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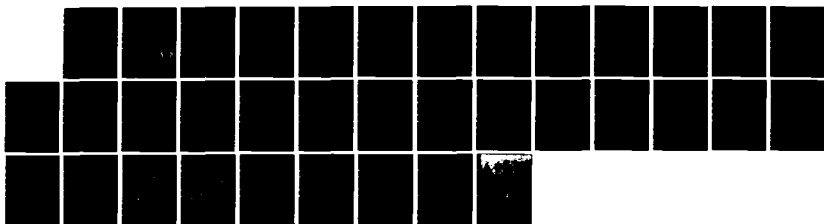
RADIOLYSIS OF RESIST POLYMERS 2  
POLY(HALOALKYLMETHACRYLATES) AND COPOLYMER (U)  
MASSACHUSETTS UNIV AMHERST MATERIALS RESEARCH LAB  
G N BABU ET AL. AUG 83 TR-2

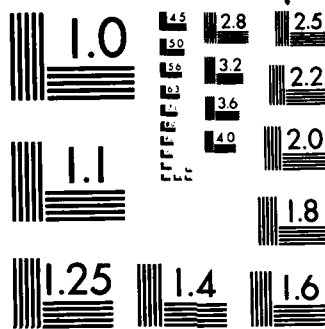
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Homopolymers of 2-fluoroethyl methacrylate (FEMA), 2-chloroethyl methacrylate (CEMA),<br>2-bromoethyl methacrylate (BEMA), 2,2,2-trichloroethyl methacrylate (TCEMA), 2,3-<br>dibromopropyl methacrylate (DBPMA) and copolymers with MMA over a range of composi-<br>tions have been synthesized. Gamma-radiolysis yields for scission (Gs), cross-<br>linking (Gx) and radical formation (Gr) were determined. The volatile products<br>were analyzed by GC-MS. Probable mechanisms of radiolysis of all polymers were<br>proposed. |                       |                                                                              |

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TECHNICAL REPORT NO. 2

Radiolysis of Resist Polymers. II.

Poly(haloalkylmethacrylates) and Copolymers with Methylmethacrylate

By

G.N. Babu, A. Narula, P.H. Lu, X. Li, S.L. Hsu and James C.W. Chien

Prepared for Publication

in

Macromolecules

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Department of Polymer Science and Engineering  
Materials Research Laboratories  
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Amherst, Massachusetts 01003

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Radiolysis of Resist Polymers: II.  
Poly(haloalkylmethacrylates) and Copolymers with Methylmethacrylate

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Homopolymers of 2-fluoroethylmethacrylate (FEMA), 2-chloroethylmethacrylate (CEMA), 2-bromoethylmethacrylate (BEMA), 2,2,2-trichloroethylmethacrylate (TCEMA), 2,3-dibromopropylmethacrylate (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 ( $G_S$ ), crosslinking ( $G_X$ ) and radical formation ( $G_R$ ) were determined, the former from  $\bar{M}$  versus 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 positive E-beam resist having  $G_S = 2.4$ ,  $G_X = 0$  and  $G_R = 4.1$ . Copolymers with < 34 mole % of TCEMA is either inferior or comparable to PMMA in these properties. The bromine containing systems show high crosslinking 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 resist material. Copolymers of FEMA and MMA have slight tendency toward crosslinking even at low dose. Poly(MMA-co-CEMA) have properties intermediate of those containing FEMA and BEMA. Based on 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 crosslinking. Both types of processes can occur simultaneously but usually one predominates<sup>2</sup>. Ideally, a positive resist should degrade exclusively by chain scission and a negative resist via crosslinking. The radiolysis pathways reflect the chemical structure of the polymer<sup>3</sup>. Polymers with activated tertiary hydrogen, such as polystyrene, mainly crosslink, whereas polymers with quaternary main chain carbon atoms, such as PMMA predominately 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 crosslinking tendencies are in the opposite order<sup>5-8</sup>. The

crosslinking yield,  $G_x$ , can be substantially lowered by copolymerizing the methyl- $\alpha$ -haloacrylate with a non-crosslinking monomer such as methacrylonitrile<sup>5</sup> and methyl-methacrylate<sup>8</sup>. However, the radiation chemistry of the copolymers is mainly determined by the  $\alpha$ -haloacrylate monomer units.

The mechanisms for crosslinking proposed for homo- and copolymers of methyl- $\alpha$ -haloacrylates<sup>8</sup> are not applicable to haloalkylmethacrylates. Poly(trichloroethylmethacrylate) (PTCEMA) has been reported<sup>9</sup> to exhibit high chain scission sensitivity toward electron irradiation at low dose and crosslinks at high dose. Fluoroalkylmethacrylate polymers were also found<sup>7,10</sup> to degrade more efficiently than PMMA. In a comparison of resists for x-ray lithography<sup>11</sup>, poly(2-fluoro-ethylmethacrylate) (PFEMA) was found to be more sensitive than poly(2-chloroethyl-methacrylate) (PCEMA) and poly(2-bromoethylmethacrylate) (PBEMA).

The central purpose of this work was to study the radiation chemistry of poly(haloalkylmethacrylates) 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-dibromopropylmethacrylate (DBPMA).



## Experimental Section

### Materials:

The 2-haloethylmethacrylates 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<sup>8</sup>.

## Results and Discussion

Copolymerization: As it was pointed out in the previous paper<sup>8</sup>, 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 (haloalkylmethacrylate) in the feed,  $m_1$  ( $m_2$ ) its content in 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 mole percent of MMA and 20 mole per cent of TCEMA. Table I summarizes the copolymerization data and molecular weights of the copolymers. Figure 1 shows the variation of copolymer composition versus comonomer feed of MMA and TCEMA and that the curve calculated from the reactivity ratio (Table II) is in good agreement with experimental results. Similar agreement was observed for the four other copolymer systems; their copolymerization curves are not included in this paper but the relevant informations are contained in Tables I and II.

Table I. Polymerization Data and Properties of Polymers

|      | Comonomer      |                | Conversion<br>% | $\bar{M}_n \times 10^5$ | $\bar{M}_w \times 10^5$ | $\bar{M}_w/\bar{M}_n$ |
|------|----------------|----------------|-----------------|-------------------------|-------------------------|-----------------------|
|      | M <sub>2</sub> | m <sub>2</sub> |                 |                         |                         |                       |
| 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  |     |      |

---

The low  $\overline{M}_w/\overline{M}_n$  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  
Haloalkylmethacrylates ( $r_2$ ) 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  |

All the homo- and copolymers of FEMA, CEMA, and BEMA are soluble in  $\text{CHCl}_3$ , THF, DMF, and toluene at room temperature. Those of TCEMA are soluble in  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CN}$  and THF but insoluble in  $\text{CH}_3\text{OH}$  and petroleum ether. PDBPMA is soluble in methacrylonitrile, dioxane,  $\text{CHCl}_3$  and THF. PTCEMA has a high  $T_g$  of  $132^\circ$ ; the  $T_g$ 's for poly(MMA-co-TCEMA) with 53, 34, 24, and 9 mole % of TCEMA are 122, 117, 114 and  $112^\circ$ , respectively.

#### Gamma Radiolysis:

a. Yields. The yields of scission and crosslinking 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 in Table III. From the EPR intensities the values of  $G_r$  were obtained and also

given in Table III.

Among the three poly(2-haloethylmethacrylates), 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  $\bar{M}_n$  versus dose plot ( $S_n$ ) is exactly twice the slope of the  $\bar{M}_w^{-1}$  versus dose plot ( $S_w$ ). Eranian et al.<sup>11</sup> found the polymer to be three times more sensitive than PMMA as an x-ray (8.34Å) resist using a 3:1 methylisobutylketone/isopropanol developer.

Table III. Gamma 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  |       |

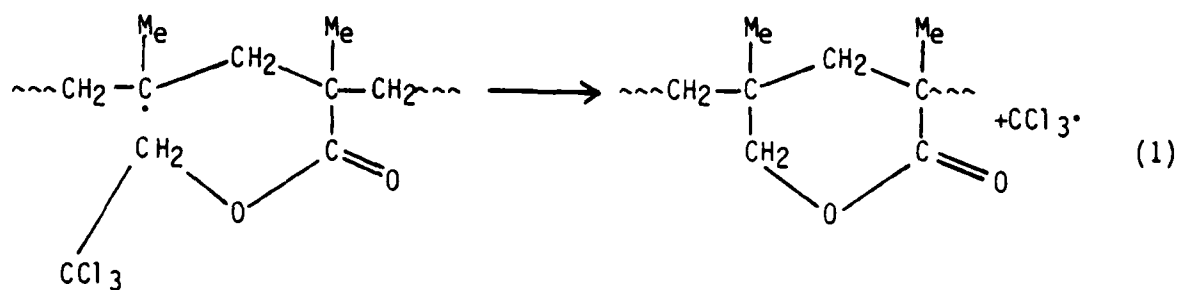
|                          |     |      |      |     |
|--------------------------|-----|------|------|-----|
| Poly(91 MMA-co-9 TCMA)   |     | 1.4  | 0    | 1.5 |
| Poly(76 MMA-co-24 TCMA)  |     | 0.54 | 0    | 1.1 |
| Poly(66 MMA-co-34 TCMA)  |     | 1.2  | 0    | 1.0 |
| Poly(47 MMA-co-53 TCMA)  |     | 1.9  | 0    | 2.6 |
| Poly(TCMA)               |     | 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 |

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 mole % of 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 mole % of one of the monomers. The values of  $G_x$  are non-zero for the FEMA-MMA copolymers. However, since the irradiated copolymers were soluble, the small values of  $G_x$  need not imply crosslinking. Since the copolymers synthesized at low conversion have  $\overline{M}_w/\overline{M}_n$  less than the most probable distribution (Table I), random radiolysis causes the polydispersity to approach the most probable distribution resulting in non-zero values for  $G_x$ <sup>8</sup>.

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

PBEMA gels upon  $\gamma$ -irradiation. There is also a definite tendency toward crosslinking 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 TCCEMA content reaching a minimum value of 0.54 at 24 mole %. Then  $G_S$  increases at small TCCEMA content and approaches the sensitivity of PMMA. At 24 mole % of TCCEMA the copolymer contains higher alternating  $M_1M_2$  diads 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:



The reaction may be favored by the elimination of the stable  $\text{CCl}_3$  radical.



Radiolysis of poly(DBPMA) and copolymers containing more than 30 mole % of this monomer were crosslinked by radiolysis. Therefore,  $G_s$  and  $G_x$  values cannot be determined by the present method. The  $G_r$  value is very high  $\sim 5$ , but the sensitivity to crosslinking rules out DBPMA in positive resist applications but may find usage as negative resist.

b. ESR. Gamma irradiated homo- and copolymers of FEMA showed only the nineline ESR spectra characteristic of the PMMA propagating radical. The radical yield is highest for the homopolymer. However, upon heating to  $50^\circ$ ,  $[R^\bullet]$  decreases by 60% (Figure 3). Between  $50^\circ$  and  $80^\circ$   $[R^\bullet]$  remained relatively constant; above  $80^\circ$  the ESR intensity decreases very rapidly and becomes unobservable at ca  $120^\circ$ . In contrast, the ESR signal intensity of  $\gamma$ -irradiated copolymers was unaffected by heating to  $60^\circ$ . Rapid decrease in  $[R^\bullet]$  commences at ca  $70^\circ$  and their curves merge with that of poly(FEMA). The differences between the homo- and copolymers may be attributed to geminal recombination of FEMA radicals in the homopolymers whereas the radicals are far separated in the copolymers and their combination occurs only above  $T_g$  of the copolymers.

Gamma irradiation of homo- and copolymers of CEMA produced nine-line spectra of PMMA type radical. The EPR intensity is stable at ambient temperatures over 100 hrs. However, it decreases rapidly with heating and the radical disappears at  $80^\circ$  (Figure 4). The CEMA copolymers have  $T_g$ 's ca  $30^\circ$  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 EPR spectra of PTCEMA and poly(MMA-co-TCEMA) are the same as that of the PMMA radicals<sup>2</sup>. Tada<sup>9</sup>, however, reported that irradiated PTCEMA produced radicals having hyperfine characteristics for a carbon centered radical having hyperfine interaction with two equivalent chlorine nuclei ( $^{35}\text{Cl}$  A = 5.2G). 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- $\alpha$ -chloroacrylate-trichloroethyl methacrylate copolymers we observed radicals attributable to a  $-\text{CCl}_2$  species. These results will be published elsewhere.

The radicals produced upon  $\gamma$ -irradiation of homo- and copolymers of DBPMA have identical ESR spectra as  $\gamma$ -irradiate PMMA.

c. GC-MS. Table IV summarizes the volatile products of  $\gamma$ -radiolysis as analyzed by GC-MS.

Table IV

Table IV. Volatile  $\gamma$ -radiolysis Products<sup>a</sup>

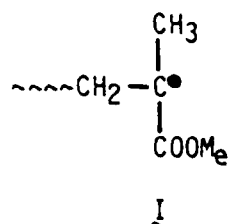
| Products                                         | Relative ion current |       |        |                         |      |      |       |
|--------------------------------------------------|----------------------|-------|--------|-------------------------|------|------|-------|
|                                                  | Homopolymers         |       |        | Copolymers <sup>b</sup> |      |      |       |
|                                                  | PFEMA                | PBEMA | PTCEMA | FEMA                    | CEMA | BEMA | TCEMA |
| CH <sub>4</sub>                                  | 2.8                  | 4.0   | 4.1    | 5.7                     | 3.9  | 1.7  | 0.4   |
| CO, CH <sub>2</sub> = CH <sub>2</sub>            | 6.3                  | 17.8  | 19.7   | 18.7                    | 10.4 | 17.6 | 0.1   |
| C <sub>2</sub> H <sub>6</sub> , HCO <sup>+</sup> | --C                  | --    | 1.0    | --                      | --   | --   | 0.1   |
| H <sup>35</sup> Cl                               | --                   | --    | 60.2   | --                      | 14.2 | --   | 18.4  |
| H <sup>37</sup> Cl                               | --                   | --    | 26.2   | --                      | 7.3  | --   | 6.6   |
| C <sub>3</sub> H <sub>6</sub>                    | --                   | --    | 0.3    | --                      | --   | --   | 0.3   |
| CO <sub>2</sub>                                  | 100                  | 100   | 100    | 100                     | 100  | 100  | 0.2   |
| C <sub>2</sub> H <sub>5</sub> F                  | 12                   | --    | --     | 30                      | --   | --   | --    |
| CH <sub>3</sub> <sup>35</sup> Cl                 | --                   | --    | 9.6    | --                      | 10.7 | --   | 0.7   |
| CH <sub>3</sub> <sup>37</sup> Cl                 | --                   | --    | --     | --                      | 3.4  | --   | --    |
| HCOOCH <sub>3</sub>                              | --                   | --    | 0.8    | 14.9                    | 3.1  | --   | --    |
| CH <sub>3</sub> CH <sub>2</sub> <sup>35</sup> Cl | --                   | --    | --     | --                      | 3.3  | --   | --    |
| CH <sub>3</sub> CH <sub>2</sub> <sup>37</sup> Cl | --                   | --    | --     | --                      | 1.3  | --   | --    |
| CH <sub>2</sub> = C(Me)CO <sup>+</sup>           | --                   | --    | 0.4    | --                      | --   | --   | 1.1   |
| CH <sub>3</sub> COOCH <sub>3</sub>               | --                   | --    | 0.7    | 7.2                     | --   | --   | 1.0   |
| CH <sub>2</sub> Cl <sub>2</sub> (Mass No. 83-88) | --                   | --    | 1.7    | --                      | --   | --   | 1.2   |

|                                                   |    |     |     |    |     |    |     |
|---------------------------------------------------|----|-----|-----|----|-----|----|-----|
| $\text{CH}_3^{79}\text{Br}$                       | -- | 2.4 | --  | -- | 3.3 | -- | --  |
| $\text{CH}_3^{81}\text{Br}$                       | -- | 1.2 | --  | -- | 3.0 | -- | --  |
| $\text{CH}_2 = \text{C}(\text{Me})\text{COOCH}_3$ | -- | --  | --  | -- | 2.4 | -- | --  |
| $\text{CHCl}_3$ (Mass No. 117-124)                | -- | --  | 6.7 | -- | --  | -- | 6.7 |
| $\text{C}_2\text{Cl}_6$                           | -- | --  | 0.4 | -- | --  | -- | 0.4 |

- 
- a. Relative yield normalized to 100 for  $\text{CO}_2$ .
- b.  $m_2 = 0.3$  (FEMA); 0.87 (CEMA); 0.22 (BEMA); 0.24 (TCEMA).
- c. Not detected.

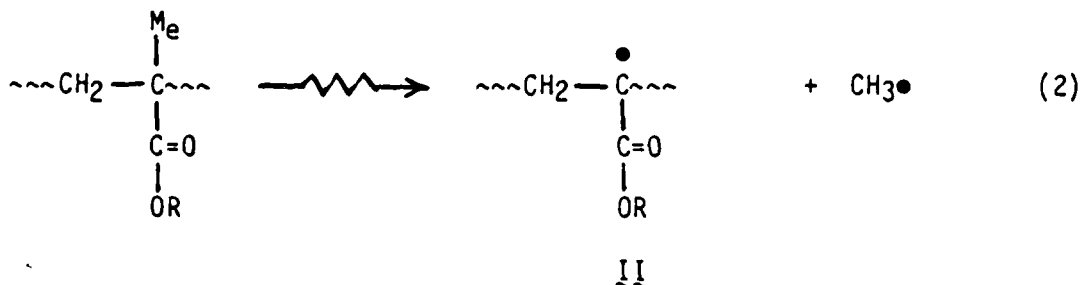
### Mechanism

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



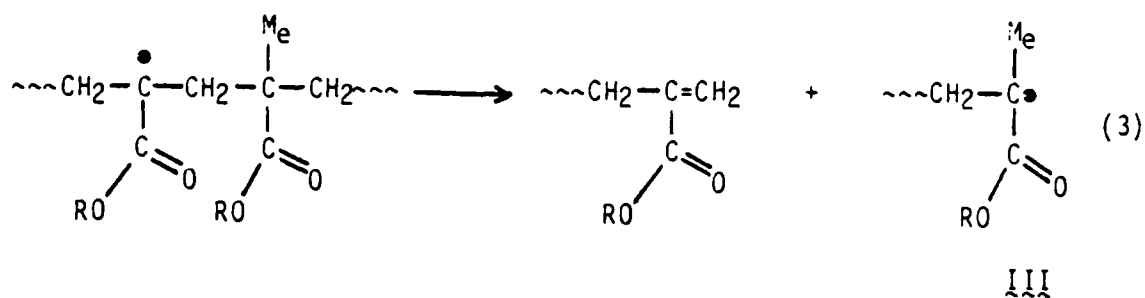
This suggests the direct radiolytic main chain scission is either of minor importance or the pair of terminal macroradicals undergo efficient cage recombination.

Let us denote R to be the  $-\text{C}_2\text{H}_4\text{F}$ ,  $-\text{C}_2\text{H}_4\text{Cl}$ ,  $-\text{C}_2\text{H}_4\text{Br}$ , or  $-\text{CH}_2\text{CCl}_3$  groups. Since all the homo- and copolymers produce methane, the common primary radiolysis event is



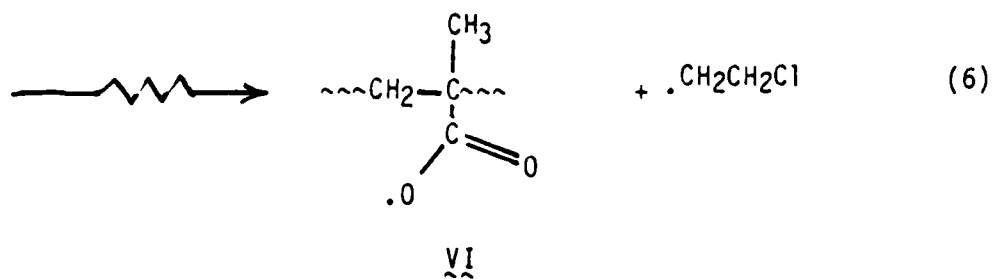
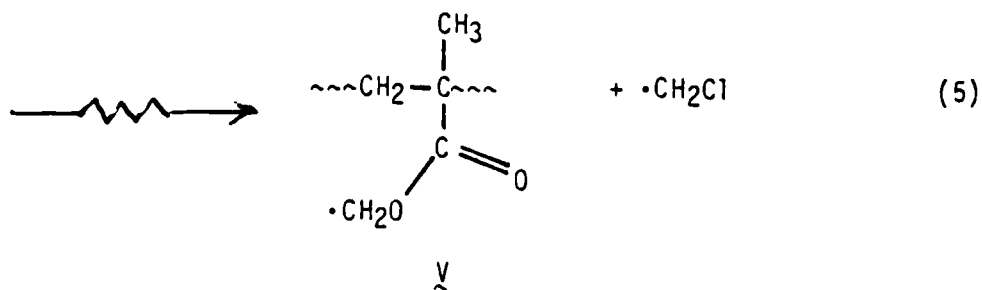
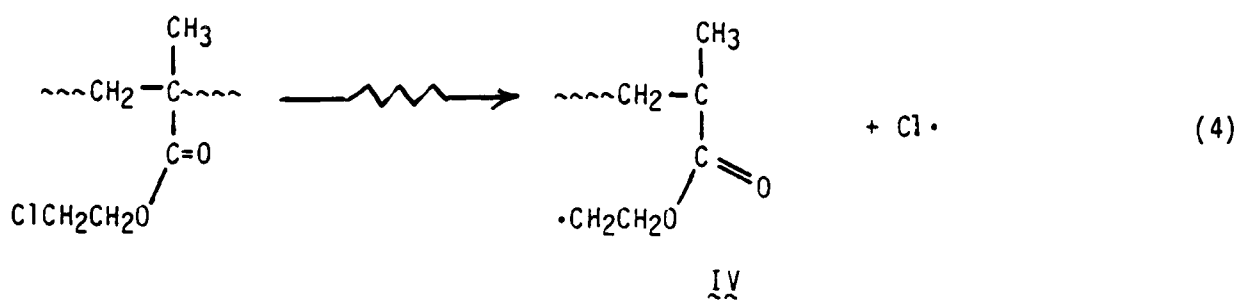
However, radical II was not observed which would correspond to the five-line or seven-line ESR spectra of  $\gamma$ -irradiated polymers of methyl- $\alpha$ -haloacrylates<sup>8</sup>.

Probably radical II readily undergoes chain scission,

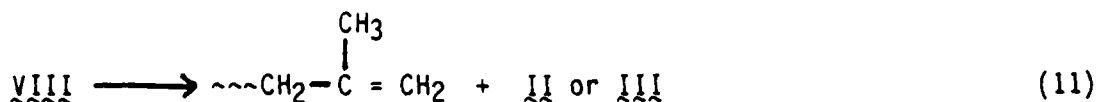
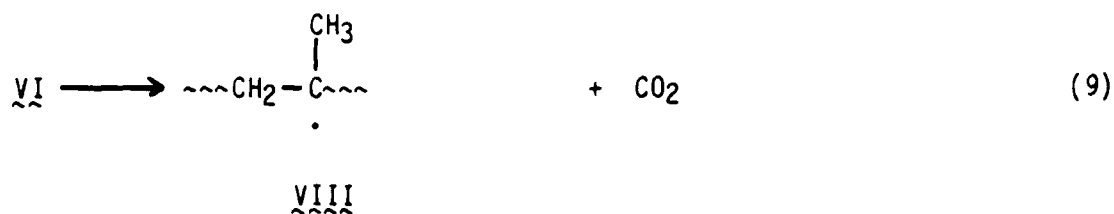
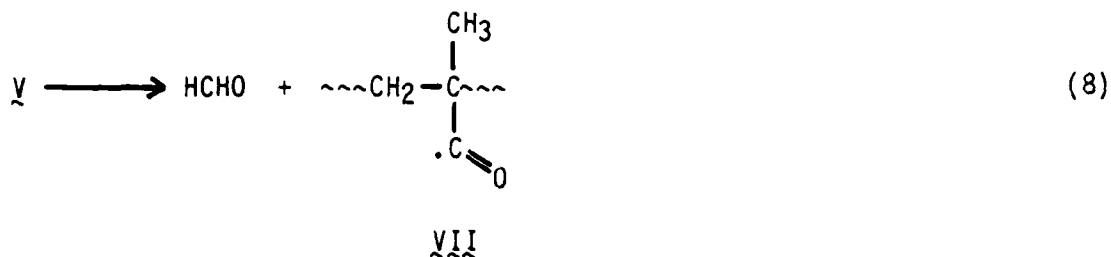


The ESR spectra of radicals I and III would be indistinguishable.

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

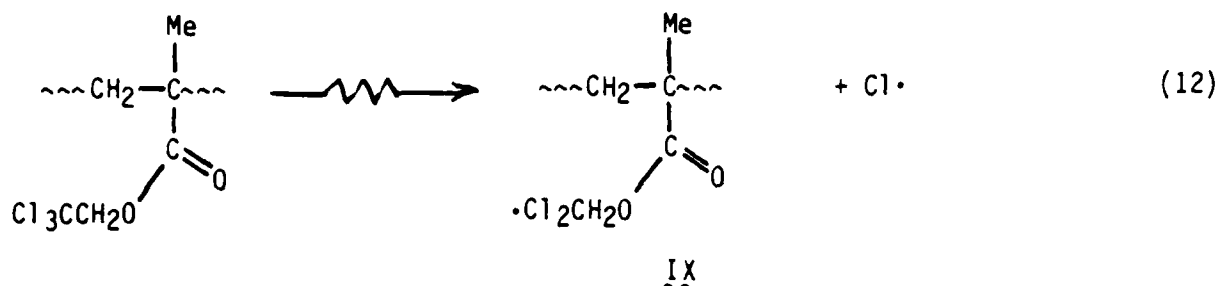


These reactions may be followed by secondary processes:

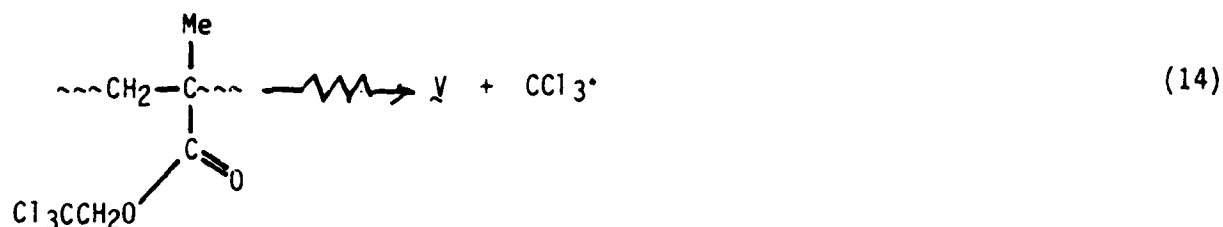


HCl, MeCl, EtCl, CO<sub>2</sub> and CO were all observed by GC-MS. The FEMA polymers undergo the similar series of reactions. One cannot say for certain whether dissociative electron capture by fluorine also occurs, because HF was not found. However, HF, if formed, will probably react with the glass container. The same cannot be said for BEMA because neither HBr nor EtBr were detected. For the bromine derivative, apparently reaction 5 is favored over reactions 4 and 6 to produce MeBr.

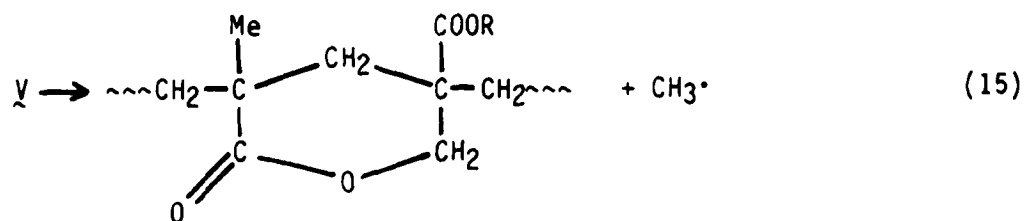
In the case of TCMA polymers, dissociative electron capture of chlorine occurs to produce HCl.



However, a very significant process is the cleavage of the stable  $\cdot\text{CCl}_3$  radical

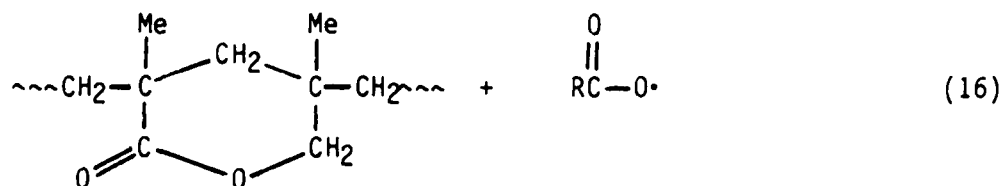


which leads to  $\text{CHCl}_3$  and  $\text{C}_2\text{Cl}_6$ . Among all the polymers investigated here, only poly(TCEMA) and copolymers with MMA show no tendency toward crosslinking. This means that main chain radicals such as II and VIII were not produced or in amounts much less than in the radiolysis of the other polymers. An intramolecular lactone formation may be proposed via reaction 1 or where R is either



or

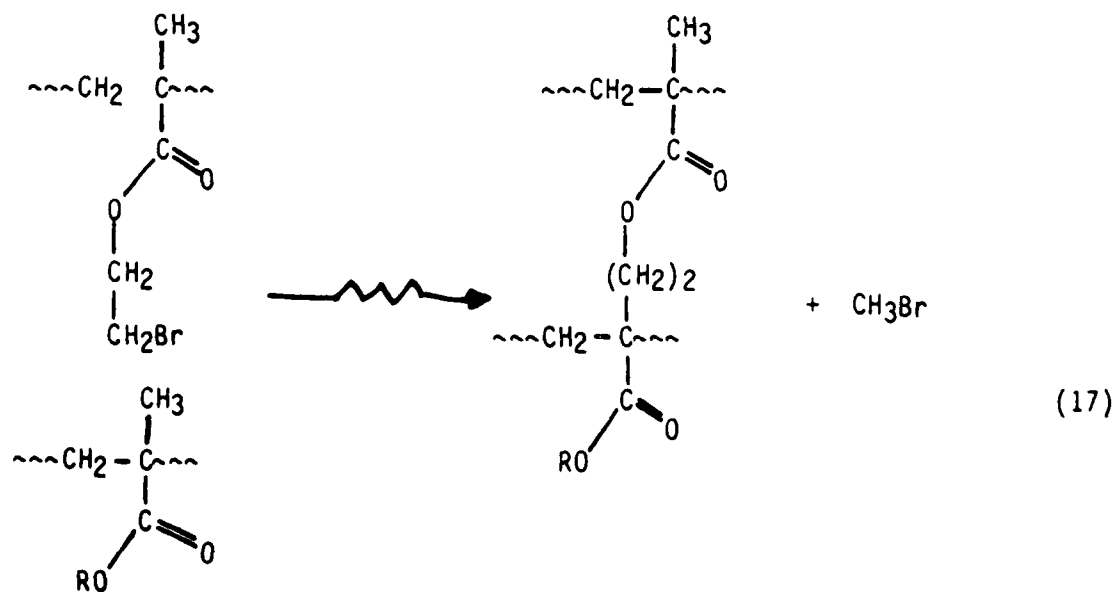




R is  $-\text{CH}_2\text{CCl}_3$  in PTCEMA or copolymers rich in TCEMA monomer, or R is  $\text{CH}_3$  for copolymers with high MMA content. Reactions 1 and 15 are apparently so efficient that the radiolysis of poly(MMA-co-TCEMA) produces very little  $\text{CO}_2$  and CO. Infrared spectroscopic evidences for lactone formation will be given in papers describing thermolysis of these polymers.

Some of the copolymers of FEMA and CEMA have  $G_x = 0$ , others have very small  $G_x$  values; the irradiated polymer remains soluble. We have pointed out<sup>8</sup> that very small  $G_x$  values may be due to chain extension more than crosslinking.

Poly(BEMA) and copolymers containing >30 mole % of DBPMA were crosslinked by radiolysis. This ease of crosslinking was also observed for polymers of methyl- $\alpha$ -bromoacrylate. This characteristic may be related to the ease of  $\text{CH}_3\text{Br}$  elimination. The possible reactions may be



and others like it.

The ease of crosslinking of the BEMA homo and copolymers as compared to the CEMA and FEMA polymers may have another 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 $\cdot$  and Cl $\cdot$  atoms can diffuse more readily from their site of formation to react elsewhere. On the other hand, the heavier Br $\cdot$  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 crosslink. We have found in our studies of other halogenated polymers that the bromine containing polymers generally crosslink much more readily than the chlorine and fluorine containing analogs in radiolysis.

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

#### Acknowledgement

The authors wish to acknowledge the GC-MS analysis by Dr. G. Riska. The work was supported in part by a grant from the Office of Naval Research.

FIGURE CAPTIONS

Figure 1: Copolymer composition versus comonomer feed of MMA and TCMA;

( $\circ$ ) experimental value; curve from copolymerization equation and reactivity ratio.

Figure 2: Effect of  $\gamma$ -ray dose on the molecular weights ( $\circ$ )  $\overline{M}_n$  and ( $\bullet$ )  $\overline{M}_w$  for a

(a) PFEMA; (b) PCEMA; (c) PBEMA; (d) PTCEMA; (e) PMA.

Figure 3: Effect of heating on the ESR spectrum of ( $\circ$ ) poly(FEMA),

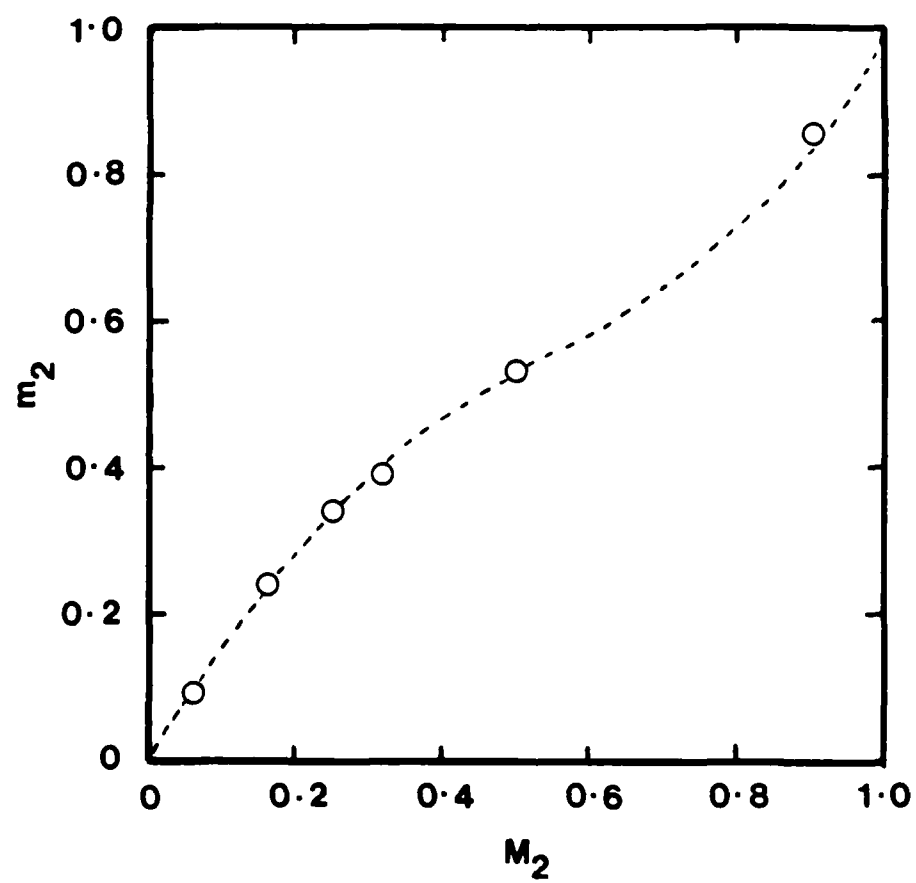
( $\bullet$ ) poly(70 MMA-co-30 FEMA) ( $\Delta$  poly(89 MMA-co-11 FEMA). Dose = 0.99

$M_{rad}$ .

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

References and Notes

1. On leave from the Department of Chemistry, Indian Institute of Technology, Powai, Bombay-400, 076, India.
2. A. Todd, J. Polym. Sci., 72, 223 (1960).
3. A.A. Miller, E.J. Lawton and J.S. Balwit, J. Polym. Sci., 14, 503 (1954).
4. L.A. Wall, J. Polym. Sci., 17, 141 (1955).
5. J.N. Helbert, C.Y. Chen, C.U. Pittman, Jr., and G.L. Hagnauer, Macromolecules, 11, 1104 (1978).
6. C.Y. Chen, C.U. Pittman, Jr., and J.N. Helbert, J. Polym. Sci., Polym. Chem. Ed., 18, 169 (1980).
7. C.U. Pittman, Jr., C.Y. Chen, M. Ueda, J.N. Helbert and J.H. Kwiatkowski, J. Polym. Sci., Polym. Chem. Ed., 18, 3413 (1980).
8. G.N. Babu, A. Narula, S.L. Hsu and J.C.W. Chien, Macromolecules, submitted.
9. T. Tada, J. Electrochem. Soc., 126, 1635 (1979).
10. H. Ito, D.C. Miller and C.G. Willson, Macromolecules, 15, 915 (1982).
11. A. Eranian, A. Couttet, E. Datamanti and J.C. Dubois, ACS Polymer Preprints, 42, 779 (1980).



**Fig. 1**

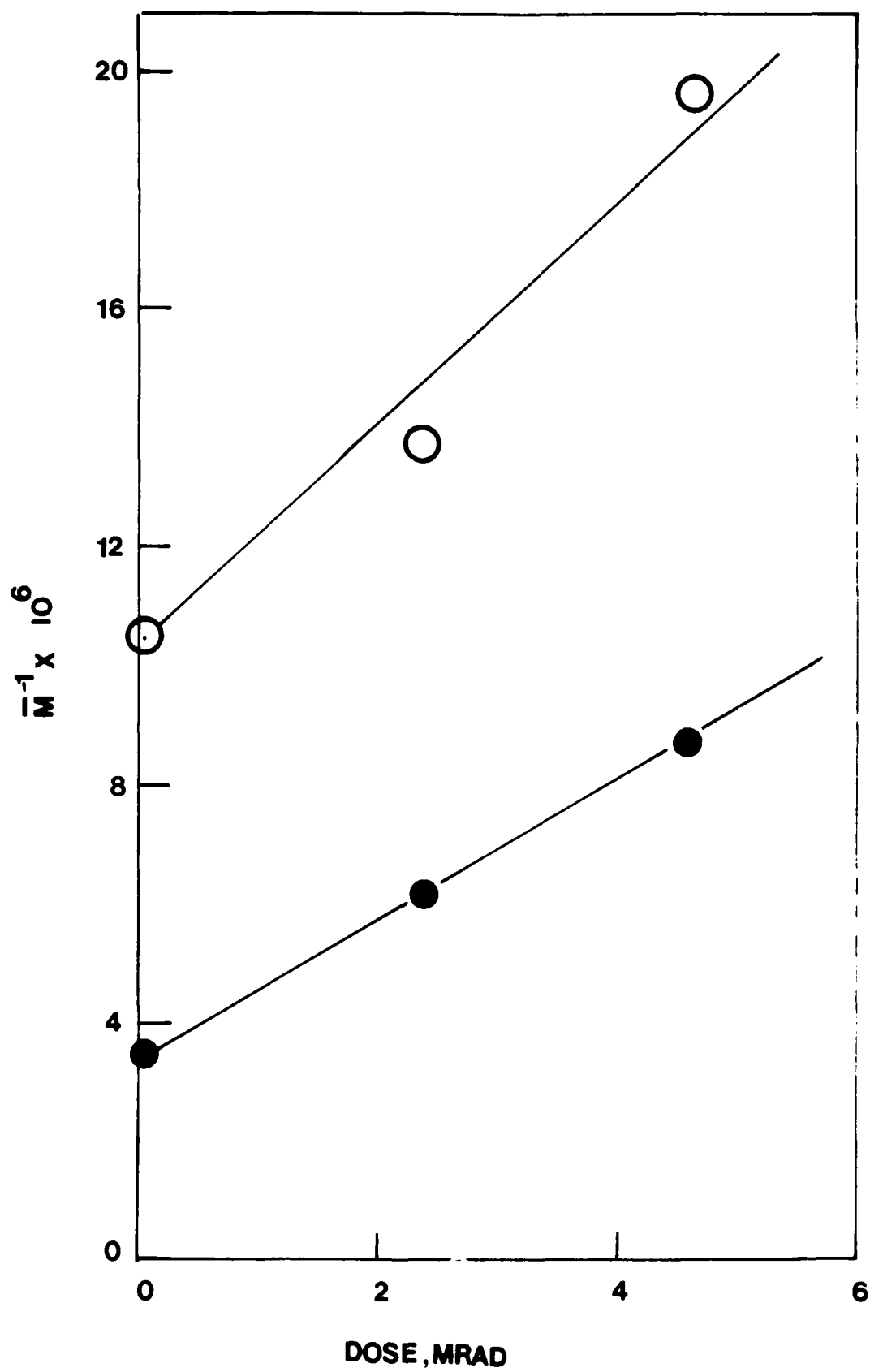


Fig.2a

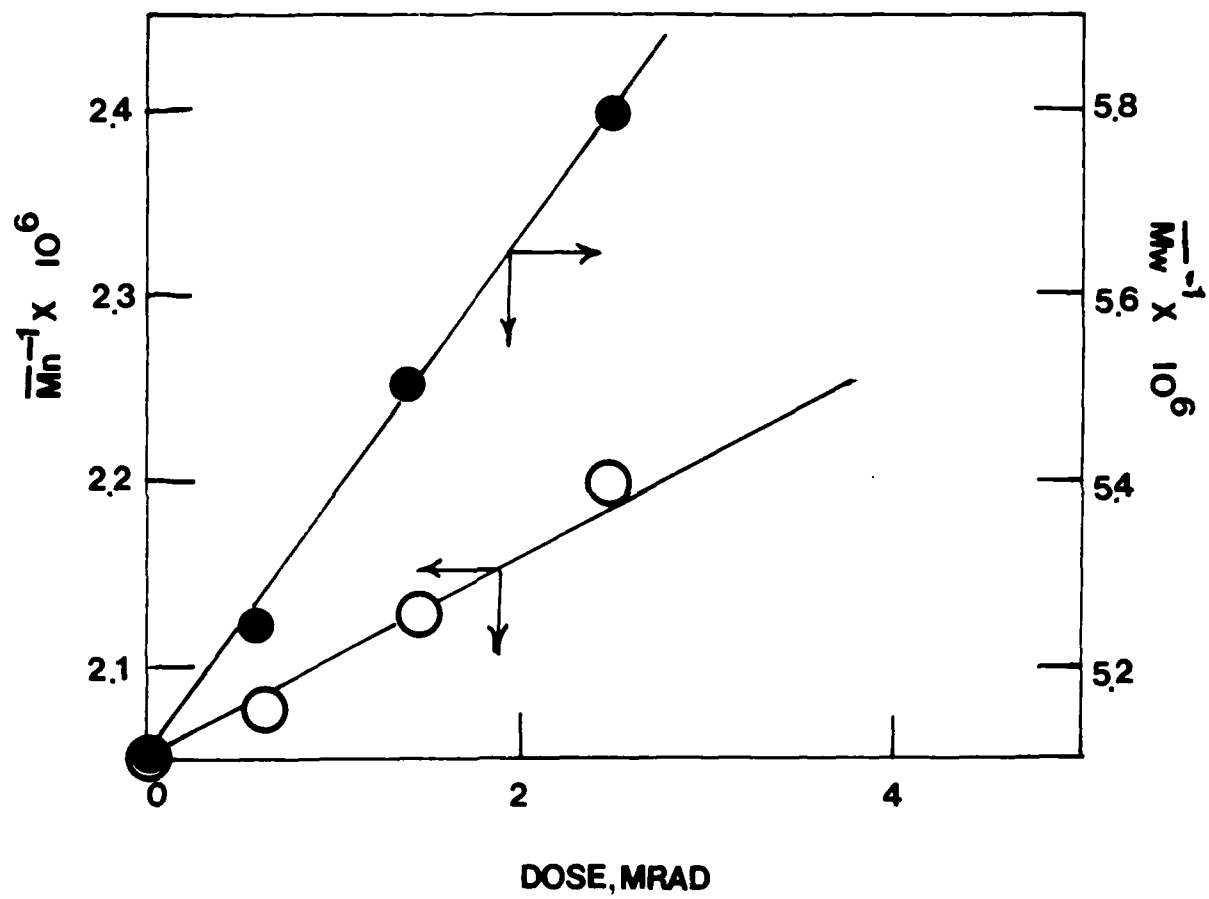


Fig. 2b

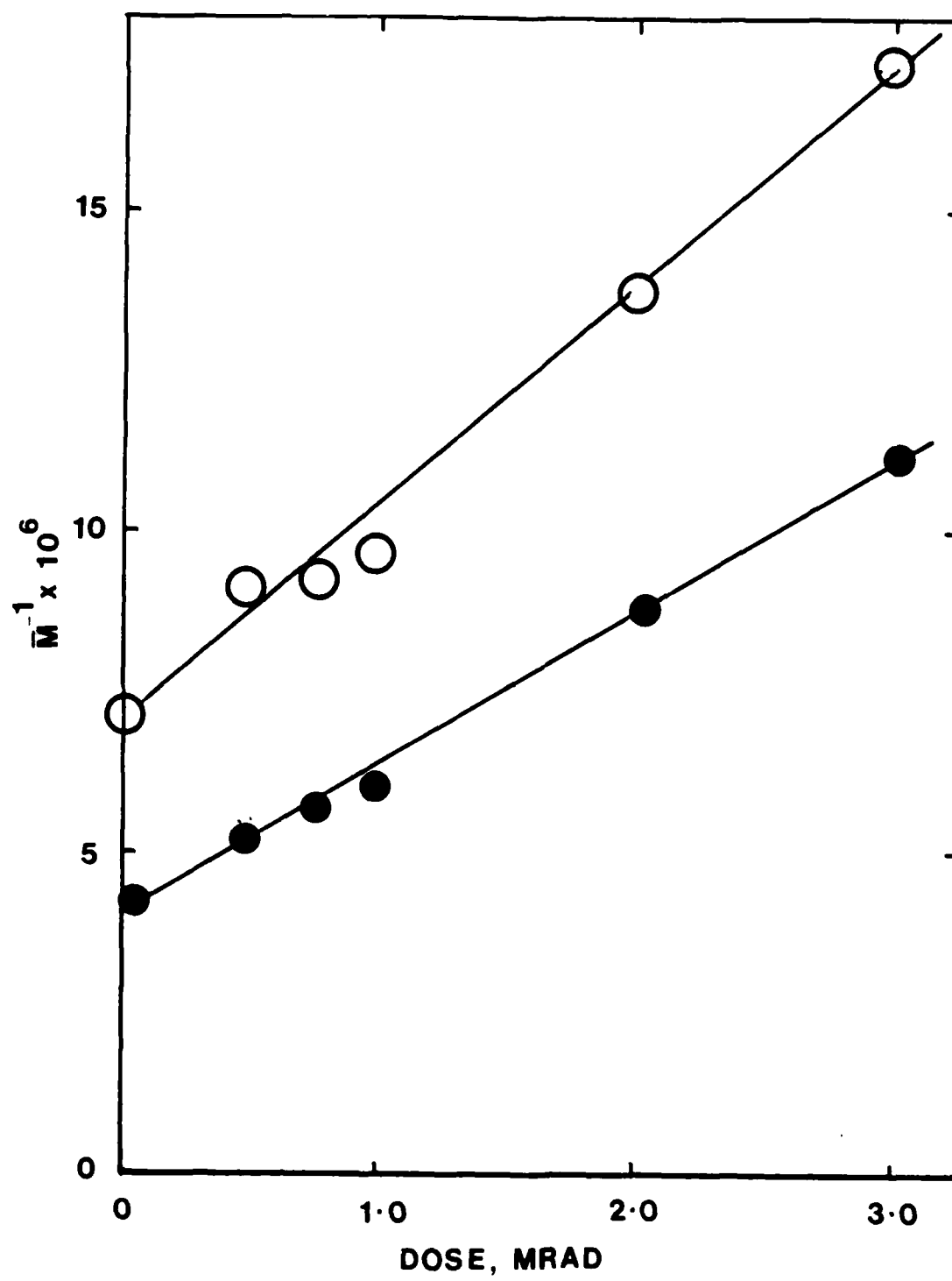


Fig.2C



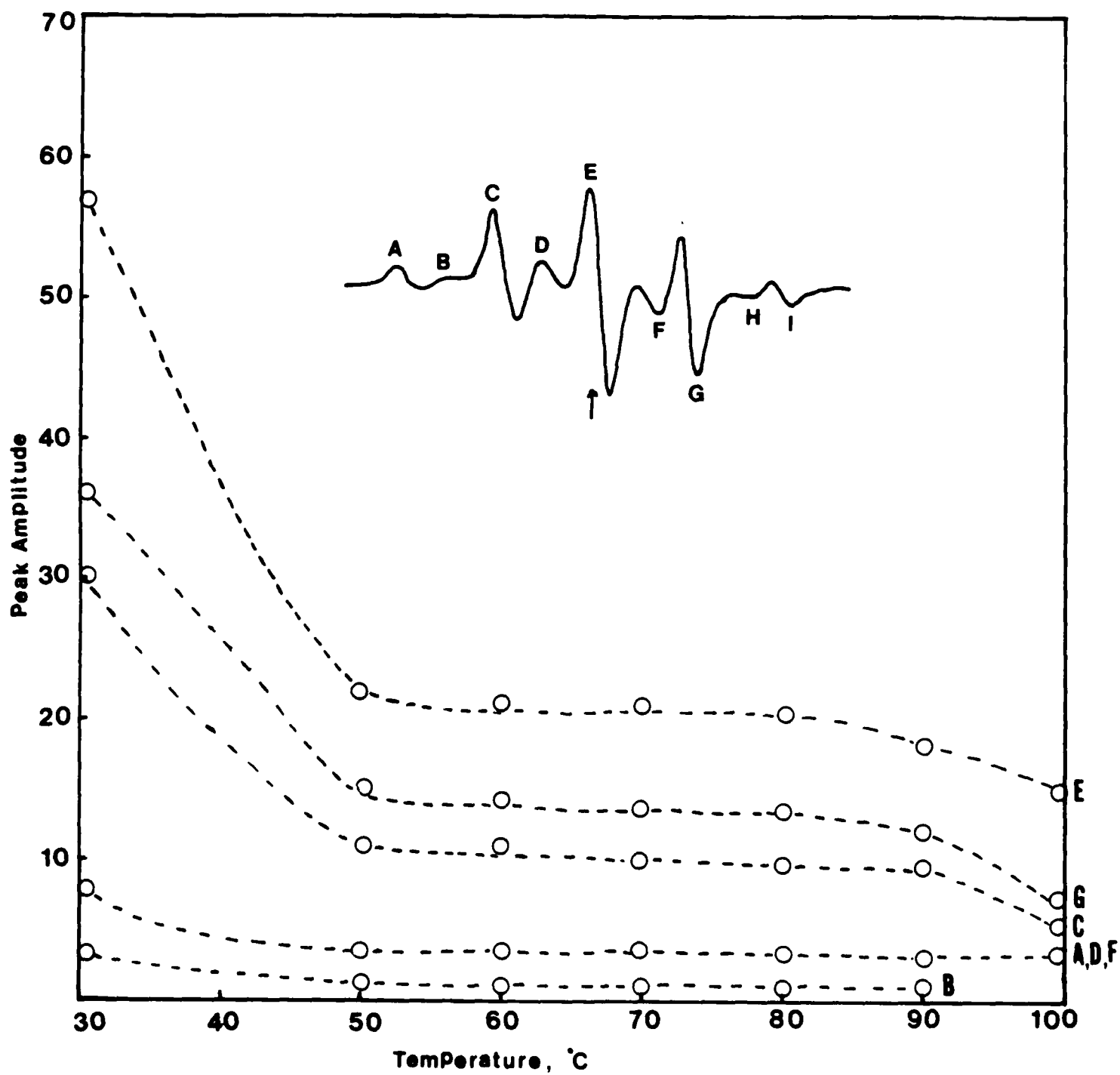


Fig. 3a

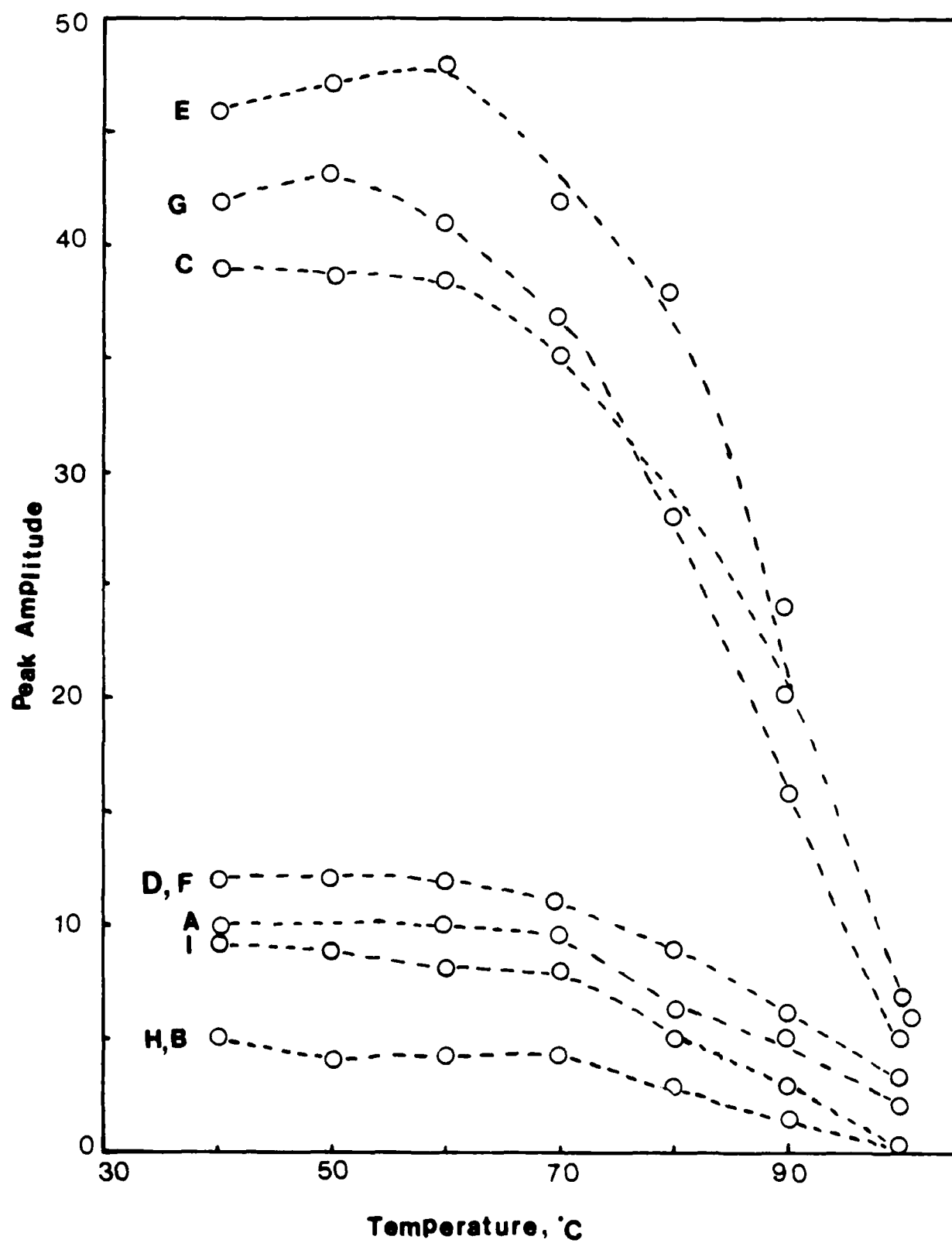


FIG. 3b

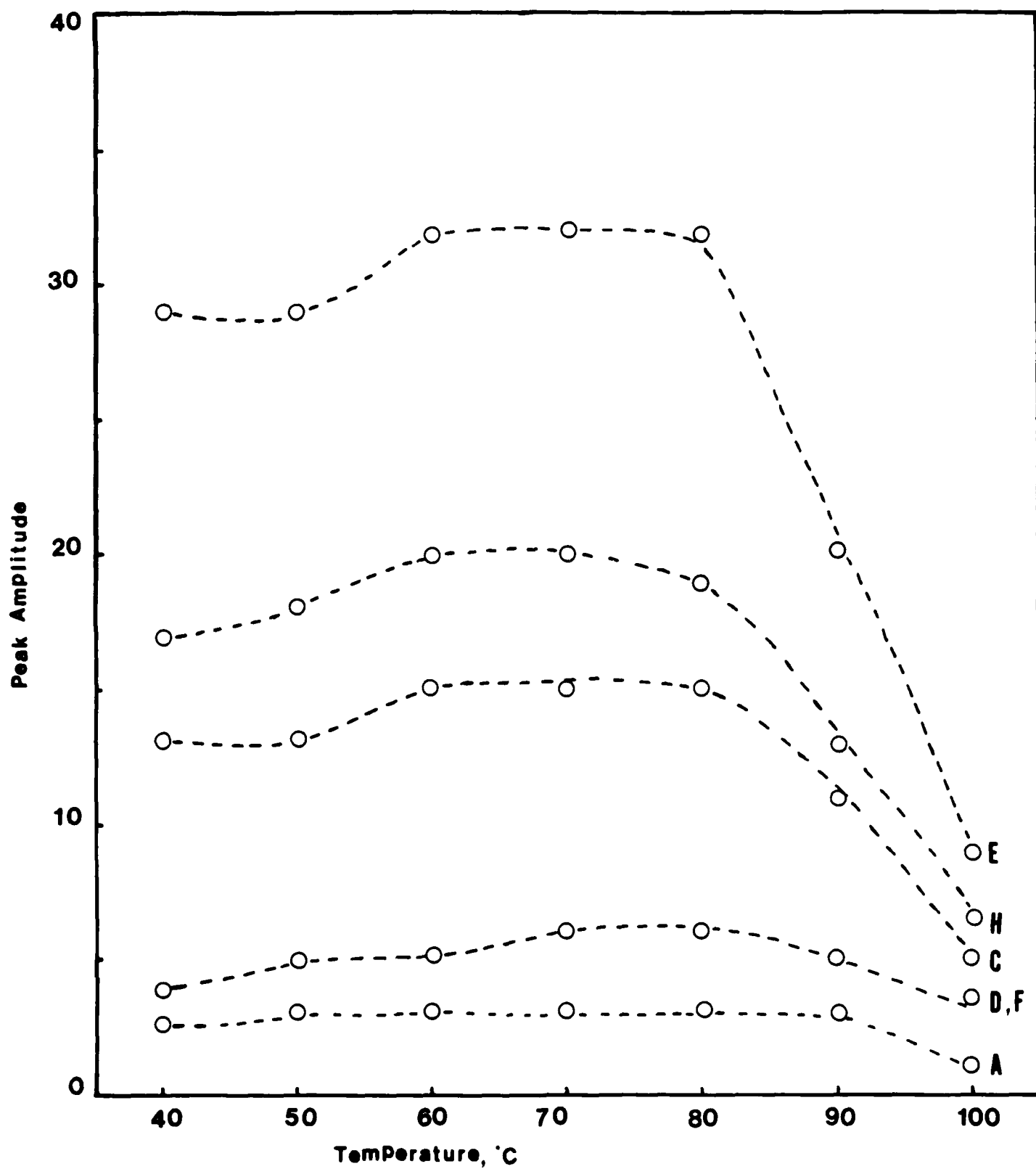
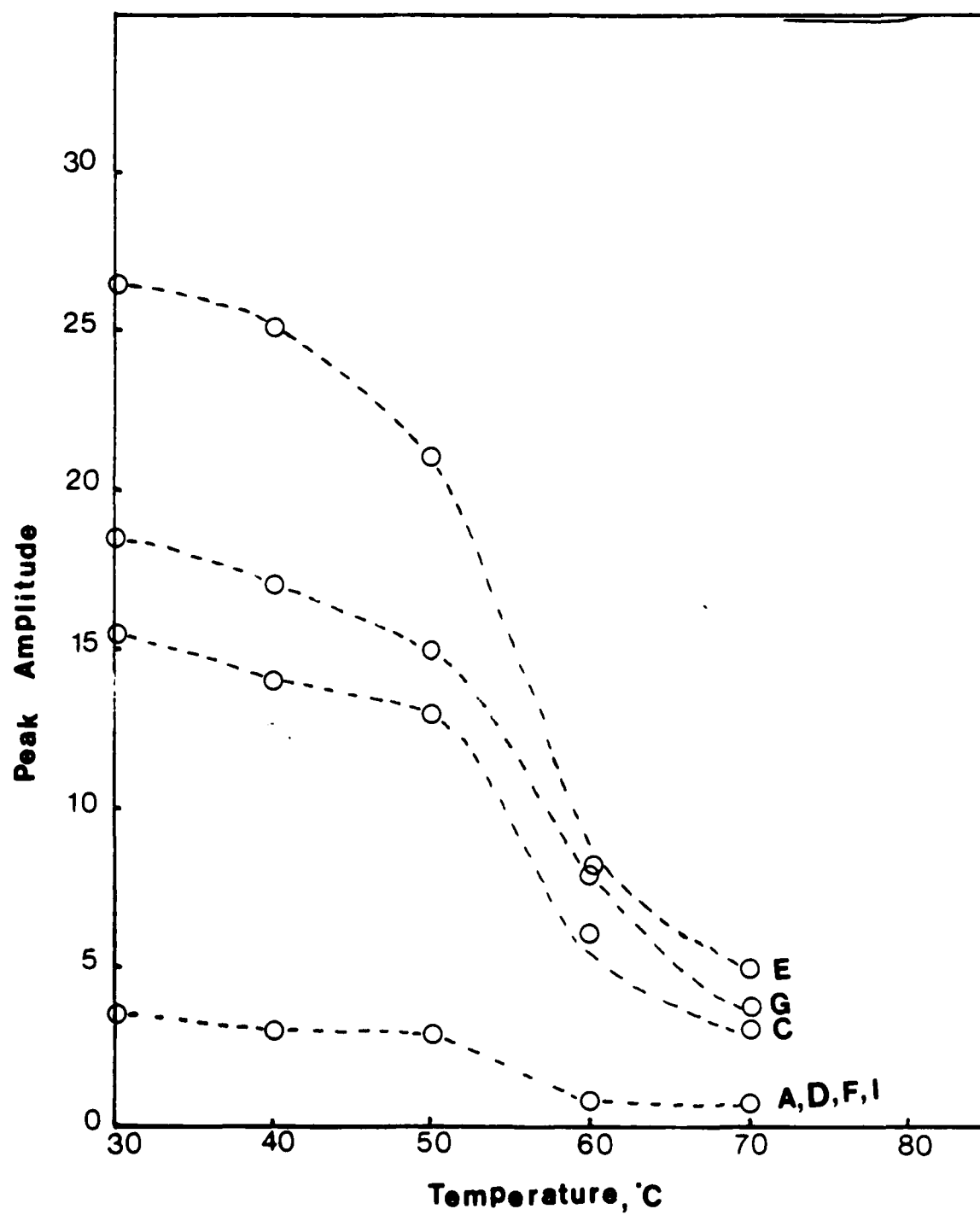


Fig. 3c



**Fig. 4**

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