °C/min in air. The sample was then cooled slowly to room temperature and the furnace was evacuated twice to replace air with nitrogen. The weight loss of the sample during this preheating period was negligible. The sample was then heated to 400 °C with a heating rate of 5 °C/min in nitrogen. TG and DTG curves of the preheated sample degraded in nitrogen are shown in Figure 1 with dashed lines. These curves are basically similar to those of PMMA degraded in nitrogen without the preheating process except at the early stage of weight loss. The preheating of the sample in air increased the threshold temperature of the first stage weight loss about 20 °C relative to the value of 160 °C for the sample without preheating. Furthermore, the maximum weight loss rate of this first reaction stage is about twice as great as that for the sample without preheating. It was observed in our study[1] that a small number of chain scissions occur around 200 °C in air without any significant weight loss. Thus, we infer that the increase in weight loss rate in nitrogen for the preheated sample is caused by chemically active sites (for example, oxygenated groups) generated during the preheating. The effects of the preheating enhance only the first reaction stage of the weight loss and not the second reaction stage. The chemically active sites are apparently consumed or deactivated during the cooling process.

Determination of Kinetic Constants. The DTG curve of PMMA degraded in air exhibits four reaction stages and the DTG curve of PMMA degraded in nitrogen shows two reaction stages, as seen in Figure 1. TG measurements in PMMA were carried out at several heating rates to determine the global kinetic constants of these reaction stages. DTG curves for PMMA degraded in nitrogen and in air are shown in Figures 2 and 3, respectively.

There are many methods to determine the kinetic constants from these results as described in ref 10. Although "differential" methods based on the rate of weight loss vs. temperature have an inherent weakness (they are sensitive to experimental scatter), more sophisticated balances and electronic signal-processing systems and computerized data collection have become available. Consequently, the "differential" method, based on rate of weight loss, has become as accurate as the "integral" methods (use of weight loss directly). Since the four reaction stages shown

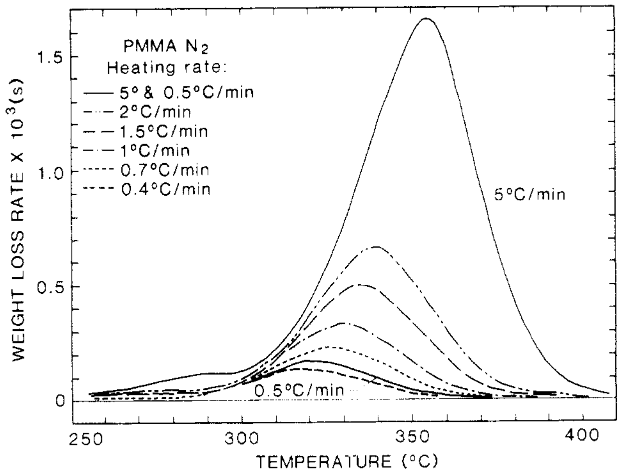

Figure 2. DTG curves of PMMA degraded in nitrogen at various heating rates.

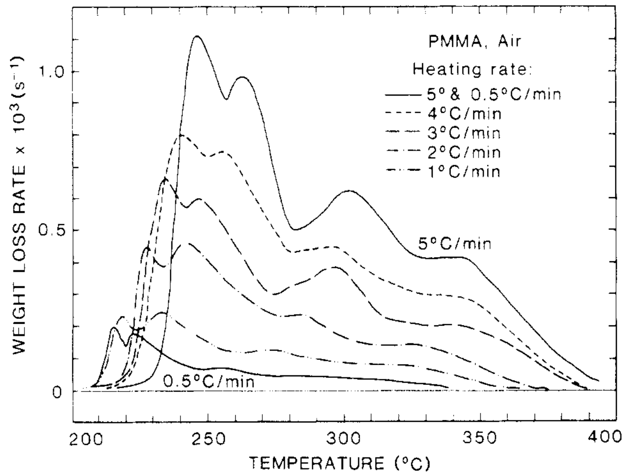

Figure 3. DTG curves of PMMA degraded in air at various heating rates.

in Figure 3 are not completely separated from each other, the relatively simple Kissinger method[11] was used to determine kinetic constants.

According to the expression derived by Kissinger

$$\ln (\phi/T_m^2) = \ln (nRAW_m^{n-1}/E) - E/RT_m$$

where ϕ is the heating rate in the TG experiment, T_m is the temperature at the maximum rate of weight loss, R is the universal gas constant, E is the activation energy, A is the preexponential factor, W_m is the weight of the sample at the maximum rate of weight loss, and n is the apparent order of the reaction with respect to the sample weight. The value of E can be determined from a plot of $\ln (\phi/T_m^2)$ vs. $1/T_m$ at various heating rates. The particular advantage of this method is that it requires only the temperature at the maximum rate of weight loss to determine the value of E and one need not a priori assume the order of the reaction. The disadvantage of this method is that it is sometimes difficult to determine the maximum rate of weight loss accurately. For example, the DTG for the first reaction stage of PMMA degraded in nitrogen exhibits a very broad, gentle curvature and it was very difficult to determine the exact location of the maximum weight loss rate. Additionally, the DTG for the fourth reaction stage of PMMA degraded in air does not have a sharp peak at slow heating rates; the location of the maximum weight loss rate cannot be determined. Thus, activation energies of these reaction stages cannot be determined from this TG study.

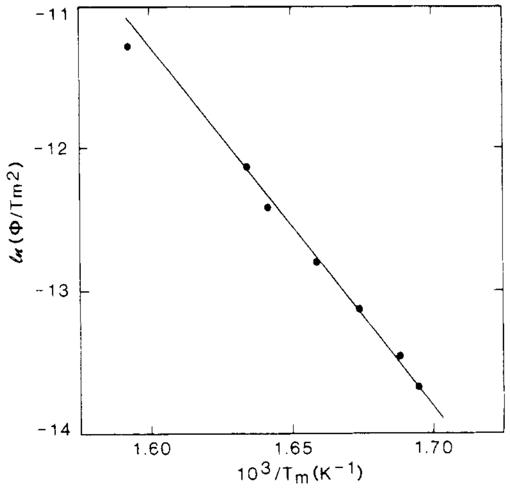

Figure 4. Kissinger plot of PMMA degraded in nitrogen by TG.

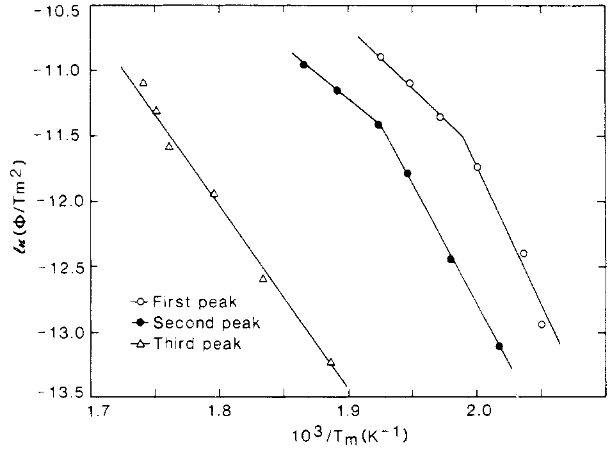

Figure 5. Kissinger plot of PMMA degraded in air by TG.

A plot of $\ln (\phi/T_m^2)$ vs. $1/T_m$ for the second reaction stage of weight loss from PMMA degraded in nitrogen is shown in Figure 4. The corresponding plots for the first, the second, and the third reaction stages of weight loss from PMMA degraded in air are shown in Figure 5. In Figure 4, a reasonable single straight line was obtained, but the plots in Figure 5 consist of two straight lines for the first and the second reaction stages of weight loss. At high values of T_m (high heating rates, >3 °C/min), the slopes of these latter two straight lines become much less than those at low values of T_m (low heating rates, <3 °C/min). The decrease in the slope of this plot may be caused by rate limitations due to the transport process of oxygen through the softened PMMA from the surface to the inside of the sample or to the transport process of decomposition products through the softened PMMA from the inside of the sample to the outside of the sample. In our previous study,[1] it was demonstrated that the sample thickness (200 μm) used in this study is thin enough so that inward diffusion of oxygen is not the rate-controlling step for weight loss in the range of temperatures where the first and the second reaction states of the weight loss occur. However, the outward transport of decomposition products, mainly monomer, may become the rate-controlling process for weight loss.[8,12] The observation of many small bubbles in the isothermally heated samples[1] indicates that the transport of monomer through the softened PMMA occurs by convection of monomer bubbles as well as by diffusion. Thus, in TG at high heating rates, it appears that the characteristic time for monomer transport becomes greater than that of the degradation. Above a 3

Table I
Kinetic Constants of TG Weight Loss from PMMA Determined by Kissinger's Method

environment	reaction stage	ϕ, °C/min	E,[a] kJ/mol	A, s^{-1}
nitrogen	second		210	2.1×10^{15}
air	first	<3	174	4.8×10^{15}
		≥3	75	9.0×10^{4}
	second	≤3	156	1.8×10^{13}
		>3	62	2.6×10^{3}
	third		114	7.4×10^{7}

[a] It is expected that the accuracy of these values is ±10%.

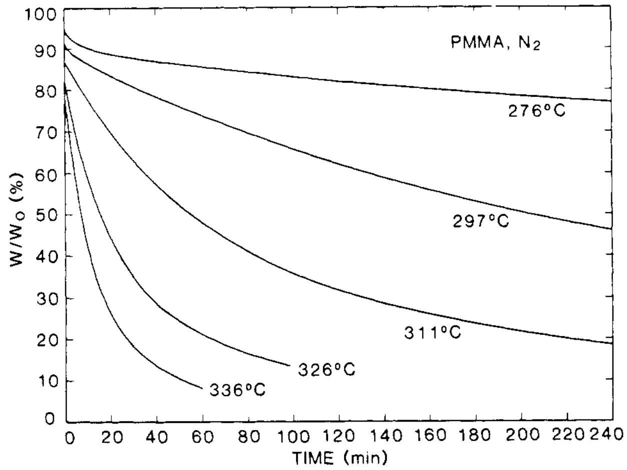

Figure 6. Weight loss curves of PMMA degraded in nitrogen by isothermal heating at various temperatures.

°C/min heating rate, the transport process of monomer apparently becomes the rate-controlling process for the first and second reaction stages of weight loss from PMMA degraded in air with the sample thickness used in this study.

As shown in Figure 5, the third reaction stage of weight loss does not show any change in slope. The molecular weight of PMMA degraded in air decreases very rapidly with an increase in heating time.[1] The decrease in molecular weight reduces the melt viscosity of softened PMMA and enhances the outward transport of monomer bubbles. For the third reaction stage of weight loss, the molecular weight of the softened PMMA evidently becomes so low that the transport of monomer by bubbles (or by diffusion) is no longer the rate-controlling process of weight loss.

Activation energies for the second reaction stage of the weight loss of PMMA degraded in nitrogen and for the first three reaction stages of PMMA degraded in air were determined from the slopes of the plots shown in Figures 4 and 5. The results are listed in Table I. Values of preexponential factors for each reaction stage were calculated, assuming a first-order reaction for all cases. These values will be compared later with those derived from our isothermal heating experiments.

Isothermal Heating. The weight loss from PMMA during isothermal heating was measured at ten different temperatures ranging from 244 to 375 °C for PMMA degraded in nitrogen and at nine different temperatures from 217 to 287 °C for PMMA degraded in air. These weight loss curves are shown in Figures 6 and 7. Five of the measured curves are not included in Figure 6 and two curves are not included in Figure 7 to keep these figures from becoming too crowded. These figures show clearly that, at high isothermal temperatures, a significant amount of weight loss occurs before the sample and furance temperature reach the specified isothermal temperature. This was due to limitations in furnace heating rate as described in the Experimental Section. The weight loss from PMMA degraded isothermally in air is much faster than that from PMMA degraded isothermally in nitrogen. This observation is consistent with the results obtained by TG and also with the results of our molecular weight study in which the molecular weight of PMMA degraded in air decreases much faster with heating time than that of PMMA degraded in nitrogen.[1]

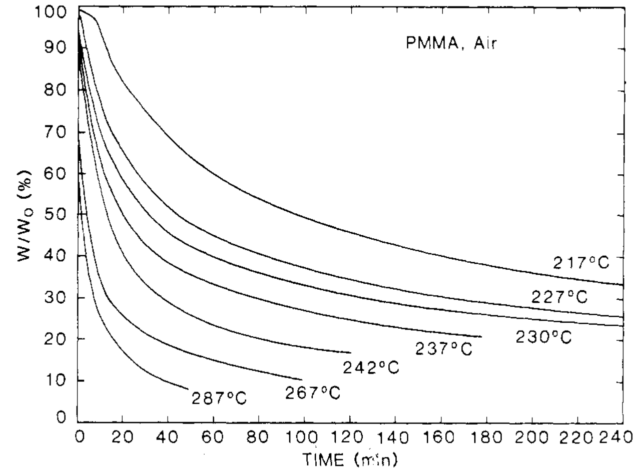

Figure 7. Weight loss curves of PMMA degraded in air by isothermal heating at various temperatures.

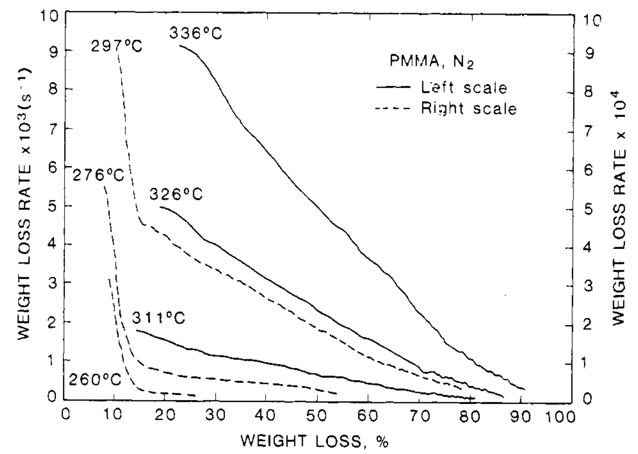

Figure 8. Plots of weight loss rate against weight loss for PMMA degraded in nitrogen by isothermal heating.

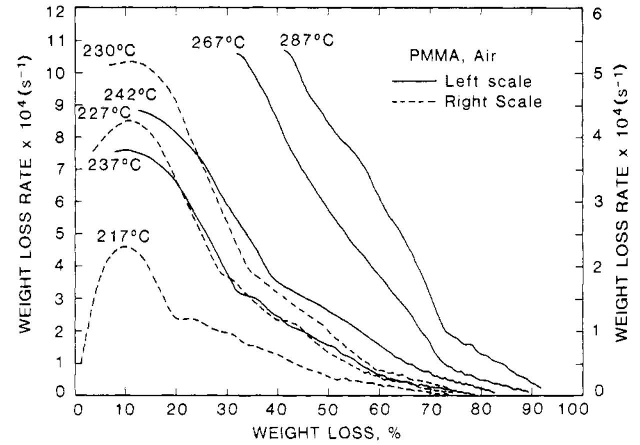

Figure 9. Plots of weight loss rate against weight loss for PMMA degraded in air by isothermal heating.

In order to determine the degradation kinetic constants based on PMMA weight loss, rates of weight loss were calculated from the data shown in Figures 6 and 7. The

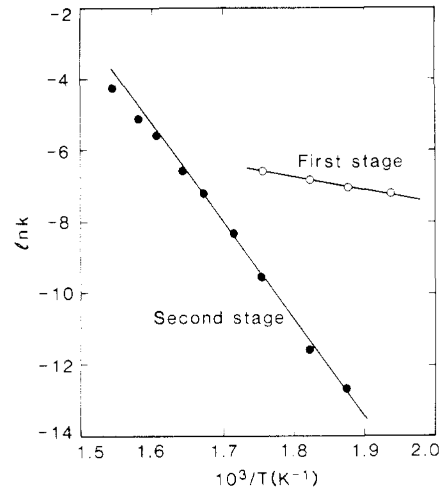

Figure 10. Arrhenius plots for weight loss of PMMA degraded in nitrogen by isothermal heating.

Table II
Kinetic Constants of Weight Loss of PMMA Determined from Isothermal Heating Experiment

environment	reaction stage	temp range, °C	E,[a] kJ/mol	A, s^{-1}
nitrogen	first		31	1.1
	second		224	2.9×10^{16}
air	first		68	1.9×10^{4}
	second	≤237	144	6.8×10^{11}
		>237	51	1.6×10^{2}
	third	≤237	125	2.2×10^{9}
		>237	57	1.9×10^{2}

[a] It is expected that the accuracy of these values is ±10%.

calculated rates of weight loss are plotted against the percentage weight loss in Figures 8 and 9. Rates of weight loss for a small weight loss percentage could not be determined above 297 °C due to the initial weight loss of the sample during the preheating period. The weight loss from PMMA degraded in nitrogen undergoes two reaction stages represented by two different nearly straight lines, i.e., two apparently first-order reactions with respect to the sample weight, as shown in Figure 8. The steep slope of the first reaction stage (below 15% weight loss) shows that the reaction is fast. The second reaction stage (over 15% weight loss) has a more gentle slope, indicating a slower reaction. We interpret the first reaction stage as being due to end-initiated reactions and to gasification of the impurities in the sample; the second reaction stage is attributed to random scission initiation. Degradation rate constants (k), based on a first-order reaction, for the first and second reaction stages were determined from the slopes of the two straight-line segments at various temperatures.

Arrhenius plots of ln (k) vs. $1/T$ are shown in Figure 10. For the second reaction stage, the plots yield straight lines except at high temperatures. The deviation from the straight line at high temperatures is probably caused by an increasing role of the transport processes of degradation products as discussed in the previous section. Values of the calculated activation energies for both reaction stages determined from the slopes of the straight lines are listed in Table II.

The relationship between the weight loss rate and the percentage weight loss for PMMA degraded in air is more complex than that for PMMA degraded in nitrogen, as shown in Figure 9. There are four reactions, all apparently first order, with respect to the sample weight. The first reaction stage proceeds up to 25–35% weight loss, the second reaction stage from roughly 30 to 65%, and the third reaction stage from roughly 65 to 85%. The fourth reaction stage appears after about 85% of the sample is lost. The weight loss rate of the fourth reaction stage is so low that the fourth reaction stage is not shown in Figure 9. As discussed in the previous section, four reaction stages of weight loss were also seen by TG. It is not clear that there is a one-to-one correspondence of reaction stages between the TG study and the isothermal heating experiment.

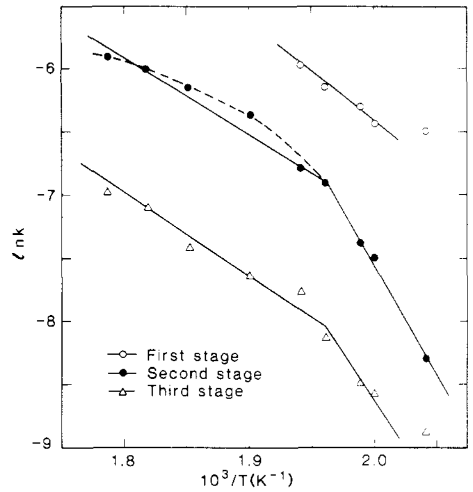

Figure 11. Arrhenius plots for weight loss of PMMA degraded in air by isothermal heating.

The degradation rate constants for each of the first three reactions at various temperatures are determined from the slope of each nearly straight-line segment in Figure 9. Arrhenius plots of the decomposition rate for each reaction stage are shown in Figure 11. The second and third reaction stages are represented by two straight lines instead of one. This trend is consistent with that observed in the TG study, shown in Figure 5. Once again we infer that the decrease in the slope of the straight line at high temperatures is caused by slow transport of the decomposition products coming from a fast chemical degradation process. The slope of the first reaction stage is close in value to those for the second and third reaction stages at high temperatures. Therefore, it is expected that the first reaction stage of the weight loss shown in Figure 11 is also limited by the outward transport of the degradation products. The activation energies determined from the slopes of the straight-line segments for each reaction stage are listed in Table II.

Discussion

Equation of Weight Loss Rate. In the isothermal heating experiments, the rate of weight loss from PMMA degraded in nitrogen decreased linearly with PMMA weight loss. This indicates an apparent first-order reaction over several segments of the weight loss. Weight loss from a polymer is generally the result of chain initiation, depropagation, transfer, and termination reactions plus the outward transport process of degradation products. Since there are no tertiary hydrogens in the PMMA structure, intermolecular chain transfer can be neglected in the PMMA depolymerization process.[13] Although there are vigorous and complete depolymerization models[14,15] reported in the literature, a simple approximate analysis was carried out to demonstrate that weight loss from PMMA degraded isothermally can be expressed by an apparent first-order reaction.

It is assumed in this analysis that the transport of degradation products is not the rate-controlling step in the weight loss and that any polymer radical has the same reactivity as a monomer radical. The weight loss caused by end initiation is less than 15% of the sample weight for PMMA degraded in nitrogen. The major weight loss for PMMA degraded in nitrogen is caused by random scission initiation.[1] Therefore, in the calculation, only random scission initiation is considered. Both first-order termination and second-order termination by disproportionation are also assumed. If the termination reaction is first order, the change in radical concentration with respect to time can be expressed as

$$d[R_n]\bar{V}/dt = \{2k_{ir}\sum_{i=n+1}[M_i] + k_{dp}([R_{n+1}] - [R_n]) - k_t[R_n]\}\bar{V} \quad (1)$$

where $[R_n]$ and $[M_n]$ are polymer radical concentration and polymer molecule concentration per unit volume, respectively.[15] $\bar{V}$ is the sample volume and k_{ir}, k_{dp}, and k_t are the rate constants for the random scission initiation, depropagation, and termination reactions, respectively. Subscript n is the number-average degree of polymerization. The summation of the above equation becomes

$$d\sum[R_n]\bar{V}/dt = \{2k_{ir}\sum\sum_{i=n+1}[M_i] + k_{dp}\sum([R_{n+1}] - [R_n]) - k_t\sum[R_n]\}\bar{V} \quad (2)$$

The second term on the right-hand side of the above equation is much smaller than the first term when the initial number-average degree of polymerization is much larger than zip length and it can be neglected. Redefining total number of radicals

$$\sum[R_n]\bar{V} = R$$

Then eq 2 becomes

$$dR/dt = 2k_{ir}\sum\sum[M_i]\bar{V} - k_tR \quad (3)$$

The physical meaning of $\sum\sum[M_i]\bar{V}$ is the total number of linkages in the polymer molecules, which is defined as L.

Then eq 3 becomes

$$dR/(L\ dt) = 2k_{ir} - k_t(R/L) \quad (4)$$

If the termination is second order, by disproportionation, eq 1 can be expressed as

$$d[R_n]\bar{V}/dt = \{2k_{ir}\sum_{i=n+1}[M_i] + k_{dp}([R_{n+1}] - [R_n]) - k_t[R_n]\sum[R_i]\}\bar{V} \quad (5)$$

Similar to the above procedure of summation of eq 5 and the approximation, eq 5 becomes

$$\frac{dR}{L\ dt} = 2k_{ir} - \frac{k_tR^2}{L\bar{V}} \quad (6)$$

The rate of weight loss can be expressed as[15]

$$dW/dt = -m_0\{k_{dp}[R_2] + 2k_{ir}\sum[M_i] + k_{dp}\sum[R_i]\}\bar{V} \quad (7)$$

where m_0 is the molecular weight of the monomer and $[R_2]$ is dimer radical concentration.

Since the major weight loss for PMMA is caused by the unzipping depropagation reaction, the contribution from the random scission initiation can be neglected in the above equation when the initial number-average degree of polymerization is much larger than zip length. Also, the first term on the right-hand side of the equation is much smaller than the third term. Then the above equation becomes

$$dW/dt = -m_0k_{dp}\sum[R_i]\bar{V} = -m_0k_{dp}R \quad (8)$$

By assuming that the total number of radicals is constant (steady state)

$$dR/dt = 0 \quad (9)$$

Then using eq 4, 6, and 9, eq 8 can be expressed as

$$\frac{dW}{dt} = -2m_0\frac{k_{dp}k_{ir}}{k_t}L \quad (10)$$

for the first-order termination reaction and

$$\frac{dW}{dt} = -m_0k_{dp}\left[\frac{2k_{ir}}{k_t}L\bar{V}\right]^{1/2} \quad (11)$$

for the second-order termination reaction. The total number of polymer molecules L can be related to the weight of the sample by

$$W = Lm_0$$

Then eq 10 and 11 become

$$\frac{dW}{dt} = -2\frac{k_{dp}k_{ir}}{k_t}W \quad (12)$$

for the first-order termination reaction and

$$\frac{dW}{dt} = -k_{dp}\left[\frac{2m_0}{\rho}\frac{k_{ir}}{k_t}\right]^{1/2}W \quad (13)$$

for the second-order termination reaction.

Therefore the rate of the weight loss of PMMA can be expressed by a first-order reaction with respect to the sample weight regardless of the order of termination. The experimentally determined relationship between dW/dt and W described in Figure 8 is linear when the weight loss is above 15–20%, corresponding to the weight loss initiated by random scission.

Degradation in Nitrogen. It is interesting to compare the activation energy values of the second reaction stage of the weight loss from PMMA degraded in nitrogen (the stage initiated by random scission) as determined by TG and by isothermal heating. The activation energy determined by TG, listed in Table I, is about 7% larger than that determined by isothermal heating listed in Table II. The preexponential factor determined from the isothermal heating experiments is about 10 times greater than that determined by TG, compensating for the difference in the activation energies. Previously published values of activation energies for PMMA corresponding to the weight loss initiated by random scission (when initial number-average degree of polymerization is larger than the zip length) were 207 kJ/mol by Brockhaus and Jenckel,[16] 230 kJ/mol by Madorsky,[17] and 275 kJ/mol by Jellinek and Luh.[18] Thus, both activation energies determined in this study agree with the previous values.[16,17]

The activation energy for the first reaction stage of weight loss of PMMA degraded in nitrogen, caused by end initiation, was determined only by isothermal heating in this study. Previously published activation energies were 113,[16] 96,[18] and 1215 kJ/mol[19] compared to 31 kJ/mol determined from this study. Our value is low compared to the previous values due to the effect of impurities, such as unreacted monomer, in the sample used in this study. The weight loss starts as low as 160 °C as shown in Figure 1. The weight loss caused by end initiation cannot be distinguished from the weight loss caused by the impurities in the sample for the isothermal heating experiments as shown in Figures 6 and 8. Purified PMMA degraded in nitrogen showed an increase in stability at low temperatures as described in a later section.

The average zip length, $1/\gamma$, is defined as the ratio of the rate of depropagation to the rate of termination. Since

Table III
Average Zip Length for PMMA Degraded in Nitrogen

	temp, °C					
	260	280	300	320	340	360
TG	2890	2390	2010	1710	1470	1270
isothermal heating	1760	1630	1520	1430	1340	1270

the total number of radicals is assumed to be constant, as described in the previous section, the rate of chain initiation becomes equal to the rate of termination. This is shown by substituting eq 9 into eq 4 or 6, depending on the order of termination. Then the average zip length for the first-order termination can be expressed as

$$\frac{1}{\gamma} = \frac{k_{\mathrm{dp}}R}{2k_{\mathrm{ir}}L} \tag{14}$$

Using eq 8 and also the apparent first-order reaction for the weight loss, which was validated by the isothermal heating experiment, we find that eq 14 becomes

$$\frac{1}{\gamma} = \frac{k_{\mathrm{w}}}{2k_{\mathrm{ir}}} = \frac{A_{\mathrm{w}}}{2A_{\mathrm{ir}}}\exp\left\{\frac{E_{\mathrm{ir}} - E_{\mathrm{w}}}{RT}\right\} \tag{15}$$

where A is the preexponential factor, E the activation energy, R the universal gas constant, and T the temperature. The subscripts w and ir represent the weight loss and the random scission initiation, respectively. The values of A_{ir} and E_{ir} as determined in our previous study[1] are 6.5×10^{13} s^{-1} and 233 kJ/mol, respectively. The average zip length was calculated at several temperatures, substituting values of A_{w} and E_{w} for the second reaction stage of PMMA degraded in nitrogen from Tables I and II; the results are listed in Table III. Since the value of E_{ir} is slightly greater than the value of E_{w}, the average zip length decreases with an increase in temperature. These results are in good agreement with those determined in our previous study[1] from the molecular weight and fall into the range 10^3–10^4 reported by Takeuchi and Tsuge[20] but are greater than those reported by Jellinek and Luh.[21]

The average zip length can be expressed in terms of the activation energies of initiation, depropagation, and termination reactions such as

$$\frac{1}{\gamma} = \frac{k_{\mathrm{dp}}}{k_{\mathrm{t}}} = \frac{A_{\mathrm{dp}}}{A_{\mathrm{t}}}\exp\{(E_{\mathrm{t}} - E_{\mathrm{dp}})/RT\} \tag{16}$$

for the first-order termination[14] and

$$\frac{1}{\gamma} = \frac{k_{\mathrm{dp}}}{(2k_{\mathrm{ir}}k_{\mathrm{t}})^{1/2}} = \frac{A_{\mathrm{dp}}}{(2A_{\mathrm{ir}}A_{\mathrm{t}})^{1/2}}\exp\left\{\left(\frac{E_{\mathrm{ir}}}{2} + \frac{E_{\mathrm{t}}}{2} - E_{\mathrm{dp}}\right)\Big/RT\right\} \tag{17}$$

for the second-order termination.[15] Combining eq 15 with eq 16 or 17, depending on the order of the termination reaction, we derive the relationship among the activation energies as

$$E_{\mathrm{w}} = E_{\mathrm{ir}} + E_{\mathrm{dp}} - E_{\mathrm{t}} \tag{18}$$

for the first-order termination and

$$E_{\mathrm{w}} = E_{\mathrm{ir}}/2 + E_{\mathrm{dp}} - E_{\mathrm{t}}/2 \tag{19}$$

for the second-order termination.

Since the depropagation step is the reverse of the propagation reaction, the value of E_{dp} should equal the sum of the heat of polymerization and the activation energy of the propagation reaction. The reported heat of polymerization is 54 kJ/mol;[22] values for the activation energy of polymerization are reported to be 26[23] and 18 kJ/mol.[24] Then E_{dp} becomes 72 or 80 kJ/mol, depending on the selected value of the activation energy of polymerization. With E_{ir} = 233 kJ/mol[1] and E_{w} = 210 kJ/mol listed in Table I, eq 18 yields 95 or 103 kJ/mol for E_{t}, depending on the value of E_{dp}. With E_{w} = 224 kJ/mol as listed in Table II, eq 18 yields 81 or 89 kJ/mol of E_{t}, depending on the value of E_{dp}. These values of E_{t} agree well with E_{t} = 84 kJ/mol determined from photodegradation of PMMA by Cowley and Melville[25] but are lower than the value of 133 kJ/mol derived by Jellinek and Luh[18] and 159 kJ/mol calculated by Grassie and MacCallum.[26] The differing value of E_{t} is due to the much greater values for E_{w} and E_{ir}, 275 and 331 kJ/mol, respectively, used by Jellinek and Luh. Grassie and MacCallum assumed a second-order termination reaction and also used the value of 110 kJ/mol for E_{dp}. This is greater than the value used in this study.

On the other hand, eq 19 yields negative values of E_{t} when based on the values of E_{dp}, E_{w}, and E_{ir} used in this study. Thus a reasonable value of E_{t} is obtained only with a first-order termination and not with a second-order termination. The same conclusion was also derived from our study of the molecular weight of isothermally heated PMMA[1] and by Jellinek and Luh.[18] Jellinek and Luh suggested that the pseudo-first-order termination took place predominantly between polymer radicals and monomer, assuming nearly constant monomer concentration.

Thermal Oxidative Degradation. Our TG and isothermal heating results from PMMA degraded in air show a more complex degradation process than that of PMMA degraded in nitrogen as seen in Figures 3 and 9. Both TG and the isothermal heating experiments indicate that there are four reaction stages. It is not clear whether each reaction stage directly corresponds in the two different heating experiments. If each reaction stage is assumed to correspond to each other, the activation energy of each stage can be compared in the two different heating experiments. There are two regimes of weight loss for the sample thickness of 200 μm used in this study. One is controlled by chemical degradation processes in slow-heating-rate experiments (<3 °C/min) with TG and low-temperature experiments (<237 °C) for isothermal heating. The other is affected by the transport of degradation products at high heating rates (>3 °C/min) for TG and at high temperatures (>237 °C) for the isothermal heating. Comparison of the activation energies and preexponential factors of each reaction stage corresponding to the above two regimes of weight loss between the TG and the isothermal heating experiments shows reasonably good agreement between the values listed in Tables I and II.

Since the weight loss from PMMA degraded in air is initiated by random scission, it is interesting to compare the activation energies corresponding to the weight loss regime controlled by chemical degradation processes with those for PMMA degraded by random scission in nitrogen. All activation energies of the first three reaction stages for PMMA degraded in air are much smaller than those of the second reaction stage for PMMA degraded in nitrogen. This differs distinctly from the result of Ohtani et al.,[7] who used the same type of PMMA as that used in this study. Although they observed the two reaction stages of weight loss due to end initiation and random scission initiation, Ohtani et al. concluded that there are no differences in activation energy for weight loss from PMMA degraded in nitrogen and in air at heating rates of 10, 20, 30, 40, and 50 °C/min. These heating rates are about an order of magnitude faster than those used in this study.

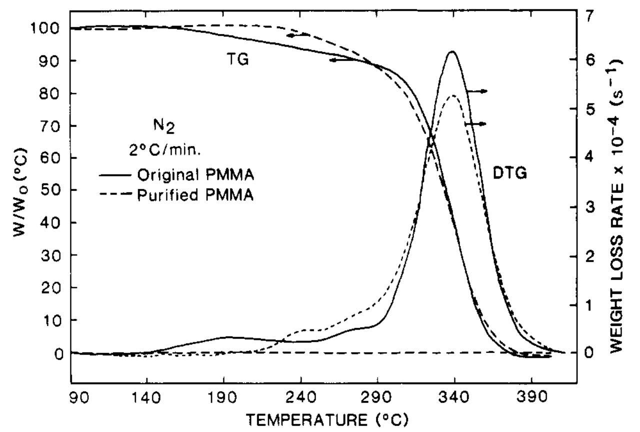

Figure 12. Comparison of TG and DTG curves of original PMMA against purified PMMA degraded in nitrogen.

Although the degradation mechanism of PMMA degraded in nitrogen is reasonably well understood, it is not clear why PMMA degrades in air via four reaction stages. Since the PMMA sample used in this study was a commercial material, it was expected that the sample would contain some impurities such as unreacted initiator, monomer, ultraviolet absorber, etc. These impurities can play an important role in the oxidation of polymers.[27] Thus, preliminary results on the weight loss from purified PMMA degraded in nitrogen and in air are described in the next section.

Weight Loss from Purified Sample. The PMMA sample was purified as follows: soluble impurities in the sample were removed by precipitating PMMA from a dilute (3–5%) solution of methylene chloride. The precipitation was achieved by slowly adding 10 volumes of methanol to each volume of methylene chloride. The precipitated polymer was filtered and rinsed several times with methanol. Dissolution, precipitation, and rinsing of the polymer were repeated three times, after which the polymer sample was dissolved in benzene and freeze-dried.

TG experiments with the purified PMMA were conducted in nitrogen and in air with a heating rate of 2 °C/min to avoid any limitations due to transport processes of the degradation products. The weight loss and DTG of the purified sample degraded in nitrogen are compared with those of the original sample degraded in nitrogen in Figure 12. The effect of sample purification on the weight loss appears only at low temperatures as a delay in the threshold of the weight loss from about 150 to 210 °C. However, the major weight loss peak in DTG, caused by random scission initiation, is almost exactly the same for both samples. Thus, for PMMA degraded in nitrogen, there are no significant effects of purification of the sample on the weight loss, except an increase in PMMA stability at low temperatures, probably by removing unreacted monomers from the sample.

The weight loss and DTG of the purified sample degraded in air are compared with those of the original sample degraded in air in Figure 13. The effect of the purification of the PMMA sample on weight loss in air is much more significant than in nitrogen. There is only one peak in the DTG for the purified sample compared with the four peaks for the original sample. Furthermore, the stability of the sample increases significantly with an increase in the threshold of weight loss from about 210 to 260 °C at a heating rate of 2 °C/min. Although it is not clear what impurities caused the four reaction stages in the original sample, it is clear that thermal oxidative degradation of PMMA is much more affected by these impurities than is thermal degradation of PMMA.

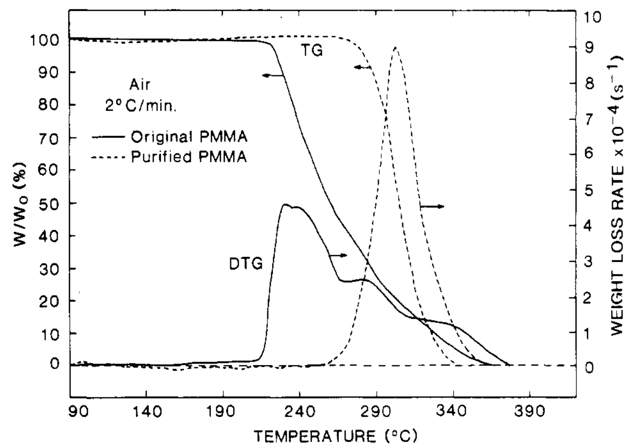

Figure 13. Comparison of TG and DTG curves of original PMMA against purified PMMA degraded in air.

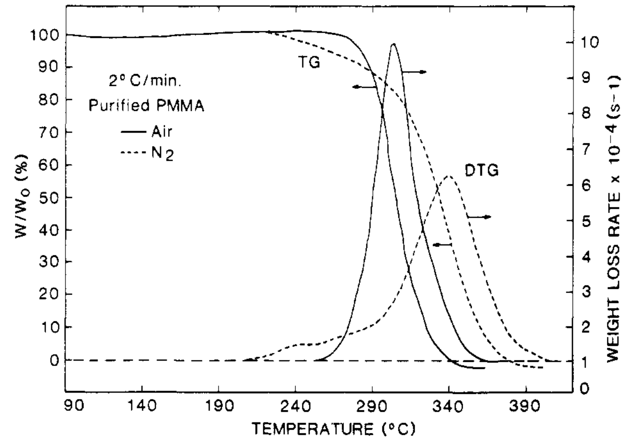

Figure 14. Comparison of TG and DTG curves of purified PMMA degraded in nitrogen against those of purified PMMA degraded in air.

Since the purification of the sample significantly increased the stability of PMMA relative to thermal oxidative degradation, the TG and DTG results of the purified PMMA degraded in air were compared with those of the purified PMMA degraded in nitrogen to find the effects of oxygen on the degradation of the purified PMMA. The comparison is shown in Figure 14. The effects of oxygen on the degradation of the purified PMMA are qualitatively the same as those of the original PMMA: (1) oxygen stabilizes PMMA at low temperatures to weight loss in the range 200–250 °C at a heating rate of 2 °C/min as shown in Figure 14, presumably due to modification of the unsaturated end of the polymer chain by oxygen or scavenging of polymeric carbon-centered radicals by oxygen at these low temperatures, and (2) oxygen destabilizes PMMA at high temperatures by shifting the DTG peak from about 340 to 300 °C at a heating rate of 2 °C/min due to the enhancement of random scission by oxygen in the polymer chain.

Further study of the degradation kinetics of purified PMMA is in progress.

Conclusions

1. There are two distinct effects of gas-phase oxygen on the degradation of PMMA: (1) an increase in stability of PMMA to loss of weight at low temperatures and (2) the destabilization of PMMA at high temperatures by enhanced random scission.

2. There are two regimes of weight loss from PMMA. In the first, the weight loss is controlled by the chemical process of degradation and in the second, weight loss is

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at least partially controlled by transport of the degradation products (by bubbles and diffusion) through the softened PMMA. For example, when 200-μm-thick PMMA was degraded in air, the latter regime was observed with heating rates above 3 °C/min for TG and at temperatures above 237 °C for isothermal heating.

3. There are two reaction stages of weight loss from PMMA degraded in nitrogen. Both reactions are apparently first order with respect to sample weight. The first reaction stage is due to end initiation but also includes some effects of impurities in the commercial PMMA used in this study. The activation energy of the first reaction stage is 31 kJ/mol as determined by isothermal heating. The second reaction stage is due to random scission initiation. The activation energy of the second reaction stage is 210 kJ/mol as determined by TG and 224 kJ/mol as determined by isothermal heating.

4. There are four reaction stages of weight loss for the commercial PMMA degraded in air in both TG and isothermal heating experiments. The first three of these reaction stages are apparently first order with respect to the sample weight. Activation energies of the first three reaction stages are much less than that of random scission initiation of PMMA degraded in nitrogen. These four reaction stages are mainly caused by impurities in the sample. The weight loss of the purified PMMA shows a single oxidative step.

5. The effects of purification of the commercial PMMA on its weight loss are small for samples degraded in nitrogen except for the threshold of the weight loss at low temperatures, but they are significant for the sample degraded in air. This indicates that thermal oxidative degradation of PMMA is very sensitive to the impurities in the sample.

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(28) Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply that the material or equipment identified is necessarily the best available for the purpose.

Observation of the Stereochemical Configuration of Poly(methyl methacrylate) by Proton Two-Dimensional *J*-Correlated and NOE-Correlated NMR Spectroscopy

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ABSTRACT: We report the one-dimensional and two-dimensional (2D) *J*-correlated (COSY) and nuclear Overhauser effect correlated (NOESY) 500-MHz spectra of isotactic and atactic poly(methyl methacrylate). The 2D spectra permit unambiguous association of nonequivalent methylene protons and thereby materially aid the assignment of resonances to configurational sequences. We also observe in the COSY spectra correlations of α-methyl and methylene protons, assumed to arise from weak (1–2 Hz) *J*-couplings through four bonds. This information is consistent with the assignments of the resonances of both types of protons.

Introduction

Conventional one-dimensional (1D) proton NMR spectroscopy has made major contributions to our understanding of the microstructure—particularly the stereochemical configuration—of synthetic macromolecules, but during the past decade has been largely eclipsed by carbon-13 NMR because of the much greater range of carbon-13 chemical shifts and consequent greater sensitivity to structural detail. Proton NMR has certain inherent advantages, however, among them the ability to measure

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