

Kinetic Study of Stabilizing Effect of Oxygen on Thermal Degradation of Poly(methyl methacrylate)

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Received: May 14, 1999; In Final Form: July 26, 1999

The thermal degradation of poly(methyl methacrylate) (PMMA) has been studied in both pure nitrogen and oxygen-containing atmospheres. The presence of oxygen increases the initial decomposition temperature by 70 °C. The stabilizing effect of oxygen may be explained by forming thermally stable radical species that suppress unzipping of the polymer. This assumption is supported by the experimental fact that introduction of NO into gaseous atmosphere increases the initial decomposition temperature by more than 100 °C. The model-free isoconversional method has been used to determine the dependence of the effective activation energy on the extent of degradation. The initial stages of the process show a dramatic difference in the activation energies that were found to be 60 and 220 kJ mol⁻¹ for respective degradations in nitrogen and air.

Introduction

The thermal degradation of PMMA has been a subject of numerous studies. The mechanism and kinetics of this process have been examined in various media such as vacuum,^{1–7} nitrogen,^{8–23} oxygen, air,^{4,5,8,11–13,17–19,21–26} argon,^{27,28} and helium.²⁹ A majority of these studies have been conducted in the nitrogen atmosphere. The thermal degradation under these conditions usually shows two steps.^{7,8,12,14,15,22,23,28} However, three-step degradations have also been reported.^{17,18,29} The stabilizing effect of oxygen on the thermal degradation of PMMA was first reported by Bresler et al.⁵ Recently, Hirata et al.¹² reported that in the oxygen-containing atmosphere, the initial temperature of degradation increases by about 50 °C compared to that for degradation in nitrogen. Kashiwagi et al.^{18,21} proposed mechanistic explanations to this effect.

A number of workers^{7,8,11,13,15,16,28,30,31} have reported the Arrhenius parameters for PMMA degradation (Table 1). As we can see, the reported values of the activation energy vary almost by an order of magnitude. Note that such a variation may simply be because of the use of inadequate computational techniques. For instance, Arrhenius parameters are most frequently evaluated by using force fitting of thermal decomposition data to various reaction models. When applied to nonisothermal data, these model-fitting methods tend to produce highly uncertain values of Arrhenius parameters that cannot be meaningfully compared with the isothermal values.³² Besides, the regular use of model-fitting methods yields a single averaged value of the activation energy for the whole process. However, thermal degradation of polymers usually involves multiple steps that are most likely to have different activation energies. The relative contribution of these steps to the overall degradation rate changes with both temperature and extent of degradation. This means that the effective activation energies determined from thermal analysis data should also be a function of these two variables. Model fitting methods are not capable of revealing this type of reaction complexity. To avoid the problems peculiar to the model-fitting, we use a model-free approach to kinetics analysis.³³ This approach rests upon the isoconversional method whose application to thermal degradations of polymers often yields an

TABLE 1: Reported Activation Energies for the Thermal Degradation of PMMA

gas	<i>E</i> /kJ mol ⁻¹			experiment	ref
	step 1 ^a	step 2	step 3		
vacuum	130–176 ^b			isothermal manometry	1, 2
vacuum	138			isothermal TGA	3
vacuum	242			isothermal TGA	3
vacuum	117	213–230		isothermal manometry	5
<i>c</i>	96	254		isothermal heating	7
N ₂	150–250 ^b			nonisothermal TGA	8
N ₂	210			nonisothermal TGA	9
N ₂	154	133		nonisothermal TGA	11
N ₂		210		nonisothermal TGA	12
air ^e	75	62	114	nonisothermal TGA	12
N ₂	31	224		isothermal TGA	12
air ^f	68	144	125	isothermal TGA	12
N ₂	233	104		isothermal heating	13
air	64			isothermal heating	13
N ₂	113			nonisothermal TGA	15
N ₂	130–180 ^b			nonisothermal TGA	16
air	250–125 ^b			nonisothermal TGA	26
	($\alpha < 0.5$)				
Ar	272	63		flash pyrolysis	28
<i>c</i>	159			pyrolysis	30
<i>c</i>	260			isothermal TGA	31

^a Single *E* values are listed under step 1 regardless of the number of steps reported. ^b *E* increases with α . ^c Not reported. ^d *E* decreases with α . ^e Heating rate was >3 °C min⁻¹. ^f Temperatures \leq 237 °C.

activation energy, which varies with the extent of conversion.³⁴ This dependence reflects the variation in relative contributions of single reaction steps to the overall reaction rate measured in a thermal analysis experiment.³³ Revealing such a dependence not only helps in detecting multistep kinetics but also assists in elucidating the reaction mechanisms.^{33,35}

In this study we employ thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to examine the thermal degradation of PMMA in both pure nitrogen and oxygen-containing atmospheres. The purpose of this work is to obtain reliable estimates for the activation energy of these processes as well as to provide further insight into the stabilizing effect of oxygen on the initial stages of PMMA degradation.

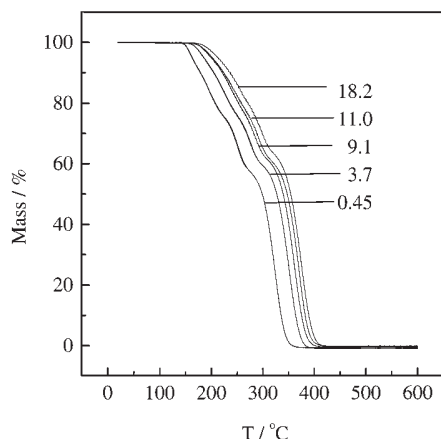


Figure 1. TGA curves at various heating rates for thermal decomposition of PMMA under nitrogen. The heating rate of each experiment (in $^{\circ}\text{C min}^{-1}$) is indicated by each curve.

Experimental Section

PMMA synthesized via radical polymerization ($M_w \approx 996\,000$) was obtained from Aldrich. The first TGA runs showed a small weight lost around $100\text{ }^{\circ}\text{C}$ that was ascribed to moisture. The latter was removed by drying samples in an oven under air at $\sim 120\text{ }^{\circ}\text{C}$ overnight. Neither we nor the vendor is aware of the presence of any thermal stabilizers in the sample. The dried samples were ground up in an agate mortar. The particle size was $<100\text{ }\mu\text{m}$ as measured by using an optical microscope. TGA experiments were performed by using a Rheometric Scientific TGA 1000M+. PMMA samples of 1–2 mg were placed in aluminum pans and heated at nominal heating rates of $0.5\text{--}20\text{ }^{\circ}\text{C min}^{-1}$ up to $600\text{ }^{\circ}\text{C}$. The actual heating rates were calculated from temperature measurements made during the period of PMMA decomposition. The experiments were conducted in flowing atmospheres of nitrogen, air, oxygen, and nitric oxide at flow rates of $100\text{--}200\text{ mL min}^{-1}$. The gas supply line was equipped with a valve that allowed for quick switch of gases while an experiment was being performed.

A Mettler-Toledo DSC821^e was used to conduct DSC runs. PMMA samples weighing 10–15 mg were placed in open aluminum pans and heated at $20\text{ }^{\circ}\text{C min}^{-1}$ up to $600\text{ }^{\circ}\text{C}$ in the atmospheres of flowing air and nitrogen (flow rate of 80 mL min^{-1}).

Results

Degradation in Nitrogen and Air. Figure 1 shows the TGA curves of PMMA degradation under nitrogen at various heating rates. At heating rates above $3.7\text{ }^{\circ}\text{C min}^{-1}$ the decomposition of PMMA shows two steps that occur in the temperature ranges $180\text{--}350$ and $350\text{--}400\text{ }^{\circ}\text{C}$, respectively. At slower heating rates (0.45 and $3.7\text{ }^{\circ}\text{C min}^{-1}$) one may observe an additional degradation step that occurs about $220\text{ }^{\circ}\text{C}$.

Figure 2 presents a nonisothermal TGA experiment conducted under air at various heating rates. Unlike the degradation under nitrogen, the process in air proceeds in one step. Additionally, we can see that the initial temperature for degradation under air is about $70\text{ }^{\circ}\text{C}$ higher than that for the process under nitrogen.

Figure 3 displays DSC data collected under nitrogen and air. The thermal degradation under nitrogen shows three overlapped endothermic peaks with minima at 260 , 300 , and $380\text{ }^{\circ}\text{C}$. Under air, DSC data show only a single broad endothermic peak that stretches from 200 to $450\text{ }^{\circ}\text{C}$. The instability of the DSC signal in the vicinity of the maximum has been found to be reproducible in three successive runs. The integral heat consumption in

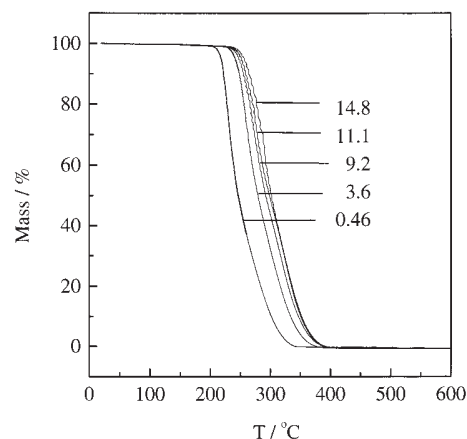


Figure 2. TGA curves at various heating rates for thermal decomposition of PMMA under air. The heating rate of each experiment (in $^{\circ}\text{C min}^{-1}$) is indicated by each curve.

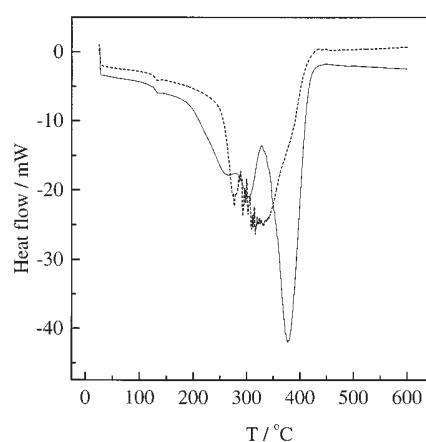


Figure 3. Overlay of DSC scans collected under air (dashed line) and nitrogen (solid line). The masses of PMMA samples are 9.8 and 15.5 mg for scans under N_2 and air, respectively. Heating rate is $20\text{ }^{\circ}\text{C min}^{-1}$.

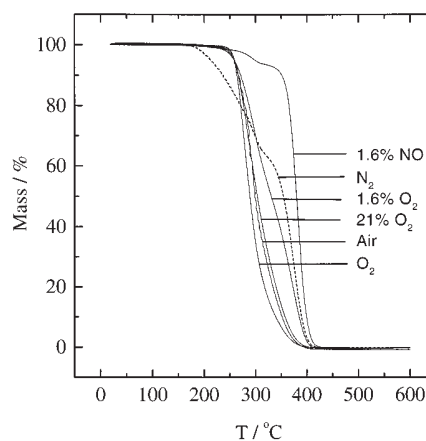


Figure 4. TGA curves for PMMA degradation under various atmospheric conditions. Percents indicate the concentration of a gas in its mixture with N_2 .

the temperature region $140\text{--}440\text{ }^{\circ}\text{C}$ has been evaluated as 1080 and 550 J g^{-1} for respective degradations under nitrogen and air.

Effect of Oxygen Concentration on Degradation. Figure 4 shows TGA curves collected for PMMA degradation in the atmospheres containing different concentrations of oxygen. As we can see, increasing the amount of oxygen above its natural concentration in air does not cause a further increase in the initial

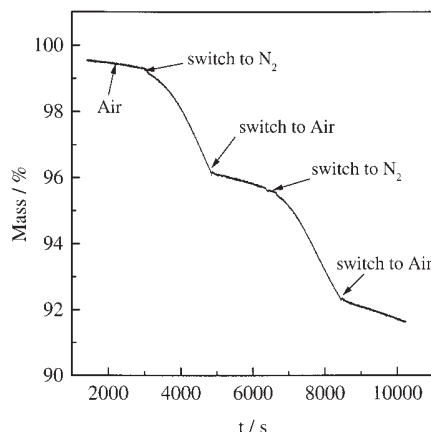


Figure 5. TGA curve showing the effect of switching of gaseous atmospheres between air and nitrogen on the thermal degradation of PMMA at 200 °C.

temperature of degradation. In other words, the stabilizing effect of oxygen has already reached its saturation in air. The use of an oxygen–nitrogen mixture containing 21% oxygen gives rise to a TGA curve that is very similar to that obtained for degradation under air. For technical reasons (the maximum gas flow should not exceed 200 mL min⁻¹), we could not obtain an oxygen–nitrogen mixture with an oxygen concentration lower than 1.6%. Even at this level, oxygen has a profound stabilizing effect on PMMA degradation.

Effect of Switching between Air and Nitrogen on Degradation. Figure 5 shows how switching of gaseous atmospheres between air and nitrogen affects the thermal degradation of PMMA. Degradation was started in the atmosphere of air. This process is characterized by a slow rate. Upon switching to a nitrogen atmosphere, the degradation rate increases significantly. Switching back to air causes the reaction rate to immediately slow down. This switching of reaction atmospheres was repeated at regular intervals until a 9% mass loss was achieved. The effect appears to be reversible.

Visual Analysis of Partially Degraded Samples. Several experiments run under air and nitrogen were stopped at 20% mass loss and analyzed visually. Note that this extent of degradation is reached at practically the same temperature for degradations performed under nitrogen and air (Figure 4). Visually, the sample degraded in air was a single chunk of clear glassy material that contained a few bubbles. The sample decomposed in nitrogen, however, was a white powder material similar to the original PMMA sample.

Kinetic Analysis of TGA Data. The kinetics of heterogeneous decompositions is traditionally described by the basic kinetic equation

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α represents the extent of reaction ($\alpha = 0-1$), t is time, $k(T)$ is the rate constant, and $f(\alpha)$ is the reaction model, which describes the dependence of the reaction rate on the extent of reaction. The value of α is experimentally determined from TGA as a relative mass loss and from DSC as a fractional peak area. In most cases the temperature dependence of $k(T)$ can be satisfactorily described by the Arrhenius equation, whose substitution into eq 1 yields

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right)f(\alpha) \quad (2)$$

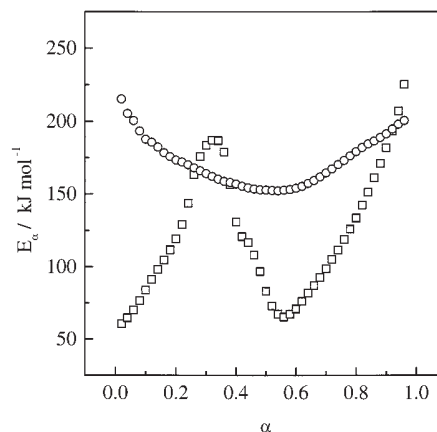


Figure 6. E_α -dependencies obtained by isoconversional analysis of TGA data for degradations under nitrogen (squares) and air (circles).

where E is the activation energy and A is the preexponential factor. To evaluate a dependence of the effective activation energy on the extent of conversion, we used an advanced isoconversional method,³⁶ which is based on the assumption that the reaction model is independent of the heating program, $T(t)$. According to this method, for a set of n experiments carried out at different heating programs, the activation energy is determined at any particular value of α by finding E_α that minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \left(\frac{\mathcal{J}[E_\alpha, T_i(t_\alpha)]}{\mathcal{J}[E_\alpha, T_j(t_\alpha)]} - 1 \right)^2 \quad (3)$$

where the subscripts i and j represent ordinal numbers of two experiments performed under different heating programs. Henceforth, the subscript α denotes the values related to a given extent of conversion. In eq 3, the integral

$$\mathcal{J}[E_\alpha, T_i(t_\alpha)] \equiv \int_0^{t_\alpha} \exp\left[\frac{-E_\alpha}{R T_i(t)}\right] dt \quad (4)$$

is evaluated numerically for a set of experimentally recorded heating programs, $T_i(t)$. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion. An advantage of the advanced isoconversional method is that it can be applied to study the kinetics under arbitrary temperature programs (e.g., under a linear heating program distorted by self-heating).³⁶

Figure 6 shows the E_α dependencies evaluated for the thermal degradation of PMMA under nitrogen and air. Under nitrogen, the initial activation energy required to initiate decomposition was about 60 kJ mol⁻¹. As the reaction approaches 30% conversion, the activation energy increases to a maximum value of about 190 kJ mol⁻¹. This is followed by a decrease from 190 to ~60 kJ mol⁻¹ in the region $0.3 < \alpha < 0.55$. This decrease falls in the transition region between the first and second step in the mass loss. Further degradation ($\alpha > 0.55$) is characterized by an increase in the activation energy from 60 to ~230 kJ mol⁻¹ near completion.

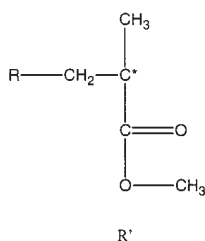
In air the thermal degradation of PMMA gives rise to a parabolic E_α dependence that decreases from about 220 kJ mol⁻¹ to a minimum value of 160 kJ mol⁻¹ at $\alpha \approx 0.55$ degradation. Then the activation energy rises to about 200 kJ mol⁻¹ at completion.

Discussion

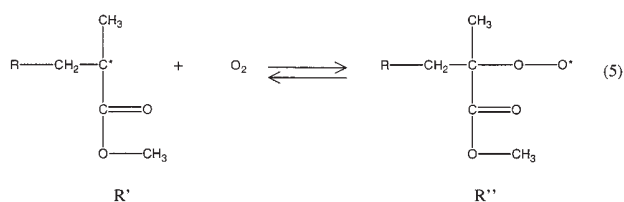
Degradation in Nitrogen. In the absence of oxygen, the thermal degradation of radically polymerized PMMA usually

shows two or three mass loss steps during decomposition. The two-step degradation was first noticed by Grassie and Melville^{1,2} who suggested that the initial degradation of PMMA is initiated at vinylidene end groups, which resulted from a bimolecular radical termination during polymerization.³⁷ Once the vinylidene-terminated chains have unzipped, the further degradation is initiated by random scission that corresponds to the second mass loss step in TGA experiments.³⁷ At slower heating rates, one may observe that the first step actually involves two substeps (Figure 1). Kashiwagi et al.¹⁸ assign the lower temperature substep to degradation initiated at abnormal head-to-head linkages that were formed as a result of termination by combination of growing polymer chains. For radically polymerized PMMA, Kashiwagi et al.¹⁸ report that the total fraction of polymer molecules that contain the head-to-head linkages and the vinylidene end groups is 28% and 36%, respectively. At faster heating rates, the first substep is not practically noticeable in TGA experiments (Figure 1) because of its strong overlap with the second substep, which corresponds to degradation initiated at the vinylidene end groups. Nevertheless, these two substeps are clearly seen in DSC experiments even if they are performed at faster heating rates (Figure 3). Therefore, one should keep in mind that the first step actually consists of two closely overlapped substeps.

Stabilizing Effect of Oxygen. The initiation at both the vinylidene end group and the head-to-head linkage results in formation of the polymer radical, R'



In an oxygen-containing atmosphere, this radical is likely to react with oxygen to form a new polymer radical R''



The peroxy radical R'' is more thermally stable than R' by about³⁸ 100 kJ mol^{-1} and thus inhibits unzipping of the polymer chain. If unzipping is suppressed, degradation occurs through random scission that produces only a small amount of low molecular weight species capable of vaporizing. As a result, the TGA experiments conducted under air show a noticeable delay in the mass loss compared to the experiments performed under nitrogen (Figure 4).

According to our TGA data (Figure 5), formation of the peroxy radical R'' is reversible. In all our experiments performed under oxygen-containing atmospheres, the amount of oxygen significantly exceeds the stoichiometry required by eq 5. This means that the reversible process is shifted toward formation of R'' . Because reaction 5 is exothermic, an increase in temperature should favor the reverse reaction. Therefore, further heating should cause R'' to ultimately decompose to oxygen

and an original radical (R'). The onset of the depolymerization reaction is thereby shifted to higher temperatures.

The proposed scheme also explains the initial acceleration in degradation rate compared with that for degradation under nitrogen. According to our mechanism, oxygen delays degradation by protecting potential reaction centers (R') formed as a result of initiation at the vinylidene end groups or the head-to-head linkages. Hence, the potential reaction centers are accumulated in a less reactive form of the peroxy radical R'' . In the vicinity of $270 \text{ }^\circ\text{C}$, R'' decomposes quickly, releasing the highly reactive reaction centers R' . The release of a great number of R' radicals over a short period of time causes a noticeable acceleration of the initial degradation of PMMA in an oxygen-containing atmosphere.

Because the degradation occurs markedly faster than under nitrogen, the corresponding TGA curve eventually crosses the curve obtained for degradation under nitrogen. The curves cross at approximately 20% of mass loss (Figure 4). At this point the PMMA samples decomposed under either air or nitrogen are at the same temperature and extent of degradation. However the appearance of the quenched samples is markedly different. Under air, the separate grains of PMMA coalesce into a single body that suggests that the decomposing polymer is a viscous liquid. Consequently, this sample has a markedly lower molecular weight than the sample decomposed under nitrogen, which consists of separate grains. This conclusion agrees with direct measurements of viscosity¹⁹ and the number-averaged molecular weight¹³ (M_n) for PMMA samples degraded under nitrogen and oxygen. The escape of gaseous products from PMMA is accompanied by the formation of bubbles, the popping of which causes the instability in the DSC signal at $270\text{--}330 \text{ }^\circ\text{C}$ (Figure 3). Since a decrease in M_n is primarily caused by random scission, we may assume that oxygen promotes this process. Besides that, oxygen causes highly exothermic oxidation that significantly diminishes the overall endothermicity of degradation. Oxidation appears to be highly exothermic because the total amount of detected²⁴ oxidation products is less than 5%.

Brown and Kashiwagi²¹ have recently proposed a mechanism to explain the stabilizing effect of oxygen. The mechanism assumes that oxygen attacks hydrogen activated by the terminal vinylidene group to form a hydroperoxide. The latter undergoes β -scission, forming a hydroxy-terminated polymer and a carbonyl vinyl ester compound. According to this mechanism, oxygen also promotes random scission that results in acceleration of degradation at the later stage. This process is accompanied by elimination of an ester compound and water. Neither the predicted ester compounds nor water has been experimentally observed by Song et al.,²⁴ who studied the products of PMMA degradation in the presence of oxygen. The major oxidation product (2.2%) was 2-methyloxirane carbonic acid methyl ester that is formed as a result of main chain scission.²⁴ The second major oxidation product was methyl pyruvate (0.37%). Therefore, the above-mentioned mechanism does not agree with the experimental data by Song et al.²⁴

Another mechanism was earlier proposed by Kashiwagi et al.¹⁸ This mechanism includes an irreversible formation of R'' (cf., eq 5), which after rearrangements traps oxygen in the polymer chain and eliminates methyl pyruvate, which has been experimentally detected by Song et al.²⁴ Note that the observed amount of methyl pyruvate (0.37%) significantly exceeds the maximum theoretical yield obtained under the assumption that methyl pyruvate is formed only in a reaction initiated at a weak link that presumably is present in each polymer chain. The

excessive amount of methyl pyruvate seems to indicate the existence of an alternative channel that also yields this product. Therefore, the detection of methyl pyruvate does not provide unequivocal evidence for the above mechanism. Nevertheless, this does not discard this mechanism as a plausible cause for explaining the stabilizing effect of oxygen.

The only weakness of the mechanism proposed by Kashiwagi et al.¹⁸ is that it is uniquely developed for oxygen. For this reason it does not allow one to predict the stabilizing effect of other substances. On the contrary, our mechanism predicts that any species of a low electron affinity should cause a stabilizing effect similar to that of oxygen. The following section provides an example of such an effect demonstrated by nitric oxide.

Degradation in NO-Containing Atmosphere. The thermal degradation of PMMA in a NO-containing atmosphere has been conducted to provide further evidence in support of radical reaction 5 as being a process that delays degradation of PMMA. Oxygen does not play a unique role in reaction 5. As a matter of fact, any other species of a low electron affinity should also demonstrate a stabilizing effect. Nitric oxide, which is a stable radical in its ground state, was therefore a natural choice. As seen in Figure 4, introduction of NO in the atmosphere of decomposing PMMA has a profound stabilizing effect on the initial degradation of PMMA. The onset decomposition temperature increases about 100 °C relative to that for degradation under nitrogen. When cooled to room temperature, the 20% degraded sample looked like a single chunk of glassy material similar to that obtained after the partial degradation under air. Unlike degradation in an oxygen-containing atmosphere, the process under NO shows the initial 5% mass loss, which is likely to result from formation of volatile byproducts of a reaction between NO and PMMA.

E_{α} Dependence for Degradation under Nitrogen. Figure 6 shows the E_{α} dependencies determined by the isoconversional method for the thermal degradation of PMMA under nitrogen and air. This graph clearly demonstrates that the degradation of PMMA cannot be adequately described by a single value of the activation energy.

For degradation under nitrogen, the first step (recall that it consists of two closely overlapped substeps) of mass loss accounts for ~30% of the initial mass (Figure 1). The effective activation energy for this step shows an increase from 60 to 190 kJ mol⁻¹ at $\alpha < 0.3$. Degradation starts at the weak linkages, whose concentration is very high at low extents of degradation. Therefore, unzipping of the polymer chain controls the overall degradation rate. The value of 60 kJ mol⁻¹ obtained at low α is consistent with the estimate of the activation energy (15 kcal mol⁻¹) for unzipping of the polymer radical.³⁹ Somewhat greater values were reported by Mita⁴⁰ (75 kJ mol⁻¹) and Cowley and Melville⁴¹ (77 kJ mol⁻¹). The concentration of the weak linkages decreases with the extent of degradation. As a result, the rate-limiting step shifts from unzipping to initiation, which has a significantly higher activation energy. This shift is observed as an increase in the effective value of E_{α} in the region $0 < \alpha < 0.35$ (Figure 6). Grassie and Melville^{2,39} and Dickens and Flynn⁸ have also observed an increase in the activation energy at the initial stage of PMMA degradation.

At $\alpha \approx 0.3$, E_{α} is about 190 kJ mol⁻¹, which gives us an estimate for the effective activation energy for degradation limited by initiation. According to TGA data (Figure 1), $\alpha \approx 0.3$ corresponds to the middle of the second substep, which is degradation initiated at the vinylidene end groups. Once initiation at the vinylidene end groups has produced a sufficient number of reaction centers, unzipping becomes the rate-

controlling step and the effective activation energy decreases to ~60 kJ mol⁻¹ in the region $0.3 < \alpha < 0.55$ (Figure 6). The second step of mass loss ($\alpha > 0.55$) seems to be associated with the change in the rate-controlling step from unzipping to initiation by random scission. This process is accompanied by an increase in the effective activation energy up to a value of ~230 kJ mol⁻¹, which gives as an estimate for the activation energy of degradation initiated by random scission.

E_{α} Dependence for Degradation under Air. According to the proposed mechanism (reaction 5), the delayed degradation under air starts as a result of decomposition of R'' to R' and oxygen. The released R' radicals immediately initiate the process of unzipping. On the other hand, we have concluded that the presence of oxygen favors random scission that is also followed by unzipping. Therefore, the overall rate of degradation should be determined by the rates of both formation of R' from R'' and random scission. The rate of forming R' is practically equal to the rate of the reverse reaction in eq 5. Because the forward reaction has essentially no activation energy,⁴² the activation energy for the reverse reaction should roughly be equal to the enthalpy of the reversible process 5 that we earlier estimated as ~100 kJ mol⁻¹. As mentioned above, the activation energy of degradation initiated by random scission in nitrogen is estimated to be ~230 kJ mol⁻¹. This value gives a rough estimate for a similar process in air.

The observed E_{α} dependence (Figure 6) is consistent with the occurrence of the two degradation pathways. At $\alpha < 0.05$, E_{α} is around 200 kJ mol⁻¹, which suggests that the initial weight loss is most likely to be associated with degradation initiated by random scission. The decrease in the effective activation energy (Figure 6) reflects an increasing contribution of the alternative pathway (formation of R' from R'') to the overall degradation rate. The contribution of this pathway reaches its maximum at $\alpha \approx 0.55$. The effective activation energy at this point is around 150 kJ mol⁻¹, which is greater than the estimated activation energy (100 kJ mol⁻¹) for forming R' from R''. This suggests that the rates of forming R' and random scission are comparable at this point. Note that Schneider and Hurduc²⁶ obtained a similar E_{α} dependence that decreased from about 250 kJ mol⁻¹ to a minimum of about 125 kJ mol⁻¹, which occurred at about 50% decomposition (the remaining part of the dependence was not reported). The increase in E_{α} at $\alpha > 0.55$ (Figure 6) is associated with the increasing contribution of degradation initiated by random scission to the overall degradation rate. The maximum value (200 kJ mol⁻¹) reached at completion gives us an estimate for the activation energy of degradation initiated by random scission under air. This value is very close to the activation energy of degradation initiated by random scission in nitrogen (230 kJ mol⁻¹).

Conclusions

A mechanism has been proposed to explain the stabilizing effect of oxygen on the thermal degradation of PMMA. This mechanism suggests an explanation for the initial delay of degradation as well as for the subsequent acceleration of the process. The proposed mechanism predicts that other species of low electron affinity should also cause a stabilizing effect, which has been confirmed by conducting degradation in the NO-containing atmosphere. Kinetic analysis suggests that the initial rates of degradation under nitrogen and air are respectively controlled by the unzipping of the polymer chain and by degradation initiated by random scission. The activation energies for these processes are found to be ~60 (unzipping) and 200 (random scission) kJ mol⁻¹. At the later stage the thermal

degradation is controlled by random scission under both air and nitrogen. A change in the gaseous atmosphere does not practically affect the activation energies for this process that were estimated to be 200 and 230 kJ mol⁻¹ under air and nitrogen, respectively.

Acknowledgment. The authors thank the Mettler-Toledo, Inc. for donating the DSC instrument used in the present study. This research is supported by the University of Utah Center for Simulations of Accidental Fires and Explosions (C-SAFE), funded by the Department of Energy, Lawrence Livermore Laboratory, under Subcontract B341493.

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