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Radiolysis of Resist Polymers. 1. Poly(methyl α-haloacrylates) and Copolymers with Methyl Methacrylate

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ABSTRACT: Methyl α-chloroacrylate (MCA) and methyl α-bromoacrylate (MBA) were copolymerized with methyl methacrylate (MMA) over a broad range of composition. The reactivity ratios for MMA and MCA are 0.36 and 0.26, respectively; they are 0.19 and 0.16 for MMA and MBA copolymerization. The tendency toward alternation of comonomer of methyl α-haloacrylates with MMA decreases in the order Br > Cl > F. The relative reactivities of these monomers toward the MMA radical also decrease in this order. The values of G_s (number of scissions per 100 eV of energy absorbed) for poly(MCA) and poly(MBA) are larger than for PMMA; values of G_r (number of radicals per 100 eV of energy absorbed) are in the range 7–9. All copolymers of MCA have nonzero G_x values (number of cross-links per 100 eV of energy absorbed), but they are soluble in common solvents after γ-radiolysis. Copolymers of MBA and MMA with >7% of the former are insolubilized due to extensive cross-linking by γ-radiolysis. ESR spectra of γ-irradiated homo- and copolymers of MCA and MBA were attributed to $-CH_2\dot{C}(COOMe)CH_2-$, $\cdot C(COOMe)ClCH_2-$, and $\cdot C(COOMe)BrCH_2-$ radicals. GC–MS analysis of the radiolysis products of the MCA homo- and copolymers, together with ESR and radiolysis yields, suggested probable mechanisms for the radiation chemistry. The high radiation sensitivity is attributable to the dissociative electron capture processes. The tendency of the MBA polymers toward cross-linking was postulated to be due to the ease of elimination of HBr giving intermediates for the formation of cross-links and CH_3Br elimination leading to cross-linking directly. The typical PMMA radical was observed for γ-irradiated poly(MMA-*co*-MCA) only when MCA content was ≤20%; it was not detected for γ-irradiated poly(MMA-*co*-MBA) even when MBA was present at 3%. The radiolysis of copolymers of MMA with MCA and MBA is dominated by the α-halogenated monomers.

Introduction

Polymers exhibiting high chain scission susceptibilities to radiation have been investigated as candidates for positive electron-beam (E beam) resists. However, as cross-linking also occurs sometimes, especially at high radiation dose, polymers which undergo scission only in the exclusion of cross-linking are required for resist applications. The relative tendency of the two reaction pathways is usually measured by one of two methods. The first is the determination of scission (cross-linking) yield per 100 eV absorbed, which is G_s (G_x). The second method is the measurement of sensitivity S_s (S_x) of the scission (cross-linking) reactions in C cm^{-2} for a given energy of electron.

Poly(methyl methacrylate) (PMMA) has been demonstrated to be a practical E-beam positive resist by the electronics industry; it is generally regarded as the reference polymer in this application. However, PMMA has only moderate sensitivity to radiation: $G_s = 1.4$, $G_x = 0$, and $S_s \simeq 5 \times 10^{-5}$ C cm^{-2} at 15 keV.[2] Hence, there have been intensive efforts to find polymers and copolymers of greater radiation sensitivity. Several general approaches have emerged.

The first is to take advantage of certain efficient radiolysis processes. An example is the dissociative electron capture. For instance, poly(methyl α-chloroacrylate) (PMCA) has a very high chain scission susceptibility ($G_s = 6.0$)[3]. Other halogen-containing polymers may also exhibit this characteristic. Elements of high atomic numbers are expected to interact with low-energy electrons efficiently. Thus, the incorporation of a few percent of alkali metal in poly(methyl methacrylate-*co*-metal methacrylate)[4] seems to increase G_s values. Polymers which upon radiolysis yield stable products appear to be good candidates for E-beam application. The likely examples are poly(butylene 1-sulfone)[5], poly(methyl isopropenyl ketone)[6], and polyaldehydes.[7,8]

Often times polymers with enhanced G_s also have increased G_x. Thus PMCA tends to cross-link ($G_x = 0.8$)[9] when the electron dose exceeds 6×10^{-4} C cm^{-2}. Copolymerization of such monomers with a non-cross-linking monomer can sometimes alleviate the cross-linking reactions. However, the G_s and G_x values of copolymers are usually not monotonic functions of comonomer composition. For instance, it was found that copolymers of MCA with MMA[10] and MCA with methacrylonitrile[11] and terpolymers of MCA with MMA and hexyl methacrylate[9] of certain compositions have greater G_s values than PMMA and without discernible cross-linking.

Though some of the current researches give results that are quite interesting, they do not contribute toward the understanding of the mechanisms of the chemical processes involved. For instance, if one evaluates a polymer as an E-beam or X-ray resist by the determination of sensitivity and contrast of the material to the radiation of particular energy, the effects of film thickness and surface regularity, of the method of developing, and of back-scattering can influence the overall performance. In the case of comparative study of a family of homopolymers and copolymers, a common developer is needed. The radiolysis products cannot be easily trapped and analyzed and the electron spin resonance (ESR) of the radicals cannot be

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Table I
Copolymerization of MMA and Methyl γ-Haloacrylates

	comonomer mole fraction		% conversion	reactivity ratios	
	in feed	in copolymer		r_1 (MMA)	r_2
MCA	0.074	0.16	8.2	0.36	0.26
	0.12	0.19	6.8		
	0.28	0.38	9.4		
	0.50	0.43	6.4		
	0.84	0.72	5.7		
MBA	0.33	0.44	6.4	0.19	0.16
	0.33	0.43	8.6		
	0.43	0.47	3.8		
	0.43	0.46	5.4		
	0.63	0.51	9.3		

obtained under controlled conditions.

The emphasis of our work is to elucidate the relationships between the chemical structure of polymer and its radiation sensitivity through the analysis of the volatile radiolysis products by gas chromatography–mass spectroscopy (GC–MS), the identification of the radical intermediates and their yields, G_r, by electron spin resonance (ESR), as well as the usual determination of G_s and G_x. γ-Radiation is used because of its penetrating power, which enables uniform irradiation of polymer sample contained in sealed ampules suited for ESR measurements and subsequent GC–MS analysis. One drawback is that the energies of the γ-rays and its secondary electrons are very high; atomic number effect is much smaller than for electron and X-ray irradiation.

In this first paper of the series we report the radiolysis results of PMCA, poly(methyl α-bromoacrylate) (PMBA), and their copolymers with methyl methacrylate (MMA), which showed that the radiolysis of the copolymers is determined by the halogenated comonomer and that the chloro and bromo derivatives differ markedly in their radiation chemistries.

Experimental Section

Materials. MMA (Aldrich) was distilled at reduced pressure prior to use. MCA was prepared by dehydrochlorination of 1,2-dichloropropionate[12] in 68% yield. Methyl α-bromoacrylate (MBA) was synthesized by a similar method. AIBN from Aldrich was recrystallized from methanol and stock solutions were made with chloroform.

Homo- and Copolymerizations. Monomer or comonomers were mixed with AIBN without solvent and freed of air by several freeze–evacuation–thaw cycles. Polymerizations were carried out at 60 ± 0.1 °C to less than 10% conversion. The product was precipitated with methanol, washed, and dried at 40 °C in vacuo to constant weight. The copolymer compositions were determined from elemental analysis. Molecular weights were obtained with a Waters Associates 201 chromatograph equipped with five μ-Styragel columns, using THF as the solvent and the universal calibration method. T_g was determined with a Perkin-Elmer differential scanning calorimeter (DSC) at a scanning rate of 20 °C min^{-1}.

γ-Radiolysis. Samples in Pyrex ampules were evacuated to less than 10^{-5} torr for 20 h and sealed. A ^{137}Cs γ-ray source was used to irradiate the polymer at ambient temperature. The dose rates varied from 0.07 to 0.03 Mrd h^{-1}, as determined by ferrous sulfate dosimetry, depending upon the total dose desired. The changes in $\bar{M}_w$ and $\bar{M}_n$ after radiolysis were determined by GPC as above.

ESR. A Varian E-9 X-band instrument was used to record the ESR spectra. The radical yield, G_r, was obtained by the double integration of the ESR signal with a Nicolet microcomputer in comparison with a standard solution of 2,2,6,6-tetramethylpiperidinoxyl.

GC–MS. The volatile products of radiolysis were analyzed by connecting the sample ampule to the inlet of a Hewlett-Packard 5840A GC coupled to a Hewlett-Packard 5985A MS. The eluted substances from the GC were identified by the MS.

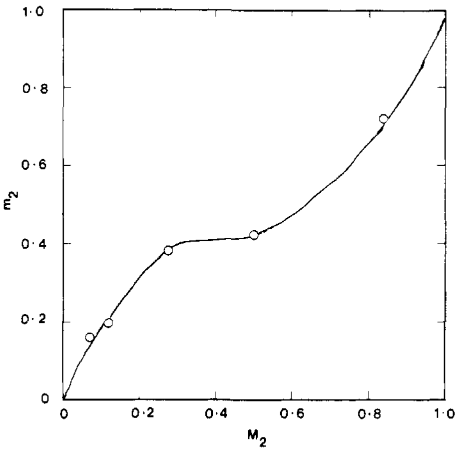


Figure 1. Plot of mole fraction of MCA (m_2) in copolymer vs. mole fraction (M_2) in feed: (○) experimental values; (—) curve calculated from copolymer equation.

Table II
Molecular Weights of Poly(MMA-*co*-methyl α-haloacrylates)

comonomer	m_2, %	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
MCA	16	2.8	3.5	1.2
	19	2.5	4.0	1.6
	38	2.1	3.4	1.6
	72	1.5	2.5	1.7
MBA	3	0.96	2.5	2.6
	5	0.40	0.91	2.2

Results and Discussion

Reactivity Ratios. The results of copolymerization of MMA (M_1) and methyl α-haloacrylate (M_2) are summarized in Table I. The reactivity ratios were calculated from the copolymer composition data with the method of Yezrielev et al.[13] based on the differential form of the copolymerization equation. This analysis was shown[14,15] to give more accurate reactivity ratios than other methods and has the advantage of being symmetrical in form. Figure 1 is a plot of the mole fraction of MCA (m_2) in the copolymer vs. the mole fraction of MCA (M_2) in the feed and the curve calculated from the copolymer equation. A similar plot was obtained for MBA. Both show good agreement between experimental results and values based on reactivity ratios.

Pittman et al.[16] have copolymerized methyl α-fluoroacrylate (MFA) with MMA and found $r_1 = 1.17$ and $r_2 = 0.36$. The products of reactivity ratios, r_1r_2, are 0.42, 0.094, and 0.03 for MFA, MCA, and MBA, respectively. Therefore, the tendency for alternation of comonomers decreases in the order of Br > Cl > F. The relative reactivity of the methyl α-haloacrylates toward an MMA radical is given by r_2^{-1}, which is 2.78, 3.85, and 6.25 for the fluoro, chloro, and bromo derivatives, respectively. The reactivities of the corresponding methyl α-haloacrylic radicals toward MMA monomer are in the opposite order. This behavior suggests that the mesomeric effect of the halogen atom in stabilizing the radical is Br > Cl > F.

The glass transition temperatures of random copolymers should lie between the T_g's of the homopolymers. This was found to be true. For instance, the values of T_g for poly(MMA-*co*-MCA) having 16, 19, 39, and 41 mol % MCA are 125, 126, 129, and 132 °C, respectively. PMCA has a T_g of 142 °C.

The molecular weights of the copolymers used for radiolysis study are summarized in Table II. In the case

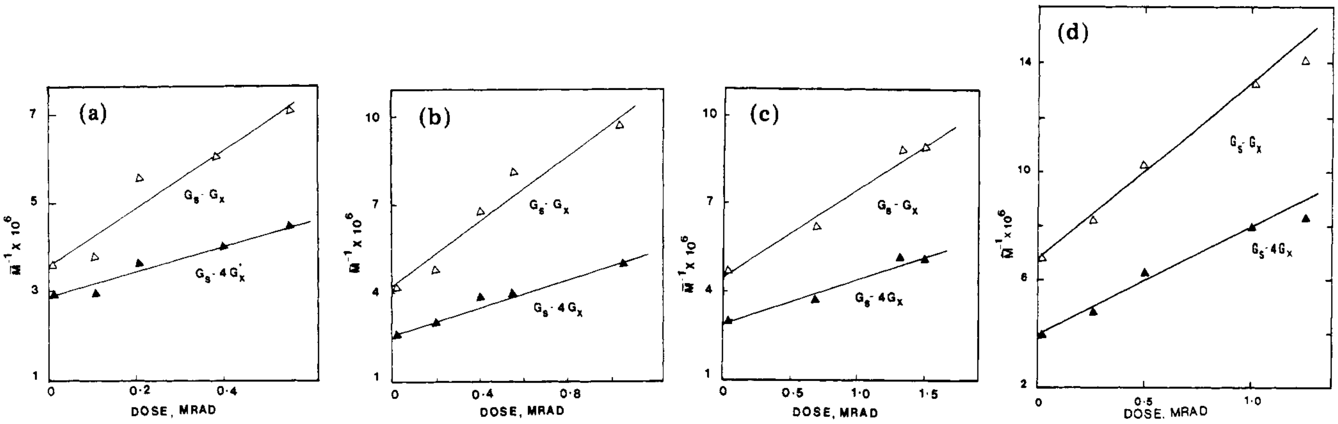


Figure 2. Variation of $\bar{M}_n$ (△) and $\bar{M}_w$ (▲) with γ dose; solid lines are least-squares fit of experimental data: (a) poly(84% MMA-*co*-16% MCA); (b) poly(81% MMA-*co*-19% MCA); (c) poly(62% MMA-*co*-38% MCA); (d) poly(57% MMA-*co*-43% MCA).

Table III
Radiolysis Yields

comonomer	M_2, %	$G_s - G_x$	G_s	G_x	G_r
none	0	1.4	1.4	0	1.4
MCA	16	4.7	5.2	0.5	4.4
	19	4.4	4.8	0.4	3.3
	38	5.4 (3.5)[a]	5.6	0.2 (0.2)[a]	
	72	6.5	6.7	0.2	9.1
	100	6.5 (5.3)[a]	7.4	0.9 (0.6)[a]	
MBA	3	5.8	5.3	0.46	2.0
	5	4.4	5.0	0.65	2.3
	7				2.3
	100				7.0

[a] From ref 3.

of MBA, only copolymers containing 5% or less of this monomer were prepared because higher contents of MBA cross-link readily upon radiolysis. The copolymers of MCA have polydispersity index less than 2. This is because we purify the polymers by repeated dissolution and precipitation (usually four or five times). Fractionation is known to occur during these processes.

γ-Radiolysis. A. Yields. The values of G_s and G_x were obtained from the values of $\bar{M}_n$ and $\bar{M}_w$ of irradiated polymers using the equations of Charlesby[17] and Kilb.[18]

$$\bar{M}_n^{-1} = \bar{M}_{n,0}^{-1} + [(G_s - G_x)D]/100N \qquad (1)$$

$$\bar{M}_w^{-1} = \bar{M}_{w,0}^{-1} + [(G_s - 4G_x)D]/200N \qquad (2)$$

where $\bar{M}_{n,0}$ and $\bar{M}_{w,0}$ are the average molecular weights of the unirradiated polymer, $\bar{M}_n$ and $\bar{M}_w$ are the values for the polymer after it has absorbed a γ-ray dose (D), and N is Avogadro's number. From the slope of the plots of $\bar{M}^{-1}$ vs. D, shown in Figure 2 for polymers of MCA, G_s and G_x values are calculated. Similar results were obtained for polymers of MBA. Table III summarizes the G_s and G_x values for both halogenated polymers. The relative determination of radiolysis yields is valid even when the GPC calibration is not accurately known.

The MMA–MCA system had been previously investigated by Helbert et al.;[3] their results are included in Table III for comparison. These authors studied the radiation degradation of PMCA and a 41% MMA–59% MCA copolymer. Emulsion polymerization was used. Consequently, the molecular weights of their polymers were generally higher (by about a factor of 10) than ours, and the molecular weight distribution was broader (also up to a factor of 10) and probably contains significant composition drifts as usually is the case with emulsion polymerizations. Helbert et al. irradiated the polymer to much higher doses than we did and noted changes in slopes of $\bar{M}_w^{-1}$ and $\bar{M}_n^{-1}$ vs. dose plots. Our dose lies in the region of their low-dose experiments. They fractionated the polymers and obtained radiolysis results generally within the experimental variabilities of unfractionated polymers; their values of G_s and G_x are somewhat smaller than ours (Table III).

On the basis of a single copolymer of 59 mol % MMA giving $G_s - G_x = 2.5$–3.0, Pittman and co-workers noted that it is exactly as expected from the average of $G_s - G_x = 5.3$ and 1.4, respectively, for PMCA and PMMA, i.e., $0.41 \times (5.3 + 1.4) = 2.7$, thus implying that $G_s - G_x$ is linear with the copolymer composition. Our data on four copolymers showed this to be untrue; all the copolymers have G_s values much closer to that of PMCA than PMMA. Even a copolymer with 16 mol % MCA has a $G_s - G_x$ value of 4.7.

PMCA and all MCA–MMA copolymers have nonzero yields for G_x. One might expect that for a monomer which tends to cross-link by radiolysis, the G_x value of copolymers with another non-cross-linking comonomer may be a monotonic function of the copolymer composition. In other words, G_x for poly(MMA-*co*-MCA) should decrease monotonically with the decrease of MCA monomer in the copolymer. This is because with the decrease of mole fraction of MCA, the probability of having two MCA monomers next to one another on adjacent chains is decreased. This expectation was not realized. The results in Table III show G_x to be 0.6–0.9 for PMCA and 0.2–0.5 for various copolymers of MCA. The G_s and G_x results indicate that the MCA monomer controls the radiolysis efficiency and chemistry of its copolymer with MMA.

The radiolysis results of MMA–MBA copolymers are quite remarkable though they are limited to very low contents of MBA. Even at 3% MBA, the G_x value is about 0.5. This implies either that the MBA units in such copolymers are situated close to each other as in the homopolymer or that its radiolysis induces cross-linking of MMA. In any case, the radiation chemistry of these copolymers is also controlled by the MBA monomer.

Both methyl α-haloacrylates are extremely sensitive to radiolysis. In the case of bromo monomer, G_r is up to 7, though G_s of PMBA itself cannot be determined due to gelation upon radiolysis. Copolymers containing a few mole percent of MBA have G_s values near 6. The G_s and G_r values for homo- and copolymers of MCA are much greater than those for PMMA. The main difference between the MCA and MBA copolymers is that the former remains soluble after irradiation through $G_x > 0$, indicative of radical coupling leading to chain extension, whereas the radical reactions of MBA copolymers containing more than 5 mol % of this monomer resulted in cross-linked net-

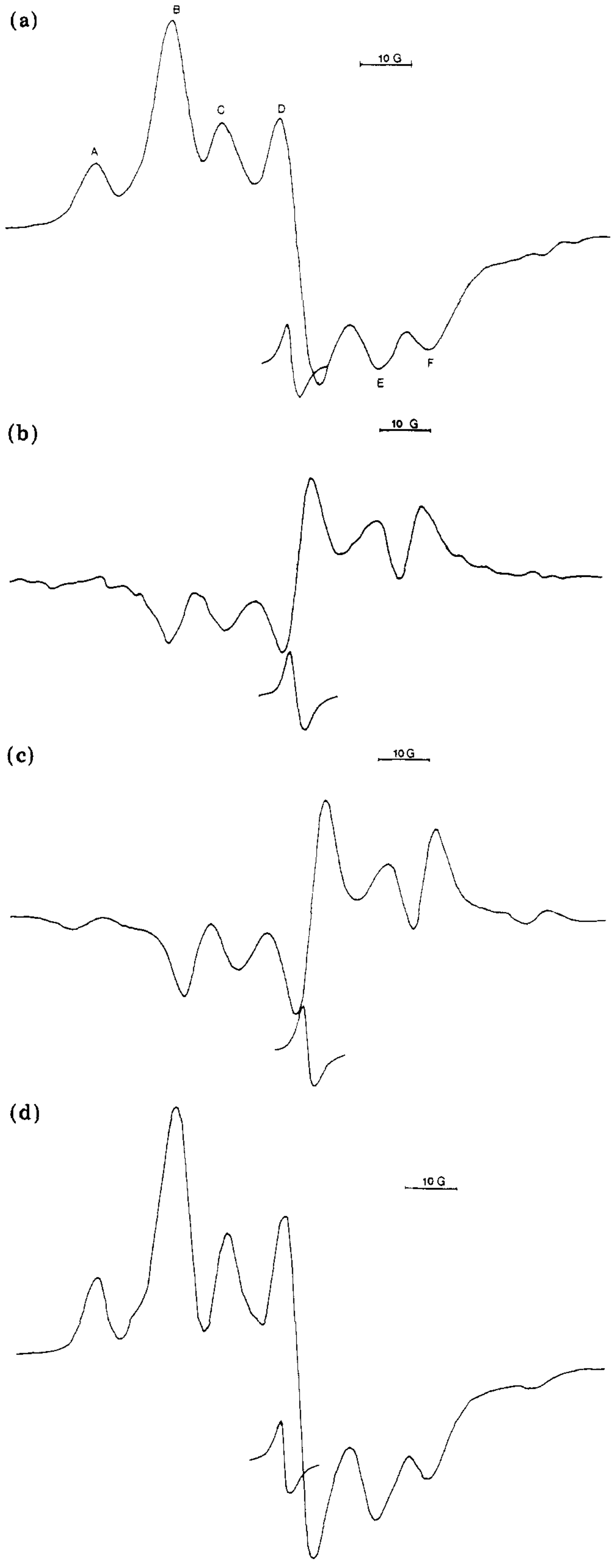


Figure 3. ESR of polymers irradiated at ambient temperature: (a) PMCA; (b) poly(57% MMA-*co*-43% MCA); (c) poly(81% MMA-*co*-19% MCA); (d) poly(84% MMA-*co*-16% MCA). Marker is DPPH.

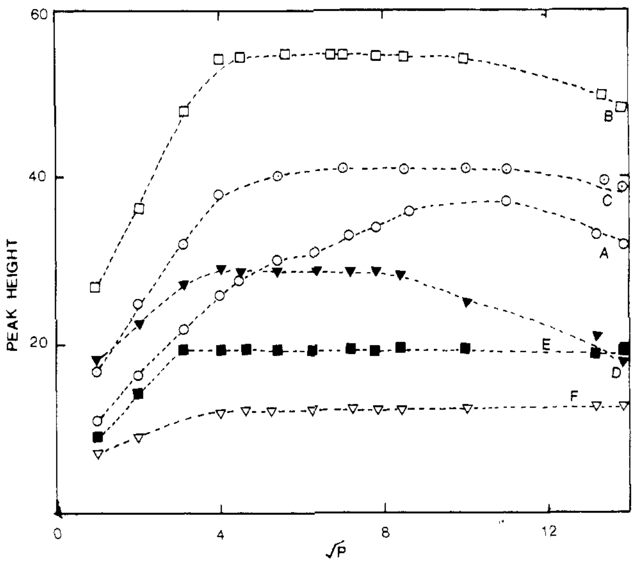
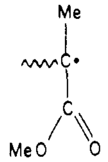


Figure 4. Effect of microwave power on the ESR spectra of γ-irradiated PMCA. The peaks correspond to those indicated in Figure 3a.

works.

B. ESR. γ-Irradiation of homopolymer of MCA at ambient temperature produced a very intense ESR spectrum as shown in Figure 3. The radicals have considerable stability as evidenced by the fact that the ESR signal did not completely disappear until the polymer was heated above 150 °C, which is 5 °C above the T_g of the polymer. The ESR spectrum essentially consists of seven hyperfine lines with spacings of about 13 G. However, there is something unusual about this spectrum. It is certainly unsymmetrical; the two outer low-field lines (indicated by A and B in Figure 3a) are much more intense than the corresponding lines at high field. This suggests the presence of more than one radical; other possible explanations such as *g* or hyperfine anisotropy are unlikely. For nearly equal molar copolymer the EPR spectrum is nearly the same as that of PMCA (Figure 3b). As the MMA content increases, the spectrum begins to contain that of the well-known PMMA radical (Figure 3c). For poly(88% MMA-*co*-12% MCA), Figture 3d showed only the nine-line ESR spectrum of the PMMA radical



(3)

To gain more insight into the ESR spectrum of irradiated PMCA, we followed the change of the peak heights with the klystron power and with temperature. If there is only one radical present than all the signals should saturate simultaneously and disappear together as radicals recombine at elevated temperatures. Figure 4 plots the intensity of the peaks as a function of microwave power. It shows that the two outer lines at the high field (E and F) are inhomogeneously broadened. On the other hand, the other lines show more homogeneous broadening, especially the two low-field lines A and B. Furthermore, the effect of heating on the ESR spectra, shown in Figure 5, is informative. The intensity of the two outer low-field lines (A and B) decreased markedly as the sample was heated to 50 °C but not the other resonance lines. Above 85 °C, A and B intensities decrease rapidly with the temperature whereas the intensities of other lines show more gradual decreases. These are incontrovertible evidences that a second radical is present which contributes to the ESR spectra in the low-field region.

We analyze the spectrum on the basis that it is composed of two species. The one at low field, designated as radical I, has $g = 2.0192$ and ${}^{H}A = 12$ G. The other radical II with $g = 2.0036$ is a triplet of triplets with two hyperfine

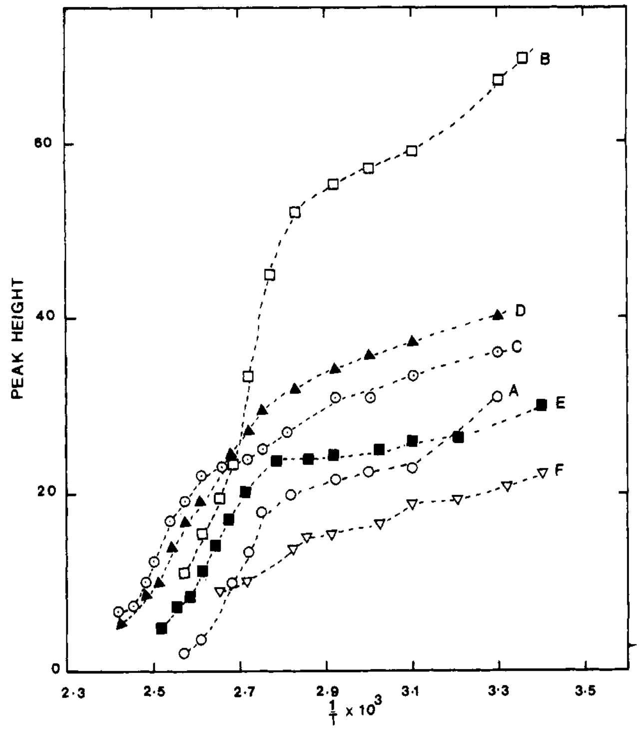
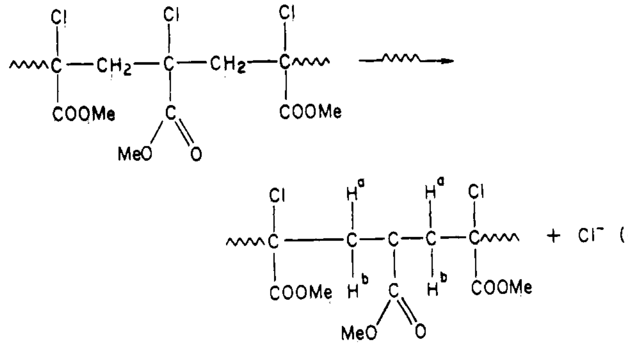


Figure 5. Effect of heating on the ESR spectra of γ-irradiated PMCA. The peaks correspond to those indicated in Figure 3a.

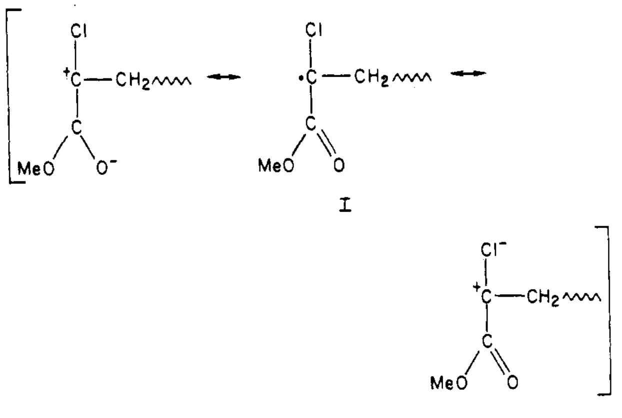
coupling constants of 24 and 12 G. Radical II is likely to be the radical produced by the dissociative electron capture:



(4)

II

This process has been proposed by Chen et al.[11] and has been suggested to be enhanced by the bond weakening along the backbone induced by the electron-withdrawing Cl atom in the quaternary carbon. The hyperfine interactions of the unpaired spin with H^a and H^b are dihedral angle dependent and have different coupling constants. Radical I is postulated to be the one formed by chain scission of radical II. It has a high *g* value because of the possible effect of spin–orbit coupling.



I

(5)

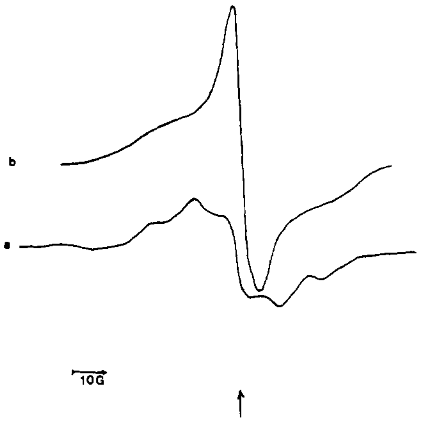
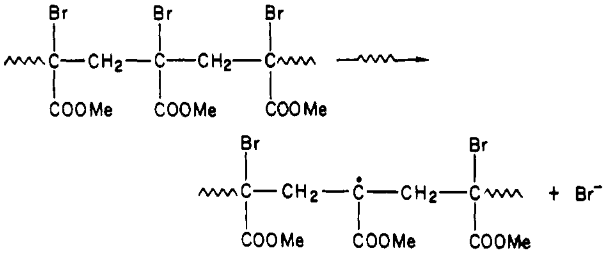


Figure 6. ESR spectrum of γ-irradiated (a) poly(97% MMA-*co*-38% MBA) (III) and (b) PMBA (IV).

Helbert et al.[3] irradiated PMCA at −195 °C and observed an ESR spectrum at that temperature which was different from the ones described above. They interpreted the spectrum as an anisotropic triplet. It is our opinion that the spectrum (Figure 4 of ref 3) contains at least seven lines. The signal was reported to disappear when the sample was warmed to room temperature.

γ-Irradiation of poly(MMA-*co*-MBA) produces a simple five-line spectrum for a single radical coupled to four equivalent protons with $^{H}A \simeq 12$ G (Figure 6a). The radical is most likely the one produced by dissociative electron capture.

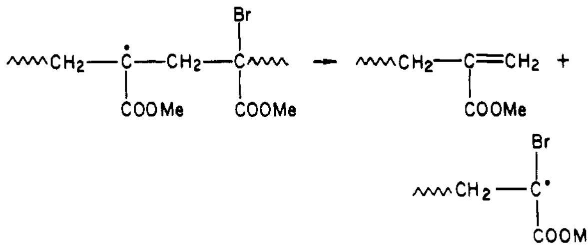


(6)

III

Radical III differs from radical II in that the methylene protons are equivalent in the former but they are non-equivalent in the latter. This may be due to the steric effects of the two neighboring C(Cl)COOMe groups in radical II and the Cl(Br)COOMe groups in radical III.

In the case of PMBA irradiated at ambient temperatures, the ESR spectrum is a simple three-line spectrum with $^{H}A \simeq 16$ G. A possible interpretation is that dissociative electron capture (eq 6) by the homopolymer is followed immediately by main-chain scission to give radical IV:



(7)

IV

One important observation is that the characteristic nine-line ESR spectrum of irradiated PMMA was not observed in the γ-irradiated poly(MMA-*co*-MBA) even when the MBA monomer was only present in 3 mol %.

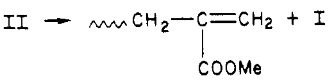
C. GC–MS. The volatile radiolysis products of MCA homo- and copolymers were analyzed by GC–MS. The

Table IV
Radiolysis Products Analyzed by GC-MS

polymer	ion mass	rel ion current	product
poly(MCA)	16	2.1	CH_4
	28	2.7	CO
	44	100	CO_2
	50	6.4	$CH_3{}^{35}Cl$
	52	1.9	$CH_3{}^{37}Cl$
poly(MMA-*co*-MCA)	16	2.1	CH_4
	28	2.7	CO
	36	2.1	$H^{35}Cl$
	38	1.1	$H^{37}Cl$
	44	100	CO_2
	50	6.4	$CH_3{}^{35}Cl$
	52	1.9	$CH_3{}^{37}Cl$
	60	4.0	HCOOMe
	69	1.8	$CH_2{=}C(Me)CO^+$

results are summarized in Table IV.

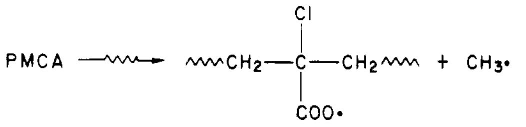
Mechanism. The radiolysis yields, ESR results, and GC–MS results for PMCA suggest the following mechanism for the γ-radiolysis of this polymer. One of the primary processes is the dissociative electron capture process (eq 1). Radical II can undergo scission to form radical I.



$$\mathrm{II} \longrightarrow \sim\!\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{COOMe}}}{\mathrm{C}}{=}\mathrm{CH_2} + \mathrm{I} \tag{8}$$

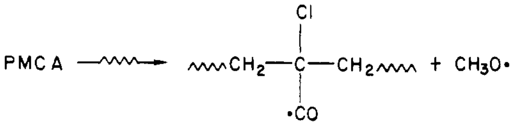
V

Other possible primary processes are



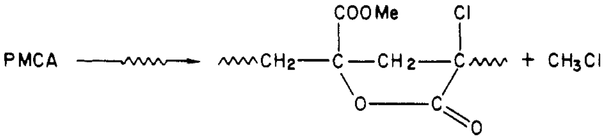
$$\mathrm{PMCA} \xrightarrow{\sim\sim} \sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{Cl}\\ |}}{\underset{\substack{|\\ \mathrm{COO\cdot}}}{\mathrm{C}}}-\mathrm{CH_2}\!\sim + \mathrm{CH_3\cdot} \tag{9}$$

VI



$$\mathrm{PMCA} \xrightarrow{\sim\sim} \sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{Cl}\\ |}}{\underset{\substack{|\\ \mathrm{\cdot CO}}}{\mathrm{C}}}-\mathrm{CH_2}\!\sim + \mathrm{CH_3O\cdot} \tag{10}$$

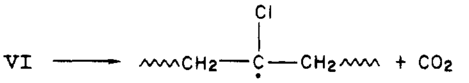
VII



$$\mathrm{PMCA} \xrightarrow{\sim\sim} \sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{COOMe}\\ |}}{\mathrm{C}}-\mathrm{CH_2}-\overset{\substack{\mathrm{Cl}\\ |}}{\mathrm{C}}\!\sim \text{ (ring: C–O–C(=O)–C) } + \mathrm{CH_3Cl} \tag{11}$$

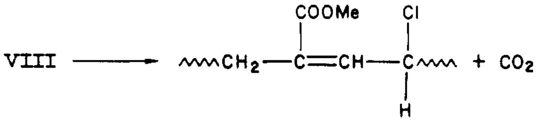
VIII

In addition to reaction 11, CH_3Cl can also be produced by the combination of $CH_3\cdot$ with $Cl\cdot$ or $CH_3\cdot$ abstraction of Cl from the polymer backbone. Methane is probably formed from methyl radicals by hydrogen abstraction. The $CH_3O\cdot$ radical was not detected as either CH_3OH or HCHO. It is possible that the GC column is not suited for their elution. Carbon dioxide is the major radiolysis product; it can be formed from VI or VIII:



$$\mathrm{VI} \longrightarrow \sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{Cl}\\ |}}{\underset{\bullet}{\mathrm{C}}}-\mathrm{CH_2}\!\sim + \mathrm{CO_2} \tag{12}$$

IX



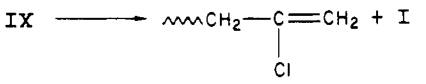
$$\mathrm{VIII} \longrightarrow \sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{COOMe}\\ |}}{\mathrm{C}}{=}\mathrm{CH}-\overset{\substack{\mathrm{Cl}\\ |}}{\underset{\substack{|\\ \mathrm{H}}}{\mathrm{C}}}\!\sim + \mathrm{CO_2} \tag{13}$$

X

The small quantity of CO can be produced from VII

$$\mathrm{VII} \longrightarrow \mathrm{IX} + \mathrm{CO} \tag{14}$$

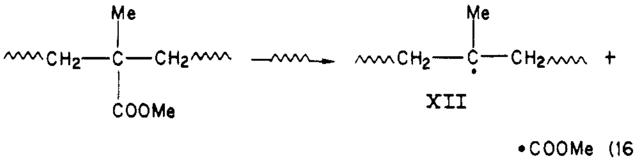
The G_s and G_x values were obtained from the $\bar{M}_n^{-1}$ and $\bar{M}_w$ vs. D plots, respectively. If the slope of the former plot S_n is equal to twice the slope of the latter plot S_w, then $G_x = 0$. However, if $S_n > 2S_w$, a nonzero value is obtained. For polymers with the most probable distribution, $S_n > 2S_w$ after radiolysis may be taken as positive evidence for cross-linking. Random scission should maintain this distribution. However, the MCA copolymers obtained at very low conversion and repeated dissolution and precipitation have $\bar{M}_w/\bar{M}_n < 2$ (Table II). Therefore, irradiation tends to increase polydispersity and $S_n > 2S_w$. The resulting nonzero G_x value probably should not be taken as evidence for cross-linking; the irradiated copolymers remain soluble. It is possible that chain scission, extension, and cross-linking all occur for PMCA. Cross-linking can occur with the reactions between two backbone radicals such as II, VI, VIII, and IX. Addition of these radicals to the double bond of X would also produce cross-links. Chain extensions can result from the combination of a backbone radical with a terminal radical I or the addition of both types of radicals to a terminal group of species V or XI, the latter being derived from radical IX



$$\mathrm{IX} \longrightarrow \sim\!\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{C}}{=}\mathrm{CH_2} + \mathrm{I} \tag{15}$$

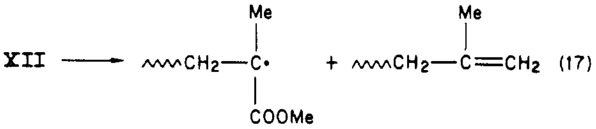
XI

The radiolysis of poly(MMA-*co*-MCA) differs from that of the MCA homopolymer in the production of HCl, HCOOMe, $CH_2{=}C(Me)CO^+$ in MS and the nine-line ESR spectra of the PMMA radical for $m_2 < 0.2$. The formation of HCl in the copolymer may be attributed to hydrogen abstraction by $Cl\cdot$ from the methylene group activated by the electron-donating methyl substituents. The methyl formate may be the result of radiolysis of the MMA units



$$\sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{Me}\\ |}}{\underset{\substack{|\\ \mathrm{COOMe}}}{\mathrm{C}}}-\mathrm{CH_2}\!\sim \xrightarrow{\sim\sim} \underset{\mathrm{XII}}{\sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{Me}\\ |}}{\underset{\bullet}{\mathrm{C}}}-\mathrm{CH_2}\!\sim} + \mathrm{\cdot COOMe} \tag{16}$$

followed by hydrogen abstraction The PMMA radical formation ensues:

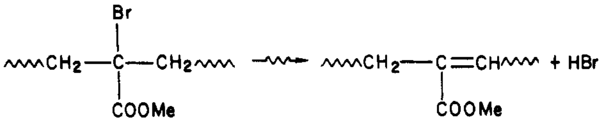


$$\mathrm{XII} \longrightarrow \sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{Me}\\ |}}{\underset{\substack{|\\ \mathrm{COOMe}}}{\mathrm{C}\cdot}} + \sim\!\mathrm{CH_2}-\overset{\substack{\mathrm{Me}\\ |}}{\mathrm{C}}{=}\mathrm{CH_2} \tag{17}$$

XIII

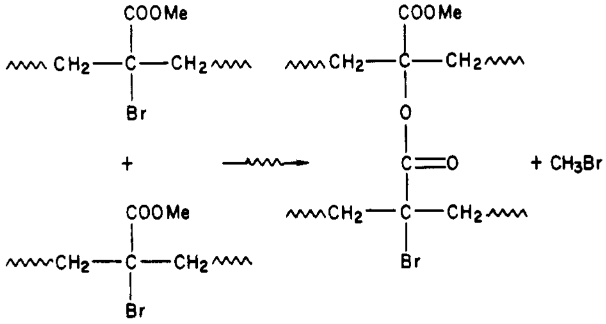
Helbert et al.[3] irradiated poly(MCA) and observed the ESR spectra at −195 °C. They propose the formation of $-(CH_2CCl(CO_2\dot{C}H_2))-$ and $\cdot CH_2CCl(COOMe)-$ radicals. The former calls for the abstraction of the least labile hydrogen in the polymer and the latter would require the intermediacy of a vinyl chloride species. Both these species do not follow naturally from the initial dissociative electron capture event. Perhaps at very low temperatures, the cage effect facilitates the formation and trapping of unstable radicals, which disappear upon warming to room temperature as observed by these workers. In contrast, the radicals produced at room-temperature irradiation led to more stable radicals. The radiation chemistry of bulk polymers can be very different at −195 °C and ambient temperature; the latter should be more relevant than the former in the context of application as resist materials.

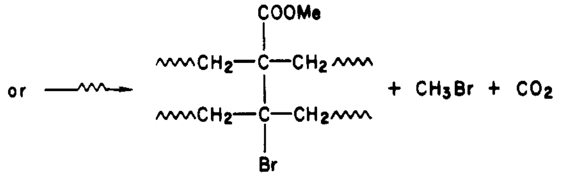
The radiolysis of homo- and copolymers of MBA led to extensive cross-linking even though the efficiency of radical formation is comparable to those of MCA. CH_3Br and HBr are the dominant products. The results may be rationalized by assuming that in addition to the analogous reactions described above for MCA polymers, there are strong tendencies for MBA polymers to undergo intramolecular elimination of HBr


(18)

XIV

and intermolecular elimination of CH_3Br


(19)


(20)

Reactions 19 and 20 rationalize why poly(MMA-*co*-MBA) containing only a few percent of the MBA monomer cross-link readily. These reactions can also be written in steps involving first the formation of Br atom which reacts near the site it is produced. In other words, the difference between PMCA and PMBA is that the Cl· diffuses away to react whereas Br· tends to react in the vicinity of where the radiolysis occurred to produce a pair of backbone radical which can combine to form cross-links. Addition of backbone radical to XIV can also produce cross-links. These processes apparently dominate over reactions involving MMA units so that radical XIII was not observed by ESR. The methyl α-haloacrylates are unsuited for resist application even though they have high scission yields. The tendency to cross-link was not eliminated completely by the introduction of a non-cross-linking MMA comonomer.

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