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NRL Report 6339

Photodegradation of High Polymers

Part VII - Photolysis of Poly (n-Butyl Methacrylate) in Vacuum

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Previous Reports in This Series

"Part I – The Homogeneous Ionic Polymerization of α-Methylstyrene," R.B. Fox and L. Isaacs, NRL Report 5518, Aug. 19, 1960

"Part II – Vacuum Photolysis of Poly-α-Methylstyrene," Suzanne Stokes and R.B. Fox, NRL Report 5591, Feb. 20, 1961

"Part III – Photolysis of Poly(Methyl Methacrylate) in Vacuum and in Air," R.B. Fox, L.G. Isaacs, Suzanne Stokes, and L.W. Daasch, NRL Report 5720, Dec. 14, 1961

"Part IV – Photolysis of Poly(Methyl Acrylate) in Vacuum and in Air," R.B. Fox, L.G. Isaacs, Suzanne Stokes, and R.E. Kagarise, NRL Report 5894, Feb. 13, 1963

"Part V – Photolysis of Poly(Alkylene Polysulfides) in Vacuum," L.G. Isaacs and R.B. Fox, NRL Report 6202, Feb. 4, 1965

"Part VI – Photolysis of Polystyrene Films in Vacuum and in Air," R.B. Fox, L.G. Isaacs, F.E. Saalfeld, and M.V. McDowell, NRL Report 6284, June 16, 1965

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ABSTRACT

The photodegradation of poly(n-butyl methacrylate) from three sources (two of the samples contained a metallic mesh) has been studied at 50° and 100°C. At 100°C, samples lost 90 to 95% of their original weight after about 30 hr of exposure and left about 4% insoluble polymer. At 50°C, about half as much material was volatilized. and one fourth was left insoluble. Most of the volatile products consisted of n-butyl methacrylate (monomer), n-butyl formate, and 1-butene; lesser amounts of n-butyraldehyde, 1-butanol, n-butane, and carbon dioxide were also produced. Increasing the temperature increased the relative yield of monomer, and, except for 1-butene, decreased the relative yields of the other products. Although films degraded at 100°C showed nearly complete volatilization, a sample exposed at 50°C and then re-exposed at 100°C showed little additional volatilization at the higher temperature. This suggests that more crosslinking occurs at the lower temperature, so that even though additional volatile products may have been formed by the 100°C exposure, their escape was prevented by the crosslinking which had taken place at 50°C. The percent volatilization varied slightly and inversely with film thickness.

The volatile products other than monomer are accounted for by cleavage reactions of the pendent ester groups, with subsequent hydrogen abstraction or disproportionation of the free radicals. Monomer results from main chain cleavage followed by depolymerization; this reaction predominates at the higher temperature.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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PHOTODEGRADATION OF HIGH POLYMERS

PART VII - PHOTOLYSIS OF POLY(n-BUTYL METHACRYLATE) IN VACUUM

INTRODUCTION

Large balloons, approximately 400 ft in diameter, constructed of aluminum mesh have been proposed for future passive communication satellites. Mesh can be made which has more than 90% open area (essentially transparent to the eye) but which will reflect more than 90% of incident radio waves. A satellite made of such material should be negligibly affected by solar pressure, a force that caused unpredictable changes in orbit and partial collapse of earlier satellite balloons. A plastic film is still necessary for inflation of the aluminum mesh, however, and it is desirable to remove this film once the mesh has attained a spherical shape. Solar radiation is a convenient source of energy for removal of the plastic by degradation reactions.

Poly(alkyl methacrylates) are known to depolymerize readily on exposure to ultraviolet radiation in vacuum, particularly at temperatures above room temperature (1). Cowley and Melville (2) found poly(methyl methacrylate) to degrade exclusively to monomer on exposure to ultraviolet radiation at temperatures of 130°C or higher. Fox, Isaacs, and Stokes (3) photolyzed poly(methyl methacrylate) at 25°C and found methyl formate and methanol as well as monomer in the small amounts of volatile products formed; chain scission was the predominating reaction. Grassie and MacCallum(1) found poly(n-butyl methacrylate) (PBMA) to depolymerize quantitatively to monomer when photolyzed at 170°C. Other poly(alkyl methacrylates) have been found to undergo scission, crosslinking, and degradation to products of low molecular weight in varying degrees, depending upon the conditions of irradiation.

Since PBMA has physical properties which make it suitable for use as the inflating bladder of passive communication satellites, it has been subjected to investigation as a photo-ablative material. The wide variation in behavior of poly(alkyl methacrylates) photolyzed under various conditions indicated the need to study the effect of temperature and film thickness and the influence of contact with the metallic mesh. Efforts have been directed at the empirical investigation of the extent and nature of the weight losses of photolyzed PBMA leading to an understanding of the mechanism of the photodegradation of this polymer.

EXPERIMENTAL METHOD

Materials

n-Butyl methacrylate monomer was washed with dilute sodium hydroxide solution and distilled water, dried over Drierite, and distilled under nitrogen at reduced pressure. A heart cut was degassed and immediately polymerized in bulk by heating 4 hr at 60° ± 2°C with 0.05% of freshly recrystallized azodiisobutyronitrile as catalyst. The polymer was isolated in 33% conversion by precipitation with methanol and purified by two reprecipitations from tetrahydrofuran solution with methanol; the polymer was dried under vacuum for several days. This PBMA was designated sample A.

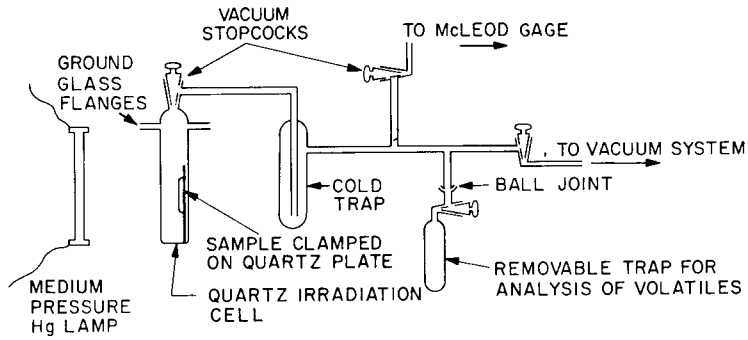

Fig. 1 - Irradiation apparatus

The PBMA referred to as sample B was obtained from Geophysics Corporation of America. A 50-μ (2-mil) film of PBMA was used to coat an aluminum mesh. The mesh was made of wires about 75μ in diameter in an elongated diamond-shaped pattern measuring about 0.65 by 0.3 cm across the diagonals.

PBMA sample C was obtained from Goddard Space Flight Center. It was a 50-μ film incorporating 50-μ-diameter copper wire in a rectangular grid measuring about 0.3 by 0.1 cm.

Apparatus

The cell, irradiation source, and vacuum system were similar to those described in a previous report in this series (4) (Fig. 1). An iron-constantan thermocouple was sealed into the top of the irradiation cell to measure temperature during degradations. A cylindrical heater with part of one side cut away to allow radiation to strike the sample was used to heat the irradiation cell for the high-temperature photodegradations.

A Gulf Research Instruments fraction collector was used to collect individual components of the volatile products as they were eluted from a gas chromatograph. A Consolidated Engineering Corp. Model 21-620 mass spectrometer was employed in the analysis of volatiles.

Procedure

Exposures and Weight Losses – A sheet of sample B or sample C of known area and weight was clamped to a supporting quartz plate and placed in the irradiation cell. A typical sample had an area of 50 cm^2 and weighed 0.15 g. The proportion of PBMA in the sample was determined by dissolving the PBMA from the wire mesh of samples B and C. The weights of PBMA only, not the total composites, were used in calculating weight losses. The irradiation cell was sealed to the Pyrex top with Apiezon W wax and the cell evacuated to about 10^{-4} torr. During exposure the cell was continuously evacuated to remove volatile products as rapidly as possible. After a suitable time of exposure, the cell was opened and the weight loss of the polymer determined. Further exposures of the same sample were made as desired.

Films of sample A, approximately 20μ in thickness, were prepared by weighing the polymer into flat rectangular Pyrex dishes of known areas, approximately 50 cm^2. The polymer was dissolved in methylene chloride and the solution allowed to evaporate at room temperature for at least 24 hr. The samples were then dried under vacuum to

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remove methylene chloride. The dishes containing the PBMA film were exposed in the irradiation cell in the same manner as the sheets of samples B and C.

The temperature within the cell increased to 50° ± 5°C within 5 min after the beginning of an ambient-temperature exposure. Temperature control was not attempted; variations in cell temperature were the result of fluctuations in room temperatures over a period of several months.

Higher temperature exposures were carried out by heating the cell to 70°C with the cylindrical heater. This required 1 to 2 hr; a PBMA sample heated at this temperature in the evacuated cell for 20 hr did not undergo weight loss. The temperature within the cell increased to 100° ± 5°C within 5 min after the start of irradiation. During most of the exposures the temperature was maintained at 100° to 102°C.

Volatile Products – Volatile products were condensed with liquid nitrogen in the large cold trap (Fig. 1). After a suitable period, the exposure was interrupted while the volatile products were transferred to the smaller removable trap for analysis. The trap was then replaced, this portion of the system was re-evacuated, and the exposure continued. This procedure was repeated when another sample of volatile products was desired.

Samples of the volatile photolysis products were separated in a gas chromatograph on the columns indicated in Figs. 2 and 3, and each component was collected as it emerged from the effluent stream (5). The compounds were identified from their mass spectra and confirmed by comparison of their retention times on the gas chromatograph with those of known compounds.

Quantitative measurements were made of the volatile products from samples A and C. These exposures were continued until the incremental yields of volatile products were extremely small; 84 and 30 hr of exposure were required for the 50° and 100°C exposures, respectively. The quantities of volatile products from sample A were measured by a gas chromatographic technique and those from sample C by mass spectrometry.

Pure samples of known volumes of each of the volatile products were injected into the gas chromatograph, using the two columns indicated in Figs. 2 and 3. Plots of the areas in the resulting chromatograms against sample volume were linear for each compound.

The volatile products resulting from photolyzing a film of sample A for a period of 1 to 5 hr were condensed with liquid nitrogen, transferred to the smaller removable trap (Fig. 1), and introduced into the gas chromatograph by means of a gas inlet device. The two different columns were used alternately to analyze either the high- or low-boiling constituents. The areas representing each compound in the chromatograms were converted to volume from the calibration plots. The weight of each compound produced during the trapping period was calculated from the density in the case of the liquid products or from the ideal gas law in the case of the gaseous products.

The volatile products from films of sample C irradiated for 1 to 2 hr periods were analyzed in the mass spectrometer. In this complex mixture almost every mass peak from 12 to 86 was present. Furthermore, since most of these compounds contain a butyl group, the largest peaks in the mass spectrum of the mixture arose from the contribution of several different compounds, making quantitative analysis difficult. The pressure of each identified component was determined by conventional methods after fragmentation patterns for the individual compounds had been measured with pure samples.

Insolubles – The gel fractions of the PBMA remaining after exposure were determined by extraction with methylene chloride for approximately 1 hr. The methylene

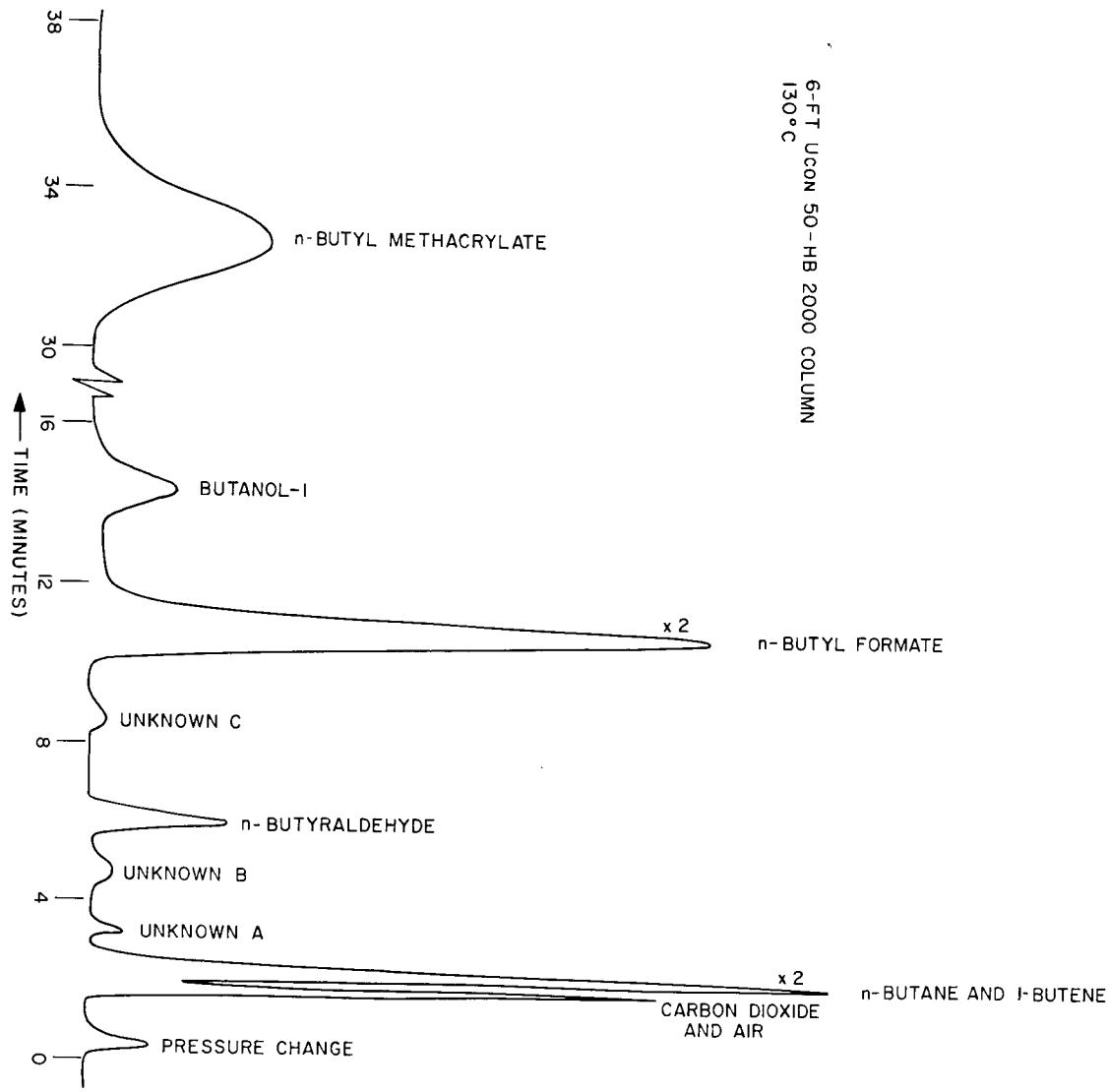

Fig. 2 - Chromatogram of the high-boiling volatile compounds of PBMA, sample C

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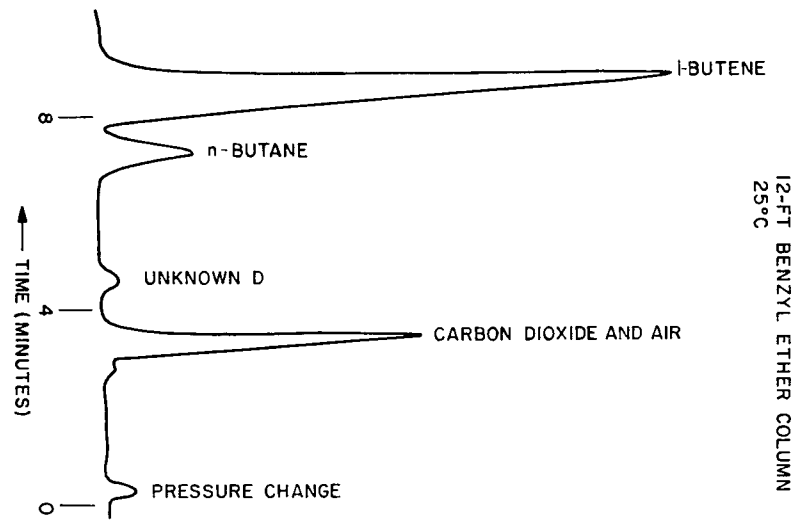

Fig. 3 - Chromatogram of the low-boiling volatile products of PBMA, sample C

chloride washings were filtered through a tared, frittered-glass filter; residues were extracted several times before it was assumed that the remaining polymer was insoluble. The filter and dish were then dried under vacuum and the total weight of the insoluble portion determined.

Non-Polymeric Esters – Methyl acetate and n-butyl acetate were purified with a preparative gas chromatograph. Approximately 1-ml portions were placed in 10-mm-diameter quartz tubes having a breakseal tube appended, degassed, and sealed under vacuum. The esters were exposed to ultraviolet radiation for 192 hr with the cell covered so that radiation was absorbed only by the liquids, rather than the gases above them. The gas chromatograph collecting method described above was used to identify the photolysis products by mass spectroscopy. Quantitative data were obtained from gas chromatograms.

RESULTS AND DISCUSSION

Weight Losses

In Fig. 4 the percent volatilization of the PBMA samples is plotted against irradiation time. Figure 4 shows that the rate of volatilization is greatly enhanced by increasing the temperature from 50° to 100°C. Points for samples B and C at 50°C are for repeated exposures of single films; all other points represent single exposures of separate film samples. Within experimental error, there appears to be little difference among the PBMA types, although values for sample A seem lower than those for the other samples. This may be the result of a slight heating effect of the wires in samples B and C.

At both 50° and 100°C the rates of volatilization decrease with increasing irradiation time, indicating that some change is taking place in the polymer as degradation proceeds. Since PBMA absorbs only part of the incident ultraviolet radiation, the energy absorbed should be proportional to the thickness of the polymer. Photolytic reactions should in turn be proportional to the thickness of the polymer and are expected to be the same throughout the film.

If diffusion of low-molecular-weight products is rapid from all parts of the film, the rate of volatilization should be independent of film thickness. This is nearly true for

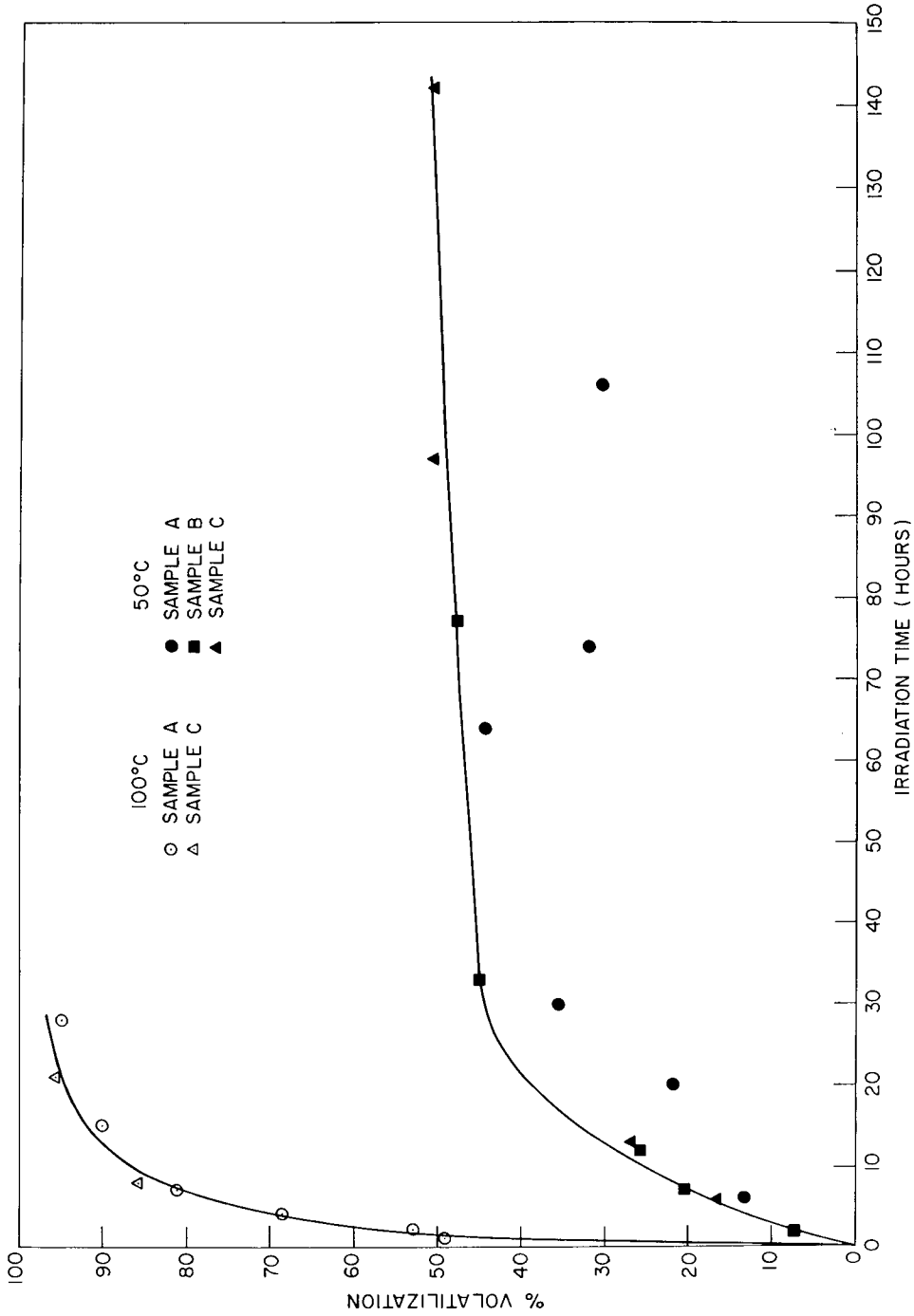

Fig. 4 - Volatilization of PBMA samples upon irradiation

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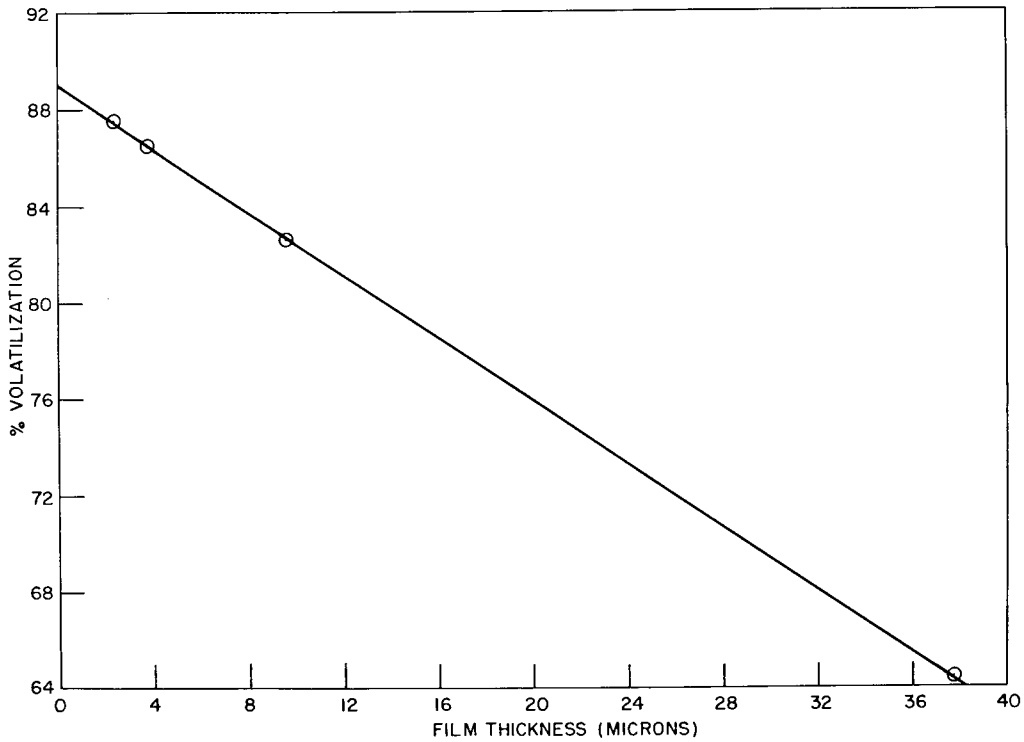


Fig. 5 - Effect of film thickness on volatilization from films of sample A degraded 5 hr at 100°C

small variations in thickness. As shown in Fig. 5, the percent volatilization of films of sample A is inversely proportional to the thickness of the film over a tenfold range, although the absolute change in volatilization rate is small. As degradation proceeds, product diffusion should be more complete because of an ever-decreasing sample thickness. Spectral changes were not recorded, but these were probably small and tended in the direction of increased absorption coefficients (3). The most likely explanation of the time-dependent volatilization rate lies in the competitive crosslinking reaction (see below) which would tend to decrease the diffusion rate of small molecules.

Volatile Degradation Products

From Figs. 2 and 3 it can be seen that photolysis of PBMA produces, in addition to monomer, almost every product that can arise from cleavage of bonds in the ester side chain. No evidence was obtained of products boiling higher than n-butyl methacrylate.

The results from gas chromatographic and mass spectrometric analyses of the volatile products, in milligrams of compound produced per square centimeter of exposed surface per hour, were plotted against irradiation time. Figure 6 is an example of the data obtained. The area under the curve represents the weight of compound produced per square centimeter of exposed surface; multiplying by the area of the film gave the weight of that compound produced during the entire exposure. These data are entered in Tables 1 and 2.

Such data are semiquantitative at best. The sensitivity of the mass spectrometer was found to have decreased during the period over which the analyses of sample C were carried out. However, a change in sensitivity should affect only the pressure found for

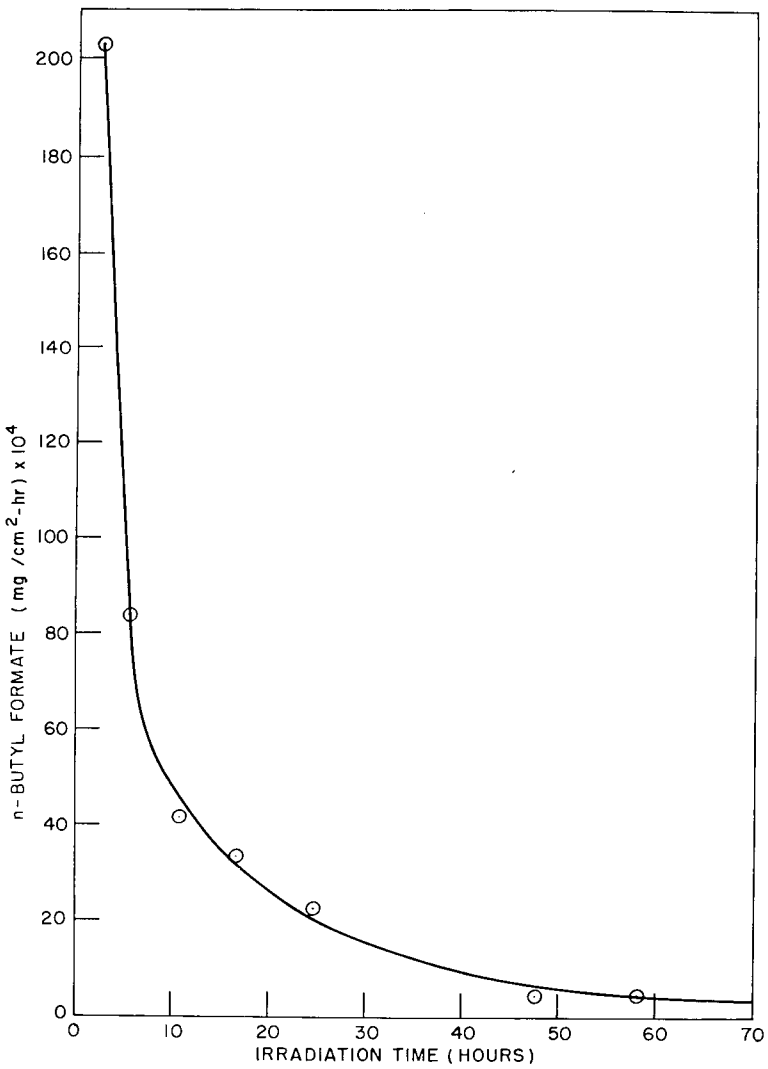


Fig. 6 - Milligrams of n-butyl formate produced per square centimeter of surface per hour against hours of irradiation

Table 1
Volatile Degradation Products from PBMA at 50°C

Compound	Sample A*			Sample C†		
	Weight (g)	Moles $\times 10^4$	Mole-%	Weight (g)	Moles $\times 10^4$	Mole-%
n-Butyl methacrylate	0.00339	0.239	12.4	0.02561	1.80	36.0
n-Butyraldehyde	0.000583	0.081	4.2	0.00350	0.486	9.7
n-Butyl formate	0.00882	0.882	45.7	0.00981	0.962	19.2
1-Butanol	0.000583	0.079	4.1	0.00433	0.585	11.7
n-Butane	0.000287	0.0495	2.6	trace	-	-
1-Butene	0.00313	0.559	29.0	0.00541	0.966	19.3
Carbon dioxide	0.00016	0.0364	1.9	0.00088	0.200	4.0
Total Weight	0.0170			0.0495		
Measured Weight Loss	0.0337			0.0590		
Original Sample Weight	0.1053			0.0927		

*Gas chromatographic analysis.
†Mass spectrometric analysis.

Table 2
Volatile Degradation Products from PBMA at 100°C

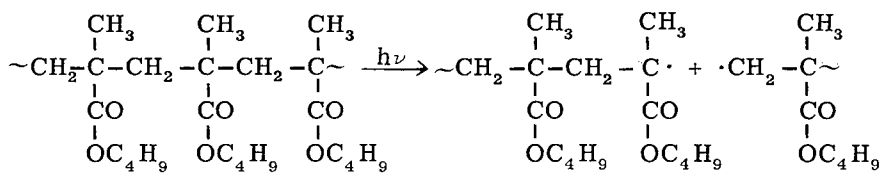
Compound	Sample C*		
	Weight (g)	Moles $\times 10^4$	Mole-%
n-Butyl methacrylate	0.0234	1.65	59.0
n-Butyraldehyde	0.00164	0.228	8.1
n-Butyl formate	0.00210	0.206	7.4
1-Butanol	trace	-	-
n-Butane	trace	-	-
1-Butene	0.00299	0.533	19.0
Carbon dioxide	0.00078	0.177	6.3
Total Weight	0.0309		
Measured Weight Loss	0.0837		
Original Sample Weight	0.0934		

*Mass spectrometric analysis.

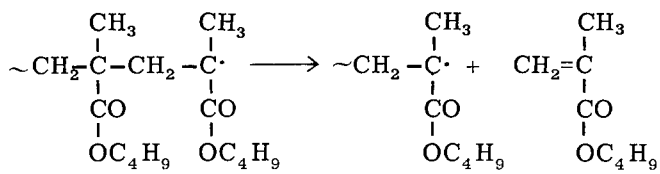
each gas and not the relative amounts of each compound. Therefore, the mole percent figures of sample C are probably reliable within 5%, but the total weights are lower than those found from the film weights. This was particularly true for the 100°C exposures, the analyses of which were the last ones carried out.

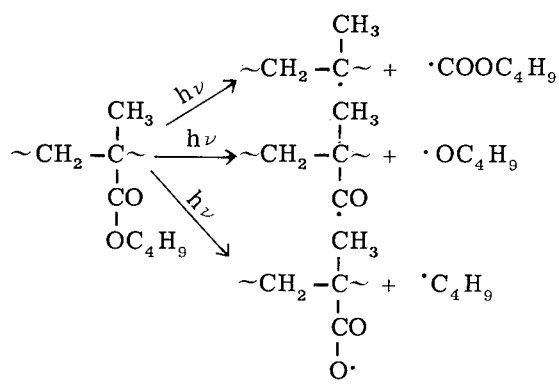
The most likely source of error in the gas chromatographic analysis is in transferring the volatile products from the detachable cold trap (Fig. 1) to the gas inlet loop of the gas chromatograph. This effect should be most pronounced for the highest boiling component, n-butyl methacrylate. The amount of n-butyl methacrylate obtained in each trapping period showed considerable scatter when plotted against irradiation time.

The volatile photolytic products can be accounted for by the following degradation pathways:



(1)



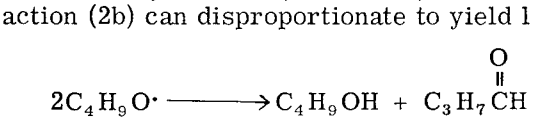


(2a)

(2b)

(2c)

Termination of the free radicals produced in reactions (2) by hydrogen atom abstraction from the polymer results in n-butyl formate, 1-butanol, and n-butane. The butoxy free radical produced in reaction (2b) can disproportionate to yield 1-butanol and n-butyraldehyde:



(3)

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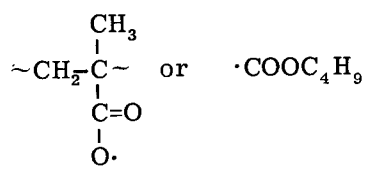
The yields of these two compounds were approximately equal. The butyl free radicals of reaction (2c) could yield 1-butene and n-butane by disproportionation:

$$2C_4H_9\cdot \longrightarrow C_2H_5CH{=}CH_2 + C_4H_{10} \tag{4}$$

Borkowski and Ausloos (6) found evidence for production of butene by a direct photolytic process in the photolysis of butyl esters:

$$RCOOC_4H_9 \xrightarrow{h\nu} RCOOH + C_4H_8 \tag{5}$$

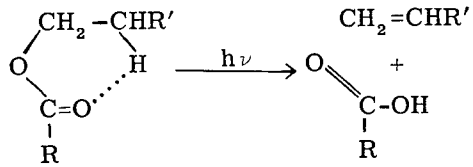
Since much more 1-butene than n-butane was found in this investigation, a process analogous to reaction (5) is more likely than reactions (2c) and (4). Carbon dioxide, a minor product of photolysis, may result from the radicals



formed in reaction (2) or from photolysis of acids formed by a reaction analogous to reaction (5). Carbon monoxide, hydrogen, and methane, if they were formed in the photolysis, would not have been condensed in the trap under the experimental conditions.

The data of Tables 1 and 2 show that n-butyl methacrylate (monomer), n-butyl formate, and 1-butene account for about three fourths of the total volatile products. Increasing the temperature of degradation from 50° to 100°C resulted in an increase in the proportion of monomer, roughly parallel to the increase in the rate of weight loss (Fig. 4). Grassie and MacCallum (1) detected only monomer in the volatile products of poly(n-butyl methacrylate) photolyzed at 170°C. Similar results were obtained by Cowley and Melville (2) in the photolysis of poly(methyl methacrylate) at 160° to 220°C.

Chromatograms of photolyzed n-butyl acetate and methyl acetate are shown in Figs. 7 and 8. In addition to the products shown in Fig. 7, n-butane, carbon dioxide, ethylene, carbon monoxide, and methane were identified in the breakseal tube which contained the gaseous photolytic products of n-butyl acetate. Acetic acid is the product present in largest yield. It has been postulated that an intramolecular elimination process is responsible for production of an acid and olefin in photolysis of esters containing a β-hydrogen atom in the alkyl group (6):



(6)

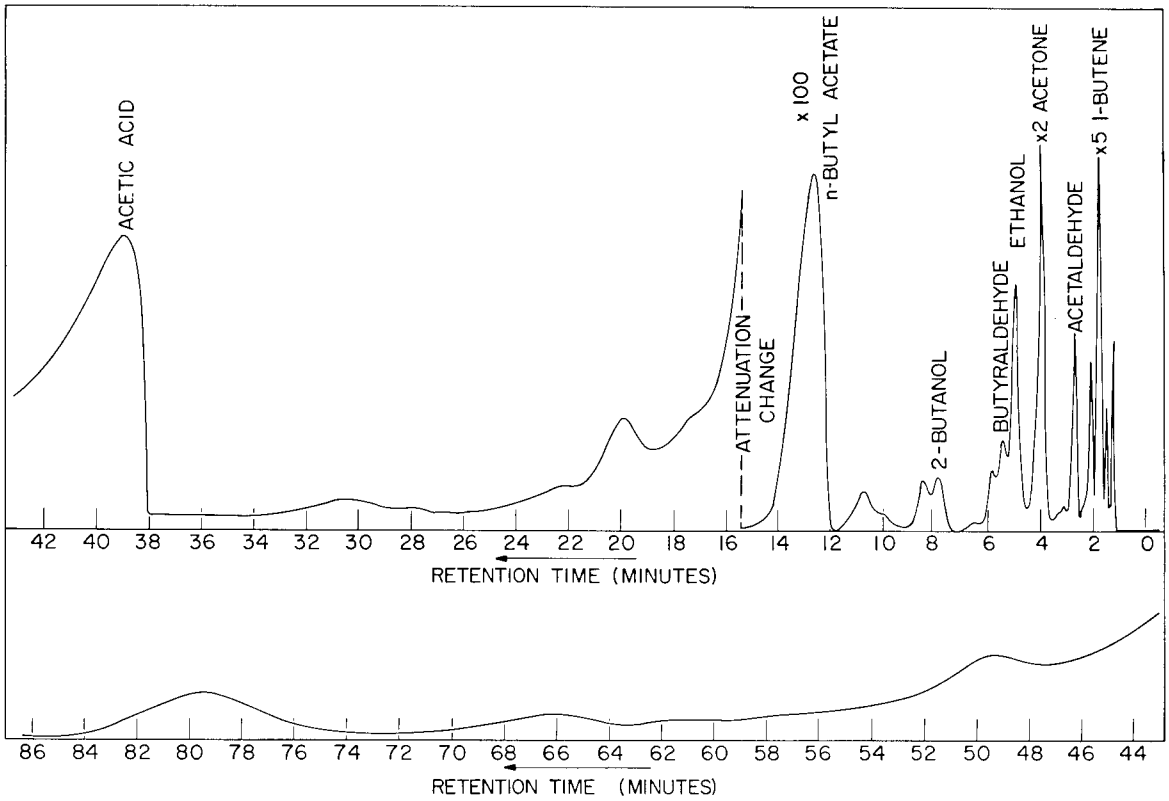


Fig. 7 - Chromatogram of photolyzed n-butyl acetate, obtained from 12-ft Ucon 50-HB 2000 column, 130°C, 50-μl sample

Although considerable evidence has been presented that the β-hydrogen of the alkyl group is involved in the production of acid by a process which does not involve free radicals (7), examination of Fig. 8 shows that acetic acid is also the principal product of methyl acetate, which does not contain β-hydrogen atoms. Data from these two photolyses are shown in Table 3.

Evidence from this study is insufficient to elucidate the mechanism of the production of acid in ester photolysis. Nevertheless, the large amounts of acetic acid and 1-butene found in the photolysis of n-butyl acetate suggest that a similar process in the photolysis of PBMA is responsible for the production of 1-butene. No attempt was made to detect acid groups in the residual polymer.

By processes analogous to reactions (2), n-butyl acetate would produce free radicals which would yield methane, n-butyl formate, acetaldehyde, 1-butanol, acetic acid, and butene simply by hydrogen atom abstraction. Examination of Fig. 7 shows that most of these compounds were present as photolysis products. 1-Butanol has the same retention time as n-butyl acetate, and thus if it were present, it could not have been detected. n-Butyl formate has a retention time on the Ucon 50-HB 2000 column of 10 min, which matches one of the peaks in the chromatogram (Fig. 7). This peak was so poorly resolved that no attempt was made to collect the material represented.

Carbon dioxide and carbon monoxide, observed as photolytic products of n-butyl acetate, may result from the decomposition of the $\dot{C}OOC_4H_9$, $CH_3\dot{C}OO$, and $CH_3\dot{C}O$ radicals. Analogous reactions were postulated with PBMA. Also, n-butyraldehyde may be produced from the $C_4H_9O\cdot$ radical (reaction (3)). The photolysis of n-butyl acetate

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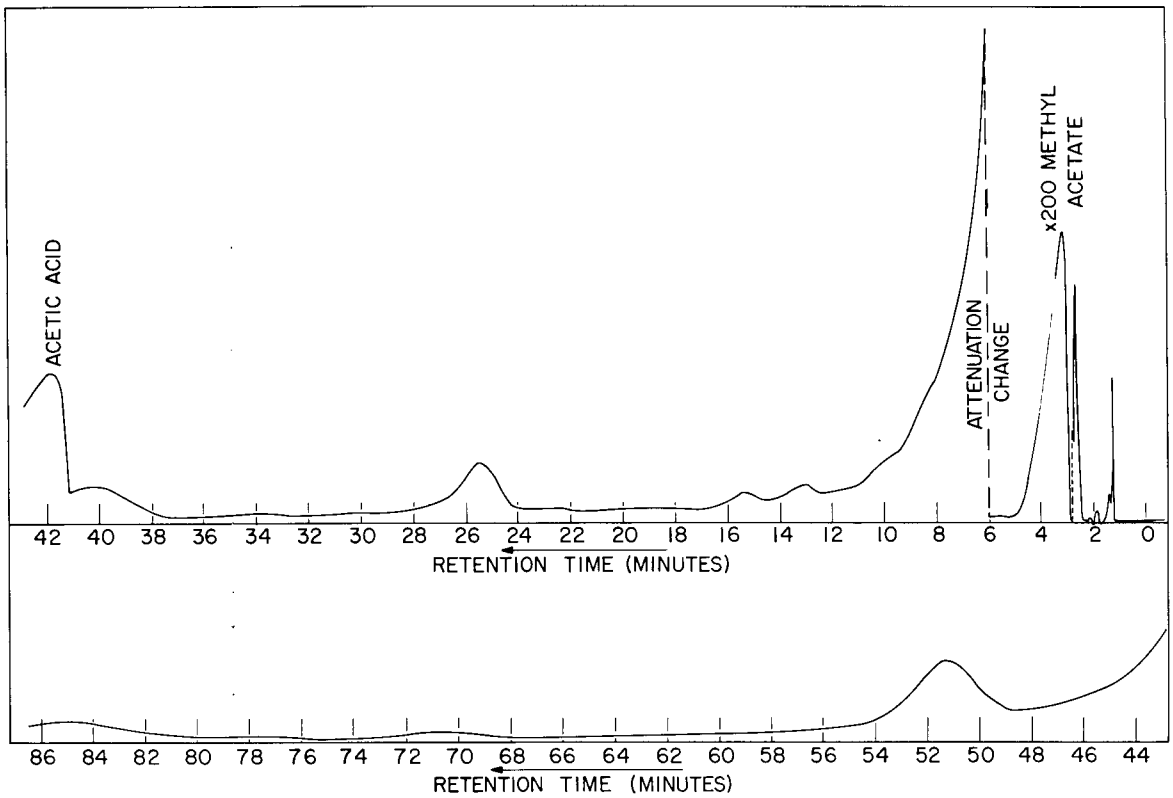

Fig. 8 - Chromatogram of photolyzed methyl acetate, obtained from 12-ft Ucon 50-HB 2000 column, 130°C, 50-μl sample

Table 3
Comparison of Yields of Products from Photolysis of n-Butyl Acetate and Methyl Acetate

Compound	Gas chromatogram areas*	
	n-Butyl acetate	Methyl acetate
Acetic acid	1.000	0.375
1-Butene	0.171	-
All other products	0.823	0.447

*Relative to acetic acid yield from n-butyl acetate

yielded many more volatile products, most of which were not identified, than did PBMA. This was probably due to secondary photolysis of initial products; unlike the PBMA photolysis, it was not possible to remove the products as they were formed. The products which had longer retention times than n-butyl acetate, except acetic acid, probably were the result of radical combination. In PBMA such products would remain part of the polymer chains and would not appear in the volatile products.

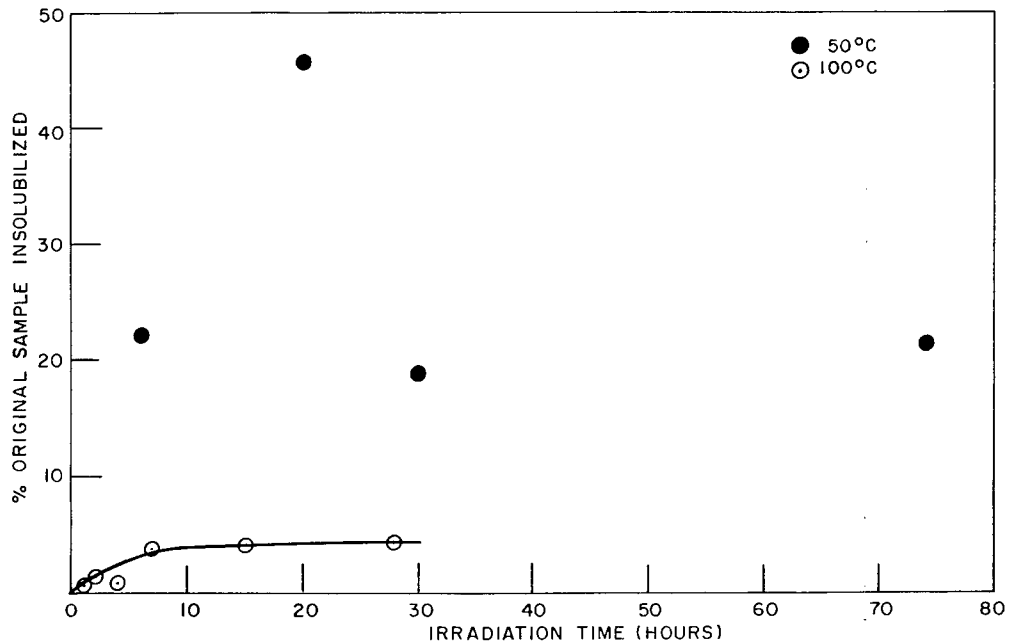

Fig. 9 - Percent of insoluble PBMA, sample A, as a function of irradiation time

Residual Polymer

Figure 9 shows the percent of insoluble, presumably crosslinked, polymer formed during photolysis plotted against irradiation time. The scatter in the data of the 50°C exposures is attributed to poor temperature control. Once crosslinked, further volatilization is markedly reduced. Thus, a film of sample A which had been exposed 64 hr at 50°C and had undergone 44% volatilization would be expected to undergo little additional weight loss on the basis of Fig. 4. This figure also shows that over 90% volatilization would take place in a film exposed 19 hr at 100°C. Experimentally, however, the residue of film initially exposed 64 hr at 50°C lost only 8.8% additional material on an exposure of 19 hr at 100°C. It might be inferred from this experiment that volatile products formed after crosslinking occurred would be trapped in the three-dimensional matrix.

Crosslinking is probably the result of combination reactions among the polymer free radicals formed in reactions (2). Such a conclusion follows also from the observation that both crosslinking and the production of small molecules via the other radicals from reactions (2) decrease with increasing temperature. The competing reaction at the higher temperature is, of course, depolymerization, which could not result in crosslinking.

SUMMARY

Samples of three different PBMA films, two of which contained metallic mesh, have been exposed at pressures of 10^{-4} torr to ultraviolet radiation. Exposures were carried out at 50° and 100°C. Weight losses, volatile material production, and formation of insoluble material were followed as a function of irradiation time.

The results from the three samples were similar. At 100°C, samples lost 90 to 95% of their original weight after about 30 hr of exposure; about 4% of insoluble polymer was formed during this process. At 50°C, only about half as much PBMA was volatilized.

After about 60 hr of exposure at 50°C, volatilization was essentially complete, and about one fourth of the original material was rendered insoluble.

The percent volatilization, the percent insoluble material formed, and the rates of production of volatile products showed some scatter in the 50°C exposures. This was probably caused by inadequate temperature control. Many of the photolytic processes are temperature dependent, and control of temperature is necessary to obtain more precise data.

Most of the volatile products consisted of n-butyl methacrylate (monomer), n-butyl formate, and 1-butene; lesser amounts of n-butyraldehyde, 1-butanol, n-butane, and carbon dioxide were also produced. Increasing the temperature increased the relative yield of monomer, and, except for butene-1, decreased the relative yields of the other products.

The percent volatilization varied slightly and inversely with film thickness.

A film of PBMA was degraded at 50°C until volatilization was essentially complete. Re-exposure of the residue at 100°C resulted in little additional weight loss.

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The photodegradation of poly(n-butyl methacrylate) from three sources (two of the samples contained a metallic mesh) has been studied at 50° and 100° C. At 100 °C, samples lost 90 to 95% of their original weight after about 30 hr of exposure and left about 4% insoluble polymer. At 50 °C, about half as much material was volatilized, and one fourth was left insoluble. Most of the volatile products consisted of n-butyl methacrylate (monomer), n-butyl formate, and 1-butene; lesser amounts of n-butyraldehyde, 1-butanol, n-butane, and carbon dioxide were also produced. Increasing the temperature increased the relative yield of monomer, and, except for 1-butene, decreased the relative yields of the other products. Although films degraded at 100° C showed nearly complete volatilization, a sample exposed at 50° C and then re-exposed at 100° C showed little additional volatilization at the higher temperature. This suggests that more crosslinking occurs at the lower temperature, so that even though additional volatile products may have been formed by the 100° C exposure, their escape was prevented by the crosslinking which had taken place at 50° C. The percent volatilization varied slightly and inversely with film thickness.

The volatile products other than monomer are accounted for by cleavage reactions of the pendent ester groups, with subsequent hydrogen abstraction or disproportionation of the free radicals. Monomer results from main chain cleavage followed by depolymerization; this reaction predominates at the higher temperature.

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