

Thermal Degradation of Poly(Methyl Methacrylate) at 50°C to 125°C

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Synopsis

Small but significant numbers of chain scissions occur in a commercial poly(methyl methacrylate) sheet exposed to temperatures between 50 and 125°C. The scission rate is initially high and then levels off to a constant rate. The short-time rate of chain scissions is temperature dependent, while the long-time rate of chain scissions appears to be temperature independent. Four possible sources of random chain scission initiation were considered: (1) the presence of unreacted initiators of polymerization, (2) free radicals generated from additives in the commercial film, (3) weak links in the polymer chain, and (4) free radicals generated from the thermal decomposition of an oxidation product of methyl methacrylate (MMA) monomer. The source most consistent with our results is the one involving free radicals generated from the oxidation product of MMA monomer.

INTRODUCTION

Specimens from a commercial poly(methyl methacrylate) (PMMA) sheet were exposed to five temperatures between 50 and 125°C in air for exposure times exceeding 2000 h. At all temperatures, a small but significant number of random chain scissions per molecule was observed (see Fig. 1) with little or no accompanying loss in film weight. Thermally induced random chain scissions in pure PMMA are typically associated with temperatures greater than 200°C.¹⁻⁴ The objective of this study was to understand the mechanism of thermal degradation of PMMA between 50° and 125°C.

EXPERIMENTAL

The experimental design is shown in Table I. It includes three different PMMA materials exposed to five different temperatures in air and in vacuum.

Characterization of the Commercial PMMA

The commercial PMMA was a sheet of Rohm & Haas's UVT.[†] According to Rohm & Haas, UVT contains no photostabilizers and only a small number of additives, one of which is an unsaturated chain transfer agent. The original

[†] Identification is made solely to define experimental materials and not to endorse a particular product.

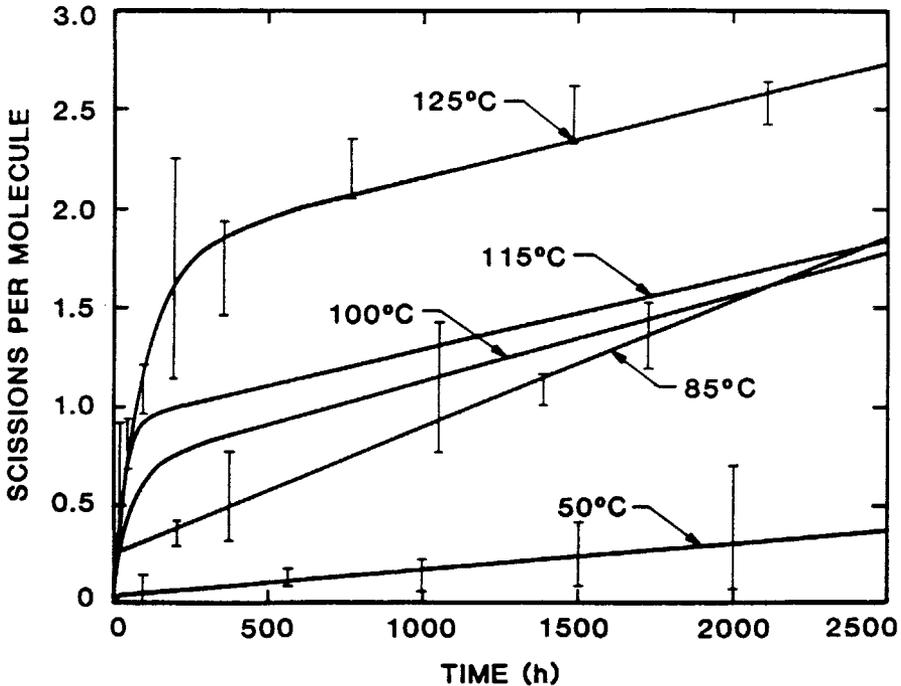


Fig. 1. Number of scissions per molecule versus exposure time for commercial PMMA films exposed in air at five different temperatures. Brackets are 90% confidence bands. Confidence bands for 100°C and 115°C data are not shown, but they are no worse than the ones displayed. The equation used in fitting the scission versus exposure time data is given in footnote on p. 385.

UVT sheet was 126 cm by 183 cm by 0.157 cm and from this sheet approximately 1500 specimens were cut, each having dimensions of 3.7 cm by 1.8 cm.

From these specimens, 20 controls were randomly selected and their number average molecule weights determined (mean = 370,000, standard deviation (SD) = 18,000) using the gel permeation chromatography programs (GPC)

TABLE I
Experimental Design

MATERIAL	TEMPERATURE									
	50°C		85°C		100°C		115°C		125°C	
	AIR	VAC	AIR	VAC	AIR	VAC	AIR	VAC	AIR	VAC
UVT	X ₅ *		X ₈	X ₆	X ₈		X ₈	X ₆	X ₈	
Rpvt UVT No monomer			X ₆	X ₅			X ₃	X ₅		
Rpvt UVT Monomer			X ₃				X ₂	X ₃		

* X_N - indicates that an exposure test was conducted for this environmental condition and temperature. Subscript N indicates the number of removal times.

described by Dickens et al.⁵ From these twenty controls, eight were further analyzed for low molecular weight constituents using a Varian Model 3700 Gas Chromatograph (GC) with 3% SP-1500 and 80/120 Carbopak B columns and a Hewlett-Packard Model 5930 GC-mass spectrometer (GC-MS) data system. Five low molecular weight constituents were identified. Two (acetone dimethylacetate and methyl, 2-hydroxy, 2-methyl propionate) did not change in concentration during exposure and, therefore, are not considered to be important to the thermal degradation process. The other three changed in concentration during thermal exposure and include (1) methyl methacrylate (MMA) monomer (mean = 3.0% by weight of the solid film, SD of 0.2%), (2) methyl pyruvate (mean 0.046% by mass of the solid film, SD 0.009%), and (3) as discussed subsequently, what we believe to be an oxidation product of monomer. In the unaged commercial films, the initial concentration of the oxidation product of monomer has a mean value of 0.015 with a 0.002 SD. These concentration units are relative to tetrahydrofuran which was added to the methylene chloride solvent in a known concentration for peak height calibration. In an analysis of variance, no significant differences were detected in the concentration of the five constituents or in the number average molecular weight of the PMMA over the unaged commercial sheet.

Evidence for an oxidation product of MMA monomer came from both our GC-MS and GC analyses. Mass fragments of 116, 101, 84, 73, 57, 45, and 43 were found. The mass fragment of 116 is suggestive of an MMA molecule with an additional oxygen atom. In an attempt to confirm this assignment, we followed the procedure given by Barnes et al.⁶ for producing the oxidation product of MMA from purified MMA. The purified MMA was heated in excess oxygen to 115°C for 10 h, whereupon it polymerized. The polymerized solid was then dissolved in methylene chloride and analyzed in a gas chromatograph. A compound eluted from the gas chromatograph at the same time as the suspected oxidation product of MMA in our commercial film, thus lending support to our identification. The chemical structure of this oxidation product, however, has not been ascertained. It may be a monomeric peroxide,⁷⁻⁹ a monomeric hydroperoxide,^{8,10} or a low molecular weight polyperoxide.^{6,11} Henceforth, this compound will be referred to as the oxidation product of monomer and its radical as the free radical from the oxidated monomer. Later in this paper, evidence is given that this oxidation product of monomer is thermally unstable.

Preparation of Purified and Doped PMMA Films

Reprecipitated and reprecipitated-plus-monomer samples were prepared by twice dissolving the specimens from the commercial UVT sheet in methylene chloride and reprecipitating with methanol. The solvent was removed by heating the reprecipitated film to 100°C in a vacuum (approximately 25 μ m Hg) for three weeks. The reprecipitated-plus-monomer films were made by soaking the reprecipitated films in a solution of 20% monomer and 80% methanol for 24 h and then removing methanol by heating the film to 100°C in a vacuum (approximately 25 μ m Hg) for three weeks. The thickness of the reprecipitated films ranged between 0.3 and 1.1 mm; each specimen, however, was uniform in thickness and had a number average molecular weight of

370,000 (SD 6000). The monomer concentration of the reprecipitated films was 0.03% (SD 0.03%) by weight while that of the reprecipitated-plus-monomer films was 0.24% by weight (SD 0.05%). Methyl pyruvate and the oxidation product of monomer were not detected in either of these films.

Experimental Conditions

Specimens were exposed at 50, 85, 100, 115, and 125°C in an air-circulating oven. The number of specimens removed for chemical analysis, the time intervals between removals, and the total number of specimen removals depended on the exposure conditions. The number of removals is given in Table I. For the commercial PMMA specimens thermally aged in air, 24 to 32 specimens were typically exposed. For the reprecipitated films, only one specimen was removed at each time interval; hence, six or fewer specimens were exposed at any temperature.

Specimens were exposed in two different air environments—closed cell and open cell. In the closed cell, specimens were placed on a glass plate which was sealed with a neoprene O-ring in a glass container. In the open cell, the specimens were placed on copper plates in an air-circulating oven. Copper is known not to catalyze the thermal degradation of PMMA.¹² We verified this by simultaneously exposing commercial PMMA specimens on copper and glass plates in an air-circulating oven at 115°C. No differences were found in the total number of scissions.

For the vacuum exposures, specimens were first placed in a vacuum at 22°C for six weeks prior to thermal exposure (approximately 25 $\mu\text{m Hg}$). These specimens were then placed on glass plates and sealed in glass containers outfitted with a vacuum port. The containers were then heated to and maintained at a designated temperature while being continuously evacuated for the length of the experiment.

RESULTS

In Figures 2, 3, and 4, the number of chain scissions per molecule, N , and the concentrations of monomer, methyl pyruvate, and the relative concentration of oxidation product of monomer are plotted against exposure time for the commercial PMMA specimens exposed in air (Fig. 2), for the commercial PMMA specimens exposed in vacuum (Fig. 3), and for the reprecipitated specimens exposed in air and vacuum (Fig. 4). In Figure 5, the number of scissions per molecule is plotted against time for the reprecipitated-plus-monomer samples exposed in air and in vacuum. The number of scissions per molecule, N , was computed from our GPC results as follows:⁵

$$N = \text{Mn}_0 / \text{Mn}_t - 1 \quad [1]$$

where

Mn_0 is the number average molecular weight of the unaged film, and

Mn_t is the number average molecular weight of film aged for time t .

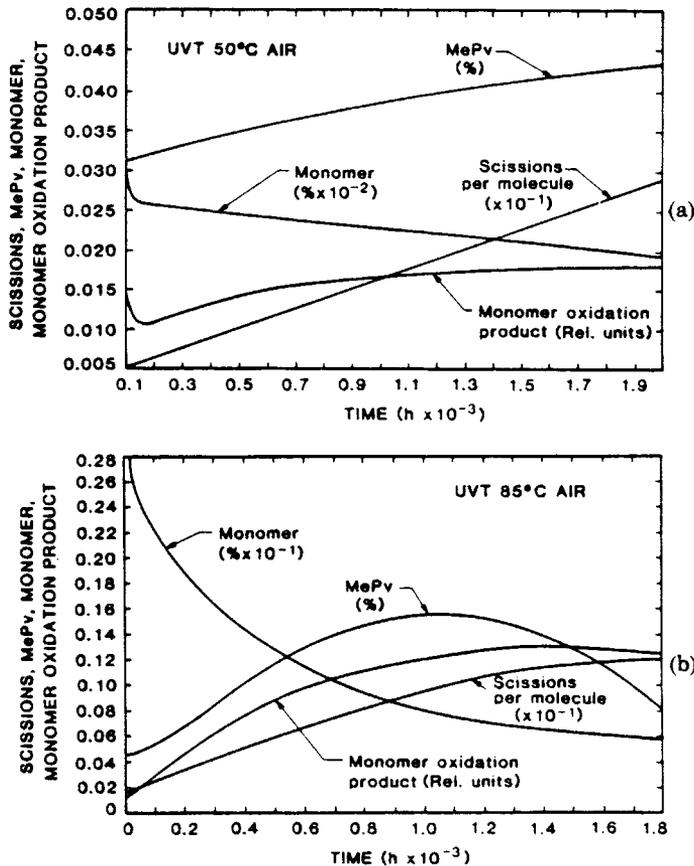


Fig. 2. Number of scissions per molecule and concentrations of methyl pyruvate, monomer, and an oxidation product of monomer with exposure time for commercial PMMA exposed in air at different temperatures.

We found that the most sensitive indicator of thermal degradation is the number of random chain scissions. The randomness of the scission process was ascertained using Scott's criterion¹³ in which Mw_t/Mw_0 is plotted against Mn_t/Mn_0 for all specimens exposed at a given temperature and in a given environment. Mw_0 and Mn_0 are the initial weight and number average molecular weights and Mw_t and Mn_t are the weight and number average molecular weights after exposure time t . Superimposed on our experimental data is the theoretical line for a polymer which maintains a polydispersity ratio (Mw_t/Mn_t) of two. Deviations from this theoretical line indicate that the polydispersity ratio is not two; hence, scissions are not random. In general, our data fell very close to the theoretical line, as shown in Figure 6 for the commercial PMMA specimens exposed in air at 100°C. We conclude, therefore, that the scission process is random.

Scissions per Molecule

For commercial PMMA specimens exposed in air, the total number of chain scissions and the short-time (less than 400 h) rate of chain scissions increase with increasing temperature (see Fig. 1). The long-time (exposure times

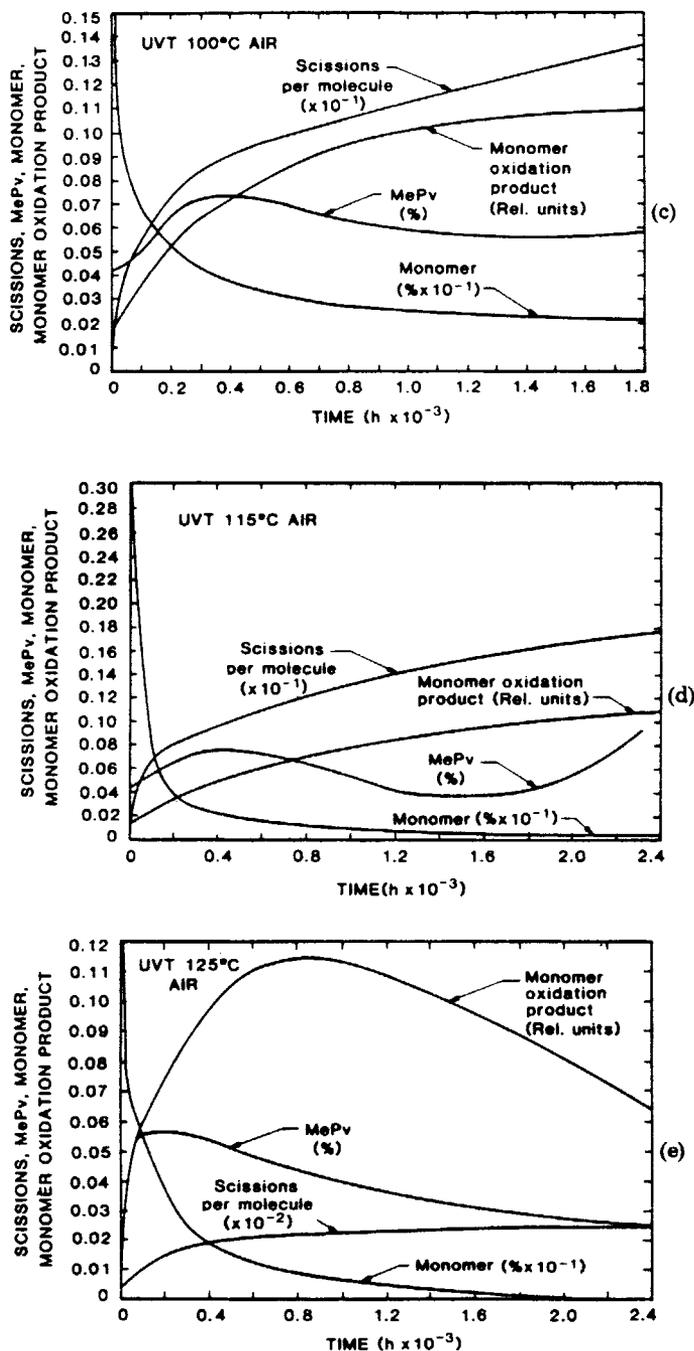


Fig. 2. (Continued from the previous page.)

exceeding 400 h) rate of chain scissions, however, is not greatly affected by an increase in temperature. Also, it remains relatively constant over time, suggesting a zeroth-order reaction (see Fig. 1). An exception to this are the 85°C results where we observe a higher long-time rate of chain scissions than at any other temperature. We suspect that this apparent higher rate of chain scission

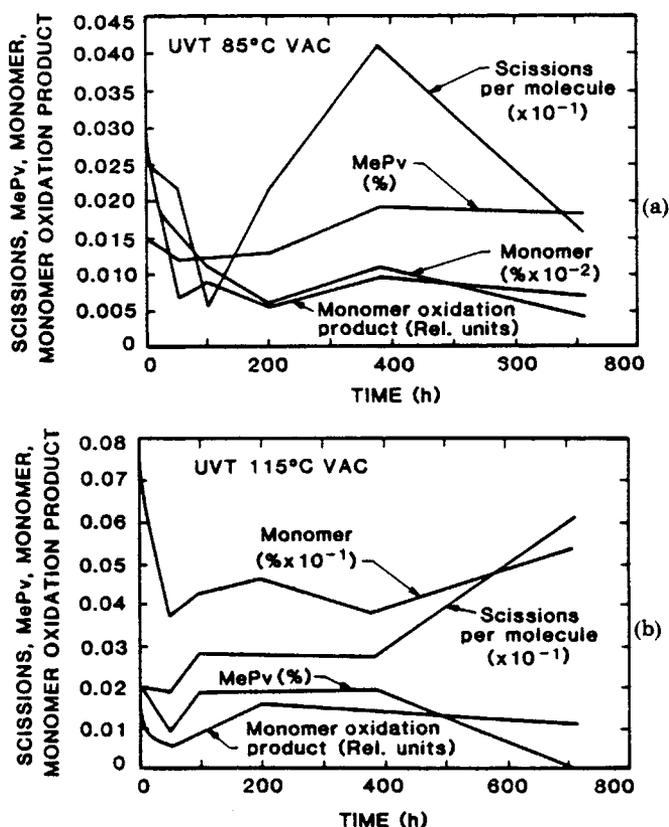


Fig. 3. Number of scissions per molecule and concentrations of methyl pyruvate, monomer, and an oxidation product of monomer with exposure time for commercial PMMA exposed in a vacuum at 85 and 115°C.

is due to a lack of sufficient data at long exposure times and that, in actuality, the true long-time rate of scissions at 85°C is the same as it is at the other temperatures. For the reprecipitated and reprecipitated-plus-monomer films exposed in air (Figs. 4 and 5), it is difficult to discern any trend in the data due to the low number of scissions per molecule and the small number of samples. Assuming a GPC measurement error of 15%, the only specimens having a significant number of scissions are the two reprecipitated-plus-monomer specimens exposed for 200 h at 115°C and for 10 h at 85°C.

For specimens exposed in a vacuum, the total number of chain scissions is always less than it is for specimens exposed in air at the same temperature and for the same exposure time (compare Fig. 3 with Fig. 2), indicating that oxygen plays an important role in the thermal degradation process. As is the case in air, most of the scissions occur a short time after the start of the vacuum exposure. Long-time trends in vacuum could not be discerned, however. Using our 15% GPC measurement error criterion, the total number of scissions per molecule is significant for the commercial specimens exposed at 85°C and 115°C in a vacuum (see Fig. 3), but is not significant for the reprecipitated (Fig. 4) and the reprecipitated-plus-monomer (Fig. 5) specimens.

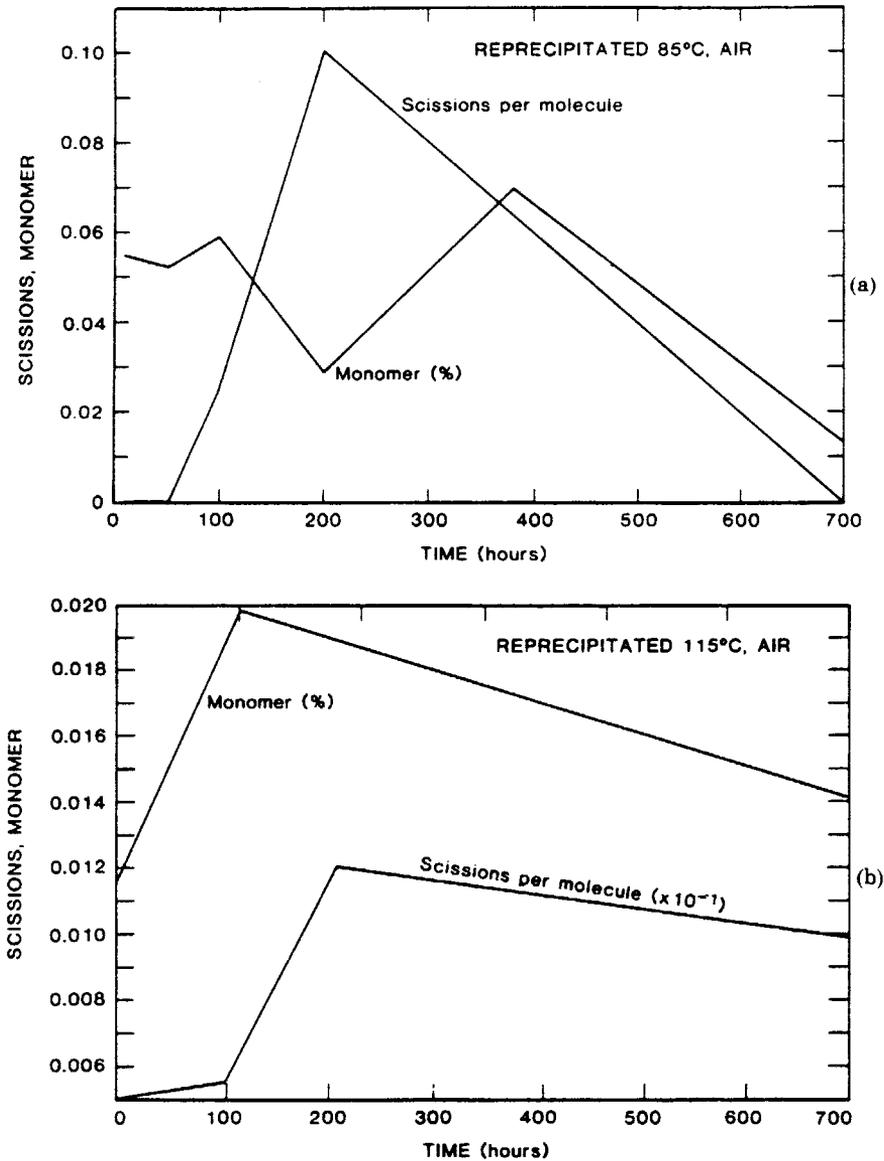


Fig. 4. Number of scissions per molecule and the concentration of monomer versus exposure time for reprecipitated commercial PMMA films exposed in air and in vacuum at 85 and 115°C.

MMA (Monomer)

For the commercial PMMA specimens exposed in air or in vacuum, the concentration of monomer changes considerably with exposure time. In both air and vacuum, the monomer concentration (initial concentration was 3.0%) decreases rapidly at first and then levels off. (The exception to this is the 50°C data where the decrease in monomer concentration appears to be relatively constant with time.) In general, the greater the temperature, the greater the short-time decrease in monomer concentration and the greater is the short-time increase in the number of scissions (Figs. 2 and 3). For long exposure times in

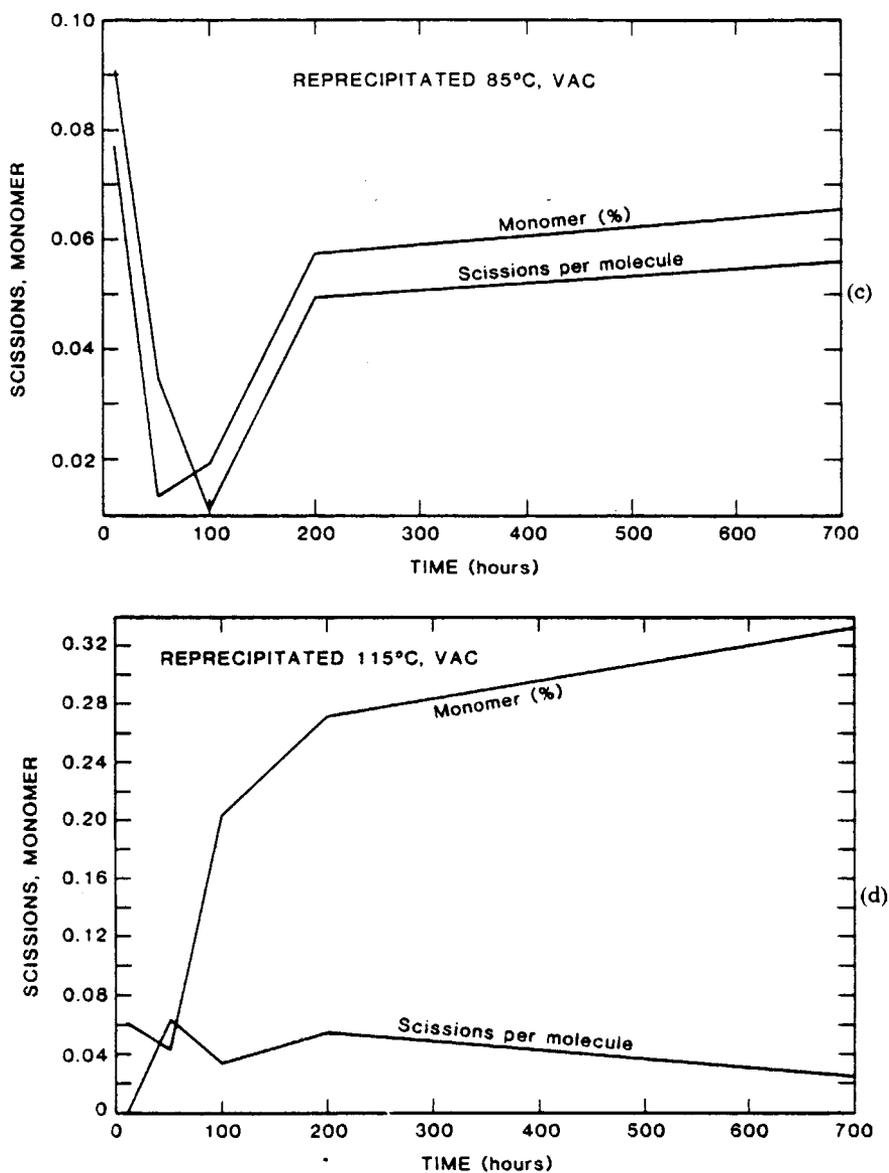


Fig. 4. (Continued from the previous page.)

air, the leveling off in monomer concentration begins at about the same time as the zeroth-order scission rate process becomes dominant.* For commercial PMMA specimens exposed for a long period of time in a vacuum, changes in

*We attempted to model the scission data in Fig. 1. The model which best fitted our data is a mixture of a first and a zeroth-order reaction rate process having the form

$$\text{number of scissions} = \alpha(1 - e^{-kt}) + k't.$$

With this model, the first-order process will effectively be completed after five time constants or $5/k$. Justification for this model will be given in a forthcoming paper.

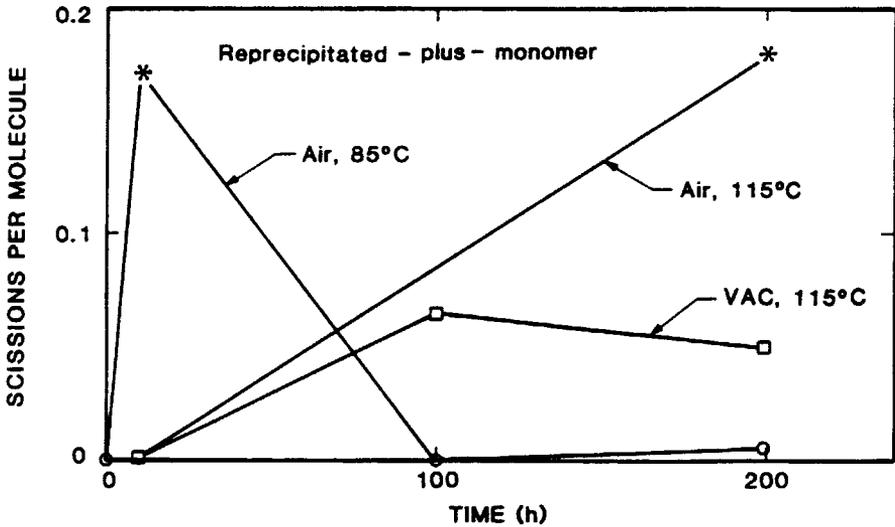


Fig. 5. Number of scissions per molecule versus exposure time for reprecipitated-plus-monomer specimens exposed at two temperatures in air and in vacuum. Specimens having a significant number of scissions are indicated with an asterisk.

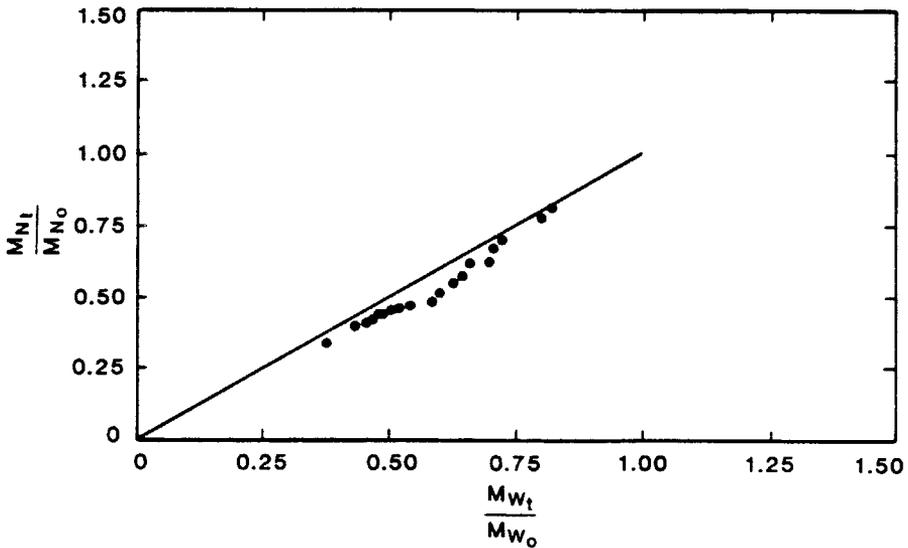


Fig. 6. Experimental data for the relative change in the number average molecular weight versus weight average molecular weight for commercial PMMA films exposed in air at 100°C compared with the theoretical behavior of random scissions of the most probable molecular weight distribution.

monomer concentration do not appear to be related to the number of chain scissions. For the reprecipitated (Fig. 4) and the reprecipitated-plus-monomer (not shown) specimens exposed in air, no trend in the monomer concentration was discerned; while for specimens exposed in a vacuum, the monomer concentration tended to increase with time.

Oxidation Product of Monomer

In air at all temperatures except 125°C, the concentration of the oxidation product of monomer in the commercial PMMA increases with increasing exposure time to an equilibrium relative concentration of approximately 0.12. The short-time increase in the concentration of the oxidation product of monomer appears to be related to the short-time increase in the number of scissions and the short-time decrease in monomer concentration. Likewise, the long-time leveling off in the concentration of the oxidation product of monomer appears to be related to the long-time leveling off in monomer concentration, and the long-time, zeroth-order scission rate process. At 125°C, the concentration of the oxidation product of monomer initially increases, levels off, and then rapidly decreases.

For commercial PMMA specimens exposed in a vacuum, the concentration of the oxidation product of monomer initially drops and then appears to level off. For the reprecipitated and reprecipitated-plus-monomer specimens, appreciable amounts of the oxidation product of monomer were not detected in any of the samples, except for the one reprecipitated-plus-monomer sample exposed at 115°C in air for 200 h.

Methyl Pyruvate

Trends in the concentration of methyl pyruvate in the commercial PMMA with time largely depend on the temperature to which the specimens were exposed. In air at 50°C, the concentration of methyl pyruvate does not change significantly from its initial value; at 85°C, the concentration of methyl pyruvate initially increases then decreases over time. At temperatures above 85°C, the concentration of methyl pyruvate at first increases, reaches a maximum, and then decreases to an equilibrium concentration between 0.04 and 0.06 wt%. An exception to this is the 125°C exposure, where the concentration of methyl pyruvate seems to continue to decrease. In air, the short-time increase in methyl pyruvate concentration corresponds to the short-time increase in chain scissions, the short-time increase in the concentration of the oxidation product of monomer, and the short-time decrease in monomer concentration. The long-time changes in methyl pyruvate concentration are poorly related to any other factor. For commercial PMMA specimens exposed in vacuum, changes in methyl pyruvate concentration appear to be closely related to changes in the concentration of the oxidation product of monomer. For the reprecipitated and reprecipitated-plus-monomer samples, methyl pyruvate was not detected.

DISCUSSION

The objective of our paper was to study the mechanism of thermal degradation occurring in our commercial and purified PMMA films in the temperature range between 50 and 125°C. After considering many possibilities, we felt it reasonable to consider four sources of initiation. These were (1) unreacted initiators of polymerization,^{14,15} (2) free radicals generated from additives in the film, (3) in-chain weak links,¹⁶⁻²⁵ and (4) free radicals generated from an oxidation product of the monomer of methyl methacrylate. Of these four, we

conclude that the generation of free radicals from the oxidation of MMA monomer best explains our results.

We reject the residual initiator and additive initiation sources because we were not able to detect any such impurities in the commercial film using Fourier transform infrared spectroscopy (FT-IR), UV spectroscopy, GC, or GC-MS analysis; a significant number of scissions were observed to occur in the reprecipitated-plus-monomer films, which should be free of residual initiators; and scissions continued to occur in the commercial PMMA film for exposure times and at temperatures (e.g., 125°C and 2500 h) long after any residual radicals should have been consumed. We reject the weak link initiation source because scissions continued to occur at a constant rate in the commercial PMMA films for long exposure times; the number of scissions for specimens exposed in a vacuum was much less than it was for specimens exposed in air at the same temperature and for the same exposure time; and a significant increase in the total number of scissions occurs when the temperature is increased from 115°C to 125°C. This increase in the total number of scissions with an increase in temperature has been observed before²⁶ and has been attributed to the presence of two different weak link structures in the same polymer chain, a low and a high temperature structure. The implausibility of two weak link structures in the same molecular chain has often been cited as a critical argument for rejecting a weak link hypothesis.²⁷

Oxidation Product of Monomer

The proposed schema for the thermal degradation of PMMA by free radicals generated from the oxidized monomer is presented in Figure 7, which is a modification of the one proposed by Panke and Wunderlich.¹⁰ The major constituents of the schema are the oxidation product of monomer, free radicals generated from the oxidized monomer, monomer, oxygen, and methyl pyruvate; all of which are present in or can be produced during the thermal aging of commercial PMMA films and all of which are either a reactant, a product, or a byproduct of the production of free radicals from oxidized monomer. Hence, the proposed schema appears to be consistent with the observed relationships between scissions, the consumption of monomer, and the production of the oxidation product of monomer and methyl pyruvate.

Free radicals from the oxidation product of monomer can be generated from the oxidation of MMA monomer or can be produced from the thermal decomposition of the oxidation product of monomer,^{6,8-11} which is present in our unaged commercial PMMA films. We independently verified that we could produce an oxidation product of monomer by heating purified MMA in air at 115°C using the procedures of Barnes et al.⁶ The solution polymerized into a solid mass and a significant concentration of the oxidation product of monomer was detected by GC analysis. In another experiment, we showed that compounds extracted with methanol from the commercial PMMA are sufficiently active to cause polymerization. From this we infer that the free radicals that were generated may be able to cause chain scissions in PMMA, especially if oxygen is present.

The total number of scissions in a specimen is greatly influenced by the concentrations of monomer and the oxidation product of monomer. Monomer

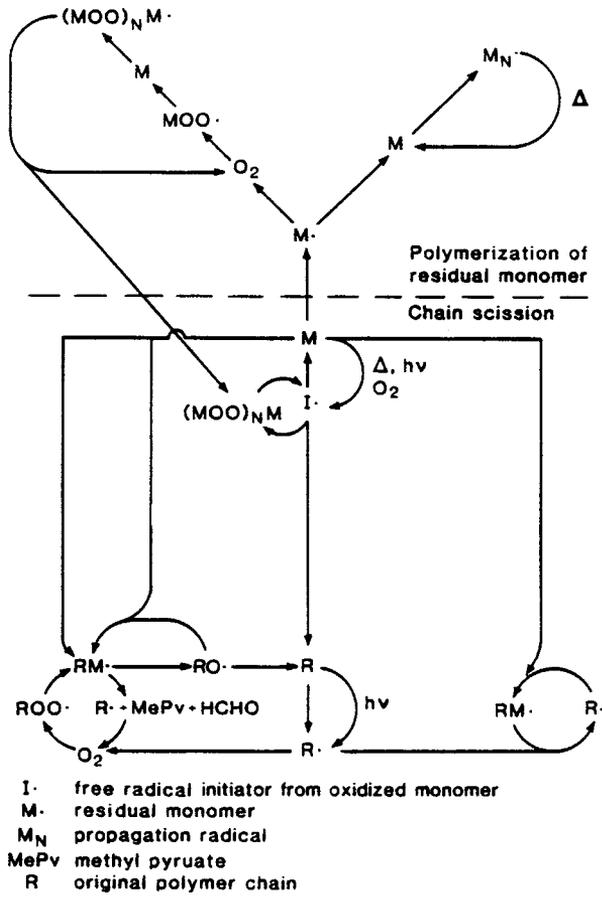


Fig. 7. Reaction schema for the thermal degradation of PMMA. Schema is a modification of the one proposed by Panke and Wunderlich.¹⁰

can be removed in several ways including (1) conversion to oxidation product of monomer, (2) addition to a propagation radical, (3) addition to a peroxy radical. Reactions for processes 1, 2, and 3 are given below



where, from Mayo et al.,^{21,24} it is known that $k_3 \gg k_2 > k_4$ and, in the case of our commercial PMMA, I^* is the free radical initiator generated from the thermal decomposition of the oxidation product of monomer which is present in the unaged film.

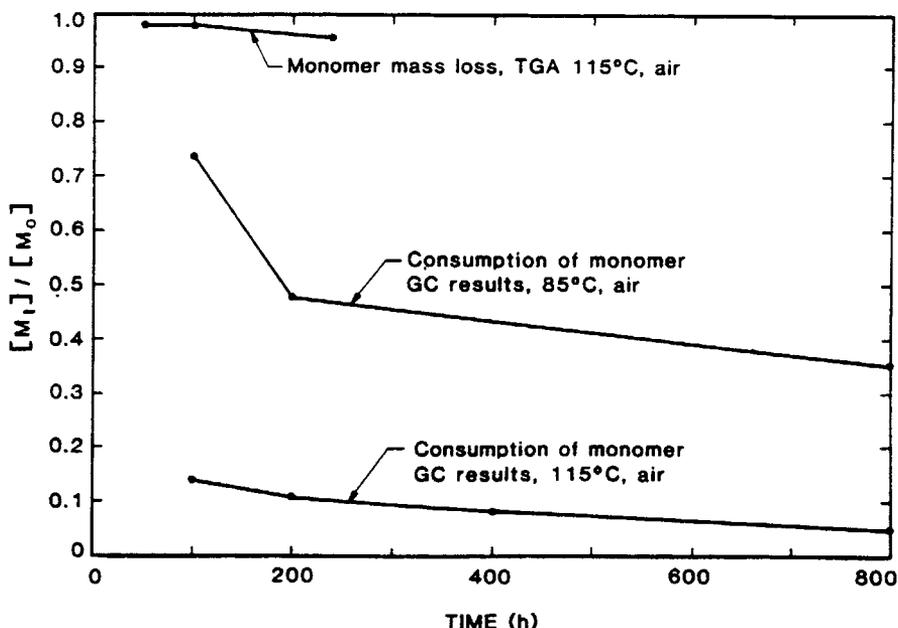


Fig. 8. Comparison of the mass loss of commercial PMMA in air to the change in monomer concentration measured by GC.

Diffusion out of the film is not considered to be a major mode of monomer depletion, since we observed little mass loss from a film during thermal aging in a TGA (thermogravimetric analysis) experiment (see Fig. 8). In this experiment, a commercial PMMA specimen was placed in a vacuum chamber at room temperature for nine days prior to the start of the TGA experiment to remove as much water as possible from the film. (We verified that monomer and the oxidation product of monomer were not removed during this conditioning by performing GC analyses on the unaged commercial PMMA specimen before and after vacuum exposure. We observed no appreciable changes in their initial concentrations.) The specimen was then heated to 115°C in air in a TGA for 240 h and the loss in mass observed over time. After 240 h exposure at 115°C (see Fig. 8), the film lost 0.11% of its mass which, if considered to be solely monomer, is equivalent to a change in the monomer concentration from 3.0% to 2.9% or $[M_1/M_0] = 0.97$. In a GC analysis of the same sample aged in the TGA in air at 115°C, however, we observed a decrease in the monomer concentration from 3.0% to 0.3% or $[M_1/M_0] = 0.10$, indicating that most of the monomer at these concentrations is consumed by reaction processes occurring within the film.

Most of the monomer is believed to be consumed by either attaching itself to a propagating radical of a peroxy radical (reactions 2 or 4). Support for these propositions comes from the comparison of monomer consumption results for our commercial PMMA specimens exposed in air and in vacuum (see Figs. 2 and 3). At the same exposure temperature, the consumption of monomer in vacuum is greater than it is in air. This is to be expected, since the reaction rate for reaction 2 is sixty times greater than that of reaction 4.^{21,24} Thus, oxygen increases the formation of the oxidation product of

monomer while lowering the monomer consumption per scission at the scission sites.

The temperature dependence of the scission process results from either an increase in the production of oxidized monomer free radicals or an increase in the scission efficiency of these free radicals. It is assumed that oxidized monomer free radicals are concurrently produced and consumed during thermal aging and that at least one oxidized monomer free radical is consumed for each chain scission. Support for these assumptions comes from the commercial PMMA specimens exposed in air and in vacuum. For commercial PMMA specimens exposed in air (see Fig. 2) at temperatures less than 125°C, the number of scissions and the concentration of the oxidation product of monomer increase with increasing temperature, thus the production rate of the oxidation product of monomer is greater in air than its consumption. For commercial PMMA specimens exposed in vacuum and in air at 125°C, however, the consumption rate of the oxidation product of monomer is greater than its production. In vacuum, (Fig. 3), monomer cannot be oxidized; therefore, scissions can only result from free radicals produced from the thermal decomposition of the oxidation product of monomer present in the unaged commercial PMMA. As these free radicals are consumed, the concentration of the oxidation product of monomer decreases to an equilibrium level. Once this equilibrium level is obtained, we do not observe a significant change in the monomer concentration or in the number of chain scissions.

The connection between scissions and the presence of the oxidation product of monomer is further supported by our reprecipitated and reprecipitated-plus-monomer exposure results. In these specimens, the oxidation product of monomer is not initially present in the film, but must be produced. In the case of the vacuum exposures, the oxidation product of monomer cannot be produced; hence, we should not and do not observe a significant number of chain scissions. For the specimens exposed in air, however, monomer can be oxidized; thus, we should detect both the oxidation product of monomer and chain scissions. Scissions and the oxidation product of monomer were detected in two of the reprecipitated-plus-monomer specimens exposed in air (Fig. 5). We would have expected similar results for the other reprecipitated specimens exposed in air, if we would have exposed them for a sufficiently long period of time. A long exposure time is necessary, since the production of monomer by unzipping is a very slow process at the temperatures of our experiment.

The thermal stability of the oxidation product of monomer depends on its structure, which we were not able to identify. Barnes et al.⁶ felt that their oxidized MMA monomer was a low molecular weight polyperoxide having a degree of polymerization of fourteen. This result was for MMA heated in excess oxygen. Our experiment is quite different in that the monomer molecules must first diffuse within a polymer film to find a peroxy radical to which they can attach. Thus, assuming that the oxidation product of monomer is a polyperoxide, we would expect its degree of polymerization to be much less than that found by Barnes et al.⁶ Mayo et al.^{21,24} studied the stability of high molecular weight polyperoxides as a function of temperature and found that polyperoxides are relatively stable at temperatures less than 60°C and are very unstable at temperatures greater than 100°C. In general, our results are consistent with Mayo's. At 50°C, the concentration of the

oxidized product of monomer continues to increase with exposure time while few scissions occur, implying that the oxidation product of monomer is relatively stable. At temperatures between 85 and 115°C, the concentration of the oxidation product of monomer reaches an equilibrium concentration, indicating an intermediate stability. At 125°C and long exposure times, the consumption of oxidation product of monomer far exceeds its production; hence, its concentration tends toward zero.

Finally, we can provide an explanation for why the scission process appears to be a mixture of a first and a zeroth-order reactions. For the commercial PMMA specimens exposed in air, an increase in temperature causes an increase in the rate of production of free radicals generated from the oxidized monomer which in turn causes an increase in the total number of scissions. This increase in the total number of scissions continues until the concentration of monomer is reduced to an equilibrium concentration of about 0.3%, at which time the concentration of the oxidation product of monomer levels off. As the concentrations of monomer and the oxidation product of monomer level off, the scission process becomes an apparent zeroth-order reaction. Our explanation for this is that even though the scission process is concentration-dependent, it is now limited by the unchanging concentration of the oxidized monomer and monomeric molecules in equilibrium with the polymer radicals in the film. Since all of these reactants are at their equilibrium concentrations, the scission process appears to become a zeroth-order reaction process.

The work discussed in this publication was funded by the Office of Solar Heat Technologies of the United States Department of Energy. Special thanks goes to Mr. Larry Masters for his continued support of this project.

References

1. G. Bagby, R. S. Lehrle, and J. C. Robb, *Makromol. Chemie*, **119**, 122-132 (1968).
2. H. H. G. Jellinek and M. D. Luh, *Makromol. Chemie*, **115**, 89-102 (1968).
3. N. Grassie, in *Polymer Science: A Materials Science Handbook*, A. D. Jenkins, Ed., Vol. 2, North-Holland, New York, 1972.
4. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964.
5. B. Dickens, J. W. Martin, and D. Waksman, *Polymer*, **25**, 706-715 (1984).
6. C. E. Barnes, R. M. Eloffson, and G. D. Jones, *J. Am. Chem. Soc.*, **72**, 210 (1950).
7. C. C. Price, *J. Appl. Polym. Sci.*, **1**, 44 (1946).
8. M. J. Bowden, E. A. Chandross, and I. P. Kaminow, *Polym. Eng. Sci.*, **1**, 494-497 (1974).
9. Von G. V. Schultz and G. Henrici, *Makromol. Chemie*, **18-19**, 437 (1956).
10. D. Panke and W. Wunderlich, *J. Appl. Polym. Sci.*, **35**, 321-328 (1979).
11. C. E. Barnes, *J. Am. Chem. Soc.*, **67**, 217-230 (1945).
12. P. R. E. Cowley and H. W. Melville, *Proc. Roy. Soc. [London]*, **A210**, 461-481 (1952).
13. K. W. Scott, *J. Polym. Sci.: Polym. Symp.*, **46**, 321-334 (1974).
14. R. B. Mesrobian and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **2(5)**, 463 (1947).
15. F. Rodriguez, *Principles of Polymer Systems*, 2nd ed., McGraw-Hill, New York, 1982.
16. J. R. MacCallum, *Makromol. Chemie*, **83**, 129 (1965).
17. G. G. Cameron and G. P. Kerr, *Eur. Polym. J.*, **4**, 709-717 (1968).
18. G. G. Cameron and G. P. Kerr, *Eur. Polym. J.*, **6**, 423-438 (1970).
19. O. Chiantore, G. Camino, L. Costa, and N. Grassie, *Polym. Degr. Stability*, **3**, 209-219 (1981).
20. I. Watcher, *J. Polym. Sci.*, **14**, 411-413 (1954).
21. F. R. Mayo, A. A. Miller, and G. A. Russell, *J. Am. Chem. Soc.*, **80**, 2500-2507 (1958).

22. I. Mita and K. Horie, in *Degradation and Stability of Polymers*, H. H. G. Jellinek, Ed., Elsevier, North Holland, 1983.
23. Y. Kamiya and E. Niki, in *Degradation and Stability of Polymers*, H. H. G. Jellinek, Ed., Elsevier, North Holland, 1983.
24. F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2493-2496 (1958).
25. L. A. Wall and D. W. Brown, *J. Res. Nat. Bur. Stand.*, **57(3)**, 131-136 (1956).
26. W. G. Oakes and R. B. Richards, *J. Am. Chem. Soc.*, **71**, 2929 (1949).
27. L. Reich and S. S. Stivak, *Elements of Polymer Degradation*, McGraw-Hill, New York, Chap. 5, 1971.

Received March 6, 1986

Accepted November 18, 1986