Ultraviolet Irradiation of Poly(alkyl Acrylates) and Poly(alkyl Methacrylates)

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Synopsis

Acrylic and methacrylic homopolymers containing different side groups were irradiated with ultraviolet light in the presence of air. The changes of molecular weight distributions of the irradiated polymers were analyzed by means of gel permeation chromatography (GPC), and the rates of chain scission and crosslinking were estimated. As the result of this study, it was found that chain scission takes place more easily in polyalkyl methacrylates than in polyalkyl acrylates.

INTRODUCTION

Recently, the studies on photodegradation of poly(alkyl acrylates) and poly(alkyl methacrylates) in vacuum or in air have been reported. The volatile products in photodegradation of poly(methyl methacrylate),[1,2] poly(n-butyl methacrylate),[3] poly(methyl acrylate),[4] and poly(ethyl acrylate)[5] have been analyzed quantitatively and the reaction mechanism has been proposed in detail for several materials. With respect to the nonvolatile residue derived from photodegradation, on the other hand, few quantitative investigations have been carried out because it was hard to obtain the molecular weight distribution of degraded polymers precisely.

Meanwhile, it is known that gel permeation chromatography technique is useful for this purpose. Therefore, this study was intended to degrade the homopolymers of acrylic and methacrylic esters with ultraviolet irradiation and to determine the degree of chain scission as well as crosslinking by using this technique.

EXPERIMENTAL

General

The polymers used in this study were polymerized in our laboratory according to usual manner and much care was taken to eliminate contaminations from monomers. In Table I, the varieties of the polymers and their number-average molecular weights are listed. A vapor pressure osmometer Hitachi-Perkins Model 115 was used to measure number-average molecular weight. The synthesized polymers were purified by reprecipitating them

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TABLE I
The Polymers and Their Number-Average Molecular Weight

Polymer	Number-average MW
Poly(methyl methacrylate) (P-MMA)	8,200
Poly(ethyl methacrylate) (P-EMA)	7,800
Poly(n-butyl methacrylate) (P-n-BMA)	8,800
	13,000[a]
Poly(lauryl methacrylate) (P-LMA)	7,500
Poly(methyl acrylate) (P-MA)	7,000
	13,000[a]
Poly(ethyl acrylate) (P-EA)	6,500
Poly(n-butyl acrylate) (P-n-BA)	6,000
Poly(isobutyl acrylate) (P-i-BA)	7,000
Poly(2-ethylhexyl acrylate) (P-2EHA)	6,500

[a]
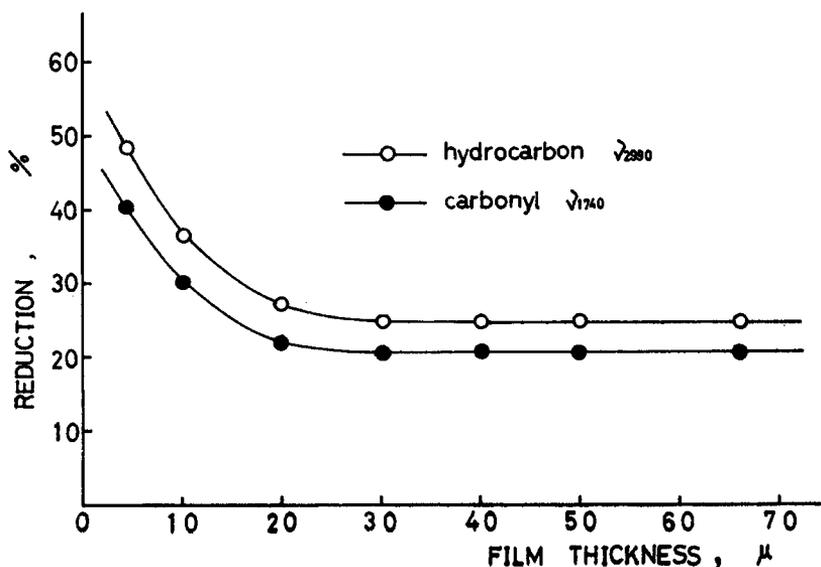
Fig. 1. Effect of film thickness in poly(n-butyl methacrylate) irradiated for 248 hr in air at room temperature.

twice with methanol from ethyl acetate solutions and drying at 60°C under vacuum for 48 hr. As main radiation source a Toshiba GL-15 low-pressure mercury lamp was employed, and a diffractional lattice radiation spectrophotometer (Japan Spectroscopy Co., Model FRM) was also used. The polymers to be irradiated were dissolved in ethyl acetate and coated onto glass or tin plates. After 24 hr of drying at 60°C under vacuum, coated panels were subjected to the irradiation.

The thickness of the dried films was controlled to fall within a range of $35 \pm 4\,\mu$. As shown in Figure 1, it seems that there would be no influence of
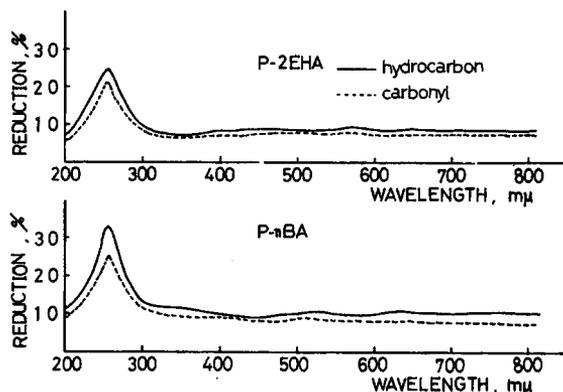
Fig. 2. Change of hydrocarbon and carbonyl absorbances as a function of wavelength.

film thickness unless it is smaller than 20 μ. Figure 1 showed the reduction rate of absorbances at 2990 and 1740 cm^{-1} obtained from IR spectra when the films of poly(n-butyl methacrylate) with different thickness were irradiated for 284 hr. In order to examine the effect of wavelength, several polymers were irradiated with a diffractional lattice radiation spectrophotometer which is able to irradiate a sample with 20 sectionalized lights separately within a range of 200 mμ to 700 mμ. The results are illustrated in Figure 2. It can be noted that the light of 254 mμ is most effective.

Spectral Changes

The infrared spectra of sample undergoing photolysis in air (Fig. 3), show that the carbonyl absorption becomes gradually broad and that the absorption at 3400 cm^{-1} increases. Figure 4 shows a progressive increase in ultraviolet absorption during the irradiation in air. The band at 285 mμ observed by Shultz[6] is also seen in these spectra and is assumed to be due to the production of aldehyde group or conjugated double bond, and the production of conjugated double bond is also assumed to be associated with the coloring of irradiated samples.

Changes in Composition During Irradiation

Figure 5 shows that the reduction of weight caused by volatilization increases linearly with increase in irradiation time, and it was also found that volatilization increases with increasing length of the side chain, except for P-n-BMA. From this behavior it is evident that the scission of side chains or the liberation of monomer units affects volatilization. Figure 6 shows the changes in gel fraction during irradiation in air at room temperature. Tetrahydrofuran was used as solvent because it is the solvent to be used for GPC. As irradiation time increases, the gel fraction of P-n-BA becomes constant while that of P-i-BA decreases. In other polymers, no gel

(a)
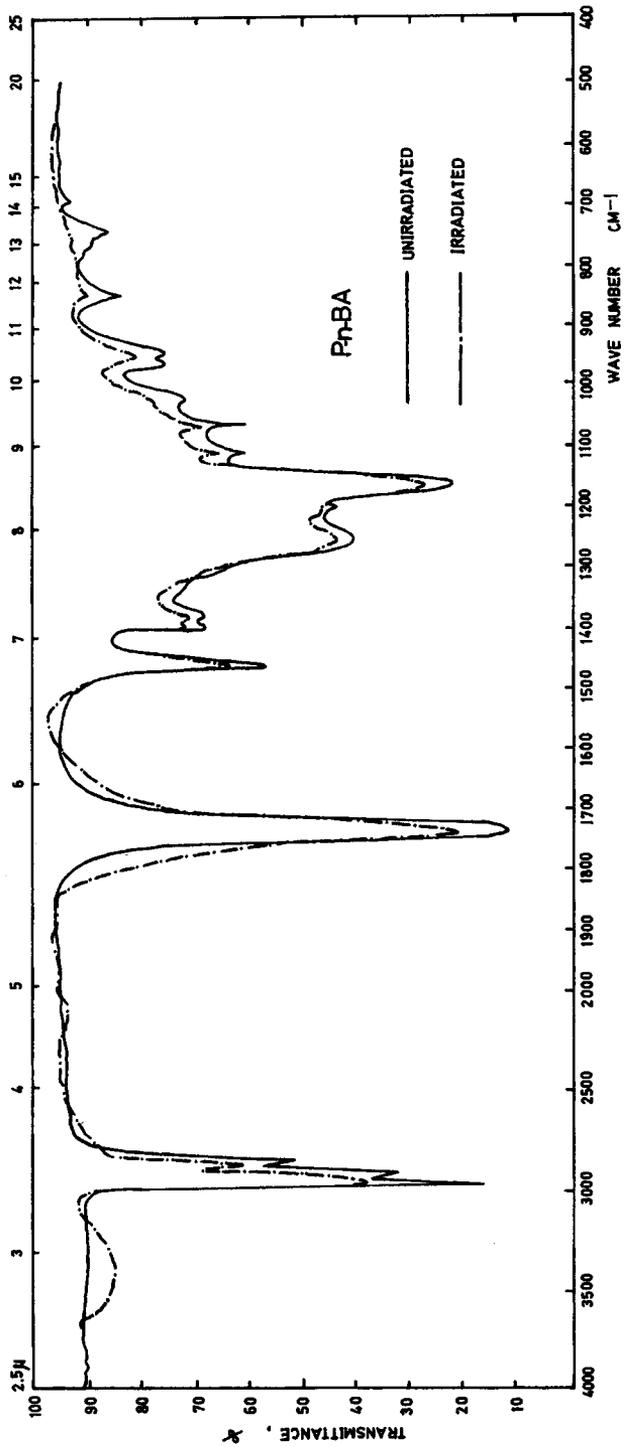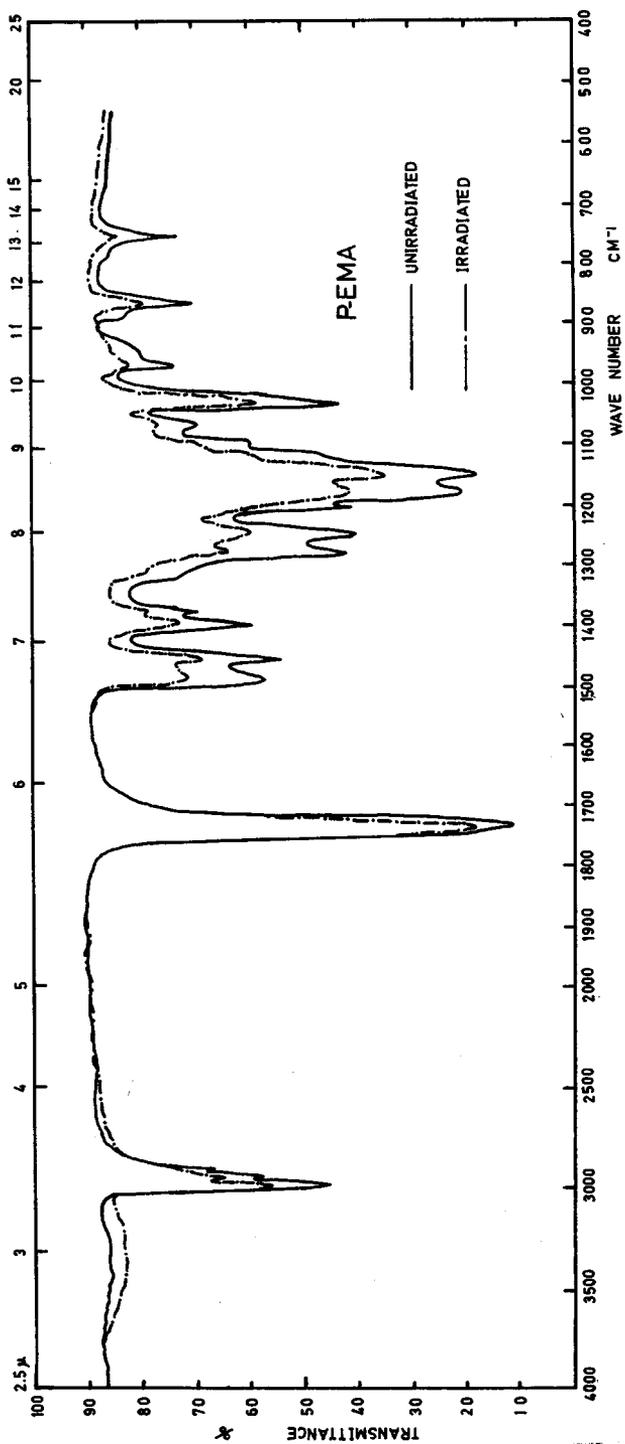
(b)

Fig. 3. Changes in infrared spectrum during irradiation in air at room temperature.

fraction was observed except for P-n-BMA, which gives a small gel fraction. It is worth noting that the gel fraction of P-n-BA is characteristically larger in comparison with other polymers and becomes constant after 60 hr. This indicates that P-n-BA forms a stable network toward ultraviolet light.
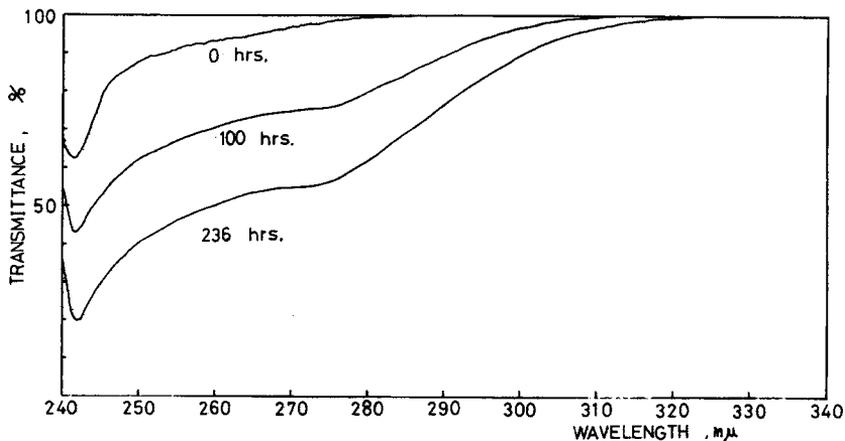
Fig. 4. Changes in the ultraviolet spectrum of P-n-BMA during irradiation in air at room temperature.
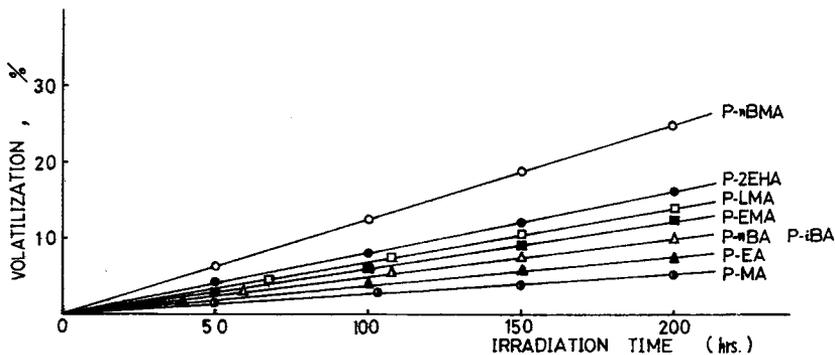
Fig. 5. Volatilization rate as a function of irradiation time in air at room temperature.
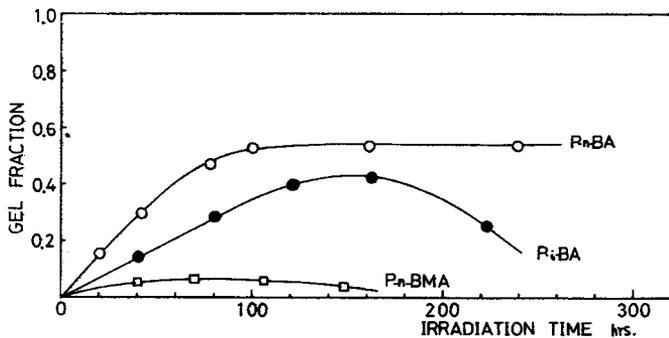
Fig. 6. Changes in gel fraction during irradiation in air at room temperature.

Molecular Weight Distributions

Molecular weight distributions were obtained by a system packed with polystyrene gel of our own making. Using the relationship between the molecular weight and the elution volume, we obtained the calibration curve shown in Figure 7. For this purpose, monodisperse polystyrenes having known molecular weights were used as standard samples. The molecular weight distributions for various polymers at different irradiation times are
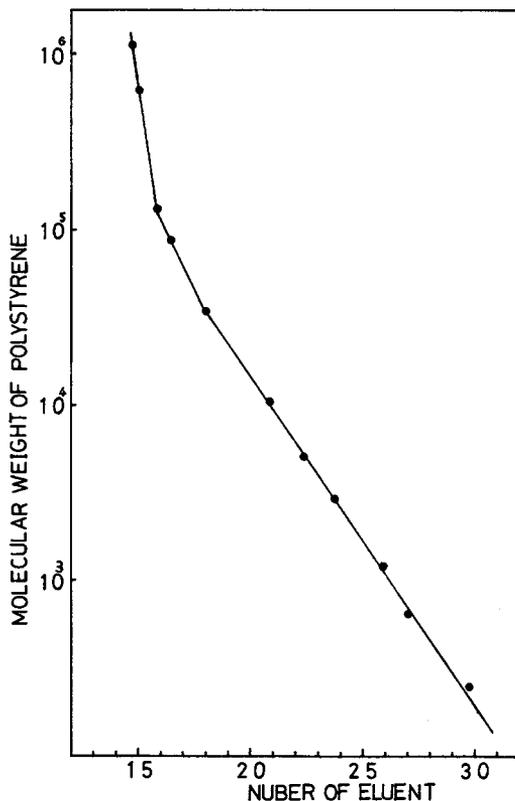
Fig. 7. Relationship between molecular weight and elution number.

shown in Figure 8. It is evident that crosslinking and decomposition occur simultaneously, except for P-MMA. The difference in side chains between P-n-BA and P-i-BA is also reflected in the change in molecular weight distribution. Qualitatively, it is clear that the crosslinking in P-n-BA, P-i-BA, and P-n-BMA takes place more easily than in other polymers. The crosslinking in poly(alkyl methacrylates) has been reported little, but it is evidently recognized that the crosslinking in P-n-BMA and P-LMA takes place considerably.
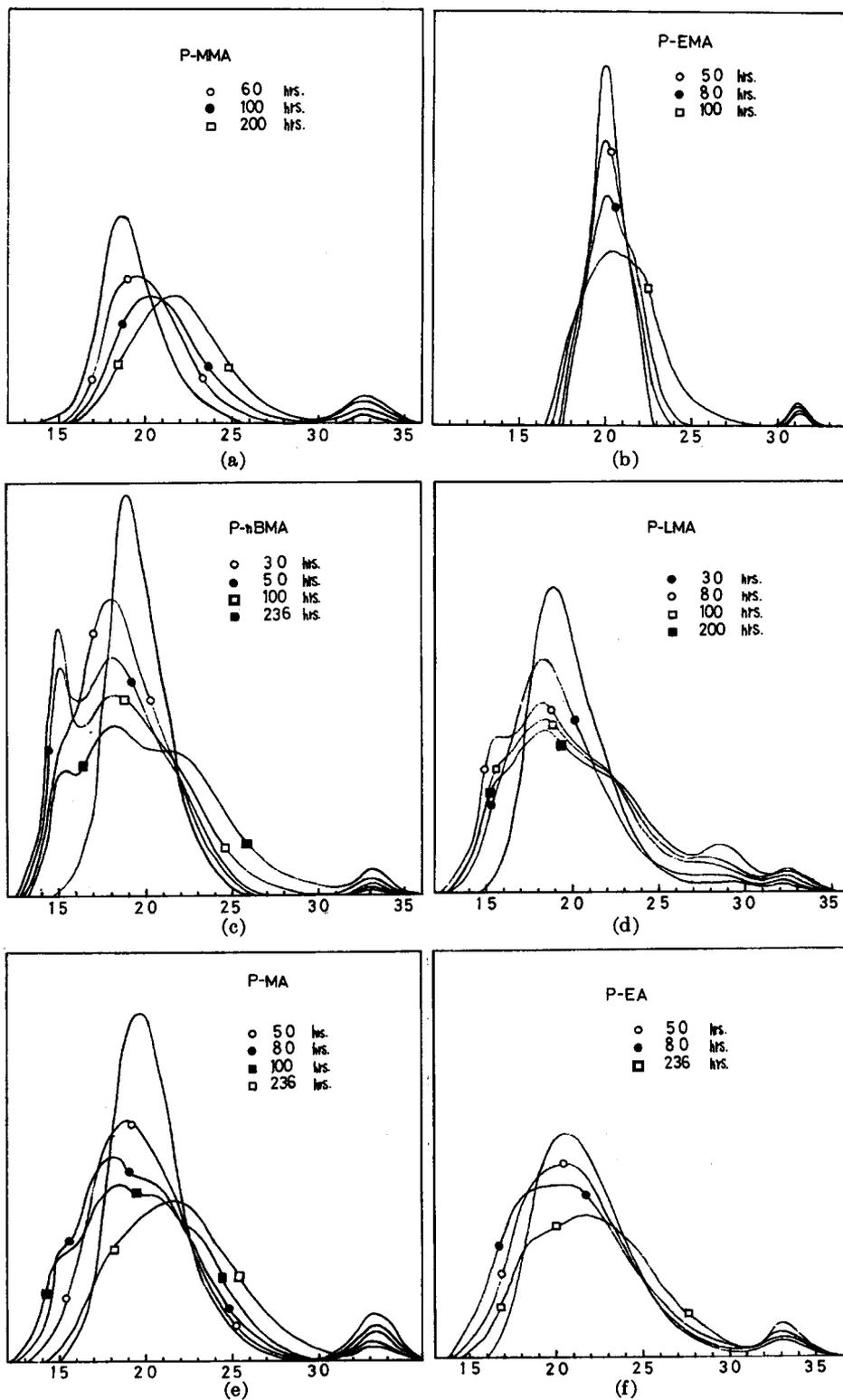
Fig. 8. (continued)
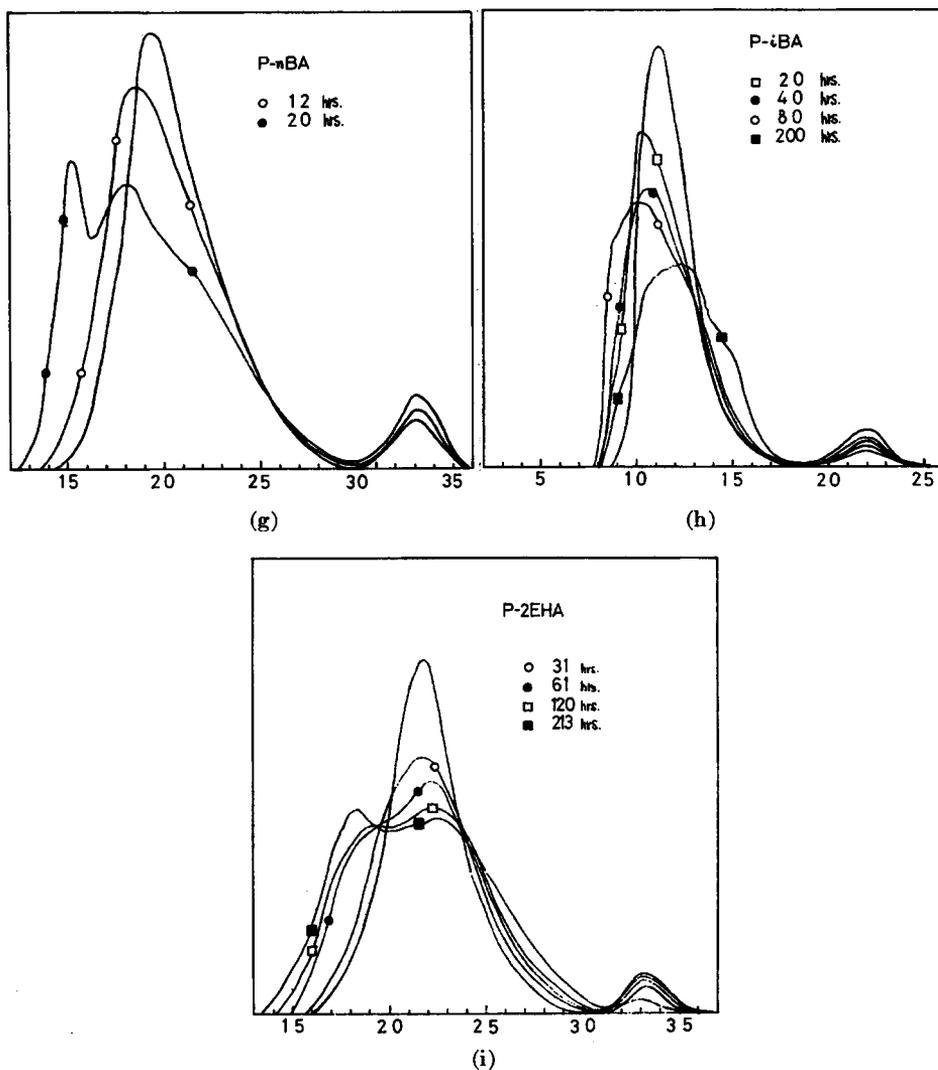
Fig. 8. Changes in molecular weight distribution during irradiation in air at room temperature.

DISCUSSION

Chain Scission

When the chain scissions occurred, the degree of degradation, expressed as the number of scissions per polymer chain was calculated from the formula.

$$n = \bar{M}_{no}/\bar{M}_n - 1$$

where $\bar{M}_{no}$ and $\bar{M}_n$ denote the number-average molecular weights before and after irradiation, respectively. The results obtained in this study are
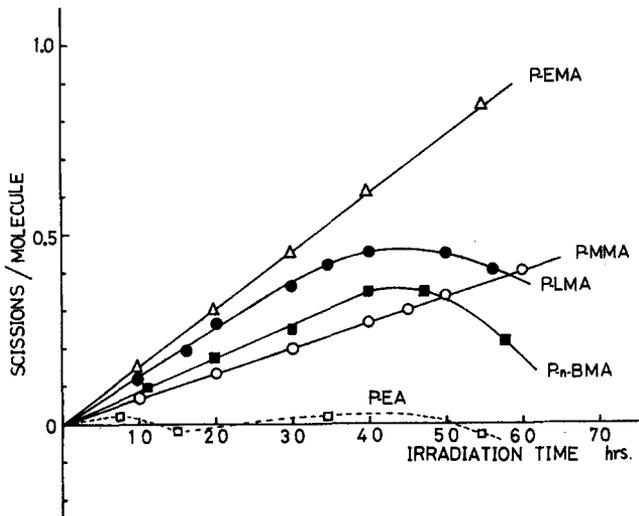
Fig. 9. Changes in chain scission as a function of irradiation time.
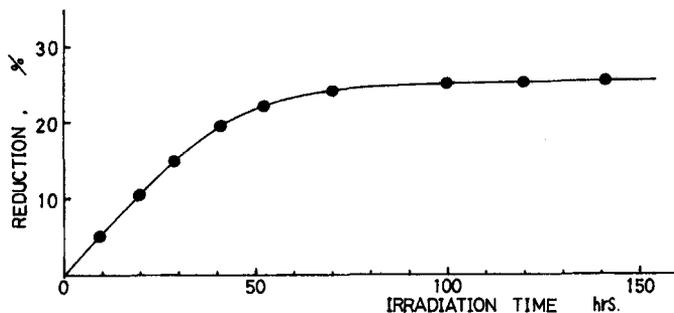
Fig. 10. Changes in intrinsic viscosity of P-MMA during irradiation in air at room temperature.

shown in Figure 9. As shown in Figure 9, the n value of P-MA and P-EMA increases linearly with increase in irradiation time; whereas in P-n-BMA and P-LMA, deviation of decrease were observed after about 60 hr of irradiation. Also, the n values of other polymers, particularly poly(alkyl acrylates) used in this study, showed no change or a negative value. The explanation for this phenomenon is sufficiently deduced from the GPC data (see Fig. 8).

The linearity obtained in the case of P-MMA and P-EMA is also shown in the reduction of intrinsic viscosity. Figure 10 shows the reduction rate of intrinsic viscosity in irradiated P-MMA as a function of irradiation time. In the case of P-n-BA and P-n-BMA, including both crosslinking and decomposition, the intrinsic viscosity shows no change or a little increase as shown in Figure 9. This is also clarified by Figure 8.

Degree of Crosslinking and Decomposition

The degree of decomposition calculated from the number-average molecular weight before and after irradiation should be considered as average value and not sufficient to discuss in this study, because the crosslinking and decomposition take place simultaneously (see Fig. 8). The reliable degree
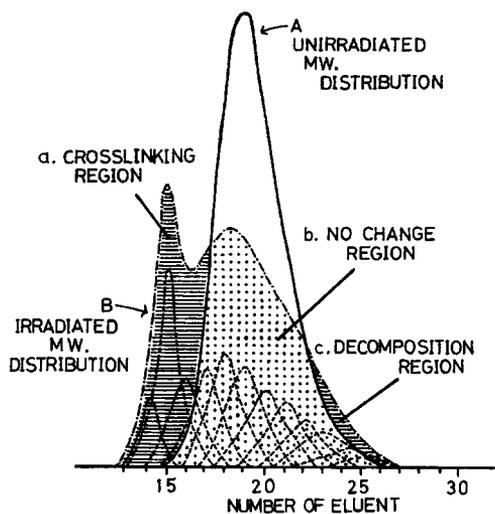
Fig. 11. Wave analysis.

TABLE II
Gel Permeation Chromatography for Sample L-8

Vol.	Ht. obs.	Sig.	Const.	Ht. Calcd	Per cent	Cumulative Per cent	MW
0.00	0.01	0.01	0.01	0.00	0.00	0.00	
0.00	0.01	0.01	0.01	0.00	0.00	0.00	
12.00	0.01	0.50	0.02	0.00	0.00	0.00	1,500,000
13.00	2.85	0.52	0.40	0.88	0.22	0.22	1,000,000
14.00	26.25	0.59	0.76	13.47	3.80	4.02	800,000
15.00	74.00	0.69	1.21	51.78	17.11	21.13	414,000
16.00	53.00	0.84	0.95	23.94	9.63	30.76	125,000
17.00	56.49	0.85	0.98	25.96	10.57	41.33	67,500
18.00	63.00	0.87	1.01	29.11	12.13	53.45	38,900
19.00	59.85	0.94	1.02	25.93	11.67	65.12	24,700
20.00	51.75	1.12	1.07	19.68	10.55	75.68	15,200
21.00	44.48	1.21	1.11	16.33	9.46	85.14	9,500
22.00	34.00	1.18	1.04	11.95	6.75	91.89	6,000
23.00	22.99	1.18	0.96	7.48	4.23	96.12	3,730
24.00	12.99	1.27	0.88	3.60	2.19	98.31	2,380
25.00	6.48	1.53	0.82	1.39	1.02	99.33	1,490
26.00	3.25	1.48	0.80	0.70	0.49	99.83	920
27.00	1.21	1.40	0.56	0.19	0.13	99.96	570
28.00	0.49	1.33	0.47	0.07	0.04	100.00	360
29.00	0.01	1.26	0.02	0.00	0.00	100.00	255
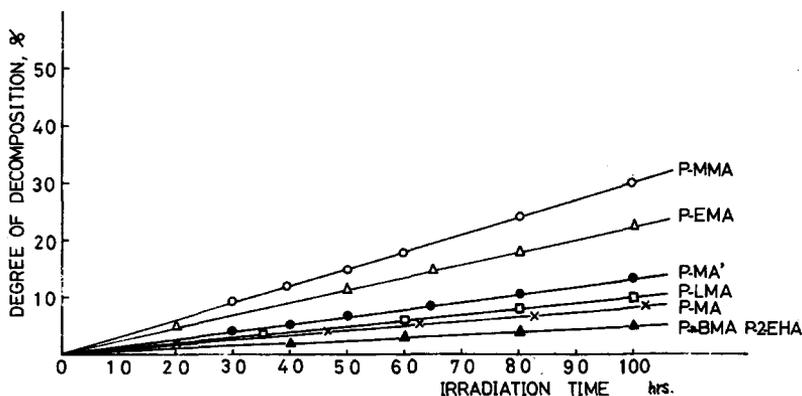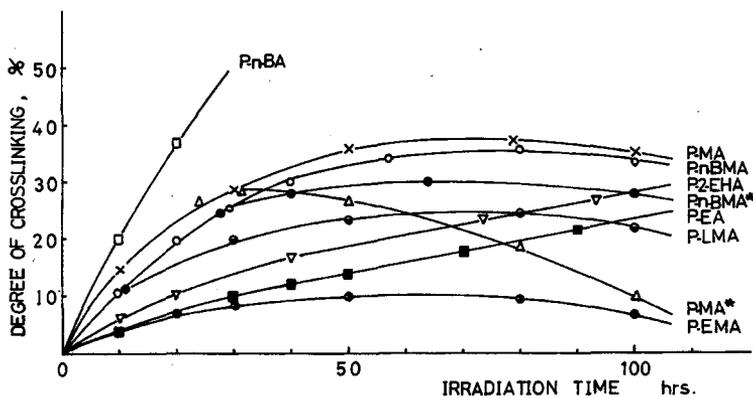
Fig. 12. Changes in the degree of crosslinking and decomposition as a function of irradiation time.

of crosslinking and decomposition could be obtained by mathematical analysis of the GPC data. As shown in Figure 11, curve B which contains a crosslinked portion as well as a decomposed portion, can be divided into individual components expressed to the dotted line at each elution volume according to the method of Smith.[7] An example of results calculated by computer is shown in Table II. The components of each the a, b, and c regions in curve B are attributable to the crosslinked, the no change, and the decomposed portions, respectively. The results calculated from molecular weight distributions which indicate the degree of crosslinking and decomposition are shown in Figure 12. From Figure 12, it is clear that crosslinking and decomposition take place simultaneously in poly(alkyl acrylates) and poly(alkyl methacrylates), except for P-MMA. The crosslinking in poly(alkyl methacrylates) seems to occur moderately and has the tendency to decrease after 100 hr of irradiation. Also, the difference of molecular

weight of initial polymer used in this study (see Table I) seems to be recognized in the degree of crosslinking rather than that of decomposition.

Perhaps this could be due to the existence of a limiting molecular weight under the experimental conditions investigated. It can also be noted that the degree of crosslinking in P-n-BA exhibits a considerable increase. Because the crosslinking is not only influenced by the chemical structure of the side chain, but also by the glass transition temperature or, in other words, by the chain mobility under the experimental conditions, it is too complex to resolve this behavior. On the other hand, it must be remembered that the insoluble fractions are not included in Figure 12; then, strictly speaking, the results mentioned above should be corrected by taking these fractions into consideration.

Mechanism

The yellowing of poly(alkyl acrylates) and poly(alkyl methacrylates), a result of exposure to ultraviolet light, is attributable to the presence of conjugated double bonds. The production mechanism of conjugated double bonds has been suggested by Allison.[2] Infrared spectrophotometer analyses were made of the gas using the gas cell attached to a quartz tube containing irradiated polymer film. The samples of gas for poly(alkyl methacrylates) were found to contain carbon dioxide and monomer. For poly(alkyl acrylates) they were found to contain carbon dioxide and acid. Therefore, crosslinking of poly(alkyl acrylates) and poly(alkyl methacrylates) is probably taking place in reactions following side-chain scission:

$$\text{---CH}_2\text{---}\underset{\underset{\text{COOR}}{|}}{\overset{\overset{\text{CH}_3\text{(H)}}{|}}{\text{C}}}\text{---} \quad \xrightarrow{h\nu} \quad \text{---CH}_2\text{---}\overset{\overset{\text{CH}_3}{|}}{\underset{.}{\text{C}}}\text{---} \; + \; \cdot\text{COOR} \tag{1}$$

$$2 \;\; \text{---CH}_2\text{---}\underset{.}{\overset{\overset{\text{CH}_3\text{(H)}}{|}}{\text{C}}}\text{---} \quad \longrightarrow \quad \begin{array}{c} \text{---CH}_2\text{---}\overset{\overset{\text{CH}_3\text{(H)}}{|}}{\underset{|}{\text{C}}}\text{---} \\ \text{---CH}_2\text{---}\underset{\underset{\text{CH}_3\text{(H)}}{|}}{\text{C}}\text{---} \end{array} \tag{2}$$
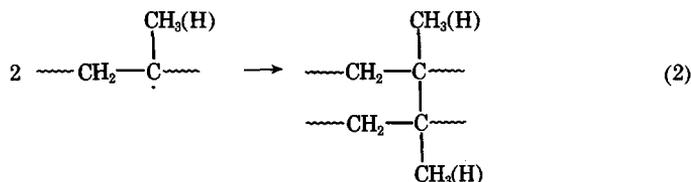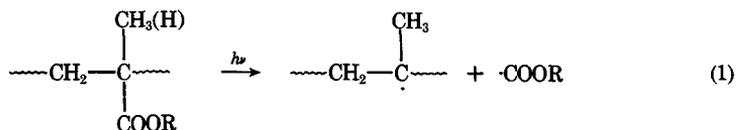
A crosslink of this type is influenced by the chain mobility. Figure 12 shows that the glass temperature of the polymer is related to the degree of crosslinking, which supports a crosslink of the type suggested. As for the main-chain scission of polystyrene in the presence of air, Grassie[3] states that hydroperoxide would decompose by way of a six-membered ring transition (see eq. (3), p. 2960).

The polymer radicals can also decompose and result in main-chain scission, but a reaction similar to eq. (3) may be considered to occur in poly(alkyl acrylates) because the α-hydrogen of poly(alkyl acrylates) would play the same role as in polystyrene. But the reactions occurring in poly(alkyl

$$\sim\sim CH_2-\underset{\underset{\displaystyle\bigcirc}{|}}{\overset{\displaystyle H}{C}}-CH_2\sim\sim \xrightarrow{h\nu} \sim\sim CH_2-\underset{\underset{\displaystyle\bigcirc}{|}}{\overset{\displaystyle H\\+\\\dot{C}}{}}-CH_2\sim\sim \xrightarrow{O_2}$$

$$\sim\sim CH_2-\underset{\underset{\displaystyle\bigcirc}{|}}{\overset{\displaystyle OOH}{C}}-CH_2\sim\sim \longrightarrow$$

$$\sim\sim CH_2-\overset{O\cdots H}{\underset{\underset{\displaystyle\bigcirc}{C}}{}}-\overset{H_2}{C}-\underset{\underset{\displaystyle\bigcirc}{C}}{C}-CH_2\sim\sim \longrightarrow$$

$$\sim\sim CH_2-\underset{\underset{\displaystyle\bigcirc}{C}}{\overset{\displaystyle O}{\|}} \quad + \; H_2O \; + \; CH_2=\underset{\underset{\displaystyle\bigcirc}{C}}{}-CH_2\sim\sim \quad (3)$$
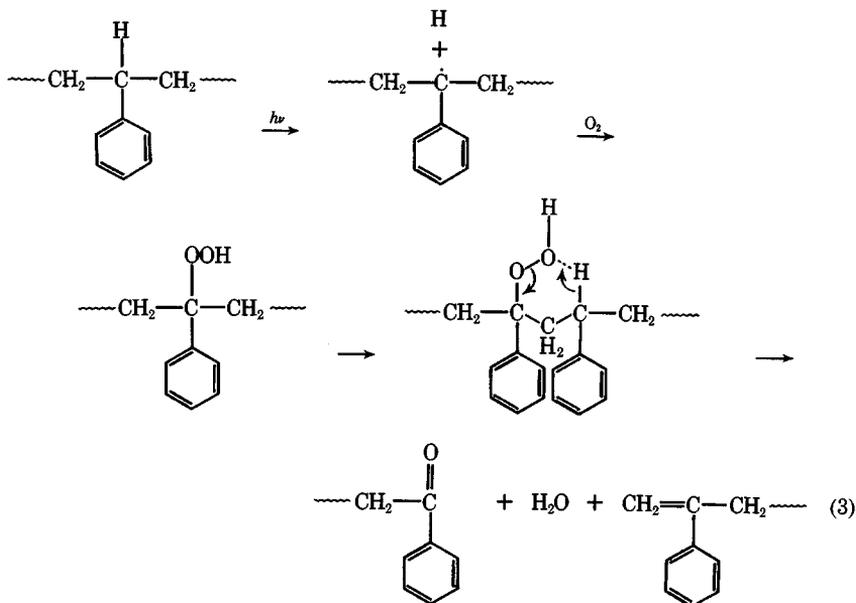
methacrylates) would be depolymerization or random scission of main chains, and be hardly influenced by oxygen. These were also investigated by determining the production of acid. The results are shown in Figure **13**. As for the reason why the crosslinking reaction of poly(alkyl acrylates) occurs more easily than that of poly(alkyl methacrylates), it should be considered that the number of crosslinking points (from the liberation of α-hydrogen and side chain) and the chain mobility (from the glass transition temperature) are more conveniently crosslinked in poly(alkyl acrylates). Clearly, a great deal of work will be necessary for the clarification of these reaction mechanisms.
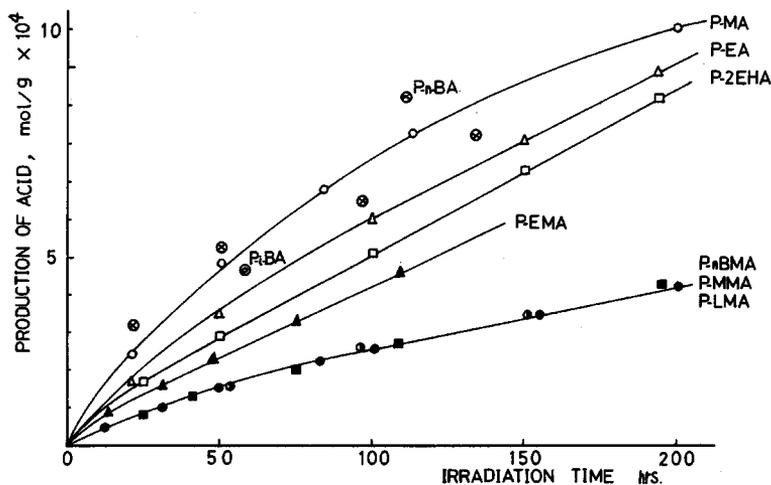
Fig. 13. Changes in production of acid during irradiation in air at room temperature.

CONCLUSIONS

In the study of the degradation of polymers, the determination of the molecular weight distribution by GPC can give more precise and useful information than other techniques. As a result of this study, it seemed that chain scission would more eaxily take place in poly(alkyl methacrylates) than in poly(alkyl acrylates), but as the length of the side chains increases, the crosslinking reaction would take place in poly(alkyl methacrylates) as well as in poly(alkyl acrylates). Also, it seemed that the reactions in poly(alkyl methacrylates) would be hardly influenced by oxygen.

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