Photolysis of Poly(benzyl methacrylate)s and Poly(benzyl acrylate)s in Solution and Films

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ABSTRACT: Methacrylate and acrylate copolymers containing benzyl or 1-phenylethyl groups and their monomeric model compounds were irradiated with a 254-nm light in CH_2Cl_2 and solid films. Low molecular weight and polymeric products were analyzed by gas chromatography (GC) and NMR spectroscopy, respectively, and main-chain scission efficiencies were determined by gel permeation chromatography (GPC). The results indicate that the ester bond cleavage in the side chain produces alkyl radicals in the main chain, leading to main-chain scission and crosslinking. The higher stability of tertiary alkyl radicals formed in methacrylate polymers lead to the predominant main-chain scission in solution. On the other hand, acrylate polymers were less susceptible to photodegradation. The degradabilities of the polymer films reflected those of the polymer solutions, although crosslinking preferentially occurred. The distinct effect of oxygen on the degradation was also observed in solution and films. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2227–2236, 2001

Key words: crosslinking; degradation; irradiation; photochemistry

INTRODUCTION

There has been considerable interest in the development of photodegradative polymers, particularly due to their potential applications in degradable plastics, lithographic techniques, and so on. Various types of photosensitive groups have been introduced to the main and side chains in polymers.[1,2]

Poly(alkyl methacrylate)s are known to have a good resistance to sunlight but to undergo chain scissions when subjected to high-energy irradiations such as γ-, X-, and vacuum UV rays and electron beams[3–7] or to long-time UV irradiation.[8–12] In the latter cases, the degradation occurs randomly over the whole polymer chains. On the other hand, polymethacrylates containing aromatic groups in the side chains are susceptible to side-chain photodegradation,[13,14] which induces main-chain scission in some cases.[15]

We previously found that methacrylate copolymers containing 1-naphthylethyl ester residues undergo facile photocleavage of ester bonds in solution and that their photoreactivities are different from those for the corresponding monomeric compounds.[16,17] We speculated some contribution of steric hindrance of substituent groups and polymer chains to the photocleavage. In fact, a detailed study on the photochemistry of α-substituted naphthylmethyl and benzyl alkanoates indicated the importance of steric hindrance around the ester bond.[18,19]
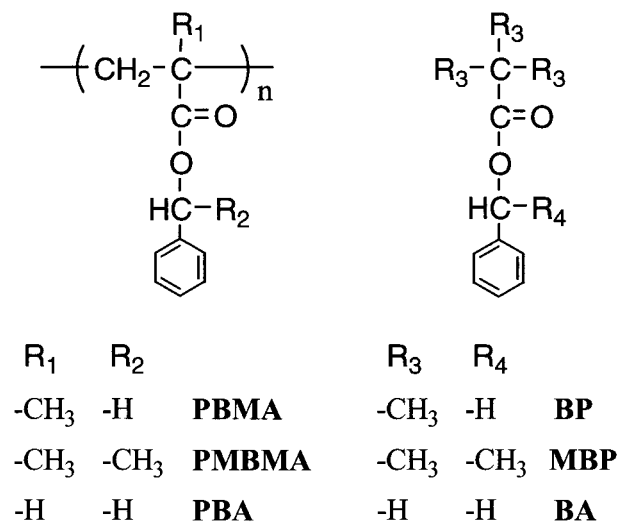
Figure 1 Structures and abbreviations of benzyl ester homopolymers and monomeric model compounds.

In many studies on polymer degradation, mechanistic interpretations are based on the estimation of photoproducts or reaction intermediates by spectroscopic analyses such as IR, UV-vis, and ESR. In a few cases, low molecular weight photoproducts for polymers and/or their model compounds were analyzed by gas chromatography (GC) and other measurements.[9,16,20,21] It should be noted again that the products are not necessarily identical in polymer and model systems. Recent development in NMR spectroscopy has permitted the identification of fine structures in polymers such as tacticity, end group, irregular linkage, and comonomer sequence.[22,23] This technique has also been applied to several mechanistic studies on polymer degradation.[3–5,21,24,25]

We report here a comparative investigation on the photolyses of benzyl ester polymers and the monomeric model compounds (Fig. 1) based on analyses of low molecular weight and polymeric products by GC and NMR measurements, respectively. The effects of substituents, comonomers, and oxygen on the photolyses were also examined in solution and films.

EXPERIMENTAL

Materials

Benzyl methacrylate (BMA), methyl methacrylate (MMA), methyl acrylate (MA), and styrene (St), purchased from Wako Chemicals (Osaka, Ja-

pan), were distilled under reduced pressure. 1-Phenylethyl methacrylate (MBMA) and benzyl acrylate (BA) were synthesized by the reaction of the corresponding alcohols with methacryloyl or acryloyl chloride in triethylamine–tetrahydrofuran (THF) mixtures[16] and purified by distillation under reduced pressure. Monomeric model compounds are those reported previously.[19]

Polymerizations were carried out at 60°C in degassed benzene using 2,2′-azobisisobutyronitrile (AIBN) as an initiator (1 mol % on the basis of total monomers) and purified by repeated precipitations from THF into n-hexane or methanol. The content of the benzyl group in the copolymer (x) was determined by absorption spectra in CH_2Cl_2 using the corresponding homopolymers and monomeric model compounds as standards.

Most of the photoproducts were commercially available. 2,2-Dimethyl-3-phenylbutane and meso- and dl-2,3-diphenylbutane were isolated from the products of preparative photolysis of 1-phenylethyl pivalate (MBP).[19]

Irradiations

For quantitative photolyses in CH_2Cl_2, irradiations were carried out with a 500-W high-pressure mercury lamp (EIKOSHA, EHB-W-500) in a merry-go-round apparatus. A 0.01M solution (4 mL) of the ester in CH_2Cl_2 was placed in a quartz tube, purged with argon or oxygen gas for 10 min, and then irradiated for 1 h at 25°C. The samples were analyzed by GC as described previously.[19]

The molecular weights of the polymers before and after irradiations were estimated by gel permeation chromatography (GPC). For comparison of the main-chain scission efficiencies for different types of homopolymers and copolymers, the efficiency per benzyl ester unit (s) was calculated with the equation that would compensate the differences in the molecular weight and composition:

$$s = (w/M_n^0)[(M_n^0/M_n) - 1]/[\text{benzyl}] \qquad (1)$$

where w is the weight of the irradiated polymer (in grams); [benzyl], the concentration of the benzyl ester unit (in mol); and M_n^0 and M_n, the initial and final polystyrene-equivalent number-average molecular weights, respectively.

Polymer films, mounted at a distance of 6 cm from the lamp, were photolyzed for 1 h under a nitrogen or oxygen atmosphere at room temperature. The films were prepared by the casting of

polymers ([benzyl] = 1×10^{-4} mol) dissolved in 3 mL of nitrogen- or oxygen-saturated CH_2Cl_2 onto a Petri dish of 42-mm diameter and dried in the dark for 24 h under nitrogen or oxygen. The film was then placed in a vacuum oven overnight at room temperature. A poly(methyl methacrylate) (PMMA) film containing 20 wt % of benzyl pivalate (BP) was prepared in the same way. The irradiated films were then dissolved in THF and the soluble potions were subjected to GC and GPC measurements.

Samples for NMR measurements were prepared as follows: A $0.01M$ solution (500 mL) of the polymer in CH_2Cl_2 was placed in a quartz vessel, purged with nitrogen for 30 min, and then irradiated for 1 h under nitrogen with the 500-W high-pressure lamp. The polymer solution was evaporated to dryness under reduced pressure and then extracted repeatedly with hot *n*-hexane. The undissolved solids were redissolved in $CDCl_3$ and subjected to the NMR measurements.

Measurements

Instrumentations for GC–MS and GC measurements were described previously.[18] For GC anal-

ysis, 2-ethylnaphthalene was used as a standard. The NMR spectra were recorded on a Bruker AVANCE400 spectrometer using a 5% (w/v) solution in $CDCl_3$ at room temperature.

Molecular weights of the polymers were estimated by using a Toyo Soda HLC-802A system with a Shodex KF-805 column. Monodisperse polystyrene samples were used as standards.

RESULTS AND DISCUSSION

Irradiation of Homopolymers and Monomeric Model Compounds in CH_2Cl_2 Under Argon Atmosphere

Irradiations were carried out in CH_2Cl_2 because of the high solubility for polymers and the transparency for a 254-nm light. No precipitation occurred for any sample. When low molecular weight model compounds, BP, MBP, and BA, were photolyzed, seven benzylic products were identified by GC and GC mass spectroscopy (MS):
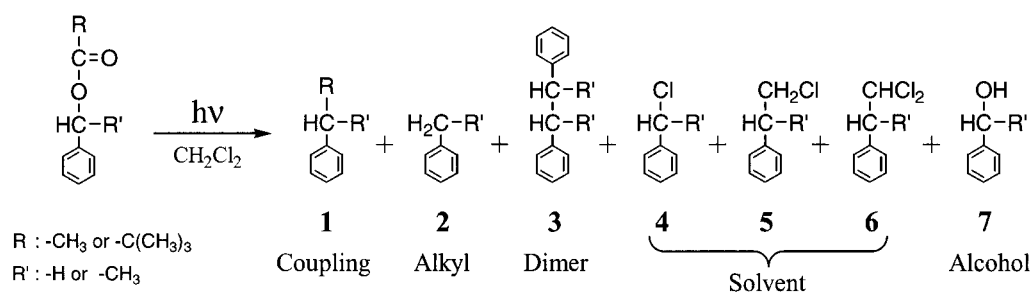
(2)

The formation of products **1–7** is rationalized by homolytic cleavage of the benzyl–heteroatom bond,[18,19,26,27] that is, the products are all derived from benzyl radicals: **1** and **3** are formed by coupling with alkyl and benzyl radicals, respectively; **2,** by hydrogen-atom abstraction; and **4–6,** by reaction with solvents. A trace amount of **7** may be an oxidized product.[19] For all polymers, the products except a polymeric one corresponding to **1,** which could not be detected by GC, were obtained, indicating that the degradation of ester groups in the polymers proceeds by the same mechanism.

The product yields for **1–6,** determined by GC, are given in Table I. As in our previous cases,[18,19]

the present experiments showed a poor mass balance of photoproducts. In contrast with the photolyses in methanol yielding both ionic and radical products,[19,26,27] substituent effects of the ester conversion and the product distribution were only moderate. The homopolymers showed a similar but somewhat complex dependence, which may be influenced by many factors, such as steric hindrance of polymer chains, the presence of active hydrogens for hydrogen abstraction, and solvent–polymer interactions. However, it can be safely said that PBMA and PMBMA are decomposed similarly and the degradation of PBA takes place inefficiently.

Figure 2 compares the GPC charts for PBMA and PBA irradiated in CH_2Cl_2. Under an argon

Table I   Product Yields (%) for Photolysis of Esters in CH$_2$Cl$_2$

Ester	Conversion[a]	Coupling **1**	Alkyl **2**	Dimer[b] **3**	Solvent **4–6**	s[c]
BP	60	5.8	5.0	2.1	5.1	—
MBP	51	4.1	5.1	1.3	6.5	—
BA	51	5.3	0.8	1.2	5.7	—
PBMA	—	—	6.0	1.4	7.4	10
PMBMA	—	—	6.3	2.7	7.6	13
PBA	—	—	1.1	0.8	1.7	0.7

[ester] = 2 × 10^{-3}M; λ_{ex} > 250 nm; irradiation time, 1 h.
[a] Yield for ester conversion in percent.
[b] Twice the molar yields.
[c] Main-chain scission efficiency in percent [see eq. (1)]; irradiation time, 5 min.

atmosphere, PBMA underwent efficient main-chain scission, while the molecular weight of PBA decreased slightly. These observations are common to degradations of methacrylate and acrylate polymers[8,11] and are explicable in terms of the stability of alkyl radicals formed in the main chain (see below). Under the present experimental conditions, neither an increase of the molecular weight nor insolubilization was observed, which indicates no crosslinking occurring in these polymers. The main-chain scission efficiency per benzyl monomer unit (s) was calculated from eq. (1) (Table I). There is little difference in the efficiencies of PBMA and PMBMA, and these values are parallel to the total yields of low molecular weight products. This strongly suggests that the side-chain degradation induces the main-chain scission. Therefore, the extremely small s value of

PBA is due not only to the instability of the main-chain radicals (see below) but also to the inefficient side-chain degradation.

NMR spectroscopy was used to investigate the formation of new structures in PBMA and PBA during photoirradiation. The molecular weights (M_n) of PBMA were 94,000 and 1800 before and after irradiation under nitrogen, respectively, and those of PBA were 130,000 and 7000. Figures 3 and 4 show the ^{1}H- and ^{13}C-NMR spectra of PBMA, respectively. Irrespective of the moderate degradation, the spectra of PBA changed only slightly.[17] For PBMA, analysis of the upfield signals for alkans in the spectra was unsuccessful because of the formation of various degradation products with different tacticities.[23] Most of new peaks in the downfield, particularly in the ^{1}H-NMR spectrum, could be assigned on the basis of the data for PMMA degraded thermally or on electromagnetic irradiations.[3–5,24] The assigned structures are indicated in the figures and a most likely mechanism for the degradation of PBMA based on these results is shown in Figure 5.

Several small peaks in the region of 4.5–5.2 ppm in Figure 3(b), overlapping with the methylene protons of benzyl groups, were assigned to olefinic protons associated with the unsaturated groups at chain ends or within the chain. The formation of the vinylidene structure at chain ends is indicative of main-chain scission, that is, an initial elimination of the benzyl radical and carbon dioxide [path (i) in Fig. 5] followed by β-scission [path (ii)]. Disproportionation between alkyl radicals formed in the midchain and benzyl or other radicals is likely to occur to produce double bonds within the chain [paths (vi) and (vii)].
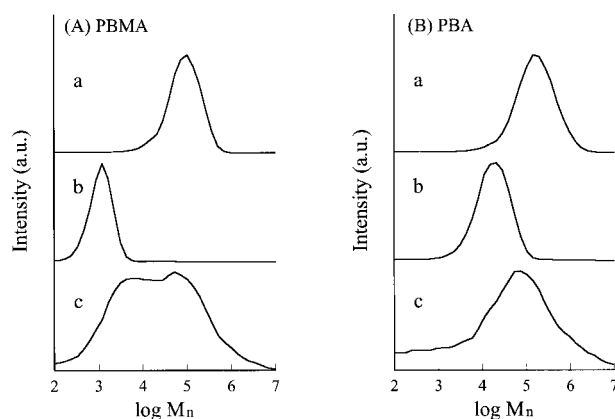

Figure 2   GPC charts of (A) PBMA and (B) PBA irradiated in CH$_2$Cl$_2$ and films at room temperature: (a) before irradiation; (b) after irradiation in CH$_2$Cl$_2$ for 5 min under argon; (c) after irradiation in films for 1 h under nitrogen (THF-soluble portions).
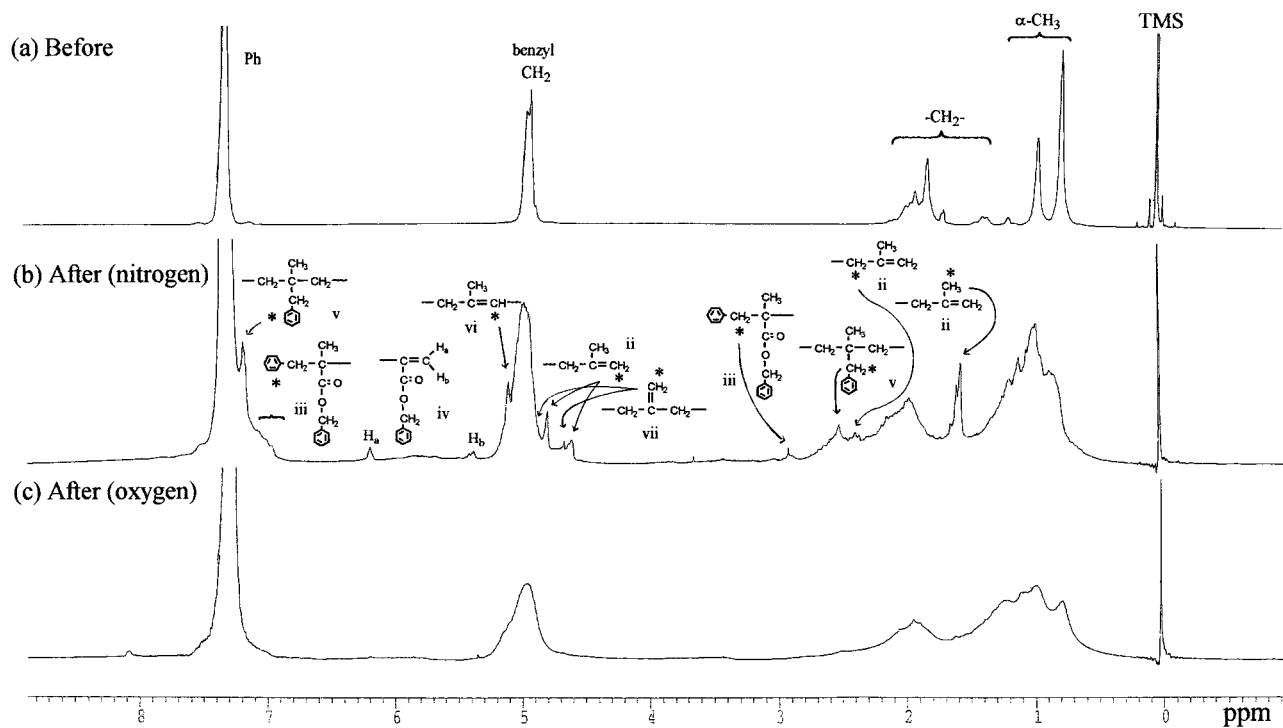
Figure 3 ¹H-NMR spectra of PBMA irradiated in CH₂Cl₂: (a) before irradiation; (b) after irradiation under nitrogen; (c) after irradiation under oxygen. Roman numerals indicate the reaction paths shown in Figure 5.

The peaks at 5.4 and 6.2 ppm in Figure 3(b) were assigned to methylene protons of another type of vinylidene structure at chain ends, which would be formed by hydrogen elimination (disproportionation) of chain-end radicals [path (iv)]. This may be consistent with the fact that
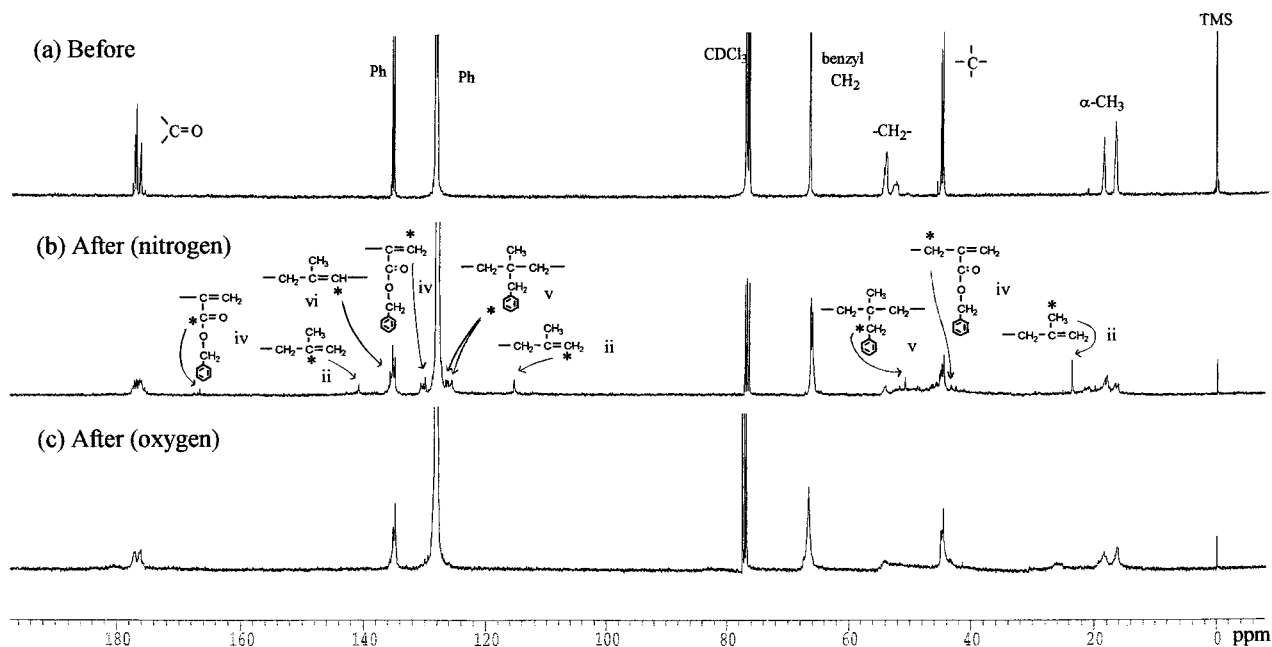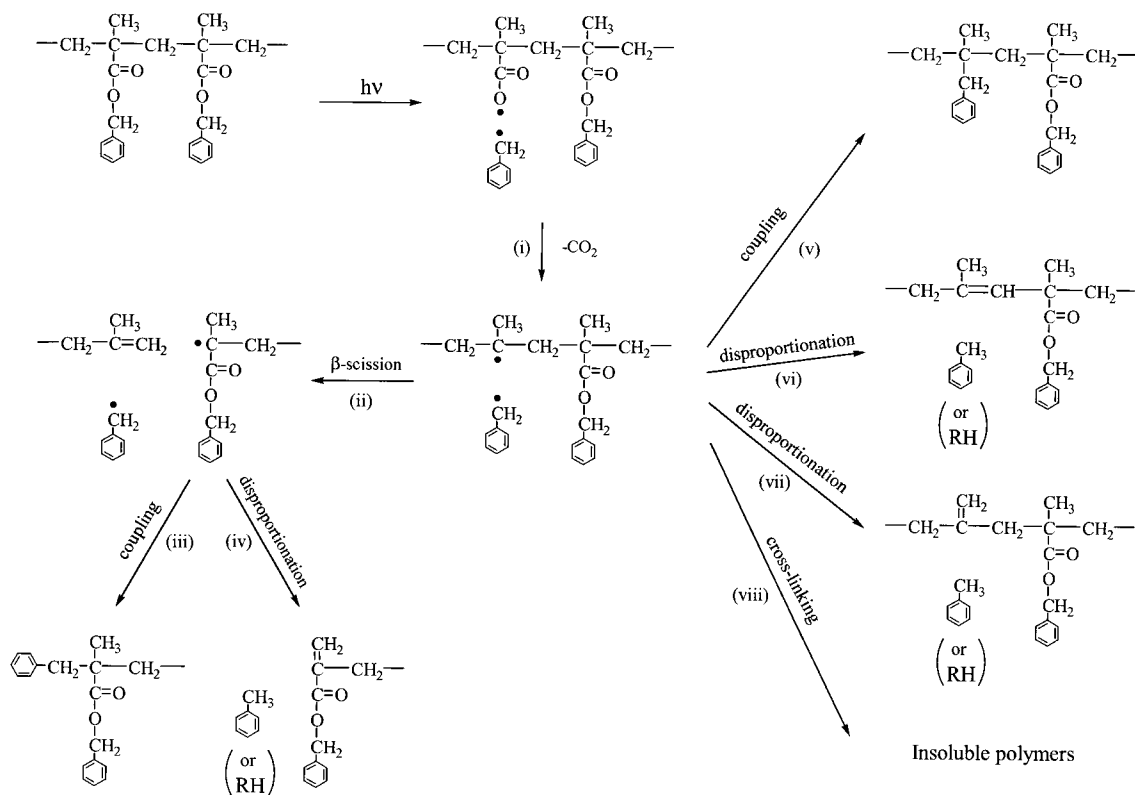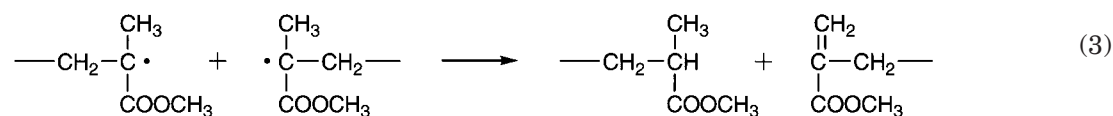

Figure 4 ¹³C-NMR spectra of PBMA irradiated in CH₂Cl₂: (a) before irradiation; (b) after irradiation under nitrogen; (c) after irradiation under oxygen. Roman numerals indicate the reaction paths shown in Figure 5.

Figure 5   Possible mechanism for the photolysis of PBMA.

termination by disproportionation in the radical polymerization of MMA results in the predominant formation of a vinylidene double bond at the chain ends[22,24]:

$$\text{—CH}_2\text{—}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\!\!\cdot \quad + \quad \cdot\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{—CH}_2\text{—} \quad \longrightarrow \quad \text{—CH}_2\text{—}\underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{CH}}} \quad + \quad \underset{\underset{\text{COOCH}_3}{|}}{\overset{\overset{\text{CH}_2}{||}}{\text{C}}}\text{—CH}_2\text{—} \tag{3}$$

The small signal and the shoulder band around 7 ppm in Figure 3(b) were assigned to phenyl protons attached to the midchain and chain ends, respectively. This indicates that the coupling of benzyl radicals with alkyl radicals in the polymer chain can occur just as in the formation of **1** for the low molecular weight models [paths (iii) and (v)].
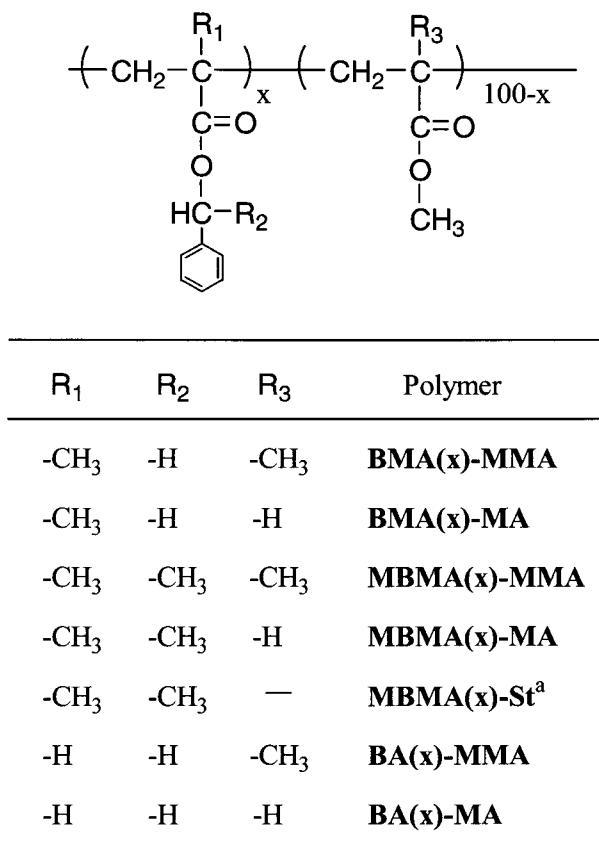
Consequently, the NMR analysis confirmed that the photodegradation of PBMA proceeds mainly by side-chain degradation followed by main-chain scission (Fig. 5), similarly to that for PMMA.[8,10] However, the "direct" generation of main-chain alkyl radicals, observed commonly for poly(alky methacrylate)s,[9] does not seem to occur, because the benzyl ester bond is cleaved quite easily. In fact, the product, benzyl

formate, could not be detected for the present polymers.

Irradiation of Copolymers in CH_2Cl_2 Under Argon Atmosphere

From the results for the homopolymers, it is anticipated that neighboring monomer units in the polymer chain will affect both side-chain degradation and main-chain scission. Then, several types of methacrylate and acrylate copolymers were prepared (Fig. 6) and photolyzed in CH_2Cl_2. Total yields of products **2–6** and main-chain scission efficiencies (s) for the copolymers are shown in Table II.

The product yields for copolymers with a comparable composition decreased in the order BMA(MB-

R$_1$	R$_2$	R$_3$	Polymer
-CH$_3$	-H	-CH$_3$	**BMA(x)-MMA**
-CH$_3$	-H	-H	**BMA(x)-MA**
-CH$_3$	-CH$_3$	-CH$_3$	**MBMA(x)-MMA**
-CH$_3$	-CH$_3$	-H	**MBMA(x)-MA**
-CH$_3$	-CH$_3$	—	**MBMA(x)-St**[a]
-H	-H	-CH$_3$	**BA(x)-MMA**
-H	-H	-H	**BA(x)-MA**

[a] St, styrene.

Figure 6 Structures and abbreviations of benzyl ester copolymers.

MA)–MMA type > BMA(MBMA)–MA(St) type > BA–MMA type ≅ BA–MA type. The higher yields for BMA- and MBMA-containing copolymers reflect the reactivities of the monomer units (Table I). The slightly lower yields for MA or St copolymers compared with those for MMA copolymers resulted from the retarded formation of "out-of-cage" products **4–6**.[17] Since MA and St residues have a tertiary hydrogen in each unit, which would be readily abstracted by radicals to form tertiary alkyl radicals in the polymer chain, benzyl radicals formed by side-chain degradation would react rapidly with these hydrogens or polymer radicals before escaping from the "polymer domain":

(4)
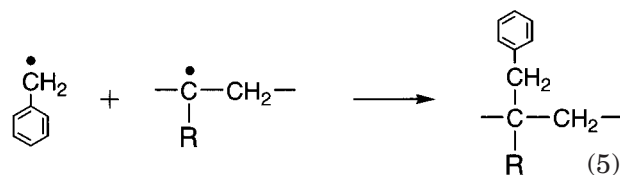
The above result also indicates that products **2** and **3** are formed exclusively in the "domain."

The yields for BMA- and MBMA-containing copolymers increased with increasing the BMA or MBMA content (x), due mainly to the increased yields of products **4–6**.[17] This means that the benzyl radicals formed in benzyl-rich copolymers escape easily from the "domain." It is reasonable to consider that, in copolymers with low x, the benzyl radicals formed are surrounded by a number of MMA or MA residues in the polymer chain and thus liable to react with these comonomers or themselves.

As expected, the efficiencies of main-chain scission for methacrylate copolymers were much larger than were those for acrylate (or St) copolymers (Table II). It has been recognized that methacrylate polymers undergo side-chain scission [path (i) in Fig. 5] and the subsequent β-scission [path (ii)] to produce tertiary radicals in the midchain and at the chain ends, respectively, which are more stable than are secondary radi-

(5)

Table II Product Yields and Main-chain Scission Efficiencies for Photolysis of Copolymers in CH$_2$Cl$_2$

Copolymer	Total Yield[a] 2–6	s[b]
BMA(10)–MMA	8	36
BMA(25)–MMA	14	20
PBMA	16	10
MBMA(12)–MMA	8	25
MBMA(27)–MMA	15	20
PMBMA	18	13
BA(12)–MMA	3	13
BMA(8)–MA	5	2
MBMA(11)–MA	6	1
MBMA(42)–MA	10	5
BA(8)–MA	3	1
PBA	4	0.7
MBMA(10)–St	6	0

[benzyl] = $2 \times 10^{-3} M$; $\lambda_{ex} > 250$ nm; irradiation time, 1 h.
[a] Total yield of products **2–6** in percent.
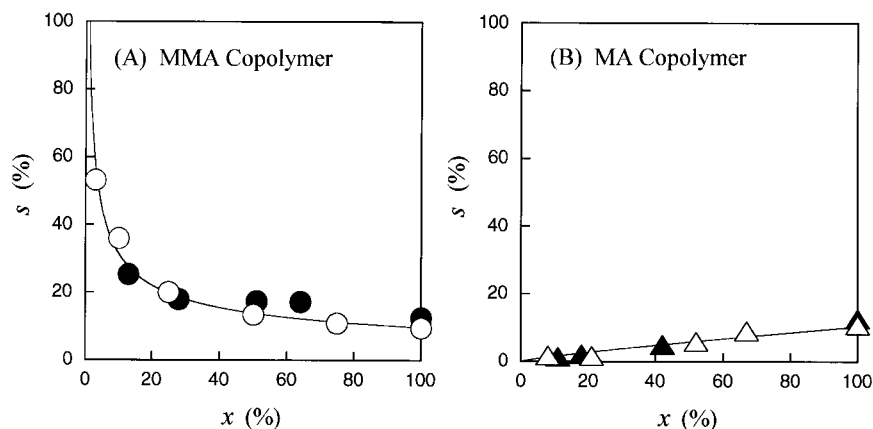[b] Main-chain scission efficiency in percent [see eq. (1)]; irradiation time, 5 min.

Figure 7 Main-chain scission efficiencies (s) for (A) MMA and (B) MA copolymers irradiated in CH_2Cl_2 under argon as a function of x in the copolymer: (○) BMA(x)–MMA; (●) MBMA(x)–MMA; (△) BMA(x)–MA; (▲) MBMA(x)–MA.

cals formed in acrylate polymers.[8,11] Thus, the former polymers should be more susceptible to main-chain scission.

The s values of BMA(MBMA)–MMA and BMA(MBMA)–MA copolymers are plotted as a function of x in Figure 7(A,B), respectively. The data for BMA and MBMA copolymers were found to lie on a single line, indicating no difference in the degradation between these polymers as in the case of homopolymers. With increasing x, the efficiencies of MMA copolymers decreased, whereas those of MA copolymers slightly increased. The latter is obviously due to the increase of the more reactive methacrylate sequences. As for the former copolymers, taking into account that MMA is smaller and more mobile than is BMA or MBMA, β-scission is likely to occur more easily in the MMA-rich sequences than in the successive BMA(MBMA) sequences. In addition, in benzyl-rich copolymers, neighboring unreacted and re-

acted benzyl groups might affect the degradation processes.

Irradiation of Homopolymer Films Under Nitrogen Atmosphere

Table III shows the results of the photolyses of homopolymer films. Toluene or ethylbenzene was identified as a single low molecular weight product in these films. For all films, irradiation caused both main-chain scission and crosslinking (i.e., insolubilization), although the latter was dominant. The broadened GPC charts of the THF-soluble portions of the films reflected these competitions (Fig. 2). In contrast, a PMMA film containing 20 wt % of BP was little changed under the same condition, despite a considerable conversion of BP. This confirms the importance of chemical bonding of degradative groups to the polymer chain. The product yield and main-chain scission

Table III   Product Yields (%) for Photolysis of Homopolymer Films

Polymer	Conversion[a]	Coupling **1**	Alkyl **2**	s[b]	Insoluble[c]
PBMA	—	—	5.7	2.3	67
PMBMA	—	—	2.9	[d]	[d]
PBA	—	—	1.0	0.2	91
BP–PMMA[e]	45	12.2	2.8	−0	0

[ester] = 1×10^{-4} mol; $\lambda_{ex} > 250$ nm; irradiation time, 1 h.
[a] Yield for ester conversion in percent.
[b] Main-chain scission efficiency in percent for THF-soluble portions of polymers.
[c] Weight fraction of THF-insoluble polymers in percent.
[d] Not determined.
[e] BP-containing PMMA film; [BP] = 1×10^{-4} mol; [PMMA] = 9×10^{-4} mol.

Table IV   Effect of Oxygen on Photolysis of Homopolymers in CH_2Cl_2 and Cast Films

| Polymer | Condition | Argon or Nitrogen/Oxygen (%) | | | |
		Products **2–6**	Alcohol **7**	s	Insoluble
PBMA	CH_2Cl_2	16/4.2	trace/1.4	9.6/5.0	0/0
	Film	5.7/[a]	trace/[a]	2.3/4.6	67/45
PBA	CH_2Cl_2	3.6/0.5	trace/0.9	0.7/1.5	0/0
	Film	1.0/[a]	trace/[a]	0.2/1.5	91/81

See footnotes to Tables II and III.
[a] Not determined.

efficiency were higher for PBMA than for PBA, which was attributable to the higher stability of the tertiary radicals formed in PBMA, as described above. On the other hand, the formation of secondary radicals in PBA would lead to the predominant crosslinking. Similar phenomena were also observed for copolymer films.[17] Therefore, the degradabilities of the polymer films parallel those of the polymer solutions. We also found that increasing the irradiation temperature (up to 100°C) facilitated the main-chain scission and retarded the crosslinking,[17] which may be due to the increased chain mobility.[15]

Effect of Oxygen on Polymer Degradation

Table IV shows the effect of oxygen on the photolyses of PBMA and PBA. When irradiated in oxygen-saturated CH_2Cl_2, the yields of radical products **2–6** remarkably decreased and the oxidized product **7** appeared. It should be noted here that the photolysis of BP under an oxygen atmosphere was not inhibited, but, if anything, slightly facilitated: The ester conversions were 60% under argon and 67% under oxygen, respectively. We previously suggested the presence of an oxygen-assisted photolysis pathway for benzyl esters.[19] It is thus likely that the side-chain ester bonds in polymers are cleaved under oxygen as efficiently as under argon and thus that the resulting benzyl and main-chain radicals react with oxygen to form benzyl alcohol **7** and other unidentified products. In fact, the ^{1}H- and ^{13}C-NMR spectra of PBMA irradiated under oxygen (M_n = 2100) showed that most of the "new structures" formed under argon disappeared [Figs. 3(c) and 4(c)].

Interestingly, the main-chain scission of PBMA was decreased in the oxygen-saturated solution, while that of PBA was facilitated. The oxidation

of tertiary alkyl radicals in the main chain would hinder the β-scission predominantly occurring in PBMA. The alkyl radicals formed in PBA, through side-chain degradation and hydrogen abstraction or other processes, would react with oxygen to produce hydroperoxide and finally carbonyl groups, which could initiate the photooxidative scission of the main chain.[8,10,12,15] It is noteworthy that oxygen facilitates the main-chain scission of the PBMA film as well as the PBA one and diminishes their crosslinking.

CONCLUSIONS

The present study elucidated the degradation mechanism of (meth)acrylate polymers containing benzyl groups based on the analyses, although not quantitative, of both low molecular weight and polymeric products. The photodegradation of PBMA was found to proceed mainly by the ester bond cleavage in the side chain followed by main-chain scission. The higher degradabilities of PBMA and the methacrylate copolymers are due to the efficient side-chain degradation and the higher stability of the main-chain alkyl radicals formed. Most of these results are qualitatively consistent with the photolyses of poly(alkyl methacrylate)s and poly(alkyl acrylate)s. However it can be said that reactive benzyl radicals play an important role in any degradation process in the present polymers.

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