

Effects of Various Ester Groups in γ -Radiation Degradation of Syndiotactic Poly(methacrylate)s

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SYNOPSIS

The γ irradiation of poly(methacrylate)s with various ester groups at room temperature was investigated by gel permeation chromatography and NMR techniques. The G values for scission and crosslinking for each of the polymers were estimated from the changes in the molecular weights and molecular weight distributions. The new structures formed during γ irradiation were examined by ¹H-NMR spectroscopy. All of the investigated poly(alkane methacrylate)s were found to produce the alkane formates during γ irradiation, and for poly(2-methyl heptyl methacrylate) $G(S)$ was less than $4G(X)$, indicating gel formation in this polymer. In the investigation of poly(benzyl methacrylate), no formate ester was found, but some small molecule compounds formed from the benzyl radical were detected. The benzyl group was also found to stabilize the polymer against radiation damage. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(methacrylate)s (PMMA)s degrade with a relatively large G value to form low molecular weight compounds (or the monomers) on irradiation.¹ Therefore, these polymers are typical positive-resist materials in deep UV, electron beam, and X-ray lithography. Many studies have been carried out to clarify the mechanism of radiation-induced degradation of PMMA.²⁻⁵ It is well known that the irradiation of PMMA at room temperature results in formation of main-chain scission-type radicals that might initiate depolymerization at temperatures above the ceiling temperature.⁶ However, little attention has been given to the comparison of the degradation properties of PMMA with various ester groups. The decomposition or stability of methacrylate polymers is related to their structure, such as the type of ester group and the tacticity. In this work, the radiation degradation behaviors for syndiotactic PMMA with various ester groups were studied. Gel permeation chromatography (GPC) and NMR

spectroscopy were used to measure the changes in the molecular weights and molecular structures after γ irradiation of the PMMA. The functions of the ester groups in the γ irradiation of PMMA will be discussed.

EXPERIMENTAL

Materials

The syndiotactic PMMA with various ester groups were supplied by Professor K. Hatada of the Department of Chemistry at Osaka University. The polymers were characterized for molecular weight and tacticity by Professor Hatada and the results are summarized in Table I.

γ Irradiation

The finely powdered PMMA with various ester groups were packed into the glass tubes and evacuated (~ 1 mPa) for at least 24 h prior to being sealed. The samples were γ irradiated at room temperature to a dose of 1600 kGy for NMR measurements and 113 kGy for GPC measurements in a ⁶⁰Co AECL Gammacell 220 radiation unit. The radiation

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Table I Properties of Syndiotactic Poly(methacrylate)s

Ester Group	Sample No.	M_n	M_w/M_n	Tacticity (%)		
				mm	mr	rr
Methyl	DPI-1	22,700	1.26	3	8	89
Ethyl	NF666-ET	29,400	1.11	0	11	89
Isopropyl	NF684-IP	30,500	1.15	0	9	91
Isobutyl	NF666-IB	28,700	1.11	1	7	92
<i>n</i> -Butyl	NF700-NB	32,400	1.13	1	9	91
2-Methyl heptyl	NF684-OCT	32,300	1.10	1	9	91
Benzyl	NF666-BZ	26,800	1.14	2	16	82

dose rates were determined by Frick dosimetry,⁷ and the values obtained were approximately 2 kGy/h.

GPC Measurement

The changes of molecular weights and molecular weight distributions for the polymers after γ irradiation were estimated by GPC in tetrahydrofuran solvent using polystyrene standards at 25°C.

NMR Measurement

The NMR spectra for all the γ -irradiated polymers except poly(*n*-butyl methacrylate) were recorded on a Bruker AMX-500 spectrometer using 7% (w/v) solution in CDCl₃ at 303 K. The NMR spectrum for the γ -irradiated poly(*n*-butyl methacrylate) was recorded on a Bruker AC-200 spectrometer using 7% (w/v) solution in CDCl₃ at room temperature.

RESULTS AND DISCUSSION

Changes of Molecular Weights and Molecular Weight Distributions after γ Irradiation

γ Irradiation of the syndiotactic PMMAs at room temperature resulted in changes in the molecular weights and molecular weight distributions, which depend on the behavior of the various ester groups. Figure 1 shows the shifts in the GPC chromatograms for syndiotactic PMMAs γ irradiated at room temperature to a dose of 113 kGy.

From the data in Figure 1, the propensities for scission and crosslinking can be compared for γ irradiation of the PMMAs with various ester groups. When the PMMAs have a short side chain, such as those with methyl, ethyl, or isopropyl groups, the polymers primarily undergo main-chain scission reactions during γ irradiation that result in a shift of the GPC chromatogram to larger elution volumes

(lower molecular weights). For poly(isobutyl methacrylate) and poly(*n*-butyl methacrylate), the changes in the average molecular weight during γ irradiation are small by comparison with those for PMMAs with a shorter side chain, such as methyl, ethyl, or isopropyl groups. In addition, there is some evidence that polymers with butyl ester groups may undergo both scission and crosslinking [see Fig. 1 (D, E)]. The GPC chromatograms in the figures suggest that crosslinking may be greater for the poly(*n*-butyl methacrylate) than for the poly(isobutyl methacrylate). Further increasing the side-chain length, for example for poly(2-methyl heptyl methacrylate), causes an obvious increase in the average molecular weight after γ irradiation. These observations are consistent with the previous report by Graham⁸ that significant yields of concurrent crosslinking and scission occur when the alkyl group in the ester of the PMMA is long. In Figure 1 (G), the molecular weight distribution for syndiotactic poly(benzyl methacrylate) is demonstrated to not change significantly during γ irradiation at room temperature. Thus it may be concluded that the benzyl group displays a significant protective effect during γ irradiation of syndiotactic poly(benzyl methacrylate) at room temperature, stabilizing the polymer against radiation damage.

The data for the change in the average molecular weights (M_n and M_w) for a single dose, which were obtained from GPC experiments, may be used to estimate the values of $G(S)$ (scission) and $G(X)$ (crosslinking) according to the method described by Dole.⁹ Table II shows the molecular weights, molecular weight distributions, and the estimated $G(S)$ and $G(X)$ values for γ -irradiated PMMAs with various ester groups.

$G(S)$ was found to be significantly greater than $4G(X)$ for all the polymers except poly(*n*-butyl methacrylate) and poly(2-methyl heptyl methacrylate), so these polymers undergo net scission.¹⁰

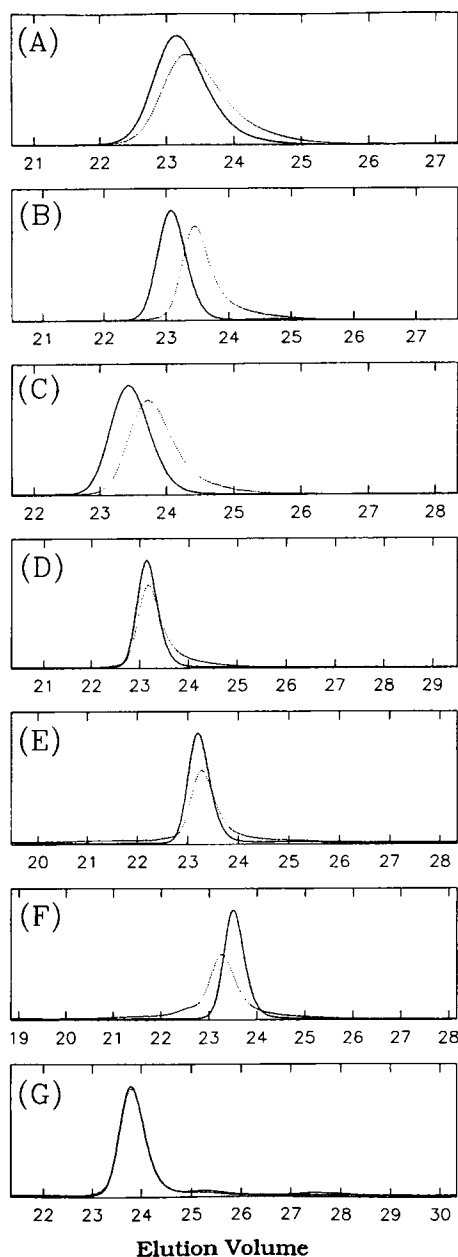


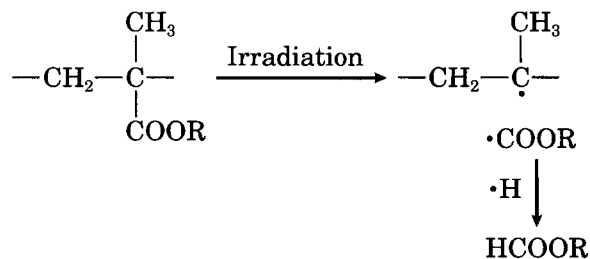
Figure 1 The GPC results for syndiotactic poly(methacrylate)s with the ester groups of (A) methyl, (B) ethyl, (C) isopropyl, (D) isobutyl, (E) *n*-butyl, (F) 2-methyl heptyl, and (G) benzyl. (—) Before γ irradiation and (· · ·) after γ irradiation at room temperature at 113 kGy.

For poly(*n*-butyl methacrylate) $G(S)$ was approximately equal to $4G(X)$ within experimental error. Poly(2-methyl heptyl methacrylate) was soluble following irradiation to a dose of 113 kGy, which indicates that the dose at the gel point is greater than this value.

New Structures Formed During γ Irradiation

The $^1\text{H-NMR}$ spectra were measured for the syndiotactic PMMAs after γ irradiation at room temperature with a dose of 1600 kGy. All of these polymers were soluble following irradiation. In this work, the focus was to compare the formation of new structures during γ irradiation for the PMMAs.

There are new peaks in the region between 7.6 and 8.4 ppm for syndiotactic poly(alkane methacrylate)s [except for poly(benzyl methacrylate)] that were γ irradiated at room temperature at 1600 kGy. Figure 2 shows the $^1\text{H-NMR}$ spectra in the region between 7.6 and 8.4 ppm for the γ -irradiated poly(alkane methacrylate)s. Previous studies of γ -irradiated PMMA and poly(2-methyl heptyl methacrylate) indicated that the protons associated with the formate groups of methyl formate or 2-methyl heptyl formate have $^1\text{H-NMR}$ resonances in this region.^{11,12} Thus, the new peaks in this region for γ -irradiated poly(alkane methacrylate)s may be attributed to the protons associated with the formate groups of alkane formate compounds formed during γ irradiation. A reaction mechanism for the formation of the alkane formates on γ irradiation is shown below.



where R is a alkane group.

The new $^1\text{H-NMR}$ peaks observed in the region between 4.3 and 5.3 ppm for PMMA, poly(ethyl methacrylate), poly(isobutyl methacrylate), and poly(2-methyl heptyl methacrylate) that were γ irradiated at room temperature at 1600 kGy are shown in Figure 3. [The new signals in this region that were formed during γ irradiation are masked by the original polymer signals for poly(isopropyl methacrylate) and poly(benzyl methacrylate) systems. The resolution of the $^1\text{H-NMR}$ spectrum in this region for γ -irradiated poly(*n*-butyl methacrylate), which was obtained using a Bruker 200-AC spectrometer, was too poor to analyze.] A sharp peak in the PMMA spectrum at 4.49 ppm was assigned to the protons associated with the structure $-\text{O}-\text{CH}_2-\text{O}-$ of dimethoxymethane, which is formed during γ irradiation.¹¹ Therefore, it may be suggested that the sharp peak

Table II Molecular Weights, Molecular Weight Distributions, and Estimated *G* Values of Scission and Crosslinking for Poly(methacrylates) after γ Irradiation

Ester Group	Molecular Weight				<i>G</i> Value		
	Before Irradiation		After Irradiation		Estimated ^a		Lit. <i>G</i> (S) ¹⁴
	<i>M_n</i>	<i>M_w/M_n</i>	<i>M_n</i>	<i>M_w/M_n</i>	<i>G</i> (S)	<i>G</i> (X)	
Methyl	24,600	1.23	18,600	1.34	1.1	0 ^b	1.3
Ethyl	35,900	1.05	19,900	1.20	1.7	0 ^b	
Isopropyl	27,400	1.10	16,800	1.25	1.8	0 ^b	
Isobutyl	41,700	1.05	31,100	1.24	0.8	0.1	0.38
<i>n</i> -Butyl	38,800	1.06	27,500	1.68	1.3	0.4	1.28
2-Methyl heptyl	40,300	1.06	43,100	1.66	0.3	0.5	
Benzyl	21,500	1.26	22,500	1.22	0 ^b	0 ^b	0.29

^a Using Dole's⁹ method with error range of ± 0.2 .

^b The calculated values are zero within experimental error.

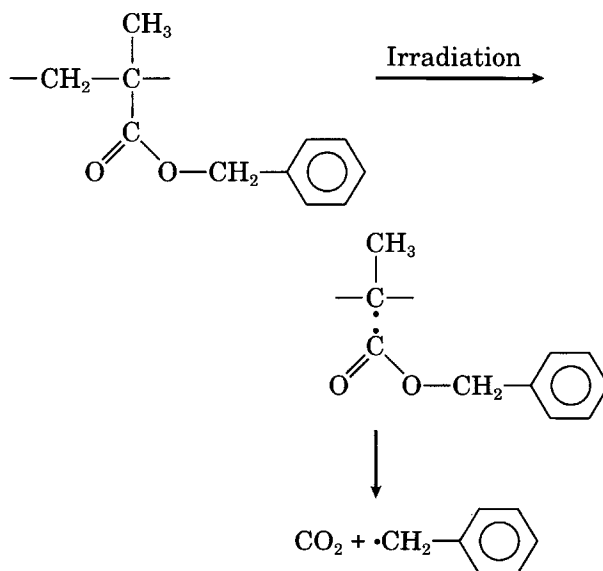
at 4.64 ppm for γ -irradiated poly(isobutyl methacrylate) is also associated with the protons with an analogous structure.

In the previous studies,^{10,13} the four relatively broad peaks at 4.53 and 4.75 ppm and 4.68 and 4.92 ppm were assigned to the protons associated with the unsaturated chain ends and with the unsaturation group within the chain, respectively. The two peaks at 4.57 and 4.78 ppm for γ -irradiated poly(2-methyl heptyl methacrylate) were assigned by 2-D NMR techniques to the protons in the unsaturated chain end in which the two protons are connected to the same carbon atom.¹² In Figure 3, the shapes and positions for the ¹H resonance peaks for γ -irradiated poly(ethyl methacrylate) and poly(isobutyl methacrylate) are similar to those for γ -irradiated PMMA. Thus, the same assignments as those for γ -irradiated PMMA may be applied to the protons in unsaturated chain ends and unsaturated groups within the chain for γ -irradiated poly(ethyl methacrylate) and poly(isobutyl methacrylate).

The radiation chemistry of poly(benzyl methacrylate) is particularly interesting. The GPC results indicated that the benzyl group displays a significant protective effect during γ irradiation of syndiotactic poly(benzyl methacrylate) at room temperature. Figure 4 shows the ¹H-NMR spectrum for the γ -irradiated poly(benzyl methacrylate), together with the spectrum of this polymer without irradiation.

There is no new peak observed in the region of 7.6–8.4 ppm, indicating that benzyl formate was not formed during γ irradiation under the prevailing experimental conditions. One explanation for this is that, due to the stability in the benzyl radical

$\cdot\text{CH}_2\text{C}_6\text{H}_5$, radiolysis would lead to decomposition of the carbonyl group of the radical $\cdot\text{COO}-\text{CH}_2\text{C}_6\text{H}_5$ formed following scission of the ester side chain. No proton resonance was found indicating the presence of a carboxylic acid group, $-\text{COOH}$, which should appear in the region of the spectrum at 9–10 ppm. Therefore, the following radiation mechanism is proposed:



Some new peaks appear in the spectrum in the region of 2.0–4.7 ppm following γ irradiation [see Fig. 4(B)]. The expansion of the ¹H-NMR spectrum in this region is shown in Figure 5.

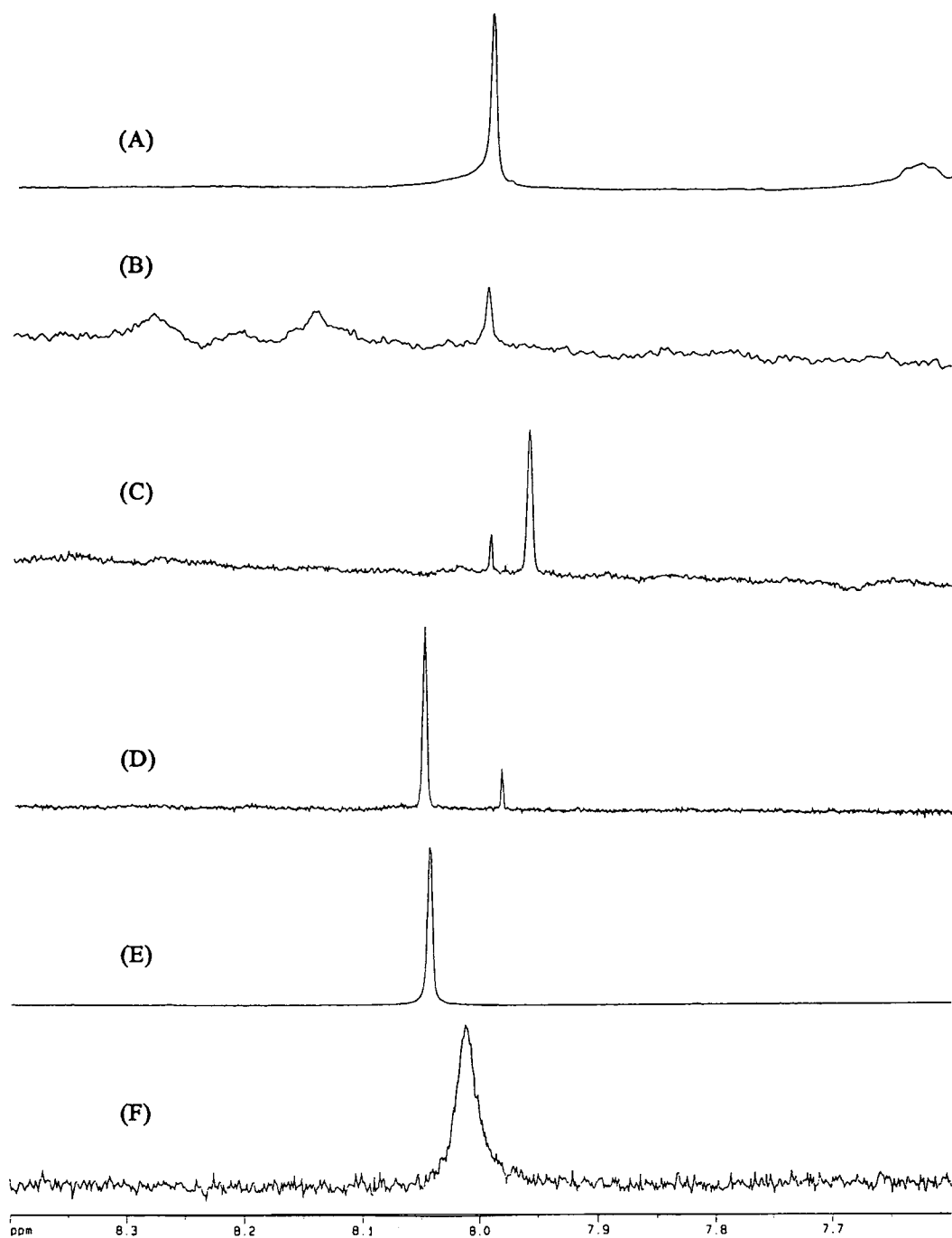


Figure 2 The ^1H -NMR spectra in the region of 7.6–8.4 ppm for the γ -irradiated poly(alkane methacrylate)s. (A) Poly(methyl methacrylate); (B) poly(ethyl methacrylate); (C) poly(isopropyl methacrylate); (D) poly(isobutyl methacrylate); (E) poly(2-methyl heptyl methacrylate); and (F) poly(*n*-butyl methacrylate). The spectrum of poly(*n*-butyl methacrylate) was recorded on a Bruker AC-200 spectrometer.

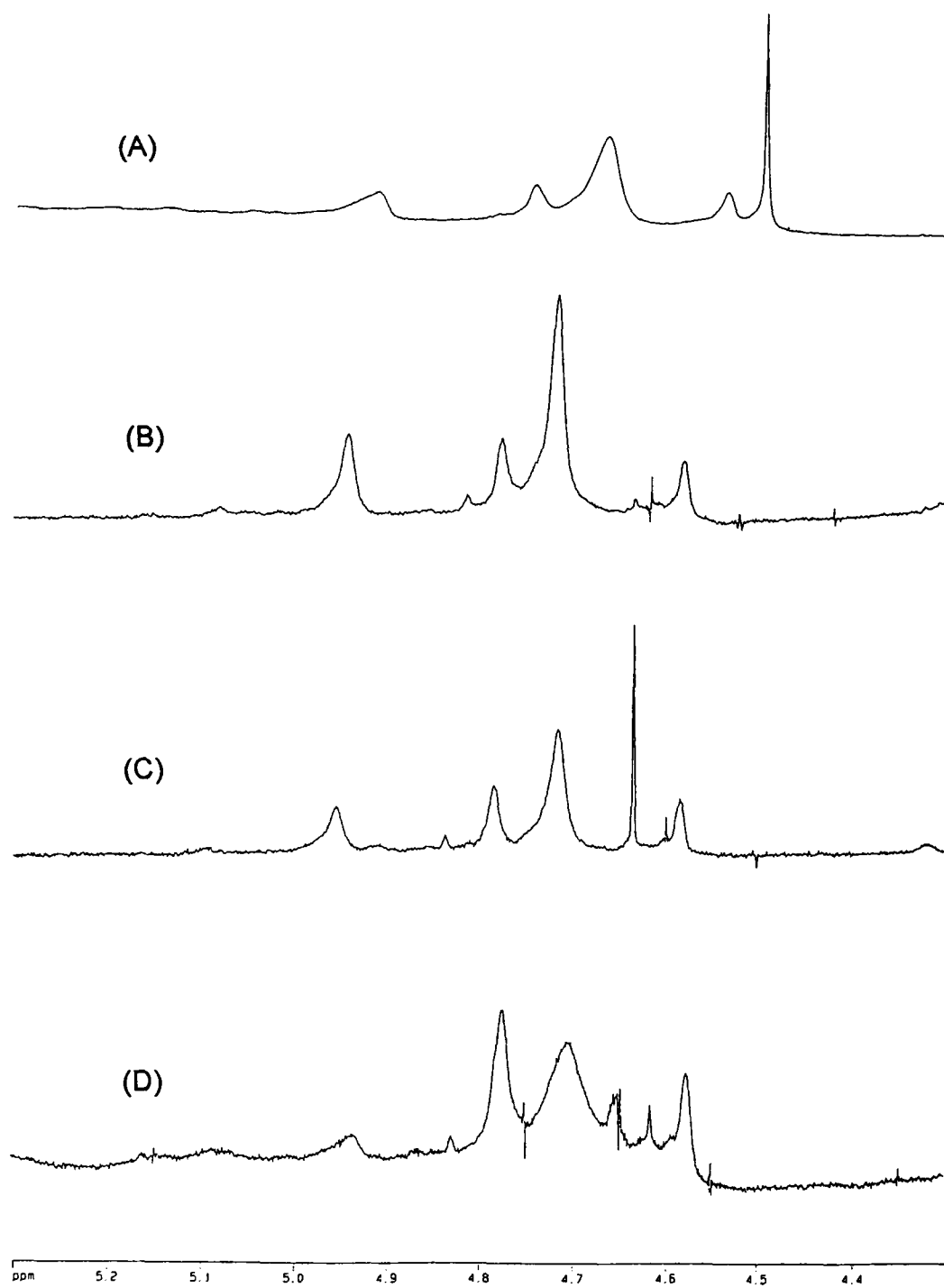


Figure 3 The $^1\text{H-NMR}$ spectra in the region of 4.3–5.3 ppm for the γ -irradiated poly(alkane methacrylate)s. (A) Poly(methyl methacrylate); (B) poly(ethyl methacrylate); (C) poly(isobutyl methacrylate); and (D) poly(2-methyl heptyl methacrylate).

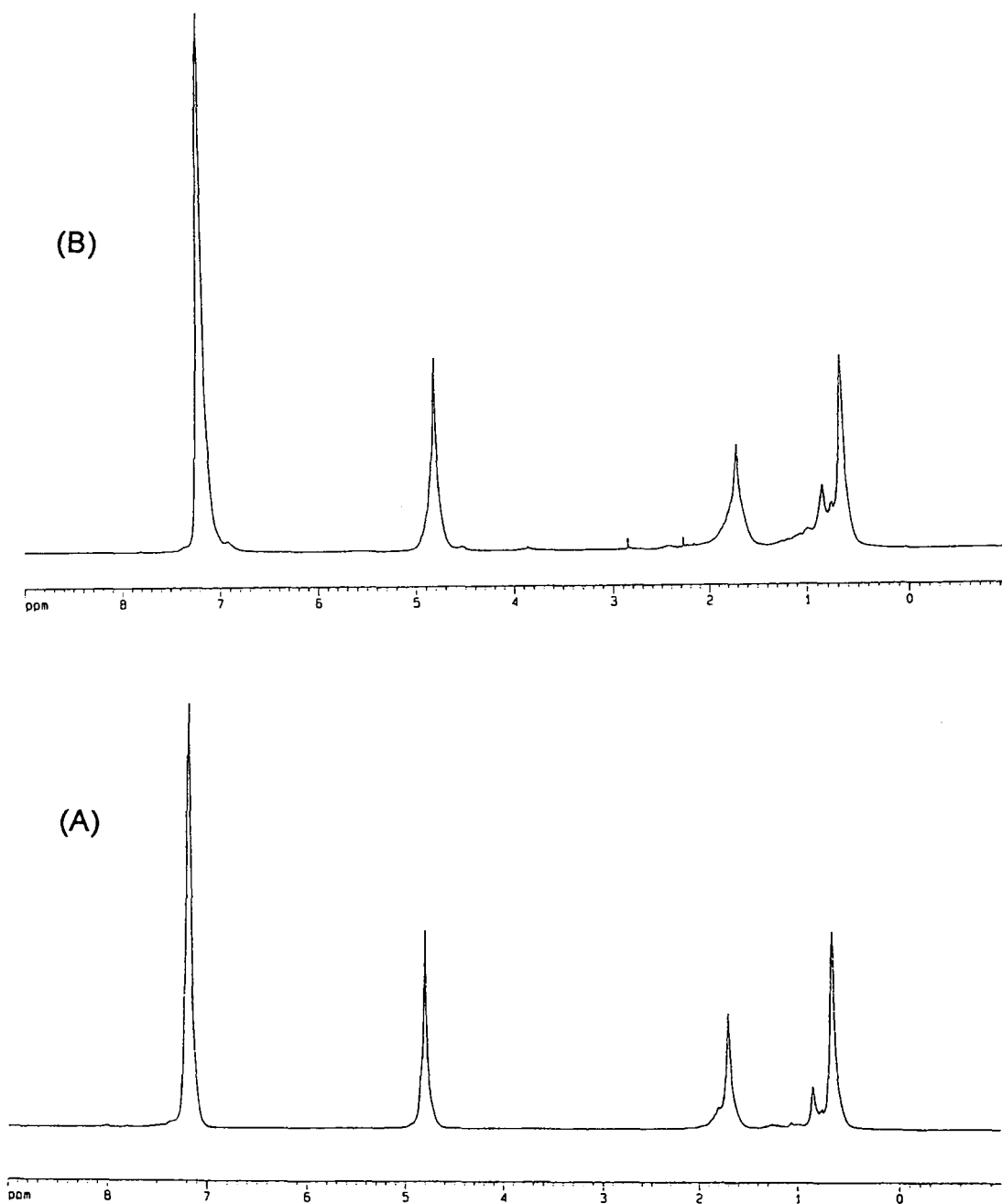
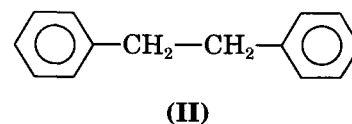
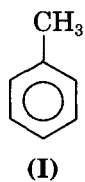


Figure 4 The ^1H -NMR spectra of poly(benzyl methacrylate): (A) no irradiation and (B) 1600 kGy γ irradiation at room temperature.

Two sharp peaks at 2.38 and 2.85 ppm may be attributed to the small molecule compounds (I) and (II), respectively, that may be formed during γ irradiation from the benzyl radical, as a result of addition or abstraction of a hydrogen atom (I) or the combination of two benzyl radicals (II).



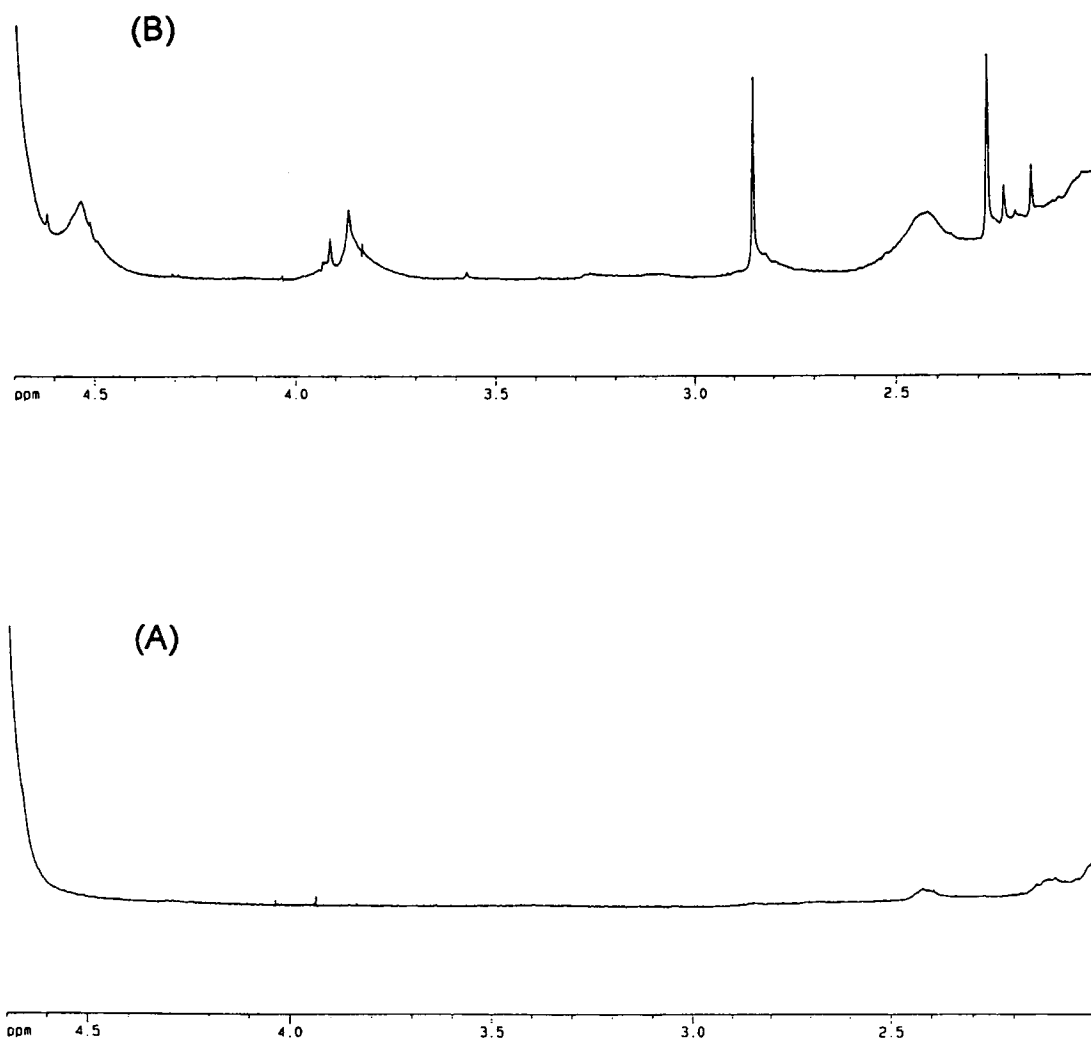


Figure 5 The expansion of the $^1\text{H-NMR}$ spectra in the region of 2.0–4.7 ppm for poly(benzyl methacrylate): (A) no irradiation and (B) 1600 kGy γ irradiation at room temperature.

CONCLUSIONS

The molecular weight changes and small molecule products formed during the γ radiolysis of a series of syndiotactic PMMAs are consistent with scission of the side-chain ester groups and β scission of the main chain on radiolysis. Formate esters were observed among the small molecule products from an analysis of the NMR spectra of the polymers with aliphatic ester side chains, but toluene and 1,2-diphenyl ethane were observed as the major products of side-chain scission in poly(benzyl methacrylate). The PMMAs with long alkyl side chains were found to undergo both scission and crosslinking, the latter through the alkyl side chain. The aromatic group in benzyl methacrylate was found to provide a stabilizing effect toward radiation damage.

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