A. B. *J. Am. Chem. Soc.* **1954**, *76*, 6185.
(5) Hendry, D. G.; Hill, M. G.; Peters, H. M. U.S. Patent 3909497, 1975.
(6) Duismann, W.; Beckhaus, H. D. Ruechardt, C. *Ann.* **1974**, *8*, 1348.
(7) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976.
(8) Engel, P. S.; Wood, J. L.; Sweet, J. A.; Margrave, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 2381.
(9) Engel, P. S.; Bishop, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 6754.
(10) Prochazka, M. *Collect. Czech. Chem. Commun.* **1976**, *41*, 1557.
(11) Prevast, C. *C. R. Hebd. Seances Acad. Sci.* **1950**, *230*, 1186.

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

Takashi Kashiwagi,* T. Hirata,[†] and J. E. Brown

National Bureau of Standards, Washington, DC 20234. *Received May 10, 1984*

ABSTRACT: The mechanisms of thermal degradation and thermal oxidation of poly(methyl methacrylate) (PMMA) were studied by measuring the molecular weight of rapidly quenched samples thermally degraded in nitrogen and air in the range of temperatures between 200 and 325 °C. Results show that thermal oxidation reduces the degree of polymerization much faster than does thermal degradation. Random scission is the initiation step for both thermal degradation and oxidative degradation. The activation energy for the random scission initiation is 233 kJ/mol for thermal degradation and 64 kJ/mol for oxidative degradation. The average zip length decreases from 2620 to 1340 with an increase in temperature from 258 to 324 °C for thermal degradation. However, the average zip length increases from 20 to 102 with an increase in temperature from 205 to 251 °C for thermal oxidative degradation. A reasonable value of activation energy for the termination reaction in nitrogen, 104 kJ/mol, is obtained only for the assumption of first-order termination.

1. Introduction

In the initiation and growth of a building fire, thermal energy fed back from an external source such as a flame heats and subsequently decomposes interior furnishings which are frequenty made from synthetic polymeric materials. This process of heating the materials and their subsequent decomposition, evolving combustible gases, controls fire initiation and growth. However, this process has often been neglected in theoretical models used to predict ignition, flame spread, and extinguishment because of an apparent lack of understanding of the physicochemical decomposition mechanism. The lack of understanding is more serious for the thermal oxidative decomposition than for the thermal decomposition of polymeric materials. Thermal oxidative decomposition occurs prior to ignition and at the leading edge of a spreading flame.

Poly(methyl methacrylate), PMMA, has been the subject of many studies of ignition[1-3] and flame spread.[4-6] It has been shown that there are two types of initiation reactions of PMMA in vacuum: one is chain-end initiated, due to double-bond terminated polymer chains, and the other is initiated at random positions by a chain scission process.[7-10] After the initiation reaction, depropagation and termination reactions follow. However, most previous studies were based on weight loss measurement to determine a value of the overall activation energy. With the assumption of a first-order termination reaction,[14] or a second-order termination reaction,[11-13] values of activation energy for the termination reaction or for the initiation reaction have been derived by using previously published activation energies for the depropagation reaction.[15,16] There are few studies reported that have directly measured the activation energy of random initiation, the average zip length (the average number of monomer units successively released by depropagation along the length of a polymer chain), and the activation energy of the termination reaction rather than inferring them from overall weight loss measurements.

The thermal oxidative decomposition mechanism of PMMA is not well understood. Kozmina and Shirshova[17] reported that the molecular weight, calculated from the measured intrinsic viscosity, decreases in the presence of oxygen at 200 °C, but not in nitrogen. It was reported[18] that oxygen affected the molecular weight in two ways; one was to accelerate degradation, probably by the formation of peroxides and hydroperoxides and the other was to deactivate free radicals and inhibit degradation. Our recent work[19,20] has shown higher rates of weight loss from thermally irradiated thick PMMA in various oxygen-containing atmospheres than from such samples irradiated in nitrogen. Molecular weights of surface layers obtained from rapidly quenched samples thermally irradiated in oxygen-containing atmospheres are lower than those of samples irradiated in nitrogen. However, there are few data available on the molecular weight, average zip length and activation energies of the various reactions in the thermal oxidation of PMMA.

In this study, molecular weights and weight losses of PMMA, degraded in nitrogen and air under isothermal heating conditions, were measured. The mechanisms of thermal decomposition and thermal oxidation of PMMA were deduced from these results and are reported in this paper.

2. Experimental Section

2.1. Material. The PMMA samples used in this study were commercial Plexiglas G (Rohm and Haas, Inc.); this material is commonly used for studies of ignition and flame spread. [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 are necessarily the best available for the purpose.] According to the manufacturer, this material contains about 0.1% of a parting agent, 0.5–0.7% of monomer, and a small quantity of ultraviolet absorber. It is made by a free radical polymerization process. One of the polymer chain ends is terminated with a double bond. The measured number average

---

[†] Guest worker from Forestry and Forest Products Research Institute, Tsukuba, Japan.

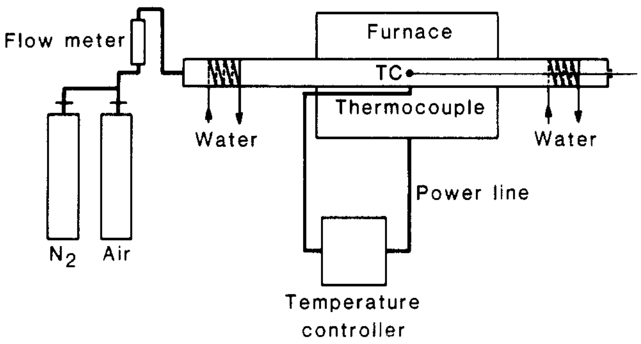

Figure 1. Schemetic illustration of the isothermal heating apparatus.

molecular weight is 402 000 and its polydispersity is about 2.4. The samples used in this study were disks, 8 mm in diameter, 200 μm thick, milled from commercially available sheet originally 900 μm thick. The weight of a sample disk was about 12 mg.

2.2. Isothermal Heating Apparatus. A schematic illustration of the isothermal heating apparatus is shown in Figure 1. The furnace was preheated to the specified temperature. A volume flow rate of 800 mL/min of dry air or nitrogen was fed through the Pyrex tube (1.4 cm inside diameter). A sample was installed in a prebaked aluminum pan and rapidly fed through the tube into the center of the furnace from the right end of the tube. When nitrogen was used as the test gas, the right end of the tube was partially closed to increase the exit gas flow velocity and thus prevent air diffusing from outside to the inside of the tube.

A 250-μm diameter chromel-alumel thermocouple was located just above the sample and it was assumed to be at the sample temperature. Temperature fluctuations were within 1 °C over the course of sample exposure. After being heated, the sample was rapidly removed from the tube and quenched in a small beaker cooled by liquid nitrogen.

2.3. Molecular Weight Measurements. The quenched sample was dissolved in tetrahydrofuran at a concentration of 10 mg of sample in 20 mL of tetrahydrofuran. The solution was filtered through a 0.47 μm pore filter prior to injecting it into a Water Associates Model ALC/GPC-150C gel permeation chromatograph equipped with a column set consisting of two Shodex A80M/S and a Waters Microstyrogel 100Å. The calibrated molecular weight range of the column set was from 8×10^2 to 7.5×10^6 g/mol. Mark–Houwink parameters for the universal calibration method[22] were taken for PMMA at 25 °C.[23]

3. Results and Discussion

3a. Role of Diffusion on Molecular Weight. Isothermal heating experiments were conducted at 229, 242, 258, 274, 295, 309, and 324 °C in nitrogen at at 190, 205, 220, 235, 251, and 265 °C in air. The molecular weight distribution of the rapidly quenched samples at each of these temperatures was measured. Typical changes in the molecular weight distribution are shown in Figure 2 for samples degraded in nitrogen and in air atmospheres. In nitrogen, the peak in the molecular weight distribution moves gradually toward lower molecular weights with an increase in heating time. In air, however, the shift toward lower molecular weights is very rapid and the peak value becomes quite low. That is, the rate of decrease in molecular weight is very large at early heating times in air. This trend is also observed at the other isothermal heating temperatures. This raises a question whether the sample used in this study is thin enough so that only chemical processes are involved as opposed to a combination of chemical processes and physical processes such as diffusion of oxygen through the sample. The narrowness of the molecular weight distribution indicates that the sample appears to be affected by oxygen relatively uniformly. Isothermal heating experiments and molecular weight measurements were repeated with 900-μm thick PMMA samples at the above various temperatures to confirm the

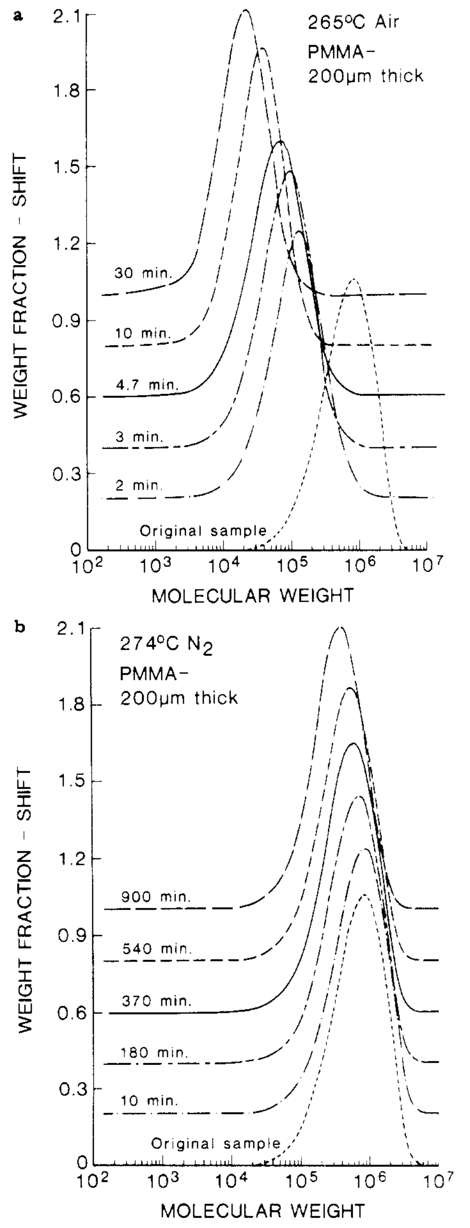

Figure 2. Changes in molecular weight distribution with heating time: (a) PMMA at 274 °C in nitrogen; (b) PMMA at 265 °C in air.

negligible effects of oxygen diffusion on the measured molecular weights. The change in the molecular weight distribution with heating time of the thicker samples is shown in Figure 3. The shape of the distributions for the thicker samples is bimodal at most heating times and quite different from the narrow distributions of the thinner samples as shown in Figure 2. The bimodal distribution is generated because the decrease in the molecular weight is much faster in air than it is in nitrogen. Therefore, the peak appearing at higher molecular weight corresponds to the thermal decomposition without the oxygen effects and the other peak appearing at lower molecular weight corresponds to oxidative degradation. This indicates that the rate of diffusion of oxygen through the thicker samples is slow compared to the rate of oxidative degradation and a part of the sample, near the surface, is degraded oxidatively while the rest of the sample is degraded thermally. Similar effects of diffusion of oxygen on the rate of the oxidative reactions for polystyrene[23] and on the rate of oxygen intake for polypropylene[24] have been reported.

The quantitative effects of oxygen diffusion as a rate-controlling process are shown in Figure 4. Figure 4a shows

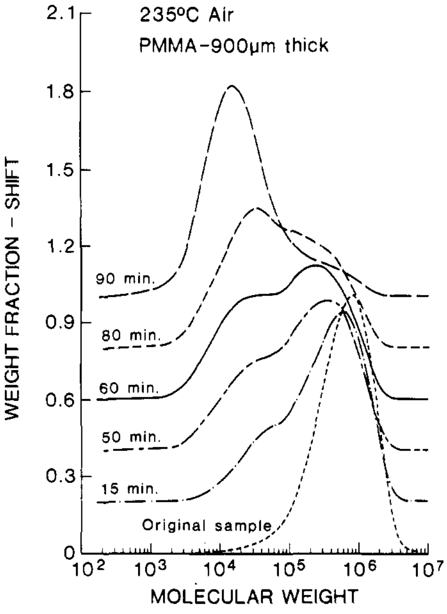

Figure 3. Changes in molecular weight distribution with heating time, 900 µm thick PMMA at 235 °C in air.

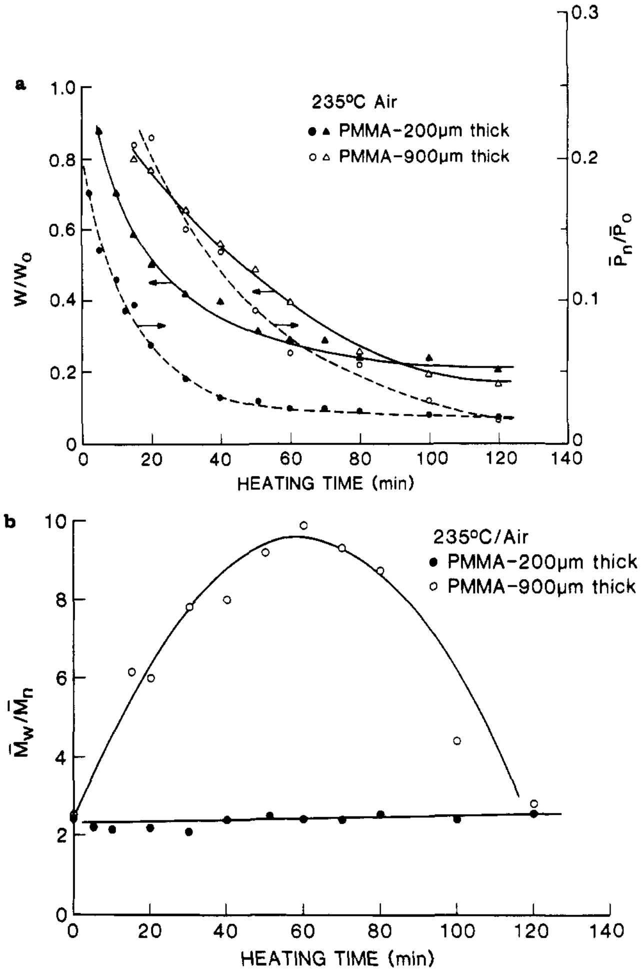

Figure 4. Effects of the sample thickness on physical and chemical parameters: (a) on normalized residue weight and normalized number-average degree of polymerization; (b) polydispersity.

the effects on the normalized residue weight W/W_0, where W_0 is the initial sample weight, and on the normalized number average degree of polymerization $\bar{P}_n/\bar{P}_0$, where $\bar{P}_0$ is the initial degree of polymerization of the unheated sample. Up to about 100 min of heating time, the thin sample loses its weight more than the thick sample by as much as 40%. Similarly, rates, of the decrease in the degree of polymerization for the thin sample are initially much faster than those for the thick sample. After about 100 min of heating time, oxygen diffuses through the residue of the thick sample and the molecular weight distribution becomes unimodal. This is also shown clearly in Figure 4b in which the change in the polydispersity of the molecular weight is compared for both samples. The value of the polydispersity for the thin sample is nearly constant between 2.2 and 2.6 for all heating times. However, the value of the polydispersity for the thick sample increases initially with the increase in heating time up to a value of 10, and then it decreases to a value close to the initial polydispersity. This observation was also confirmed at all other isothermal heating temperatures in air used in this study. From these observations, it was concluded that the thickness of the sample (200 µm) used in this study was thin enough to exclude the rate-limiting effects of oxygen diffusion for the isothermal heating temperatures used in this study. This does not necessarily mean that the rates of oxygen diffusion are always faster than the rates of thermal oxidation. They depend on experimental conditions such as the temperature, the sample thickness, and the sample physical characteristics.

Besides oxygen diffusion, another important transport process is the transport of monomer generated by degradation through the softened PMMA to the outside of the sample. Rapidly quenched samples often contained a number of small bubbles. Since PMMA starts to degrade above 200 °C, the monomer molecules (boiling temperature 100 °C) are superheated and nucleate to form bubbles. It appears that the monomer is mainly transported out of the sample by means of slow-moving bubbles rather than by diffusion. Our separate study[25] of the weight loss process using the same size of PMMA demonstrated that the transport of monomer does not limit the weight loss process in the majority of our experimental conditions. Small effects were observed at 265 °C in air and at 324 °C in nitrogen. Since the lowest molecular weight calibrated by the column set used for gel permeation chrmotography was 800, the contribution from monomer molecules was not included in our molecular weight measurements. Therefore, there are no effects of monomer transport on the measured molecular weights.

3b. Initiation Reaction. Changes in the normalized number-average degree of polymerization with heating time at different isothermal temperatures are shown in Figure 5. PMMA samples degraded in nitrogen are shown in Figure 5a and in air in Figure 5b. The decrease in normalized number-average molecular weight for the samples degraded in air is much faster than that for the samples degraded in nitrogen. Roughly, the rate of decrease at 205 °C in air corresponds to that of 324 °C in nitrogen. The initiation mechanism can be determined by use of the relationship between the number-average degree of polymerization and the heating time. Since the number-average degree of polymerization of the sample used in this study is about 4000, the effect of the end initiation on the molecular weight is small. The major initiation mechanism is known to be random scission, at least in vacuum.[7-11] Since there are no tertiary hydrogens in the PMMA structure, the intermolecular chain transfer process can be neglected in the depolymerization process.[16] Then, with the assumption of random scission initiation for our PMMA the degree of polymerization can be expressed as[25]

$$\frac{1}{(\bar{P}_n)^2}\frac{d\bar{P}_n}{dt} = k_{ir} \qquad (1)$$

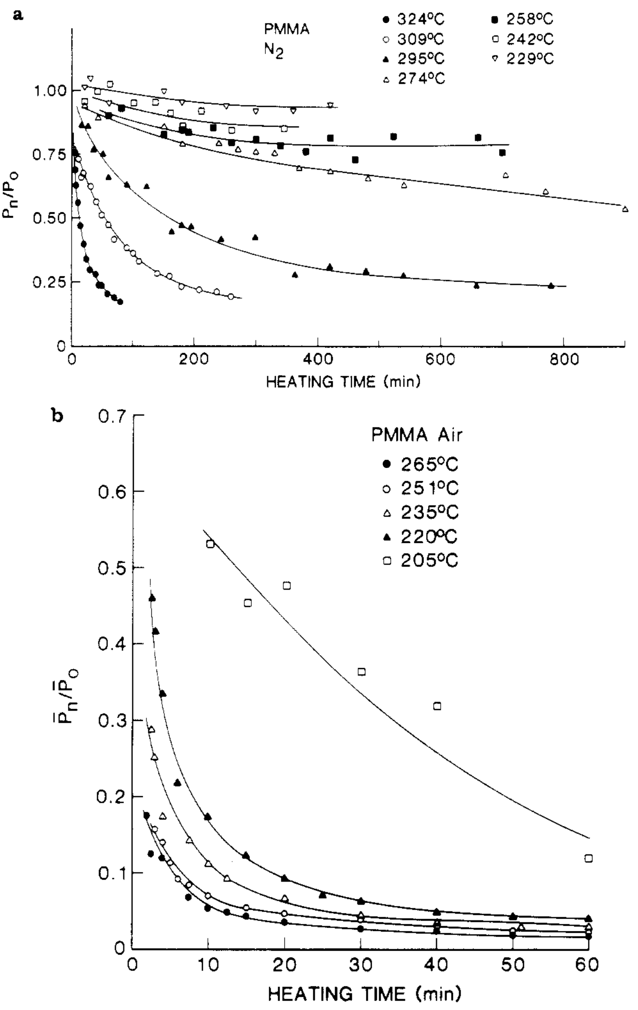

Figure 5. Changes in normalized number average degree of polymerization with heating time at different isothermal temperatures (a) in nitrogen and (b) in air.

with the first-order termination or second-order disproportionation termination, where k_{ir} is the rate constant for random scission initiation reaction. Random chain scission is defined here as any set of one or more elementary reactions whose net result is a randomly located break of the polymer backbone. This may be caused by, for example, a concerted reaction, oxygen attack or radical attack via impurities. It is assumed in deriving eq 1 that, (1) monomer is the only volatile and it does not stay in the sample, (2) any radical has the same reactivity as a monomer radical, and (3) total number of radicals is constant as a result of using the steady-state assumption. All equations referenced to Boyd[26] in this paper are derived from the same assumptions. Since the polydispersity of the thin sample degraded in nitrogen and air is close to 2 (observed values between 2.2 and 2.4) as shown in Figure 4b and the observed molecular weight distribution is nearly symmetric, the molecular weight distribution of the sample can be adequately expressed as the "most probable" distribution.[27] Then, eq 1 is applicable to all average zip lengths.[26] The solution of eq 1 is

$$\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_0} = k_{ir}t \tag{2}$$

Plots of $1/\bar{P}_n$ vs. heating time t are shown in Figure 6 at different isothermal temperatures using the data shown in Figure 5. Both plots yield a reasonable straight line over most of the heating times. Only at long heating times do the plots start to deviate from straight lines. This confirms the assumption that the initiation of degradation of high molecular weight PMMA in nitrogen and the net effect of oxygen attack is mainly random scission along the polymer chain.

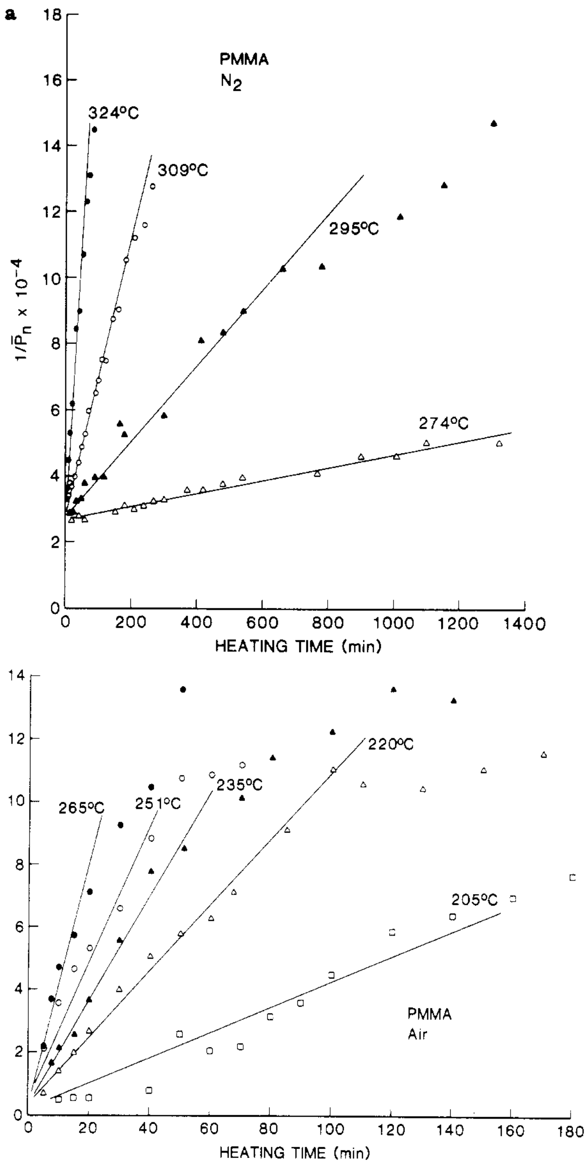

Figure 6. Relationship between $1/\bar{P}_n$ and heating time at different isothermal tempeatures (a) in nitrogen and (b) in air.

The slope of each line is the value of k_{ir} at the corresponding temperature. An Arrhenius plot of k_{ir} is shown in Figure 7 for nitrogen and air. The values of the activation energy for random scission, E_{ir}, are 233 kJ/mol (56 kcal/mol) for nitrogen and 64 kJ/mol (15 kcal/mol) for air. The values of the preexponential factor, A_{ir}, are 6.5 × 10^{13} s^{-1} for nitrogen and 8.5 s^{-1} for air. The reduction in activation energy for random scission by oxygen is very large.

The measured activation energy, 233 kJ/mol, is much smaller than the estimated bond dissociation energy for the rupture of the backbone C–C bond for small molecules, 326 kJ/mol.[27] This large difference indicates that chain scission of the polymer sample used in this study may be attributed to a number of causes more complex than a single one-step break in the backbone, such as the impurities in the sample (ultraviolet absorber and monomer), some type of concerted reaction, or steric strain on the bonds caused by rigidity and the conformation of the

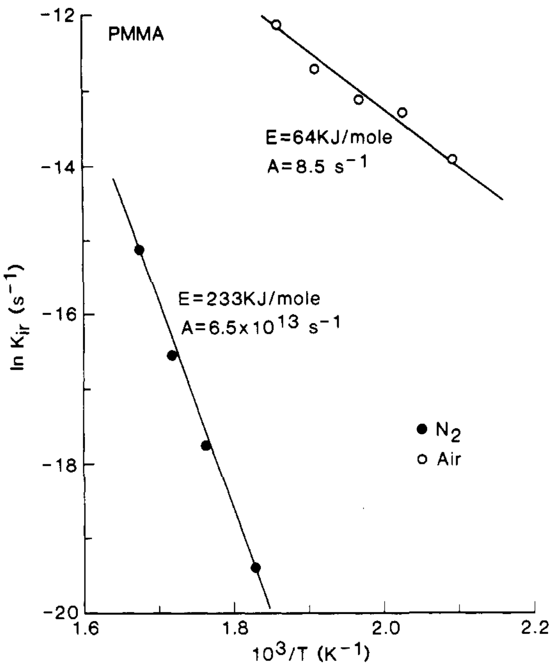

Figure 7. Arrhenius plot of the random scission rate constant.

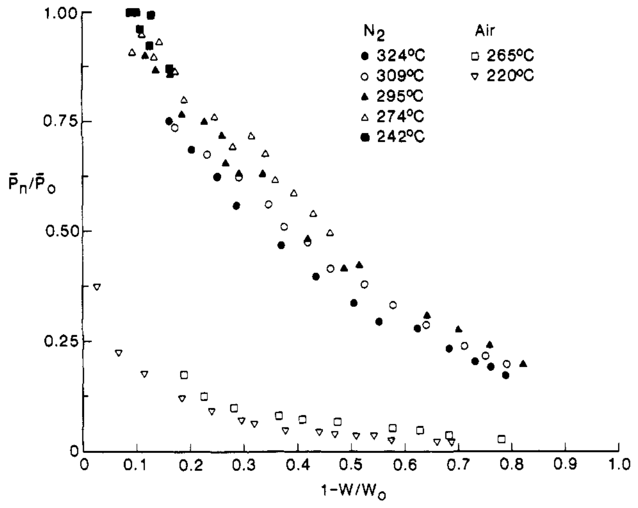

Figure 8. Normalized number-average degree of polymerization plotted against conversion of isothermally heated PMMA.

polymer. The reduction in the activation energy of random scission initiation induced by oxygen is very large. At present, it is not clear where oxygen attacks the chain at these temperatures.

Further information on the mechanism of degradation may be derived from the relationship between the degree of polymerization and the conversion of the sample, $1 - W/W_0$. This relationship is shown in Figure 8. The figure shows that the degree of polymerization of the sample degraded in air is clearly much lower than that of the sample degraded in nitrogen at the same conversion. There are slight temperature effects on the relationship. In nitrogen, an increase in temperature tends to decrease the degree of polymerization at the same conversion. This trend becomes reversed when PMMA is degraded in air, although the effect of temperature on the relationship becomes less than that for nitrogen. It appears that the degree of polymerization in nitrogen may stay constant when the conversion is below 0.1. This early weight loss, $0 < 1 - W/W_0 < 0.1$, may be caused by end initiation from the unsaturated ends created during polymerization processing. Under these conditions, the degree of polymerization remains nearly constant with the "most probable" distribution of molecular weight in the absence of recombination terminations, even though the sample loses weight.[25] Our thermogravimetric study of PMMA also shows a small amount of weight loss in nitrogen in the early stage of degradation.[28]

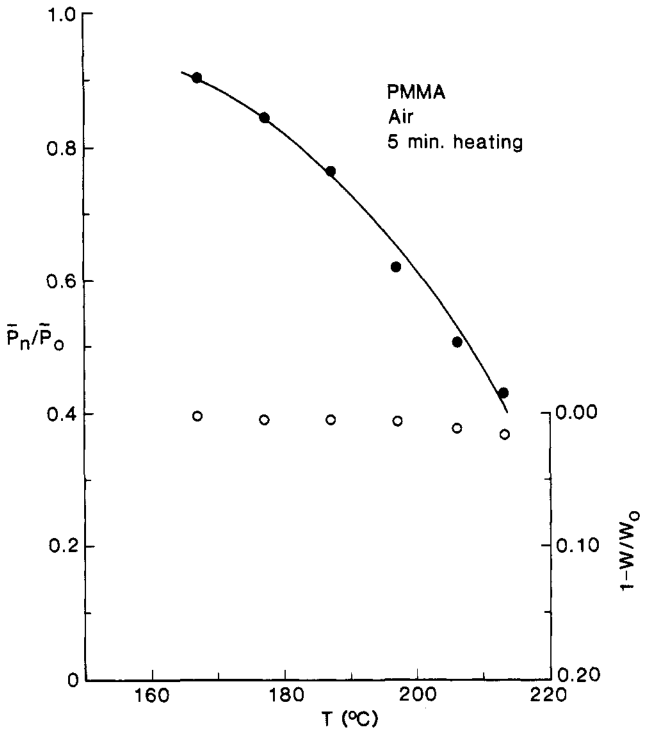

Figure 9. Changes in normalized degree of polymerization and conversion at different low isothermal temperatures after 5 min heating in air.

In Figure 8, the degree of polymerization in air drops very rapidly even before appreciable weight loss. To investigate whether the degree of polymerization decreases before the start of weight loss in air, the degree of polymerization and weight loss were measured after 5 min at temperatures of 167, 177, 187, 197, 206, and 213 °C. The results are shown in Figure 9. This figure shows a rapid decrease in the degree of polymerization, but the weight loss is extremely small below 200 °C. Extremely small initial weight losses (less than 1%) may be due to initially trapped monomer and other small molecules such as water. However, the degree of polymerization dropped about 25% even at 190 °C. The observation of extremely small weight loss below 200 °C is consistent with the ceiling temperature which is 197 °C for PMMA.[29] However, this ceiling temperature was obtained in inert atmosphere and some caution is necessary to apply the ceiling temperature to PMMA degraded in air in our study. The degree of polymerization decreases before the start of the weight loss in air at the temperatures used in this study. It appears that some types of polymerization, as suggested by Bresler et al.[18] (the monomer combining with free radicals, thus directing the reaction toward polymerization) or some type of termination, may take place at these low temperatures after the chain scission by oxygen. Otherwise, weight loss should be observed due to fast depropagation.

3c. Average Zip Length in Nitrogen. The relationship between the degree of polymerization and conversion, shown in Figure 8, can be analyzed further to obtain details of the mechanism of the degradation. The value of average zip length may be obtained from the relationship. According to Boyd,[25] the normalized degree of polymerization drops more rapidly than the conversion for short zip

Table I
Average Zip Length of PMMA Degraded in Nitrogen

T, °C	258	274	295	309	324
$1/\gamma$	2620	2460	1740	1480	1340

lengths, i.e., the $\bar{P}_n/\bar{P}_0$ curve lies far below a 45° diagonal on a plot of $\bar{P}_n/\bar{P}_0$ vs. conversion shown in Figure 8. This is true for PMMA degraded in air but not for PMMA degraded in nitrogen. The curve derived for PMMA degraded in nitrogen lies only slightly below the 45° diagonal line. Therefore, the degradation in nitrogen cannot be considered as involving either particularly short zip length or particularly long zip length.

The relation between the sample weight and the degree of polymerization applicable to degradation in nitrogen with random scission initiation is[26]

$$\frac{1}{W}\frac{\mathrm{d}W}{\mathrm{d}t} = -\frac{2k_{\mathrm{ir}}\bar{P}_{\mathrm{n}}}{(1+\bar{P}_{\mathrm{n}}\gamma)} \tag{3}$$

In eq 3, $1/\gamma$ is the average zip length. This equation is applicable for all zip lengths with the "most probable" distribution of molecular weight which was confirmed above. Since the order of the termination reaction is not well-known, first and second orders for this reaction are considered. The average zip length can be expressed as

$$\frac{1}{\gamma} = \frac{k_{\mathrm{dp}}}{k_{\mathrm{t}}} \tag{4}$$

for first-order termination and as

$$= k_{\mathrm{dp}}\left(\frac{M_0}{2k_{\mathrm{ir}}k_{\mathrm{t}}d_0}\right)^{1/2}$$

for second-order termination,[25] where k_{dp} and k_{t} are the rate constants for the depropagation and termination reactions, respectively. The symbol, d_0, denotes the initial density of the sample and M_0 is the molecular weight of a repeat unit.

The solution of eq 3 is

$$\frac{W}{W_0} = \left(1 + \frac{k_{\mathrm{ir}}\bar{P}_0 t}{1+\gamma\bar{P}_0}\right)^{-2} \tag{5}$$

Substituting eq 2 into eq 5, the normalized weight loss becomes

$$\frac{W}{W_0} = \left\{\frac{(1/\gamma + \bar{P}_0)}{\bar{P}_0}\,\frac{\bar{P}_{\mathrm{n}}}{(1/\gamma + \bar{P}_{\mathrm{n}})}\right\}^2 \tag{6}$$

Values of the average zip length at different temperatures can be determined by a numerical nonlinear curve fit between W/W_0 and $\bar{P}_n/\bar{P}_0$ using the data shown in Figure 8. The results are shown in Table I. These values are in good agreement with those derived from our thermogravimetric study.[28] However, they are roughly a factor of 2 larger than those obtained by Jellinek and Luh.[30] It is interesting to note that values of average zip length become about 40% of those listed in Table I if the average zip length is calculated by assuming a short average zip length as was assumed in the study of Jellinek and Luh.[30] However, the short average zip length approximation cannot be made for our thermal degradation results as shown by the data in Figure 8.

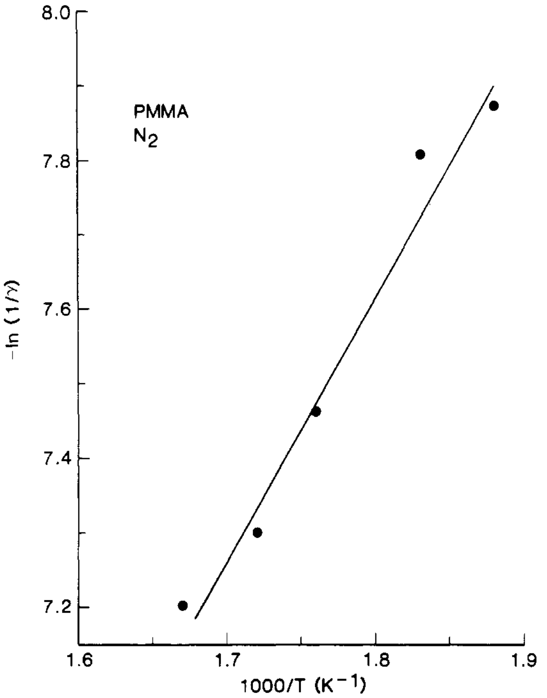

Figure 10. Arrhenius plot of kinetic chain length of PMMA degraded in nitrogen.

3d. Termination Reaction in Nitrogen. The temperature dependence of the average zip length can be expressed as

$$\frac{1}{\gamma} = \frac{k_{\mathrm{dp}}}{k_{\mathrm{t}}} = \frac{\{A_{\mathrm{dp}}\exp[-E_{\mathrm{dp}}/(RT)]\}}{A_{\mathrm{t}}\exp\{-E_{\mathrm{t}}/(RT)\}} = C\exp\{-(E_{\mathrm{dp}} - E_{\mathrm{t}})/(RT)\} \tag{7}$$

for a first-order termination reaction and

$$= \left(\frac{M_0 A^2{}_{\mathrm{dp}}}{2d_0 A_{\mathrm{ir}} A_{\mathrm{t}}}\right)^{1/2} \exp\left[-\left\{E_{\mathrm{dp}} - \left(\frac{E_{\mathrm{ir}} + E_{\mathrm{t}}}{2}\right)\right\}/(RT)\right] \tag{8}$$

for the second-order termination reaction. Subscripts dp, t and ir are for depropagation, termination, and random scission initiation, respectively. E is the activation energy, A the preexponential factor and R the universal gas constant. From the slope of the Arrhenius plot of ln $(1/\gamma)$ vs. $1/T$, the value of $-(E_{\mathrm{dp}} - E_{\mathrm{t}})/R$ and $-\{E_{\mathrm{dp}} - (E_{\mathrm{ir}} + E_{\mathrm{t}}/2)\}/R$ can be determined. The Arrhenius plot is shown in Figure 10. The values obtained are $-(E_{\mathrm{dp}} - E_{\mathrm{t}}) = 29$ kJ/mol (7 kcal/mol) for first-order termination and $-\{E_{\mathrm{dp}} - (E_{\mathrm{ir}} + E_{\mathrm{t}})/2\} = 29$ kJ/mol for 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. Two values of E_{dp} have been reported, 77.4 kJ/mol[15] and 75 kJ/mol (18 kcal/mol).[16] If the value of E_{dp} is taken as 75 kJ/mol, E_{t} becomes 104 kJ/mol (25 kcal/mol) for first-order termination. However, E_{t} becomes negative for second-order termination with $E_{\mathrm{dp}} = 75$ kJ/mol and the measured value $E_{\mathrm{ir}} = 233$ kJ/mol. A reasonable value for the activation energy of the termination reaction is only obtained for first-order termination and not with second-order termination. The value of 84 kJ/mol for E_{t} was reported previously.[15] These values, 84 or 104 kJ/mol, were much greater than the energy of activation of radical termination reactions in dilute solutions, but it should be remembered that the termination occurs in a highly viscous polymer medium. With first-order termination and random scission initia-

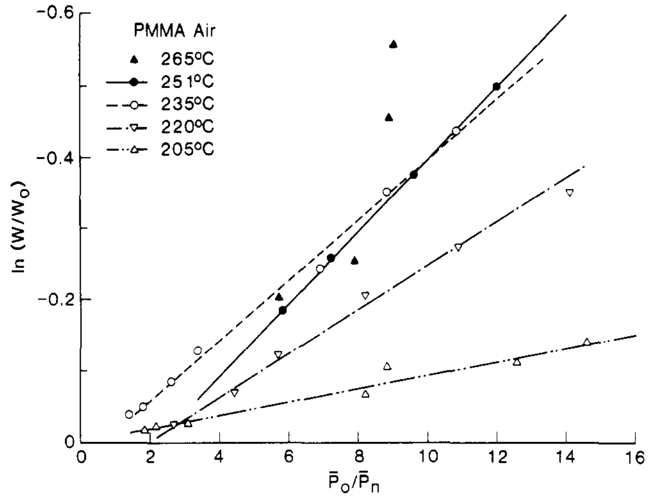

Figure 11. Plot of ln (W/W_0) vs. $\bar{P}_0/\bar{P}_n$ for PMMA degraded in air.

tion, the overall activation energy of the weight loss, $E_{o.w}$, can be expressed as[25] $E_{o.w} = E_{ir} + E_{dp} - E_t = 233 + 75 - 104 = 204$ kJ/mol for the case of the short average zip length and $E_{o.w} = E_{ir} = 233$ kJ/mol for the case of the long average zip length. These expressions apply only to the weight loss in the absence of any effect of the transport of monomer through the softened PMMA. Since our previously derived average zip lengths lie between the short and the long average zip length, it is expected that the measured value of $E_{o.w}$ lies between 204 and 233 kJ/mol. The values of $E_{o.w}$ measured in our thermogravimetric study without the effect of the transport of monomer are 210 and 224 kJ/mol,[28] which lies between 204 and 233 kJ/mol. Therefore, it is suggested that the termination reaction is first order instead of second order as was often assumed previously.[11-13] Jellinek and Luh[14] have also suggested that the termination reaction is first order. They suggested that the first-order termination reaction took place predominantly between polymer radicals and monomer, assuming near constant monomer content.

3e. Average Zip Length in Air. In a similar manner, the values of average zip length are obtained for PMMA degraded in air. In this case, for reasons discussed above, the average zip length is much shorter than the initial average length of the chain. Then, the relationship between the weight loss and the degree of polymerization is[25]

$$\frac{1}{W}\frac{\mathrm{d}W}{\mathrm{d}t} = -\frac{2k_{ir}}{\gamma} \tag{9}$$

The solution of eq 9 can be modified by using eq 2. Then

$$\ln\left(\frac{W}{W_0}\right) = \frac{2}{\gamma\bar{P}_0}\left(1 - \frac{\bar{P}_0}{\bar{P}_n}\right) \tag{10}$$

In a plot of ln (W/W_0) vs. $\bar{P}_0/\bar{P}_n$ as shown in Figure 11, the slope of the straight line is the value of $-2/(\gamma\bar{P}_0)$, and $1/\gamma$ can be calculated from this result. At 265 °C, the rates of weight loss and of oxidative degradation are so fast that there is a lot of scatter in the data as shown in Figure 11. Consequently, the value of the average zip length could not be determined for 265 °C. Average zip lengths calculated from the slopes of the lines shown in Figure 11 are listed in Table II. Average zip lengths for PMMA degraded in air are much shorter than those for nitrogen. Since the chain length is rapidly shortened by random scission induced by oxygen, the average zip length is correspondingly reduced.

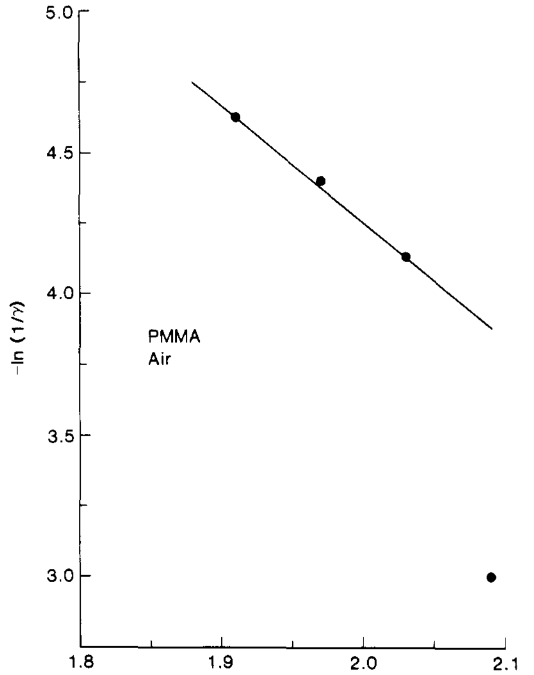

Figure 12. Arrhenius plot of kinetic chain length of PMMA degraded in air.

Table II
Average Zip Length of PMMA Degraded in Air

T, °C	205	220	235	251
$1/\gamma$	20	62	85	102

For degradation of PMMA in nitrogen, the average zip length decreases with an increase in temperature; however, it increases with an increase in temperature for PMMA degradation in air. The same trend is also observed in our thermogravimetric study.[28] This indicates that the value of $-(E_{dp} - E_t)$ in eq 7 is negative for air assuming first-order termination. The Arrhenius plot of average zip length for air is shown in Figure 12. It is not clear, at present, why the data point at 205 °C is far off the straight line. Only three data points at 220, 235, and 251 °C are used to obtain the value of the slope of the straight line shown in Figure 12. The value of $-(E_{dp} - E_t)$ for air is −33 kJ/mol (−8 kcal/mol). To obtain the value of E_t, it is assumed that the depropagation reaction in air is the same as the one in nitrogen. This assumption is consistent with our preliminary study in which predominant product from PMMA degradation in both air and nitrogen is monomer in the temperature range used in the study. If E_{dp} is assumed to have a value of 75 kJ/mol, the value of E_t for air is found to be 42 kJ/mol (10 kcal/mol). This is much less than that for nitrogen. This indicates that the termination process may not be important for PMMA degradation in air because of the short available chain length. However, the mechanism of thermal oxidation of PMMA is far more complex than is that of thermal degradation. There are apparently four different degradation steps for thermal oxidation.[28] Therefore, until the mechanism of thermal oxidation of PMMA is more clearly understood, some caution is suggested in using the value of E_t obtained in air.

4. Conclusions

(1) The value of the activation energy for random scission initiation of PMMA in nitrogen is 233 kJ/mol. This was directly determined from the measurement of molecular weight. The average zip length decreases from 2620 to 1340 with an increase in temperature from 258 to 324 °C. A reasonable value of the activation energy for the

termination reaction, 104 kJ/mol, is obtained only for a first-order termination reaction and the value of activation energy becomes negative if the termination reaction is assumed to be second order.

(2) Thermal oxidation of PMMA reduces the degree of polymerization much more rapidly than does thermal degradation. It appears that the reduction in the degree of polymerization occurs before the onset of weight loss. Initiation of thermal oxidation is due to random scission and its activation energy is 64 kJ/mol. The kinetic chain length of thermal oxidation increases from 20 to 102 with an increase in temperature from 205 to 251 °C. The average zip lengths for thermal oxidation are about 1 order of magnitude shorter than those for thermal degradation.

Acknowledgment. We thank Drs. J. D. Barnes and F. L. McCracken of NBS for interfacing a computer with the GPC and writing a series of computer programs for collection and processing of the GPC data. Dr. Bert Rust is acknowledged for use of his nonlinear curve fit program and David Tate for implementation of the latter program.

References and Notes

(1) Mutoh, N.; Hirano, T.; Akita, K. Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1979, 1183.
(2) Kashiwagi, T. *Combust. Flame* **1979**, *34*, 231.
(3) Clark, F. R. S. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2323.
(4) Orloff, L.; de Ris, J. N.; Markstein, G. H. Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1975, 183.
(5) Fernandez-Pello, C. A.; Ray, S. R.; Glassman, I. Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1981, 579.
(6) Altenkirch, R. A.; Eichhorn, R.; Rizvi, A. R. *Combust. Sci. Technol.* **1983**, *32*, 49.
(7) Grassie, N.; Melville, H. W. *Proc. R. Soc. London, Ser. A* **1949**, *199*, 14.
(8) Jellinek, H. H. G. "Degradation of Vinyl Polymers"; Academic Press: New York, 1955; p 74.
(9) MacCallum, J. R. *Makromol. Chem.* **1965**, *83*, 137.
(10) Cameron, G. G.; Kerr, G. P. *Makromol. Chem.* **1968**, *115*, 268.
(11) Grassie, N.; Melville, H. W. *Proc. R. Soc. London, Ser. A* **1949**, *199*, 24.
(12) Grassie, N.; MacCallum, J. R. *J. Polym. Sci., Part B* **1963**, *1*, 551.
(13) Jellinek, H. H. G.; Luh, M. D. *J. Phys. Chem.* **1966**, *70*, 3672.
(14) Jellinek, H. H. G.; Luh, M. D. *Makromol. Chem.* **1968**, *115*, 89.
(15) Cowley, P. R. E. J.; Melville, H. W. *Proc. R. Soc. London Ser. A* **1952**, *211*, 461.
(16) Mita, I. In "Aspects of Degradation and Stabilization of Polymers"; Jellinek, H. H. G., Ed.; Elsevier Scientific: Amsterdam, 1978; pp 247–294.
(17) Kozmina, O. P.; Shirshova, A. N. *Zh. Prikl. Khim.* **1957**, *30*, 1878.
(18) Bresler, S. E.; Os'minskaia, A. T.; Popov, A. G.; Saminskii, E. M.; Frenkel, S. Ia. *Colloid J.* (*U.S.S.R*) **1958**, *381*, 20.
(19) Kashiwagi, T.; Ohlemiller, T. J. Nineteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1982, p 815.
(20) Brown, J. E.; Ohlemiller, T. J.; Kashiwagi, T. "Polymer Gasification and Ignition", presented at Symposium on the Chemistry of Combustion Processes, 185th National Meeting of the American Chemical Society Seattle, WA, May 1983; American Chemical Society: Washington DC.
(21) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753.
(22) Janca, J.; Blcek, P.; Trekoval, J.; Kolinsky, M. *J. Polym. Sci., Part A-1* **1975**, *13*, 1471.
(23) Jellinek, H. H. G.; Lipovac, S. N. *Macromolecules* **1970**, *3*, 231.
(24) Boss, C. R.; Chien, J. C. W. *J. Polym. Sci., Part A-1* **1966**, *4*, 1543.
(25) Boyd, R. H. In "Thermal Stability of Polymers"; Conley, R. T., Ed.; Marcel Dekker: New York, 1970; pp 47–89.
(26) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; p 318.
(27) Weast, E. "Handbook of Chemistry and Physics", 64th ed.; CRC Press Inc.: Boca Raton, FL, 1983; F-188.
(28) Hirata, T.; Kashiwagi, T.; Brown, J. E. "Thermal and Oxidative Degradation of Poly(methyl methacrylate): Weight Loss", to appear in *Macromolecules*.
(29) Busfield, W. K. In "Aspects of Degradation and Stabilization of Polymers"; Jellinek, H. H. G., Ed.; Elsevier Scientific: Amsterdam, 1978; pp 39–78.
(30) Jellinek, H. H. G.; Luh, M. D. *J. Phys. Chem.* **1966**, *70*, 3672.