Radiation Degradation Study of Poly(methyl α-chloroacrylate) and the Methyl Methacrylate Copolymer

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ABSTRACT: High molecular weight samples of poly(methyl α-chloroacrylate) and poly(methyl α-chloroacrylate-*co*-methyl methacrylate) were prepared by emulsion polymerization techniques. These polymers were fractionated and exposed to varying doses of γ radiation from a ^{60}Co source. The $G_s - G_x$, G_s, and G_x values were determined from $\bar{M}_n^{-1}$ vs. dose and $\bar{M}_w^{-1}$ vs. dose plots. Analysis of the molecular weights was performed by membrane osmometry, light scattering, and gel permeation chromatography (GPC). The value of G_s for poly(methyl α-chloroacrylate) was found to be 6.0 ± 0.9 and $G_x = 0.7 \pm 0.2$ from a combination of light scattering and osmometry measurements. The corresponding values from GPC studies were 7.4 ± 0.9 and 0.9 ± 0.2, respectively. G_s and G_x were not dependent on molecular weight. The homopolymer undergoes ready scission which is complicated by concurrent cross-linking. The $G_s - G_x$ value for a copolymer with 41% methyl α-chloroacrylate was 2.8 ± 0.3 and this value was independent of molecular weight. Furthermore, this value is about 41% of the difference between that of the two homopolymers suggesting that $G_s - G_x$ may be linearly related to copolymer composition. The degradation mechanism is discussed in light of these data and ESR measurements.

As part of a study to determine the susceptibility of vinyl polymers to chain scission upon irradiation, we have examined a variety of structures including poly(α-substituted acrylates),[1] poly(α-hydroxyisobutyric acid),[2] poly(glycollic ester),[2] poly(methacrylonitrile),[3] poly(α-chloroacrylonitrile),[3] poly(methacrylic anhydride)[3], poly(acrylic anhydride),[3] and poly(dimethylitaconate). Preliminary studies pointed out that poly(methyl α-chloroacrylate), 1,

$$-(\mathrm{CH_2CCl(CO_2CH_3)})_n-$$

1

$$-(\mathrm{CH_2CCl(CO_2CH_3)})_n-(\mathrm{CH_2CCH_3(CO_2CH_2)})_m-$$

2

and its methyl methacrylate copolymer, **2**, undergo extensive degradation when subjected to ionizing radiation in vacuo.[1,4] Since poly(methyl α-chloroacrylate) is an acrylate which has a quaternary carbon (known to be important in promoting chain scission[2,5]), we have carried out a critical study of its decomposition upon irradiation. These studies supplement the recent reports of Lai[6] and our group[7] establishing poly(methyl α-chloroacrylate) and copolymers of methyl α-chloroacrylate and methyl methacrylate as sensitive positive electron beam resists.

Radiation degradation behavior is determined by a positive value for $G_s - G_x$ and a high value of G(rads). Here, G_s is the yield of scission events, G_x is the number of cross-linking events, and G(rads) is the number of scission radicals formed per 100 eV of absorbed dose. Since previous studies employed membrane osmometry and low-temperature ESR, only values of $G_s - G_x$ and G(rads) were obtained.[1,4] In fact, separate values of G_s and G_x are desirable.

In this paper, we report further studies of the degradation of **1** and **2**, based on membrane osmometry data augmented by viscosity, light-scattering, and gel permeation chromatography measurements. Determinations of the weight-averaged molecular weights permitted both G_s and G_x to be determined. The G values are then compared to G values reported for other α-chlorinated vinyl polymers and to poly(methyl methacrylate), PMMA. Polymers **1** and **2** are of further interest because they serve as model systems for applications where polymers are subjected to ionizing radiation during processing.[8]

It has been generally recognized that the sensitivity of a positive resist is a function of its molecular weight and molecular weight distribution. For example, Gipstein et al.[9] demonstrated that the sensitivity of PMMA increased as the dispersity ($\bar{M}_w/\bar{M}_n$) increased at constant $\bar{M}_n$. Unlike PMMA, narrow distributions appear to give higher sensitivities with poly(methyl α-chloroacrylate).[10]

However, sensitivity is not a fundamental polymer property since it depends on the nature of the solvent selected to define sensitivity. In contrast, G_s and G_x are fundamental properties.

The dependence of G_s and G_x on molecular weight distribution is not well studied. Usually, it is assumed these quantities are independent of molecular weight. At molecular weights in excess of 55×10^3, this is true for PMMA.[9] Since very few studies of this type have appeared, we have examined the G_s and G_x values of **1** at different molecular weights. In order to prepare high molecular weight samples of **1** and **2**, emulsion polymerization techniques were employed. This method achieves both high polymerization rates and molecular weights by lowering termination rates.[11,12] This permits the synthesis of poly(methyl α-chloroacrylates) with molecular weights in excess of those reported by Lai.[13]

Experimental Section

Materials. Methyl α-chloroacrylate was obtained from Monomer-Polymer Laboratories and vacuum distilled before use. Methyl methacrylate was obtained from Aldrich Chemical Co. (99%) and vacuum distilled before use. Sodium lauryl sulfate was used as received (Matheson Co.) as was potassium persulfate

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Table I
Molecular Weight and Viscosity Measurements for Poly(methyl α-chloroacrylate), 1

polymer (fraction)	light scattering $\bar{M}_w \times 10^{-6}$	MOSM[a] $\bar{M}_n \times 10^{-5}$	GPC $\bar{M}_w \times 10^{-6}$	GPC $\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	$[\eta]_{CHCl_3}{}^{30°}$, dL/g
1 (unfractionated)	9.9	9.4	*b*	*b*	11	4.0
1 (a)	7.8	13.3	*b*	*b*	5.9	6.4
1 (b)	2.4	10.2	*b*	*b*	2.4	3.2
1 (c)	1.8	6.0	1.6	6.2	2.6[c]	2.7
1 (d)	0.34	1.2	0.27	1.2	2.3[c]	0.65

[a] MOSM stands for membrane osmometry. [b] The molecular weights were beyond the reliable resolution range of the GPC columns. No reliable calibration was available beyond $\bar{M}_w > 3 \times 10^6$. [c] $\bar{M}_w$(GPC)/$\bar{M}_n$(GPC).

(J. T. Baker Chemical Co.). All water used in emulsion polymerizations was distilled and boiled for 10 min and purged with nitrogen on cooling to ambient temperature. All other solvents were purified by distillation.

Poly(methyl α-chloroacrylate). An aqueous stock solution was prepared by dissolving potassium persulfate (0.05 g, 0.18 mmol) and sodium lauryl sulfate (0.4 g, 1.3 mmol) into distilled water (100 g). The aqueous solution was charged into a flask (250 mL) followed by the addition of methyl α-chloroacrylate (50 g, 0.417 mol). The flask, fitted with a condenser, was heated in a constant temperature bath (oil) at 50 °C for 14 h with rapid stirring. A steady nitrogen purge was employed throughout the reaction. The resulting latex was cooled and poured into rapidly stirring methanol (500 mL). The coagulated polymer (50 g, 100% yield) was filtered and dried in vacuo at 40 °C overnight. The polymer was purified by dissolving 25-g portions into acetonitrile (2500 mL). These 1% solutions were filtered through Whatman qualitative grade filter paper. The filtrate was concentrated by rotary evaporation to a viscous fluid. The fluid was added very slowly to a large excess of rapidly stirred methanol. The resulting poly(methyl α-chloroacrylate) was dried under vacuum and stored in the dark and cold.

Fractionation of Poly(methyl α-chloroacrylate). A 4% poly(methyl α-chloroacrylate) solution was prepared at room temperature by dissolving the polymer (25 g) in acetonitrile (625 mL). Next, methanol (nonsolvent) was added to the solution dropwise with stirring. The addition was continued, intermittently, until permanent cloudiness resulted. The polymer solvent/nonsolvent mixture was then heated until it turned clear. Then it was slowly cooled back to room temperature and was allowed to stand overnight. Two phases were then clearly observed. The upper layer was removed for further fractionation. The bottom layer was a semifluid. It was directly coagulated by precipitation into methanol. The upper layer was then treated by the same procedure several times to generate fractions.

Copolymer of Methyl α-Chloroacrylate and Methyl Methacrylate. A procedure similar to that used to make the homopolymer was employed. The initiator–emulsifier stock solution (100 g) was mixed with premixed methyl α-chloroacrylate (23 g, 192 mmol) and methyl methacrylate (23 g, 230 mmol). The emulsion was heated at 50 °C for 18 h with rapid stirring. The resulting latex was coagulated, the copolymer isolated, and purification effected in the same manner described above for the homopolymer. The polymer yield was 97%. The mole ratio of methyl α-chloroacrylate to methyl methacrylate, based on elemental analysis, was 41/59.

Polymer Irradiation. Polymer samples were sealed into 5-mm o.d. Pyrex tubes at pressures of 10^{-4} torr. Irradiations were carried out at 25 °C using a ^{60}Co source at dose rates ranging from 0.01 to 0.8 Mrad h^{-1} as described previously.[1-4]

Analytical Methods. Intrinsic viscosity measurements employed a standard Cannon-Ubbelohde dilution viscometer (25-mL capacity) in a 30 ± 0.03 °C constant temperature external water bath. Chloroform was employed as the solvent. Solutions were filtered before measurement.

Number-averaged molecular weights, $\bar{M}_n$, were determined using Hewlett-Packard Model 502 and Wescan Model 230 osmometers operating at 25 and 28 °C, respectively. Membrane osmometry solutions were prepared using acetonitrile solutions of homopolymer 1 and THF for copolymer 2. All THF solution measurements were carried out with the HP-502 unit. All solutions were filtered (coarse) before measurement.

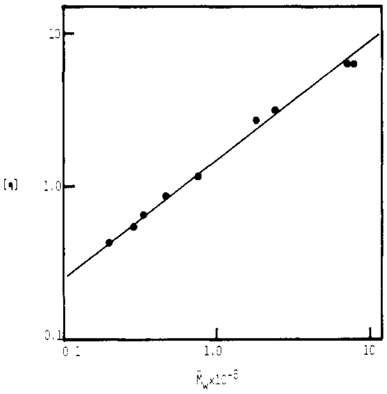


Figure 1. Mark-Houwink plot for $CHCl_3$ solutions of poly(methyl α-chloroacrylate). The equation for the best-fit of the data is $[\eta] = 3.08 \times 10^{-5}\ M^{0.78}$.

An Applied Reseach Laboratory FICA 50 instrument, operated with unpolarized light of wavelength λ 4358 Å and calibrated with benzene ($R_B = 45.6 \times 10^{-6}$), automatically measured scattered light intensities at present angles between 30 and 150°. Matheson Coleman and Bell reagent ACS chloroform was used as the solvent. Solutions were filtered through 0.45-μm Gelman Metricel alpha-6 filters directly into the measuring cell. The refractive index increment as determined using a Brice-Phoenix differential refractometer was (dn/dC) = 0.0721 mL/g. A computer program incorporating a polynominal equation for the least-squares analysis of data and a plotting routine for the construction of Zimm light-scattering plots were used to evaluate weight-average molecular weights, $\bar{M}_w$.

Gel permeation chromatograms for irradiated polymer samples were obtained by using a Waters Model 201 GPC. Chloroform was employed as the mobile phase for both the homopolymer and the copolymer samples. Polymer solutions were filtered through a millipore 0.5-μm Teflon filter before GPC injection. Polystyrene standards were employed to calibrate the 10^6, 10^5, 10^4, and 10^3 Å microstyrogel column bank.

GPC $\bar{M}_w$ and $\bar{M}_n$ values were calculated by utilizing calibration curves generated by the "Universal Calibration" method.[14] Mark-Houwink constants used for PMMA were determined by Bischoff and Desreaux.[15] Mark-Houwink constants for poly(methyl α-chloroacrylate) were determined from the log $\bar{M}_w$–log $[\eta]$ plot shown in Figure 1. The calibration curves are found in Figure 2. The calibration curve found to be satisfactory for GPC analysis of the copolymer samples was simply an average curve between the two homopolymer curves. Sample results for the polymers of this study are found in the tables.

Results

The molecular weight data from light scattering, membrane osmometry, and GPC measurements for poly(methyl α-chloroacrylate) samples are summarized in Table I together with intrinsic viscosity measurements. A very high molecular weight was achieved ($\bar{M}_w$ in excess of 9×10^6). Similarly, the molecular weight, viscosity, and glass transition temperature measurements on the copolymers are summarized in Table II. A copolymer with M_1/M_2 of 41/59 was fractionated into three samples **2**

Table II
Molecular Weight, Viscosity, and Glass-Transition Temperatures of Poly(methyl α-chloroacrylate-*co*-methyl methacrylate), 2

copolymer (fraction)	M_1/M_2[a]	GPC $\bar{M}_w \times 10^{-6}$	GPC $\bar{M}_n \times 10^{-5}$	MOSM[b] $\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	$[\eta]_{CHCl_3}^{30}$, dL/g	T_g,[e] °C
2 (unfractionated)	41/59	1.4	5.9	4.5	3.0[c]	3.7	129
2 (a)	41/59	1.9	9.1	6.6	2.9[c]	2.6	132
2 (b)	41/59	1.3	7.8	5.4	2.4[c]	2.4	134
2 (c)	41/59	1.0	3.7	2.8	2.7[d]	2.2	134
2 (unfractionated)	20/80	0.34	0.94	1.2	2.8	0.57	

[a] M_1/M_2 = methyl α-chloroacrylate/methyl methacrylate mole ratio. [b] MOSM means membrane osmometry. [c] $\bar{M}_w$(GPC)/$\bar{M}_n$(MOSM). [d] $\bar{M}_w$(GPC)/$\bar{M}_n$(GPC). [e] Measured by DSC using a Dupont Model 990 thermal analyzer.

Table III
Molecular Weight vs. Radiation Dose for Fraction 1 (c) of Poly(methyl α-chloroacrylate)

dose, Mrad	light scattering $\bar{M}_w \times 10^{-5}$	MOSM[a] $\bar{M}_n \times 10^{-5}$	GPC $\bar{M}_w \times 10^{-5}$	GPC $\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$[b]	$[\eta]_{CHCl_3}^{30}$, dL/g
0	18	6.0	16	6.2	2.6	2.7
0.46	7.6	2.4	4.1	2.0	2.1	1.1
0.93	4.6	1.9	3.8	1.8	2.1	0.86
2.3	2.9	1.5	2.9	1.5	1.9	0.59
4.6	2.0	1.1	2.0	0.93	2.1	0.43

[a] MOSM means membrane osmometry. [b] $\bar{M}_w$(GPC)/$\bar{M}_n$(MOSM).

Table IV
Molecular Weight vs. Radiation Dose for Fraction 2 (b) of Poly(methyl α-chloroacrylate-*co*-methyl methacrylate)

dose, Mrad	GPC $\bar{M}_w \times 10^{-5}$	GPC $\bar{M}_n \times 10^{-5}$	MOSM[a] $\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$[b]	$[\eta]_{CHCl_3}^{30}$, dL/g
0	13.0	7.8	5.4	2.4	2.4
0.9	4.1	2.1	2.0	2.1	1.1
2.4	1.7	0.73	0.86	2.0	0.68
4.8	1.1	0.50	0.54	2.0	0.44
38	0.4	0.19	0.17	2.1[c]	0.17

[a] MOSM means membrane osmometry. [b] $\bar{M}_w$(GPC)/$\bar{M}_n$(MOSM). [c] $\bar{M}_w$(GPC)/$\bar{M}_n$(GPC).

(a–c). Also a lower molecular weight sample with M_1/M_2 = 20/80 was studied.[1] The molecular weight measurements after irradiation to various doses are given in Table III for one fraction 1 (c) of poly(methyl α-chloroacrylate). Table IV presents the same data for fraction 2 (b) of the copolymer (M_1/M_2 = 41/59).

Plots of $\bar{M}_n$ vs. dose yield $G_s - G_x$ in accord with eq 1;[16]

$$\bar{M}_n^{-1} = \bar{M}_n^{0\,-1} + [G_s - G_x]D/100N_A \tag{1}$$

where D is the irradiation dose in Mrad, N_A is Avogadro's number, and M_n^{0-1} is the number-averaged molecular weight inverse of the unirradiated polymer. Similarly, a plot of $\bar{M}_w^{-1}$ vs. dose permits the evaluation of $G_s - 4G_x$ according to eq 2.[17] Derivation of eq 2 is based upon the

$$\bar{M}_w^{-1} = \bar{M}_w^{0\,-1} + [G_s - 4G_x]D/200N_A \tag{2}$$

assumption that $\bar{M}_w^0/\bar{M}_n^0$ is 2; therefore, use of this equation is only rigorously valid for analysis of polymers with this initial ratio. Our results for PMMA (some unpublished) and the polymers of this work indicate, however, that eq 2 may be employed to calculate G_s and G_x accurately when $\bar{M}_w^0/M_n^0$ is as high as 2.5–2.7. The slopes of the two experimental plots can then be used to determine individual values of G_s and G_x.

GPC measurements are capable of determining both G_s and G_x while membrane osmometry can only give $G_s - G_x$ (eq 1) and light scattering can only give $G_s - 4G_x$ (eq 2). The availability of data from all three techniques provides two sets of data from which two independent evaluations of G_s and G_x may be made. The slope ratio from the $\bar{M}_w^{-1}$ vs. D and $\bar{M}_n^{-1}$ vs. D plots provides a check for nonzero values of G_x. If $\bar{M}_n^{-1}$ vs. D has a slope greater than 1.6–1.8 times that of $\bar{M}_w^{-1}$ vs. D, then G_x is probably nonzero and significant. Furthermore, if $\bar{M}_w/\bar{M}_n > 2$ for the unirradiated polymer, then $\bar{M}_w/\bar{M}_n$ should approach 2 with increasing D if cross-linking is absent.[18] If $\bar{M}_w/\bar{M}_n$ does not approach 2 or if it increases, then G_x is clearly nonzero. Two examples of the latter behavior have recently been found by Lai and Helbert.[19]

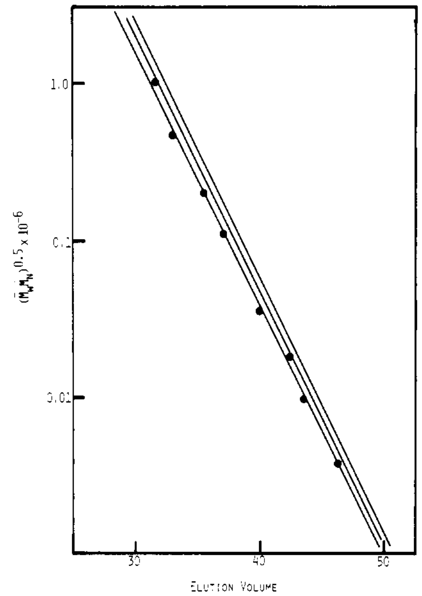


Figure 2. $(\bar{M}_w\bar{M}_n)^{0.5}$ vs. elution volume GPC calibration curves. Solid circles are polystyrene calibration points, and the lower line is the best first-order polynomial fit of data. The middle line is the calibration curve for the copolymer samples and the upper the calibration curve for PMMA.

Poly(methyl α-chloroacrylate) and its methyl methacrylate copolymers predominantly degrade by scission as can be seen in Tables III and IV. At low doses, the $G_s - G_x$ value of poly(methyl α-chloroacrylate) is about 5. This is much higher than that of PMMA ($G_s - G_x$ = 1.4). This is in accord with the higher sensitivity reported for this homopolymer.[7,13] Sample $\bar{M}_n^{-1}$ vs. dose plots of the membrane osmometry data are shown in Figure 3. The

Table V

$G_s - G_x$ and $G_s - 4G_x$ Determinations from Molecular Weight vs. Dose Measurements on Poly(methyl α-chloroacrylate)

homopolymer fraction	low dose $G_s - G_x$ (MOSM)	high dose $G_s - G_x$ (MOSM)	low dose $G_s - 4G_x$	high dose $G_s - 4G_x$
1 (unfractionated)	5.0 ± 0.3			
1 (a)	5.3	2.0 ± 0.3		
1 (b)	5.3	2.1	3.5 ± 0.3[a]	1.4 ± 0.3[a]
1 (c)	5.3	2.7	3.8[b]	1.2[b]
1 (d)	5.0			
PMMA	1.4[b]	1.4[b]	1.6[b]	1.6[b]

[a] Light-scattering data in $CHCl_3$. [b] GPC data in $CHCl_3$.

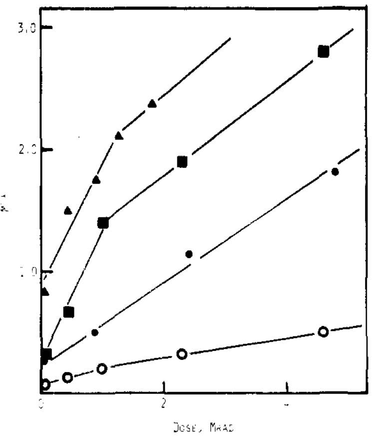


Figure 3. Molecular weight inverse ($\bar{M}^{-1}$) vs. dose for irradiated poly(methyl α-chloroacrylate) samples. The triangles and squares are MOSM data for 1 (d) and 1 (c), respectively. Solid circles are MOSM data for copolymer 2 (b). Lower open circles are from LS($\bar{M}_w$) experiments of 1 (c) in $CHCl_3$.

experimental points were fit by a linear equation indicating that radiation processes are random. The homopolymer 1 requires two linear fits with different slopes: one at high doses and one at low doses (see Figure 3). The loss in accuracy of osmometry determinations for samples with $\bar{M}_n < 10\,000$ precluded the use of higher doses.

The values of $G_s - G_x$ and $G_s - 4G_x$ for the homopolymer fractions are given in Table V. The value of $G_s - G_x$ (low dose) is constant over a large molecular weight range ($\bar{M}_w = 9.5 \times 10^6$–$3.4 \times 10^5$, $\bar{M}_n = 13.3 \times 10^5$ to 1.2×10^5). Also changes in the dispersity of poly(methyl α-chloroacrylate) do not cause a change in $G_s - G_x$. Employing eq 1 and 2, with light-scattering $\bar{M}_w$ values and osmometry $\bar{M}_n$ values, gives $G_s = 6.0 \pm 0.9$ and $G_x = 0.7 \pm 0.2$ for poly(methyl α-chloroacrylate) at low doses. Employing GPC values of $\bar{M}_w$ and $\bar{M}_n$, the values of G_s and G_x were independently determined to be 7.4 ± 0.9 and 0.9 ± 0.2, respectively, at low doses. The agreement is remarkably good. Clearly, poly(methyl α-chloroacrylate) has a high susceptibility to chain scission, but it also undergoes cross-linking. The corresponding high dose values from light scattering and osmometry are $G_s = 3.9 \pm 0.9$ and $G_x = 0.3 \pm 0.2$. These may be compared to the high dose values from GPC data, which were $G_s = 3.2 \pm 0.9$ and $G_x = 0.5 \pm 0.2$. Again, the agreement is good.

The ESR spectrum of γ-irradiated poly(methyl α-chloroacrylate) at 77 K is an anisotropically broadened triplet with a proton hyperfine splitting, a_H, of 22 ± 1 G (see Figure 4). Upon warming to room temperature, the radical concentration decays below the detection limit. G(rads) vs. PMMA as a reference is determined to be 5.7 ± 1.2 for polymer 1. If one assumes $G(\text{rads}) = G_s$, G_x is independently estimated to range between 0.3 and 0.9 in fair agreement with the G_x values from molecular weight dose measurements.

These results establish, without doubt, that cross-linking occurs concurrently with main-chain degradation in homopolymer 1. However, it is significant to point out that polymer 1 does not gel for doses up to 56 Mrad where $\bar{M}_w/\bar{M}_n$ decreases to 1.9 ± 0.1, the most probable distribution.

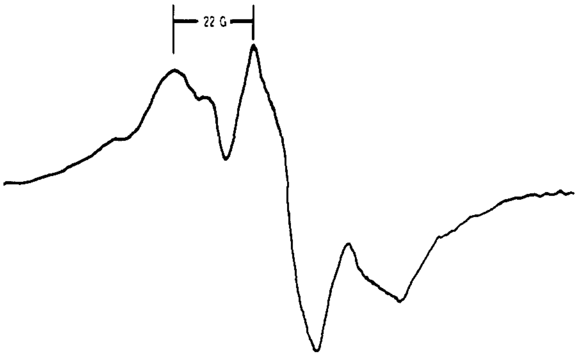


Figure 4. Electron paramagnetic resonance spectrum of irradiated poly(methyl α-chloroacrylate) observed in liquid nitrogen following irradiation at that temperature.

Table VI

$G_s - G_x$ and $G_s - 4G_x$ Determinations from Molecular Weight vs. Dose Measurements on Poly(methyl α-chloroacrylate-*co*-methyl methacrylate)

copolymer fraction	MMA, mol %	$G_s - G_x$ (MOSM)	$G_s - G_x$[a] (GPC)	$G_s - 4G_x$[a] (GPC)
2 (unfractionated)	59	2.5 ± 0.3	- -	- -
2 (a)	59	2.8	3.5 ± 0.3	- -
2 (b)	59	3.0	3.5	3.0 ± 0.3
2 (c)	59	2.7	3.3	3.2
2 (unfractionated)	80	2.0	- -	- -

[a] For the 41/59 copolymer $G_s = 3.1 \pm 0.5$ and $G_x = 0.06 \pm 0.04$.

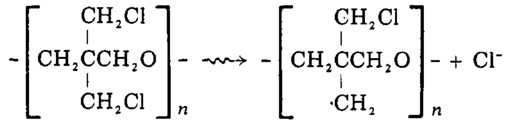
Poly(methyl α-chloroacrylate-*co*-methyl methacrylate) also exhibits linear $\bar{M}_n^{-1}$ vs. dose plots. The linearity occurs over a wider dose range than was observed for homopolymer 1. The $G_s - G_x$ values for the copolymer with 59 mol % MMA was 2.5–3.0 (see Table VI). This value remained constant as molecular weight varied. It is interesting to note that the value of $G_s - G_x$ (2.8–3.0) for the copolymer is exactly what one would calculate from 0.41 (5.3 + 1.4), which assumes the $G_s - G_x$ value of the copolymer directly reflects the M_1/M_2 ratio between the values of $G_s - G_x$ for the homopolymers. From GPC data, the individual values of G_s and G_x were 3.1 ± 0.5 and 0.06 ± 0.04, respectively, for copolymer 2 (59% MMA). The propensity toward cross-linking is greatly reduced in the copolymer. Most significantly the ratio, G_s/G_x, is larger for copolymer 2 than homopolymer 1. While G_s is a factor of 2 smaller for the copolymer G_x is reduced by a factor of approximately 15. Finally, $\bar{M}_w/\bar{M}_n$ approaches 2 rapidly for the copolymer.

The slope ratio of $\bar{M}_n^{-1}$ vs. dose and $\bar{M}_w^{-1}$ vs. dose for homopolymer **1** is 3.3 to 3.8 at low dose. This again emphasizes that G_x is nonzero. At higher doses the ratio is between 3 and 4. This should be compared to the slope ratios observed for the 41/59 copolymer **2** which were 2.0–2.2. Thus, the slope ratio of the copolymer is fairly close to 1.6–1.8 which indicates G_x is qualitatively lower for the copolymer.

Discussion

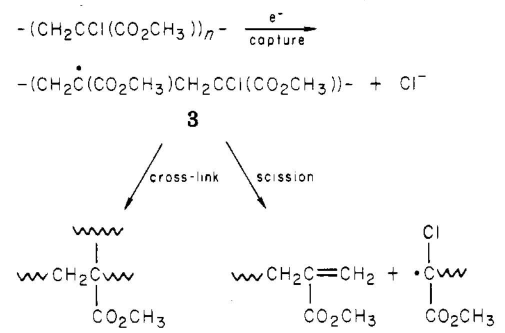
Poly(methyl α-chloroacrylate) differs from PMMA only in its α substituent. However, G_s is increased by a factor of 4 by changing the α substituent from methyl to chlorine. Also, G_x goes from zero to 0.7–0.9. The chlorine, paradoxically, increases the tendency toward main-chain scission while promoting concurrent cross-linking. This result should be compared to other vinyl polymers with α-chlorines. Poly(vinyl chloride), $-(CH_2C(Cl)H)-$, was found to cross-link predominately, when irradiated in vacuo; it exhibited $G_x = 0.33$.[20] Electron scavenging experiments with poly(vinyl chloride) detected the formation of the radical, $-(CH_2\dot{C}H)-$, and evidence was presented that it results from a dissociative electron capture reaction of the carbon–chlorine bond.[21]

Chung et al.[22] observed an analogous radical (see eq 3)



$$-\left[\begin{matrix}CH_2Cl\\|\\CH_2CCH_2O\\|\\CH_2Cl\end{matrix}\right]_n- \rightsquigarrow -\left[\begin{matrix}CH_2Cl\\|\\CH_2CCH_2O\\|\\\cdot CH_2\end{matrix}\right]_n- + Cl^- \quad (3)$$

in irradiated poly(3,3-bis(chloromethyl)oxetane) (i.e., Penton), which would result from dissociative electron capture at the chloromethyl side chain. They reported a G value for radical formation of 0.5. Since dissociative electron capture is thermodynamically favorable,[23] we postulate that this reaction plays an important role in the cross-linking reaction mechanism for poly(methyl α-chloroacrylate) (see eq 4). This suggestion is further warranted since there is substantial experimental evidence for its occurrence in macromolecular[20-22] and molecular systems.[23] Thus, radical **3**, produced in this fashion, could lead to either a cross-linking or a scission event. The high value of G_s for **1** may be the result of the ease of formation of radical **3** by dissociative electron capture. This suggestion is attractive because radical **3** could then give a main-chain break without the intervention of the cage effect. Furthermore, cleavage by this mechanism results in the formation of a tertiary radical, **4**. It is interesting to note that the G_x and G(rads) values for PVC and Penton are similar in magnitude to the G_x value reported for poly(methyl α-chloroacrylate), **1**.



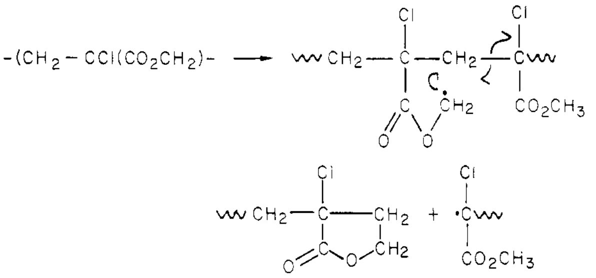
(4)

4

The dominant triplet of the ESR spectrum observed for irradiated **1** can be attributed to $\cdot CH_2CCl(CO_2CH_3)\sim$, radical **4**, or $-(CH_2CCl(CO_2\dot{C}H_2)-$, radical **5**. The observed hyperfine splitting constant of 22 G is similar to the splitting of 19 G observed for a similar ESR triplet detected in irradiated PMMA. That triplet has been the subject of intense study[24-27] and is assigned to the $-(CH_2CCH_3(CO_2\dot{C}H_2))-$ radical. Thus, by analogy, it seems likely that radical **5** is responsible for the triplet in poly(methyl α-chloroacrylate). Furthermore, main-chain radicals **4** and $\cdot CH_2CCl(CO_2CH_3)\sim$ are not going to be formed from a direct main-chain scission due to the "cage effect". An analogous radical in PMMA, $\cdot CH_2CCH_3(CO_2CH_3)\sim$, has not been detected during careful ESR investigations.[24-27] These arguments correspond directly to those advanced by Geuskens[24] to explain the initial absence of $\sim CH_2\dot{C}CH_3(CO_2CH_3)$ in the low-temperature ESR spectrum of PMMA.

It should be pointed out that the observed ESR spectrum of Figure 4 could be a composite spectrum dominated by the triplet. In fact, the hyperfine lines of the triplet are broadened (i.e., the line widths are almost equal to the hf splitting), possibly by unresolved hyperfine lines of less abundant radicals such as radicals **3**, $\cdot CO_2CH_3$, $-(CH_2\dot{C}Cl)-$, or $\cdot CCl(CO_2CH_3)\sim$. The central hyperfine line of the triplet is anomalously larger than the theoretical 1:2:1 intensity ratio calls for; thus, formation of $\cdot CO_2CH_3$ is possible. The spectrum of $\cdot CO_2CH_3$ would be a singlet (i.e., no interacting α or β protons) centered on and overlapping with the central hyperfine line of the triplet. An analogous singlet ESR spectrum observed in PMMA has been assigned to this radical.[24]

Radical **5** may be a primary precursor in the scission process for poly(methyl α-chloroacrylate) as shown in eq 5. It is possible that chain scission may occur as shown in both eq 4 and 5. Arguments against scission via eq 5 may be raised, thus it may be instructive to consider existing thought on the mechanism of PMMA scission.

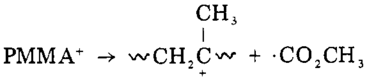


(5)

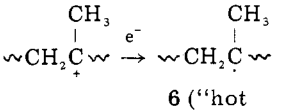
5

$$\mathrm{PMMA} \overset{\gamma}{\rightsquigarrow} \mathrm{PMMA}^+ + e_m^- \text{ (Compton)} \quad (6)$$

David et al. have proposed eq 6–10 for radiation degradation in PMMA.[24,28,29] The crucial step in this mechanism is the ion recombination in eq 8 to form the "hot radical". Protection of irradiated PMMA toward degradation by the presence of electron scavenger (ethyl mercaptan) is the basis for eq 8. This important finding combined with the fact that there was no effect of ethyl



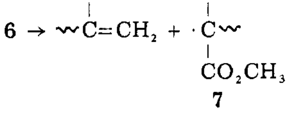
$$\mathrm{PMMA}^+ \rightarrow \sim CH_2\overset{CH_3}{\underset{+}{C}}\sim + \cdot CO_2CH_3 \quad (7)$$



$$\sim CH_2\overset{CH_3}{\underset{+}{C}}\sim \xrightarrow{e^-} \sim CH_2\overset{CH_3}{\underset{\cdot}{C}}\sim \quad (8)$$

6 ("hot radical")

$$\cdot CO_2CH_3 \rightarrow 0.26CO_2 + 0.26CH_3 + 0.50OCH_3 + 0.50CO + \text{other products} \quad (9)$$



$$\mathbf{6} \rightarrow \sim\overset{CH_3}{C}=CH_2 + \cdot\overset{CH_3}{\underset{CO_2CH_3}{C}}\sim \quad (10)$$

7

mercaptan on the volatile product yields strongly favors a free-radical mechanism for main-chain degradation in PMMA. A macromolecular cation radical has recently been observed in irradiated PMMA,[30] which supports the idea of an ionic ester removal mechanism as written in eq 7.

Todd[31] and Kirchner et al.[27] have put forth a mechanism for scission in PMMA as follows:

$$\text{PMMA} \xrightarrow[\text{ionization}]{\text{following}} \underset{\mathbf{8}}{\sim\!\sim\dot{\text{C}}\text{HCCH}_3(\text{CO}_2\text{R})\sim\!\sim} \rightarrow$$
$$\sim\!\sim\text{CH}{=}\text{CCH}_3(\text{CO}_2\text{R}) + \underset{\mathbf{9}}{\cdot\text{CH}_2\text{CCH}_3(\text{CO}_2\text{CH}_3)\sim\!\sim} \quad (11)$$

This mechanism would be consistent with the electron-scavenging results of ref 29 because there is some evidence that C–H bond cleavage can occur to form H^- [32] and radical **8**. In addition, the analogous radical to radical **8** in irradiated polysobutylene, $\sim\!\sim\dot{C}HC(CH_3)_2\sim\!\sim$, has been observed by ESR.[33] Kirchner et al. further hypothesize that radical **8** may be formed by a hydrogen abstraction reaction of radical **5**, which is observed in irradiated PMMA and poly(methyl α-chloroacrylate).

Evidence favoring the overall mechanism of eq 6–10 for degradation in PMMA is substantial. This mechanism, however, can only account for about 80% of the degradation since $G(CO_2CH_3)/G_s$ is 0.8. It seems logical that some other mechanism involving the methylene group as in eq 11 or the α-methyl group is responsible for the remaining portion of degradation in PMMA. The simple fact that polyisobutylene degrades more efficiently than PMMA is supportive to this claim.

It is not yet possible to say what path is mainly responsible for chain scission in poly(methyl α-chloroacrylate). By analogy to PMMA, a large portion of the degradation is most likely due to the mechanism proposed by David et al.[24] (see eq 6–10). The mechanism of eq 4, however, must be considered of importance due to the large observed effect on G_s of the α-chlorine substituent. The mechanisms of eq 5 and 11 may also contribute, but to a lesser degree. It is very possible that main-chain degradation in poly(methyl α-chloroacrylate), the MMA copolymer, and PMMA for that matter proceeds via several concurrent mechanisms.

Summary

The predominance of radiation degradation is quantitatively established for poly(methyl α-chloroacrylate), as manifested by the observed G_s/G_x ratios of 8.5 and 6.2 at low and high dose. In addition, concurrent cross-linking in irradiated poly(methyl α-chloroacrylate) is established. The larger G_s value observed for poly(methyl α-chloroacrylate) vs. PMMA is attributed to the electronegative α-chlorine substituent,[4] while the nonzero value of G_x is attributed to dissociative electron capture reaction of the C–Cl bond.

Cross-linking in the copolymer occurs, but to a lesser degree than for the homopolymer. This suggests that intermolecular cross-linking may involve adjacent α-chlorine sites or that the methyl groups of the comonomer are capable of sterically hindering the cross-linking reaction.

We intend to study poly(methyl α-fluoroacrylate) to further investigate the importance of an electronegative α substituent. The C–F bond is stronger than the C–Cl bond and may lower the propensity for polymer dissociative electron capture. Thus, the tendency to form $\sim\!\sim CH_2\dot{C}(CO_2CH_3)\sim\!\sim$ may decrease which may decrease G_x and even possibly G_s.

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