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# Radiolysis of Resist Polymers. 2. Poly(haloalkyl methacrylates) and Copolymers with Methyl Methacrylate

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ABSTRACT: Homopolymers of 2-fluoroethyl methacrylate (FEMA), 2-chloroethyl methacrylate (CEMA), 2-bromoethyl methacrylate (BEMA), 2,2,2-trichloroethyl methacrylate (TCEMA), and 2,3-dibromopropyl methacrylate (DBPMA) and copolymers with MMA over a range of compositions have been synthesized. The copolymerization reactivity ratios have been determined for copolymers obtained at low conversions. $\gamma$-Radiolysis yields for scission ($G_s$), cross-linking ($G_x$), and radical formation ($G_r$) were determined, the former from $\bar{M}$ vs. dose data and the last with quantitative ESR. The volatile products were analyzed by GC-MS. With the exception of the BEMA system, which does not form a stable radical, all the other systems produce radicals similar to the PMMA radicals upon radiolysis. PTCEMA is the most promising candidate as a positive E-beam resist, having $G_s = 2.4$, $G_x = 0$, and $G_r = 4.1$. Copolymers with <34 mol % TCEMA are either inferior or comparable to PMMA in these properties. The bromine-containing systems show high cross-linking tendencies and are without merits for E-beam applications. PFEMA has $G_s = 2.0$, $G_x = 0$, and $G_r = 2.8$, showing promise as a resist material. Copolymers of FEMA and MMA have a slight tendency toward cross-linking even at low dose. Poly(MMA-*co*-CEMA) have properties intermediate of those containing FEMA and BEMA. On the basis of the product analysis and other data, mechanisms of radiolysis for these polymers were proposed.

## Introduction

There has been a renewed interest in the radiation chemistry of macromolecules stimulated by searches for electron beam (E-beam) resists for lithographic applications in the electronics industry. Interaction of ionizing radiation with polymers causes chain scission and/or cross-linking. Both types of processes can occur simultaneously but usually one predominates.[2] Ideally, a positive resist should degrade exclusively by chain scission and a negative resist via cross-linking. The radiolysis pathways reflect the chemical structure of the polymer.[3] Polymers with activated tertiary hydrogen, such as polystyrene, mainly cross-link, whereas polymers with quaternary main-chain carbon atoms such as PMMA predominatly undergo chain scission. The tendency of a polymer to undergo scission has been attributed to steric strain in its structure and has been correlated with low heats of polymerization. However, such conclusions are too general and qualitative to be of real value in predicting the radiation sensitivity of a particular polymer.

Halogen-containing polymers have received much attention because of their high radiation sensitivity in dissociative electron capture. Poly(methyl $\alpha$-haloacrylates) have backbone quaternary carbon atoms and are expected to have high chain scission efficiency. In the bromo, chloro, and fluoro series one might expect $G_s$ (scission yield per 100 eV absorbed) to decrease in this order since the mesomeric effect in stabilizing a main-chain terminal radical and steric effect are greater for the methyl $\alpha$-bromoacrylate. However, the tendency toward chain scission by radiolysis increases in the order of Br < F < Cl and cross-linking tendencies are in the opposite order.[5-8] The cross-linking yield, $G_x$, can be substantially lowered by copolymerizing the methyl $\alpha$-haloacrylate with a non-cross-linking monomer such as methacrylonitrile[5] and methyl methacrylate.[8] However, the radiation chemistry of the copolymers is mainly determined by the $\alpha$-haloacrylate monomer units.

The mechanisms for cross-linking proposed for homo- and copolymers of methyl $\alpha$-haloacrylates[8] are not applicable to haloalkyl methacrylates. Poly(trichloroethyl methacrylate) (PTCEMA) has been reported[9] to exhibit high chain scission sensitivity toward electron irradiation at low dose and cross-links at high dose. Fluoroalkyl methacrylate polymers were also found[7,10] to degrade more efficiently than PMMA. In a comparison of resists for X-ray lithography,[11] poly(2-fluoroethyl methacrylate (PFEMA) was found to be more sensitive than poly(2-chloroethyl methacrylate) (PCEMA) and poly(2-bromoethyl methacrylate) (PBEMA).

The central purpose of this work was to study the radiation chemistry of poly(haloalkyl methacrylates) and copolymers with MMA in order to understand the effects of halogen substitution on the pendant ester groups in contrast to those on the main-chain quaternary carbon atoms. The systems investigated are FEMA, CEMA, BEMA, TCEMA, and 2,3-dibromopropyl methacrylate (DBPMA).

## Experimental Section

**Materials.** The 2-haloethyl methacrylates were prepared by the reaction of the corresponding haloethanol with methacryloyl chloride. 2,3-Dibromopropanol and 2,2,2-trichloroethanol were used to synthesize DBPMA and TCEMA, respectively, by the same acylation method.

**Methods.** The methods for homopolymerization, copolymerization, polymer characterization, $\gamma$-radiolysis, determinations of $G_s$, $G_x$, and $G_r$ (radical yield per 100 eV absorbed), ESR (electron spin resonance), and GC-MS analysis of volatile radiolysis products are the same as given previously.[8]

## Results and Discussion

**Copolymerization.** As pointed out in the previous paper,[8] the radiolysis yields are not monotonic functions of the copolymer composition. Therefore, copolymers with a wide range of compositions were synthesized in this work. The copolymerizations were stopped after a few percent conversion to avoid composition drift and to obtain good reactivity ratios.

In the copolymerizations, $M_1$ ($M_2$) refers to the MMA (haloalkyl methacrylate) in the feed, $m_1$ ($m_2$) its content in the copolymer, and $r_1$ ($r_2$) the corresponding reactivity ratio. The copolymer composition is indicated by the number in mole percent before the particular monomer. Thus poly(80 MMA-*co*-20 TCEMA) is a copolymer containing 80 mol % MMA and 20 mol % TCEMA. Table I summarizes the copolymerization data and molecular weights of the copolymers. Figure 1 shows the variation of copolymer composition vs. comonomer feed of MMA and TCEMA and that the curve calculated from the reactivity ratio (Table II) is in good agreement with exper-

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**Table I**
**Polymerization Data and Properties of Polymers**[a]

| comonomer | $M_2$ | $m_2$ | convsn, % | $\bar{M}_n \times 10^{-5}$ | $\bar{M}_w \times 10^{-5}$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|---|
| FEMA | 0.1 | 0.05 | 11 | 3.6 | 6.3 | 1.7 |
| | 0.2 | 0.11 | 12 | 2.6 | 4.2 | 1.6 |
| | 0.5 | 0.30 | 10 | 2.3 | 4.2 | 1.8 |
| | 1.0 | 1.0 | 9 | 0.96 | 2.8 | 2.9 |
| CEMA | 0.18 | 0.28 | 4.2 | 2.2 | 3.9 | 1.8 |
| | 0.2 | 0.33 | 6.4 | 2.7 | 4.1 | 1.5 |
| | 0.58 | 0.60 | 9.5 | | | |
| | 0.78 | 0.86 | 10 | 1.8 | 3.6 | 2.0 |
| | 1.0 | 1.0 | 8.2 | 0.47 | 2.0 | 4.9 |
| BEMA | 0.08 | 0.10 | 4.8 | 3.1 | 5.0 | 1.6 |
| | 0.16 | 0.22 | 7.2 | 4.0 | 6.1 | 1.5 |
| | 0.40 | 0.48 | 6.4 | 2.9 | 5.3 | 1.8 |
| | 0.62 | 0.65 | 8.6 | | | |
| | 0.80 | 0.79 | 10.2 | | | |
| TCEMA | 0.06 | 0.09 | 6.4 | 3.0 | 4.3 | 1.4 |
| | 0.16 | 0.24 | 9.8 | 2.2 | 3.2 | 1.45 |
| | 0.25 | 0.34 | 8.4 | 1.7 | 2.6 | 1.55 |
| | 0.32 | 0.39 | 4.6 | | | |
| | 0.50 | 0.53 | 6.8 | 1.55 | 2.3 | 1.5 |
| | 0.90 | 0.87 | 6.2 | | | |
| | 1.0 | 1.0 | 6.0 | 1.5 | 2.3 | 1.55 |
| DBPMA | 0.41 | 0.31 | 8.2 | 2.2 | 4.3 | 2.0 |
| | 0.46 | 0.35 | 5.9 | | | |
| | 0.56 | 0.44 | 4.3 | 1.6 | 2.3 | 1.5 |
| | 0.75 | 0.61 | 6.8 | | | |
| | 0.93 | 0.61 | 6.8 | | | |
| | 1.0 | 1.0 | | 1.5 | | |

[a] The low $\bar{M}_w/\bar{M}_n$ values for most of the polymers can be attributed to some fractionation effect by the repeated dissolution and precipitation used to purify the polymers.

**Table II**
**Copolymerization Reactivity Ratios for Haloalkyl Methacrylates ($r_2$) with MMA ($r_1$)**

| comonomer | $r_1$ | $r_2$ |
|---|---|---|
| FEMA | 1.50 | 0.62 |
| CEMA | 0.49 | 1.47 |
| BEMA | 0.61 | 0.95 |
| TCEMA | 0.40 | 0.62 |
| DBPMA | 1.75 | 0.82 |

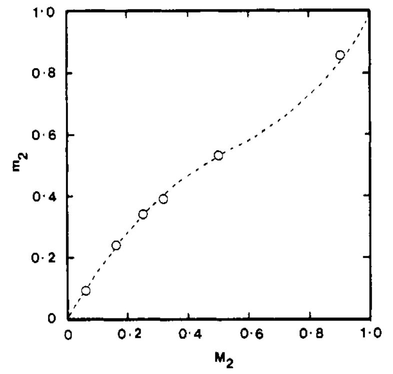


**Figure 1.** Copolymer composition vs. comonomer feed of MMA and TCEMA: (○) experimental value; curve from copolymerization equation and reactivity ratio.

imental results. Similar agreement was observed for the four other copolymer systems; their copolymerization curves are not included in this paper but the relevant information is contained in Tables I and II.

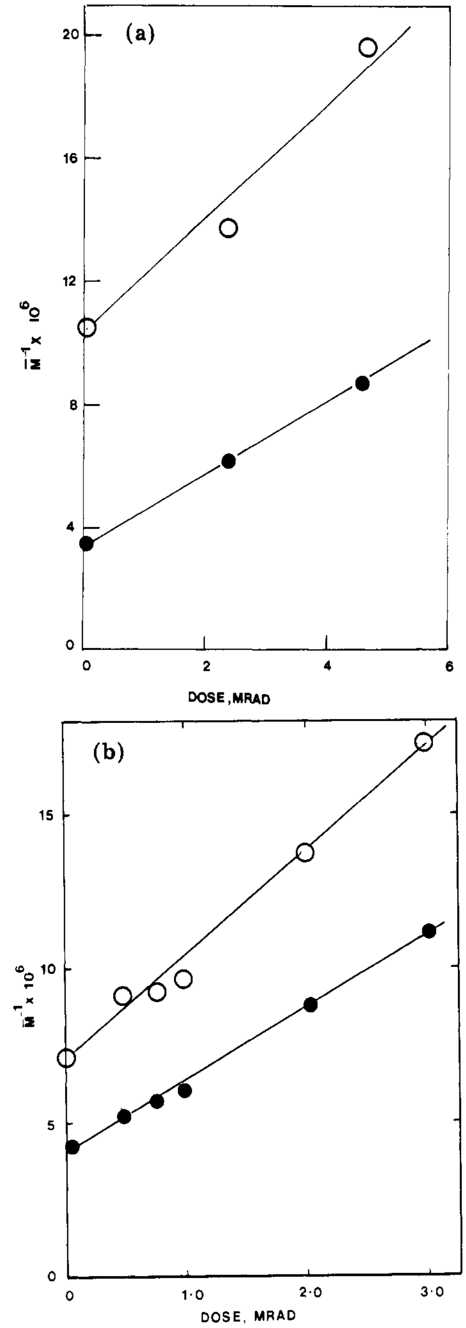


**Figure 2.** Effect of γ-ray dose on the molecular weights (○) $\bar{M}_n$ and (●) $\bar{M}_w$ for (a) PFEMA and (b) PTCEMA.

All the homo- and copolymers of FEMA, CEMA, and BEMA are soluble in $CHCl_3$, THF, DMF, and toluene at room temperature. Those of TCEMA are soluble in $CHCl_3$, $CH_3CN$, and THF but insoluble in $CH_3OH$ and petroleum ether. PDBPMA is soluble in methacrylonitrile, dioxane, $CHCl_3$, and THF. PTCEMA has a high $T_g$ of 132 °C; the $T_g$'s for poly(MMA-*co*-TCEMA) with 53, 34, 24, and 9 mol % TCEMA are 122, 117, 114, and 112 °C, respectively.

**γ-Radiolysis. (a) Yields.** The yields of scission and cross-linking were obtained from the changes in $\bar{M}_n$ and $\bar{M}_w$ with dose, shown in Figure 2 for the homopolymers. Similar measurements were made on all the other copolymers but the plots are not included in this paper. The value of $G_s$ and $G_x$ thus calculated are summarized in Table III. From the EPR intensities the values of $G_r$ were obtained and also are given in Table III.

Among the three poly(2-haloethyl methacrylates), PFEMA appears to be the best candidate for positive resist. Its $G_s$ value of 2.0 is larger than that of PMMA ($G_s$ = 1.4), and $G_x$ = 0. That is the slope of the $\bar{M}_n$ vs. dose plot ($S_n$) is exactly twice the slope of the $\bar{M}_w^{-1}$ vs. dose plot ($S_w$). Eranian et al.[11] found the polymer to be 3 times more

**Table III**
**γ-Radiolysis Yields**

| polymer | $G_r - G_x$ | $G_s$ | $G_x$ | $G_r$ |
|---|---|---|---|---|
| poly(95 MMA-*co*-5 FEMA) | 1.85 | 1.90 | 0.05 | 1.6 |
| poly(89 MMA-*co*-11 FEMA) | 0.96 | 0.95 | 0.01 | |
| poly(70 MMA-*co*-30 FEMA) | 1.75 | 1.6 | 0.15 | 2.4 |
| poly(FEMA) | 2.0 | 2.0 | 0 | 2.8 |
| poly(83 MMA-*co*-27 CEMA) | 0.45 | 0.45 | 0 | |
| poly(78 MMA-*co*-32 CEMA) | 1.7 | 1.5 | 0.18 | |
| poly(13 MMA-*co*-87 CEMA) | 1.0 | 1.0 | 0 | |
| poly(CEMA) | 0.54 | 0.58 | 0.08 | |
| poly(90 MMA-*co*-10 BEMA) | 0.81 | 0.91 | 0.10 | 0.5 |
| poly(78 MMA-*co*-22 BEMA) | 0.65 | 0.85 | 0.2 | |
| poly(52 MMA-*co*-48 BEMA) | 0.45 | 0.70 | 0.35 | |
| poly(91 MMA-*co*-9 TCEMA) | | 1.4 | 0 | 1.5 |
| poly(76 MMA-*co*-24 TCEMA) | | 0.54 | 0 | 1.1 |
| poly(66 MMA-*co*-34 TCEMA) | | 1.2 | 0 | 1.0 |
| poly(47 MMA-*co*-53 TCEMA) | | 1.9 | 0 | 2.6 |
| poly(TCEMA) | | 2.4 | 0 | 4.1 |
| poly(93 MMA-*co*-7 DBPMA) | 1.8 | 1.8 | 0.06 | |
| poly(84 MMA-*co*-16 DBPMA) | 1.3 | 1.0 | 0.26 | |
| poly(69 MMA-*co*-31 DBPMA) | | | | 3.9 |
| poly(39 MMA-*co*-61 DBPMA) | | | | 4.7 |
| poly(16 MMA-*co*-84 DBPMA | | | | 5.2 |

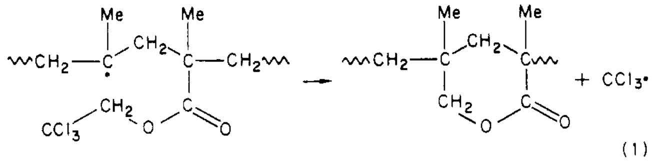
sensitive than PMMA as an X-ray (8.34 Å) resist using a 3:1 methyl isobutyl ketone/2-propanol developer.

Copolymers of FEMA and MMA have lower $G_s$ values than PFEMA. A minimum value of 0.95 for $G_s$ was obtained for copolymers with 11 mol % FEMA. However, the scission yields for copolymers of greater and smaller contents of FEMA are all larger than the yield for PMMA. It is not uncommon that copolymers show either a maximum or a minimum in radiolysis yields containing 10–20 mol % of one of the monomers. The values of $G_x$ are nonzero for the FEMA–MMA copolymers. However, since the irradiated copolymers were soluble, the small values of $G_x$ need not imply cross-linking. Since the copolymers synthesized at low conversion have $\bar{M}_w/\bar{M}_n$ less than the most probable distribution (Table I), random radiolysis causes the polydispersity to approach the most probable distribution, resulting in nonzero values for $G_x$.[8]

PCEMA is less sensitive to radiative degradation than PMMA. The copolymers have $G_s$ values which lie between those of the two homopolymers but show no definite trend in the variation of $G_s$ with copolymer composition.

PBEMA gels upon γ-irradiation. There is also a definite tendency toward cross-linking for the copolymers of BEMA and MMA. Table III shows that $G_s$ decreases and $G_x$ increases monotonically with the increase of BEMA content. This monomer has no merit as a positive resist material.

PTCEMA has the highest $G_s$ of the systems studied here and zero value for $G_x$. Furthermore, $G_x = 0$ for copolymers of all compositions with MMA. The scission yield decreases with the decrease of TCEMA content, reaching a minimum value of 0.54 at 24 mol %. Then $G_s$ increases at small TCEMA content and approaches the sensitivity of PMMA. At 24 mol % of TCEMA the copolymer contains higher alternating $M_1M_2$ dyads than copolymers of other compositions. The low $G_s$ yield may be due to an intramolecular reaction which prevents the scission of a PMMA radical, such as



(1)

The reaction may be favored by the elimination of the stable $CCl_3\cdot$ radical.

Radiolysis of poly(DBPMA) and copolymers containing more than 30 mol % of this monomer were cross-linked by radiolysis. Therefore, $G_s$ and $G_x$ values cannot be determined by the present method. The $G_r$ value is very high, ~5, but the sensitivity to cross-linking rules out DBPMA in positive resist applications; however, DBPMA may find usage as a negative resist.

**(b) ESR.** γ-Irradiated homo- and copolymers of FEMA showed only the nine-line ESR spectrum characteristic of the PMMA propagating radical. The radical yield is the highest for the homopolymer. However, upon heating to 50 °C, [R·] decreases by 60% (Figure 3). Between 50 and 90 °C, [R·] remained relatively constant; above 90 °C, the ESR intensity decreases very rapidly and becomes unobservable at ca 120 °C. In contrast, the ESR signal intensity of γ-irrdiated copolymer containing 30 mol % FEMA was unaffected by heating to 60 °C. Rapid decrease in [R·] commences at ca. 70 °C and their curves merge with that of poly(FEMA). The differences between the homo- and copolymer may be attributed to geminal recombination of FEMA radicals in the homopolymer whereas the radicals are far separated in the copolymer and their combination occurs only above $T_g$ of the copolymers.

γ-Irradiation of homo- and copolymers of CEMA produced the nine-line spectrum of the PMMA-type radical. The ESR intensity is stable at ambient temperatures over 100 h. However, it decreases rapidly with heating and the radical disappears at 80 °C (Figure 4). The CEMA copolymers have $T_g$'s ca. 30 °C lower than the FEMA-containing polymers.

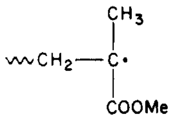
Radiolysis of polymers containing BEMA gave no detectable ESR signal. Apparently the radicals were too reactive and unstable at ambient temperatures. The ESR spectra of PTCEMA and poly(MMA-*co*-TCEMA) are the same as that of the PMMA radicals.[2] Tada,[9] however, reported that irradiated PTCEMA produced radicals having hyperfine characteristics for a carbon-centered radical having hyperfine interaction with two equivalent chlorine nuclei ($^{Cl}A = 5.2$ g). This spectrum is said to be superimposed on the normal PMMA radical. We did not observe any such ESR spectra in the radiolysis of either PTCEMA or poly(MMA-*co*-TCEMA). On the other hand, in our study of the radiolysis of methyl α-chloroacrylate–trichloroethyl methacrylate copolymers, we observed radicals attributable to a $CCl_2$ species. These results will be published elsewhere.

The radicals produced upon γ-irradiation of homo- and copolymers of DBPMA have ESR spectra identical with the spectrum of γ-irradiated PMMA.

**(c) GC–MS.** Table IV summarizes the volatile products of γ-radiolysis as analyzed by GC–MS.

## Mechanism

Most of the polymers and copolymers of this work, except those of BEMA, gave the PMMA type of radical (nine-line ESR spectrum) upon radiolysis:



$$\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOMe}{C\cdot}}$$

I

The fact that $G_r$ is dependent upon the haloalkyl group (–COOR) suggests that direct radiolytic main-chain scission is of minor importance. Instead, the common primary radiolysis event is[12]

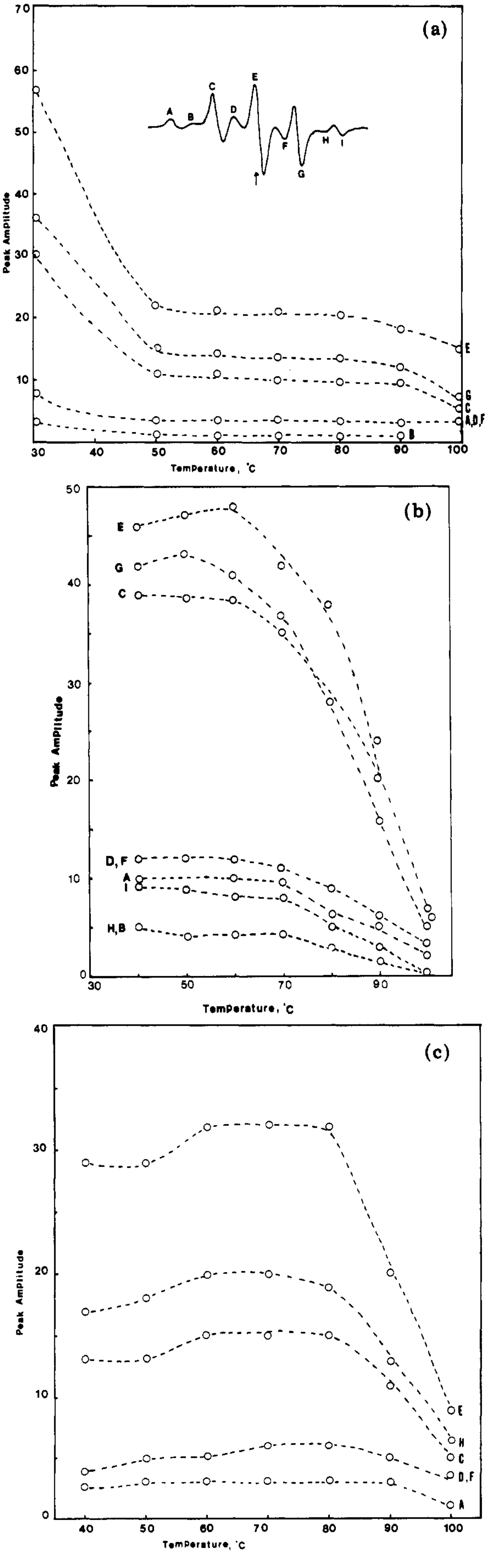
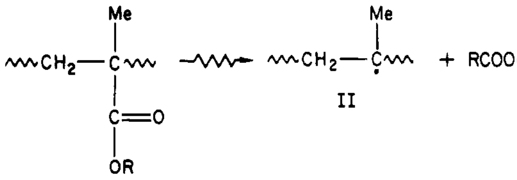
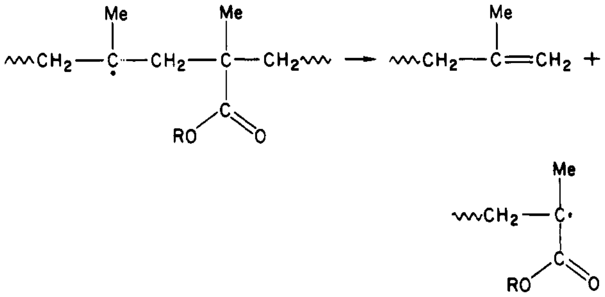


Figure 3. Effect of heating on the ESR spectra of (a) poly(FEMA), (b) poly(70 MMA-*co*-30 FEMA), and (c) poly(89 MMA-*co*-11 FEMA). Dose = 0.99 Mrd.



$$\sim CH_2-\overset{Me}{\underset{\underset{OR}{C=O}}{C}}\sim \;\rightsquigarrow\; \sim CH_2-\overset{Me}{\underset{\bullet}{C}}\sim + RCOO\cdot \qquad (2)$$

II

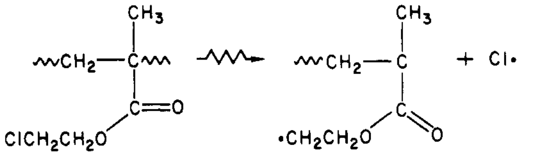


(3)

III

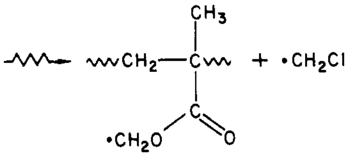
The analogous ionization, neutralization, and cleavage of the methyl group followed by scission like eq 3 probably also occur. The ESR spectral of radicals I and III would be indistinguishable.

Radiolytic dissociation of the pendant group of CEMA polymers is also expected.



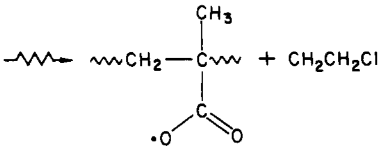
(4)

IV



(5)

V

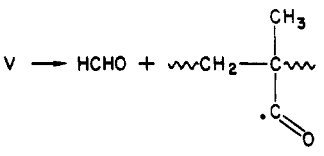


(6)

VI

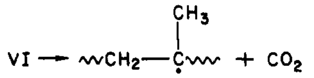
These reactions may be followed by secondary processes:

$$IV \rightarrow CH_2{=}CH_2 + VI \qquad (7)$$



(8)

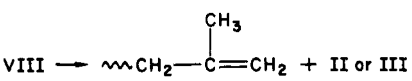
VII



$$VI \rightarrow \sim CH_2-\overset{CH_3}{\underset{\bullet}{C}}\sim + CO_2 \qquad (9)$$

VIII

$$VII \longrightarrow VIII + CO \qquad (10)$$



$$VIII \rightarrow \sim CH_2-\overset{CH_3}{C}{=}CH_2 + \text{II or III} \qquad (11)$$

HCl, MeCl, EtCl, $CO_2$, and CO were all observed by GC–MS. The FEMA polymers undergo a similar series of

**Table IV**
**Volatile γ-Radiolysis Products**[a]

| products | relative ion current: homopolymers PFEMA | PBEMA | PTCEMA | copolymers[b] FEMA | CEMA | BEMA | TCEMA |
|---|---|---|---|---|---|---|---|
| $CH_4$ | 2.8 | 4.0 | 4.1 | 5.7 | 3.9 | 1.7 | 0.4 |
| CO, $CH_2{=}CH_2$ | 6.3 | 17.8 | 19.7 | 18.7 | 10.4 | 17.6 | 0.1 |
| $C_2H_6$, $HCO^+$ | *c* |  | 1.0 |  |  |  | 0.1 |
| $H^{35}Cl$ |  |  | 60.2 |  | 14.2 |  | 18.4 |
| $H^{37}Cl$ |  |  | 26.2 |  | 7.3 |  | 6.6 |
| $C_3H_6$ |  |  | 0.3 |  |  |  | 0.3 |
| $CO_2$ | 100 | 100 | 100 | 100 | 100 | 100 | 0.2 |
| $C_2H_5F$ | 12 |  |  | 30 |  |  |  |
| $CH_3{}^{35}Cl$ |  |  | 9.6 |  | 10.7 |  | 0.7 |
| $CH_3{}^{37}Cl$ |  |  |  |  | 3.4 |  |  |
| $HCOOCH_3$ |  |  | 0.8 | 14.9 | 3.1 |  |  |
| $CH_3CH_2{}^{35}Cl$ |  |  |  |  | 3.3 |  |  |
| $CH_3CH_2{}^{37}Cl$ |  |  |  |  | 1.3 |  |  |
| $CH_2{=}C(Me)CO^+$ |  |  | 0.4 |  |  |  | 1.1 |
| $CH_3COOCH_3$ |  |  | 0.7 | 7.2 |  |  | 1.0 |
| $CH_2Cl_2$ (mass no. 83–88) |  |  | 1.7 |  |  |  | 1.2 |
| $CH_3{}^{79}Br$ |  | 2.4 |  |  | 3.3 |  |  |
| $CH_3{}^{81}Br$ |  | 1.2 |  |  | 3.0 |  |  |
| $CH_2{=}C(Me)COOCH_3$ |  |  |  |  | 2.4 |  |  |
| $CHCl_3$ (mass no. 117–124) |  |  | 6.7 |  |  |  | 6.7 |
| $C_2Cl_6$ |  |  | 0.4 |  |  |  | 0.4 |

[a] Relative yield normalized to 100 for $CO_2$. [b] $m_2$ = 0.3 (FEMA), 0.87 (CEMA), 0.22 (BEMA), and 0.24 (TCEMA). [c] Not detected.

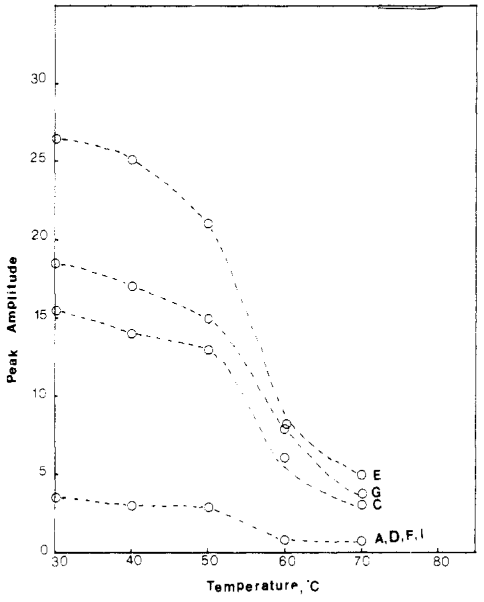
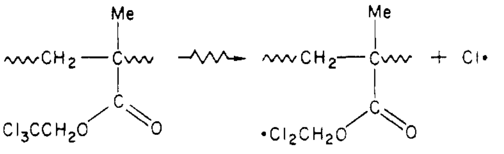


Figure 4. Effect of heating on the ESR intensity of poly(CEMA).

reactions. One cannot say for certain whether dissociative electron capture by fluorine also occurs, because HF was not found. However, HF, if formed, will probably react with the glass container. The same cannot be said for BEMA because neither HBr nor EtBr was detected. For the bromine derivative, apparently reaction 5 is favored over reactions 4 and 6 to produce MeBr.

In the case of TCEMA polymers, dissociative electron capture of chlorine occurs to produce HCl.

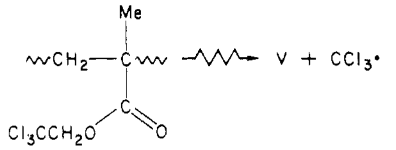


$$\sim CH_2-\overset{Me}{\underset{C(=O)OCH_2CCl_3}{C}}\sim \rightsquigarrow \sim CH_2-\overset{Me}{\underset{C(=O)OCH_2Cl_2\cdot}{C}}\sim + Cl\cdot \qquad (12)$$

IX

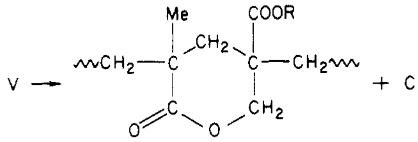
$$IX \longrightarrow CH_2Cl_2 + VI \qquad (13)$$

However, a very significant process is the cleavage of the stable $\cdot CCl_3$ radical

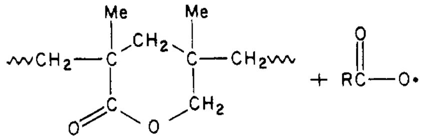


$$\sim CH_2-\overset{Me}{\underset{C(=O)OCH_2CCl_3}{C}}\sim \rightsquigarrow V + CCl_3\cdot \qquad (14)$$

which leads to $CHCl_3$ and $C_2Cl_6$. Among all the polymers investigated here, only poly(TCEMA) and copolymers with MMA show no tendency toward cross-linking. This means that main-chain radicals such as II and VIII were not produced or were produced in amounts much less than in the radiolysis of the other polymers. An intramolecular lactone formation may be proposed via reaction 1 or



(15)



(16)

where R is $CH_2CCl_3$ in PTCEMA and copolymers rich in TCEMA monomer, or R is $CH_3$ for copolymers with high MMA content. Reactions 1 and 15 are apparently so efficient that the radiolysis of poly(MMA-*co*-TCEMA) produces very little $CO_2$ and CO. Infrared spectroscopic evidence for lactone formation will be given in papers describing thermolysis of these polymers.

Some of the copolymers of FEMA and CEMA have $G_x = 0$, while other have very small $G_x$ values; the irradiated polymers remain soluble. We have pointed out[8] that very small $G_x$ values may be due to chain extension more than cross-linking.

Poly(BEMA) and copolymers containing >30 mol % DBPMA were cross-linked by radiolysis. This ease of cross-linking was also observed for polymers of methyl

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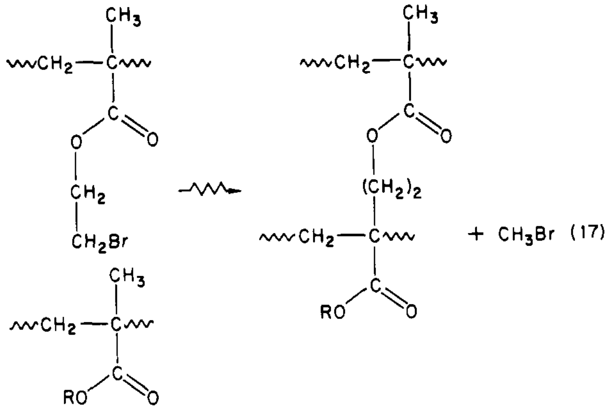
α-bromoacrylate.[8] This characteristic may be related to the ease of $CH_3Br$ elimination. The possible reactions may be



(17)

and others like it.

The ease of cross-linking of the BEMA homo- and copolymers as compared to the CEMA and FEMA polymers may have other explanation. The size of the halogen atoms should govern their rates of diffusion, which are approximately inversely proportional to the square root of their masses. Thus the lighter F· and Cl· atoms can diffuse more readily from their site of formation to react elsewhere. On the other hand, the heavier Br· atom probably reacts in the close vicinity of its site of formation, i.e., hydrogen abstraction. Combination of the two resulting macromolecular radicals would tend to cross-link. We have found in our studies of other halogenated polymers that the bromine-containing polymers generally cross-link much more readily than the chlorine- and fluorine-containing analogues in radiolysis.

In conclusion, PTCEMA has high scission efficiency without tendency of cross-linking. It can be superior to PMMA as an E-beam resist. This optimism should be tempered by the report of Tada[9] that poly(TCEMA) will cross-link at high dose. More work needs to be done for TCEMA polymers at high dose and search for a comonomer to reduce the cross-linking tendency. The bromine-containing systems have no merit for resist applications. The FEMA and CEMA systems are marginal in this respect.

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# Radiolysis of Resist Polymers. 5. Poly(haloalkyl α-chloroacrylates) and Copolymers with Methyl Methacrylate

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ABSTRACT: Homopolymers of 2,2,2-trifluoroethyl α-chloroacrylate (PTFECA) and of hexafluoroisopropyl α-chloroacrylate (PHFPCA) and copolymers with MMA have been synthesized. The homopolymers have $G_s \approx 3.6$ and $G_x = 0$. Their glass transition temperatures are high and the polymers form strong films. These polymers may prove to be excellent candidates for positive electron-beam resist materials, superior to PMMA. A relative comparison of the radiation sensitivity of haloalkyl α-chloroacrylate polymers with homo- and copolymers of methyl α-chloroacrylate is discussed.

## Introduction

Research on positive electron-beam resist polymers has mainly been directed toward polymers which are highly sensitive toward radiolytic chain scission without cross-linking. Of course, other considerations such as high $T_g$, ability to form mechanically strong thin films, and good differential solubility, which depends on molecular weight, are also important.

Poly(methyl α-chloroacrylate) has very high $G_s$ (number of chain scissions per 100 eV absorbed) values of 6–7.4[1,2] Unfortunately, the polymer also tends to cross-link upon irradiation; $G_x \sim 0.6$–0.9. Attempts to eliminate the cross-linking reactions by copolymerizing methyl α-chloroacrylate with methyl methacrylate (MMA) were unsuccessful.[2] Copolymers of all compositions have $G_s$ values lying between that for each corresponding homopolymer but nonzero $G_x$ values.

Halogens placed on the pendant group slightly enhanced $G_s$ without inducing cross-linking.[3] For instance, poly(2,2,2-trifluoroethyl methacrylate)[4-6] and poly(2,2,2-trichloroethyl methacrylate)[6,7] have $G_s$ values of 2.0 and 2.4, respectively, and these $G_s$ values are greater than $G_s = 1.4$ for PMMA. However, based on the $G_s$ and $G_r$ (radical yield) values, dissociative electron capture by halogen atoms on the backbone is more effective in generating radicals than similar capture by halogen atoms on the pendant group. Recently, Tada[8] reported that poly(2,2,2-trifluoroethyl α-chloroacrylate) was found to exhibit