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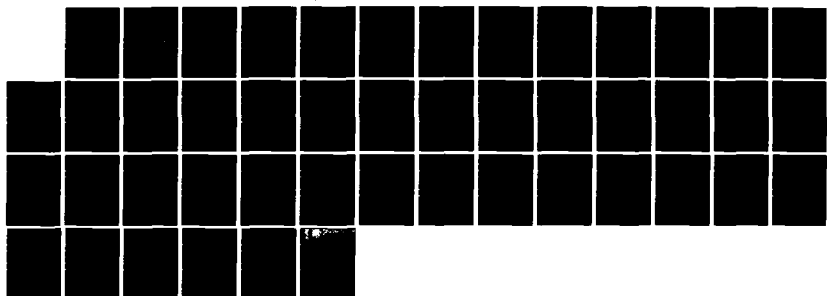
RADIOLYSIS OF RESIST POLYMERS 1  
POLY(METHYL-ALPHA-HALOACRYLATES) AND COPO. (U)  
MASSACHUSETTS UNIV AMHERST MATERIALS RESEARCH LAB  
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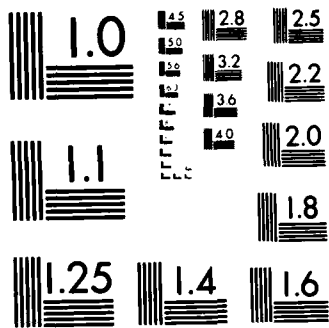
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TECHNICAL REPORT NO. 1

Radiolysis of Resist Polymers. I.

Poly(methyl- $\alpha$ -haloacrylates) and Copolymers with Methylmethacrylate

By

G.N. Babu, A. Narula, S.L. Hsu, and James C.W. Chien

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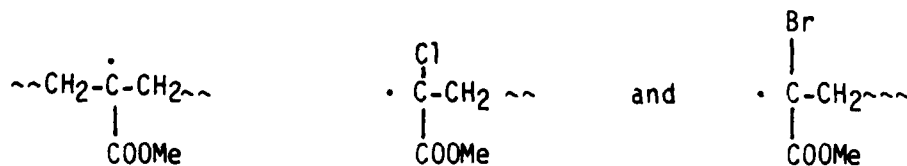
Radiolysis of Resist Polymers. I. Poly(methyl- $\alpha$ -haloacrylates) and  
Copolymers with Methylmethacrylate

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Abstract

Methyl- $\alpha$ -chloroacrylate (MCA) and methyl- $\alpha$ -bromoacrylate (MBA) were copolymerized with methylmethacrylate (MMA) over a broad range of composition. The reactivity ratios for MMA and MCA are 0.36 and 0.26, respectively; they are 0.19 and 0.16 for MMA and MBA copolymerization. The tendency toward alternation of comonomer of methyl- $\alpha$ -haloacrylates with MMA decreases in the order Br>Cl>F. The relative reactivities of these monomers toward the MMA radical also decrease in this order. The values of  $G_s$  (number of scissions per 100 eV of energy absorbed) for poly(MCA) and poly(MBA) are larger than for PMMA;  $G_r$  (number of radicals per 100 eV of energy absorbed) values are in the range of 7 to 9. All copolymers of MCA have non-zero  $G_x$  values (number of crosslinks per 100 eV of energy absorbed), but they are soluble in common solvents after  $\gamma$ -radiolysis. Copolymers of MBA with MMA with >7% of the former are insolubilized due to extensive crosslinking by gamma radiolysis. ESR spectra of  $\gamma$ -irradiated homo- and co-polymers of MCA and MBA had been attributed



to radicals. GC-MS analysis of the radiolysis products of the MCA homo- and co-polymers, together with ESR and radiolysis yields, suggested probable mechanisms for the radiation chemistry. The high radiation

sensitivity is attributable to the dissociative electron capture processes. The tendency of the MBA polymers toward crosslinking was postulated to be due to the ease of elimination of HBr giving intermediates for the formation of crosslinks and CH<sub>3</sub>Br elimination leading to crosslinking directly. The typical PMMA radical was observed for  $\gamma$ -irradiated poly(MMA-co-MCA) only when MCA content is  $\leq 20\%$ ; it was not detected for  $\gamma$ -irradiated poly(MMA-co-MBA) even when MBA is present at 3%. The radiolysis of copolymers of MMA with MCA and MBA are dominated by the  $\alpha$ -halogenated monomers.

### Introduction

Polymers exhibiting high chain scission susceptibilities to radiation have been investigated as candidates for positive electron-beam (E-beam) resists. However, as crosslinking also occurs sometimes, especially at high radiation dose, polymers which undergo scission only in the exclusion of crosslinking are required for resist applications. The relative tendency of the two reaction pathways is usually measured by one of two methods. The first is the determination of scission (crosslinking) yield per 100 eV absorbed, which is  $G_S$  ( $G_X$ ). The second method is the measurement of sensitivity  $S_S$  ( $S_X$ ) of the scission (crosslinking) reactions in coulomb cm<sup>-2</sup> for a given energy of electron.

Poly(methyl methacrylate) (PMMA) has been demonstrated to be a practical E-beam positive resist by the electronics industry; it is generally regarded as the reference polymer in this application. However, PMMA has only moderate sensitivity to radiation:  $G_S = 1.4$ ,  $G_X = 0$  and  $S_S = 5 \times 10^{-5}$  coulomb  $\text{cm}^{-2}$  at 15 keV.<sup>2</sup> Hence, there have been intensive efforts to find polymers and copolymers of greater radiation sensitivity. Several general approaches have emerged from these researchers.

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

Often times polymers with enhanced  $G_S$  also have increased  $G_X$ . Thus PMCA tends to crosslink ( $G_X = 0.8$ )<sup>9</sup> when the electron dose exceeds  $6 \times 10^{-4}$  coulomb  $\text{cm}^{-2}$ . Copolymerization of such monomers with a

noncrosslinking monomer can sometimes alleviate the crosslinking reactions. However, the  $G_S$  and  $G_X$  values of copolymers are usually not monotonic functions of comonomer composition. For instance, it was found that copolymers of MCA with MMA,<sup>10</sup> methacrylonitrile,<sup>11</sup> and terpolymers of MCA with MMA and hexylmethacrylate<sup>9</sup> of certain compositions have greater  $G_S$  values than PMMA and without discernible crosslinking.

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

The emphasis of our work is to elucidate the relationships between the chemical structure of polymer and its radiation sensitivity through the analysis of the volatile radiolysis products by gas chromatography-mass spectroscopy (GC-MS), the identification of the radical intermediates and their yields,  $G_r$ , by electron spin resonance (ESR), as well as the usual determination of  $G_S$  and  $G_X$ . Gamma radiation is used because

of its penetrating power which enables uniform irradiation of polymer sample contained in sealed ampules suited for ESR measurements and subsequent GC-MS analysis. One drawback is that the energies of the  $\gamma$ -ray and its secondary electrons are very high; atomic number effect is much smaller than for electron and x-ray irradiation.

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

#### Experimental Section

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

Homo- and Co-polymerizations. Monomer or comonomers were mixed with AIBN without solvent and freed of air by several freeze-evacuation-thaw cycles. Polymerizations were carried out at  $60 \pm 0.1^\circ$  to less than 10%

conversion. The product was precipitated with methanol, washed, and dried at 40° in vacuo to constant weight. The copolymer compositions were determined from elemental analysis. Molecular weights were obtained with a Waters Associates 201 chromatograph equipped with five micron styrogel columns using THF as the solvent and the universal calibration method.  $T_g$  was determined with a Perkin-Elmer differential scanning calorimeter (DSC) at a scanning rate of 20°min<sup>-1</sup>.

Gamma radiolysis. Samples in pyrex ampules were evacuated to less than 10<sup>-5</sup> torr for 20 hrs and sealed. A <sup>137</sup>Cs  $\gamma$ -ray source was used to irradiate the polymer at ambient temperature. The dose rates varied from 0.07 to 0.03 Mrad hr<sup>-1</sup>, as determined by ferrous sulfate dosimetry, depending upon the total dose desired. The changes in  $\bar{M}_w$  and  $\bar{M}_n$  after radiolysis were determined by GPC as above.

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

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

Results and Discussion

Reactivity ratios. The results of copolymerization of MMA ( $M_1$ ) and methyl- $\alpha$ -haloacrylate ( $M_2$ ) are summarized in Table I. The reactivity ratios were calculated from the copolymer composition data with the method of Yezrielev et al.<sup>13</sup> based on the differential form of copolymerization equation. This analysis was shown<sup>14,15</sup> to give more accurate reactivity ratios than other methods and has the advantage of being symmetrical in form. Figure 1 is a plot of the mole fraction of

Table I

Fig. 1

Table I. Copolymerization of MMA and methyl- $\gamma$ -haloacrylates

	<u>Comonomer</u>		<u>% Conversion</u>	<u>Reactivity ratios</u>	
	<u>Mole fraction in feed</u>	<u>Mole fraction in copolymer</u>		<u><math>r_1</math></u> (MMA)	<u><math>r_2</math></u>
MCA	0.074	0.16	8.2	0.36	0.26
	0.12	0.19	6.8		
	0.28	0.38	9.4		
	0.50	0.43	6.4		
	0.84	0.72	5.7		
MBA	0.33	0.44	6.4	0.19	0.16
	0.33	0.43	8.6		
	0.43	0.47	3.8		
	0.43	0.46	5.4		
	0.63	0.51	9.3		

MCA ( $m_2$ ) in copolymer versus MCA ( $M_2$ ) in feed and the curve calculated from the copolymer equation. A similar plot was obtained for MBA. Both show good agreement between experimental results and values based on reactivity ratios.

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

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

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

Table II

Table II Molecular weights of poly (MMA-co-methyl- $\alpha$ -haloacrylates)

Comonomer		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
m <sub>2</sub> , %				
MCA	16	2.8	3.5	1.2
MCA	19	2.5	4.0	1.6
MCA	38	2.1	3.4	1.6
MCA	72	1.5	2.5	1.7
MBA	3	0.96	2.5	2.6
MBA	5	0.40	0.9'	2.2

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

Gamma radiolysis

A. Yields.—The values of  $G_S$  and  $G_X$  were obtained from the values of  $\bar{M}_n$  and  $\bar{M}_w$  of irradiated polymers using the equations of Charlesby,<sup>17</sup> and Kilb.<sup>18</sup>

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

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

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

Fig. 2

Table III

The MMA-MCA system had been previously investigated by Helbert et al.<sup>3</sup>, their results are included in Table III for comparison. These authors studied the radiation degradation of PMCA and one copolymer of 41MMA-59MCA composition. Emulsion polymerization was used.

Table III Radiolysis yields

Comonomer		$G_{S-G_X}$	$G_S$	$G_X$	$G_r$
	$M_2, \%$				
None	0	1.4	1.4	0	1.4
MCA	16	4.7	5.2	0.5	4.4
MCA	19	4.4	4.8	0.4	3.3
MCA	38	5.4(3.5) <sup>a</sup>	5.6	0.2(0.2) <sup>a</sup>	-
MCA	72	6.5	6.7	0.2	9.1
MCA	100	6.5(5.3) <sup>a</sup>	7.4	0.9(0.6) <sup>a</sup>	-
MBA	3	5.8	5.3	0.46	2.0
MBA	5	4.4	5.0	0.65	2.3
MBA	7	-	-	-	2.3
MBA	100	-	-	-	7.0

<sup>a</sup>From reference 3.

Consequently, the molecular weights of their polymers were generally higher (by about a factor of 10) than ours, the molecular weight distribution was broader (also up to a factor of 10), and probably contains significant composition drifts as usually is the case with emulsion poly-

merizations. Helbert et al. irradiated the polymer to much higher doses than we did and noted changes in slopes of  $\overline{M}_w^{-1}$  and  $\overline{M}_n^{-1}$  versus dose plots. Our dose lies in the region of their low dose experiments. They fractionated the polymers and obtained radiolysis results generally within the experimental variabilities of unfractionated polymers; their values of  $G_S$  and  $G_X$  are somewhat smaller than ours (Table III).

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

PMCA and all MCA-MMA copolymers have non-zero yields for  $G_X$ . One might expect that for a monomer which tends to crosslink by radiolysis, then the  $G_X$  value of copolymers with another non-crosslinking comonomer may be a monotonic function of the copolymer composition. In other words  $G_X$  for poly(MMA-co-MCA) should decrease monotonically with the decrease of MCA monomer in the copolymer. This is because with the decrease of mole fraction of MCA, the probability of having two MCA monomers next to one another on adjacent chains is decreased. This expectation was not realized. The results in Table

III show  $G_x$  to be 0.6-0.9 for PMCA and 0.2-0.5 for various copolymers of MCA. The  $G_s$  and  $G_x$  results indicate that the MCA monomer controls the radiolysis efficiency and chemistry of its copolymer with MMA.

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

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

B. ESR.-Gamma irradiation of homopolymer of MCA at ambient temperature produced a very intense ESR spectra as shown in Figure 3. The radicals

Fig. 3

are considerably stable as evidenced by the fact that the ESR signal did not completely disappear until the polymer was heated above 150° which is 5° above the  $T_g$  of the polymer. The ESR spectrum essentially consists of seven hyperfine lines with spacings of about 13 Gauss. However, there is something unusual about this spectrum. It is certainly unsymmetrical; the two outer low-field lines (indicated by A and B in Figure 3a) are much more intense than the corresponding lines at high field. This suggests the presence of more than one radical, other possible explanations such as  $g$  or hyperfine anisotropy is unlikely. For nearly equal molar copolymer the EPR spectrum is nearly the same as that of PMCA (Figure 3b). As the MMA content increases the spectrum begins to contain that of the well known PMMA radical (Figure 3c). For poly(88MMA-co-12MCA), Fig. 3d showed only the 9-line ESR spectrum of the PMMA radical,

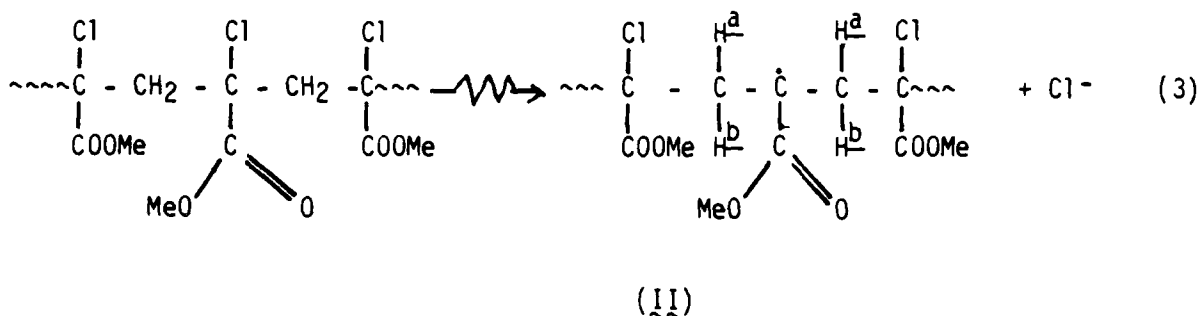


To gain more insight into the ESR spectrum of irradiated PMCA, we followed the change of the peak heights with the klystron power and with temperature. If there is only one radical present then all the signals should saturate simultaneously and disappear together as radicals recombine at elevated temperatures. Figure 4 plots the intensity of the

Fig. 4

peaks as a function of microwave power. It shows that the two outer lines at the high field (E and F) are inhomogeneously broadened. On the other hand the other lines show more homogeneous broadening, especially the two low-field lines A and B. Furthermore, the effect of heating on the Fig. 5 ESR spectra, shown in Figure 5, is informative. The intensity of the two outer low-field lines (A and B) decreased markedly as the sample was heated to 50° but not the other resonance lines. Above 85° A and B intensities decrease rapidly with the temperature whereas the intensities of other lines show more gradual decreases. These are incontrovertible evidences that a second radical is present which contributes to the ESR spectra in the low field region.

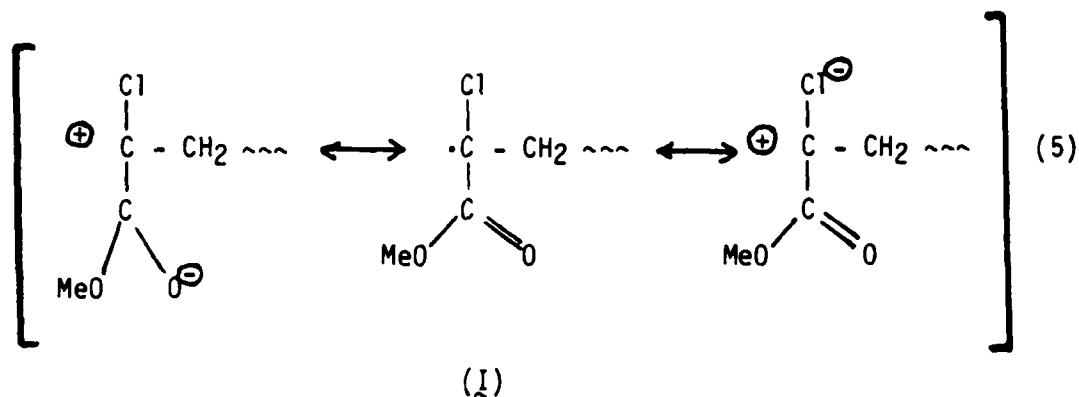
We analyze the spectra on the basis that it is composed of two species. The one at low field designated as radical I, has  $g = 2.0192$  and  $H_A = 12$  Gauss. The other radical II with  $g = 2.0036$  is a triplet of triplet with two hyperfine coupling constants of 24 and 12 Gauss. Radical II is likely to be the radical produced by the dissociative electron capture:



This process has been proposed by Chen et al.<sup>11</sup> and suggested to be enhanced by the bond weakening along the backbone induced by the electron withdrawing Cl atom in the quaternary carbon.

The hyperfine interactions of the unpaired spin with  $H_A$  and  $H_B$  are dihedral angle dependent and have different coupling constants.

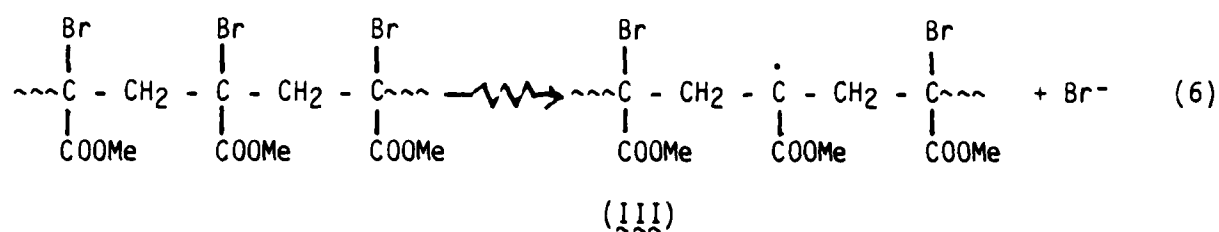
Radical I is postulated to be the one formed by chain scission of radical II. It has high  $g$  value because of the possible effect of spin orbit coupling.



Helbert et al.<sup>3</sup> irradiated PMCA at  $-195^\circ$  and observed an ESR spectra at that temperature which was different from the ones described above. They interpreted the spectra as an anisotropic triplet. It is our opinion that the spectra (Figure 4 of reference 3) contains at least seven lines. The signal was reported to disappear when the sample was warmed to room temperature.

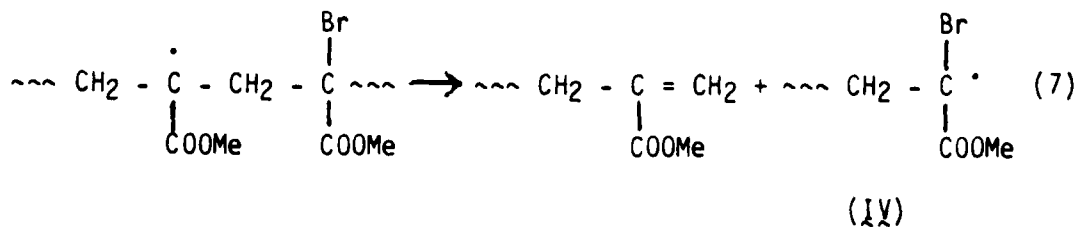
Gamma irradiation of poly(MMA-co-MBA) produces a simple five-line spectrum for a single radical coupled to four equivalent protons with  $H_A = 12$  G (Figure 6a). The radical is most likely the one produced by dissociative electron capture.

Fig. 6



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

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



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

C. GC-MS.-The volatile radiolysis products of MCA homo- and co-polymers were analyzed by GC-MS. The results are summarized in Table IV.

Table IV

Table IV Radiolysis products analyzed by GC-MS

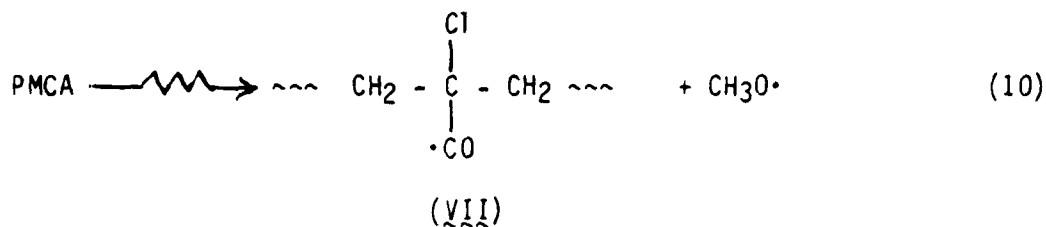
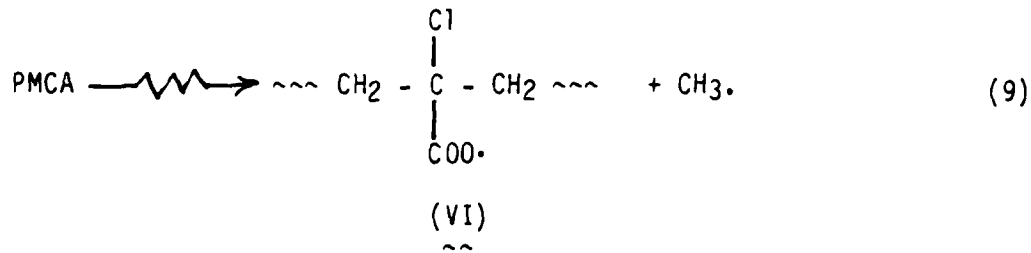
Polymer	Ion mass	Relative ion current	product
poly(MCA)	16	2.1	CH <sub>4</sub>
	28	2.7	CO
	44	100	CO <sub>2</sub>
	50	6.4	CH <sub>3</sub> <sup>35</sup> C1
	52	1.9	CH <sub>3</sub> <sup>37</sup> C1
poly(MMA-co-MCA)	16	2.1	CH <sub>4</sub>
	28	2.7	CO
	36	2.1	H <sup>35</sup> C1
	38	1.1	H <sup>37</sup> C1
	44	100	CO <sub>2</sub>
	50	6.4	CH <sub>3</sub> <sup>35</sup> C1
	52	1.9	CH <sub>3</sub> <sup>37</sup> C1
	60	4.0	HCOOMe
69	1.8	CH <sub>2</sub> =C(Me)CO <sup>+</sup>	

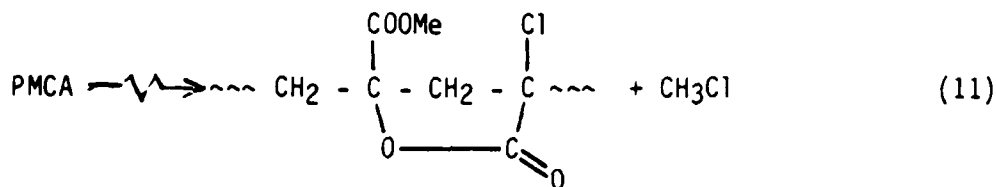
Mechanism

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



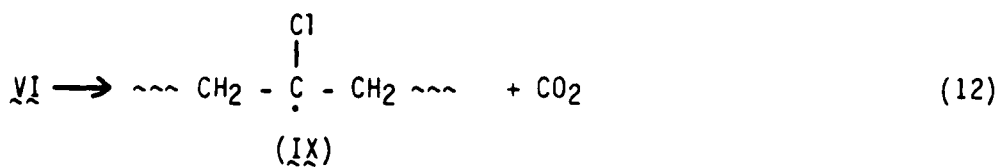
Other possible primary processes are:

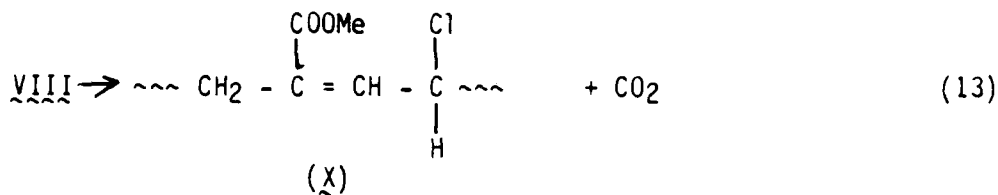




(VIII)

In addition to reaction 11,  $\text{CH}_3\text{Cl}$  can also be produced by the combination of  $\text{CH}_3\cdot$  with  $\text{Cl}\cdot$  or  $\text{CH}_3\cdot$  abstraction of  $\text{Cl}$  from the polymer backbone. Methane is probably formed from methyl radicals by hydrogen abstraction. The  $\text{CH}_3\text{O}\cdot$  radical was not detected as either  $\text{CH}_3\text{OH}$  or  $\text{HCHO}$ . It is possible that the GC column is not suited for their elution. Carbon dioxide is the major radiolysis product; it can be formed from VI or VIII:



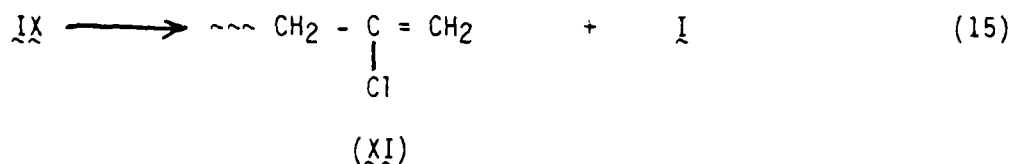


The small quantity of CO can be produced from VII,

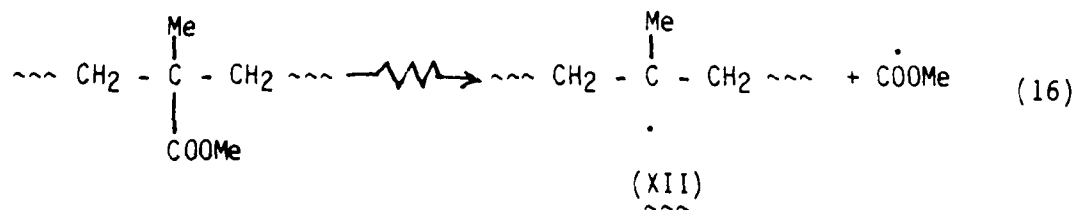


The  $G_s$  and  $G_x$  values were obtained from the  $\bar{M}_n^{-1}$  and  $\bar{M}_w^{-1}$  versus D plots, respectively. If the slope of the former plot  $S_n$  is equal to twice of the slope of the latter plot  $S_w$ , then  $G_x = 0$ . However, if  $S_n > 2S_w$  a non-zero value is obtained. For polymers with the most probable distribution, then if  $S_n > 2S_w$  after radiolysis it may be taken as positive evidence for crosslinking. Random scission should maintain this distribution. However, the MCA copolymers obtained at very low conversion and repeated dissolution and precipitation have  $\bar{M}_w/\bar{M}_n < 2$  (Table II). Therefore, irradiation tends to increase polydispersity and  $S_n > 2S_w$ . The resulting nonzero  $G_x$  value probably should not be taken as evidence for crosslinking, the irradiated copolymers remain soluble. It is possible that chain scission, extension, and crosslinking all occur to

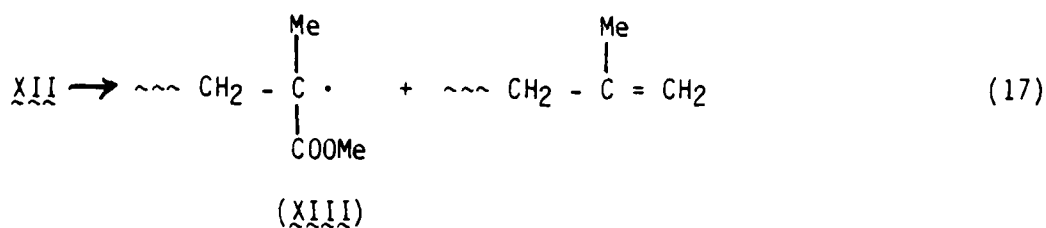
of PMCA. Crosslinking can occur with the reactions between two backbone radicals such as  $\underline{\text{II}}$ ,  $\underline{\text{VI}}$ ,  $\underline{\text{VIII}}$ , and  $\underline{\text{IX}}$ . Addition of these radicals to the double bond of  $\underline{\text{X}}$  would also produce crosslinks. Chain extensions can result from the combination of a backbone radical with a terminal radical  $\underline{\text{I}}$  or the addition of both types of radicals to a terminal group of species  $\underline{\text{Y}}$  or  $\underline{\text{XI}}$ , the latter being derived from radical  $\underline{\text{IX}}$ ,



The radiolysis of poly(MMA-co-MCA) differs from that of the MCA homopolymer in the production of HCl, HCOOMe,  $\text{CH}_2=\text{C}(\text{Me})\text{CO}^\cdot$  in MS and the nine-line ESR spectra of the PMMA radical for  $m_2 < 0.2$ . The formation of HCl in the copolymer may be attributed to hydrogen abstraction by  $\text{Cl}\cdot$  from the methylene group activated by the electron donating methyl substituents. The methyl formate may be the result of radiolysis of the MMA units



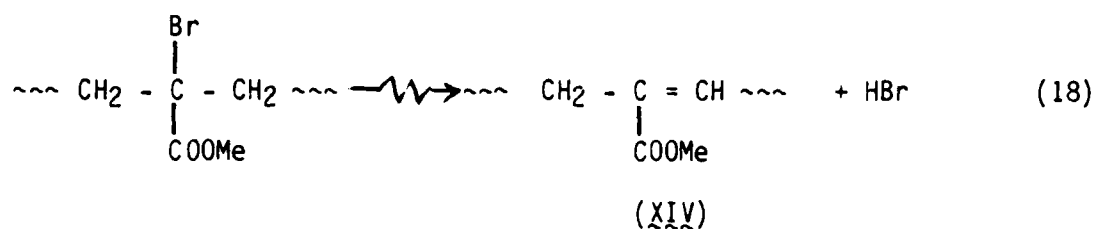
followed by hydrogen abstraction. The PMMA radical formation ensues:



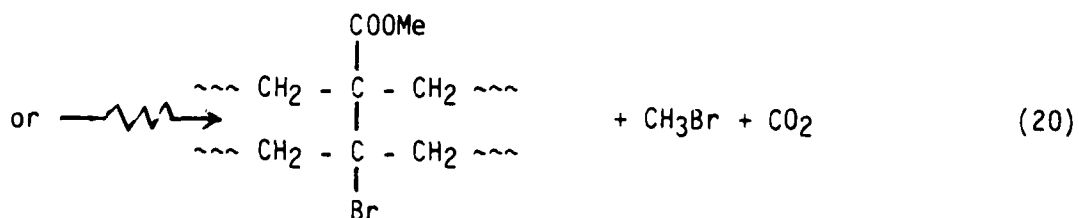
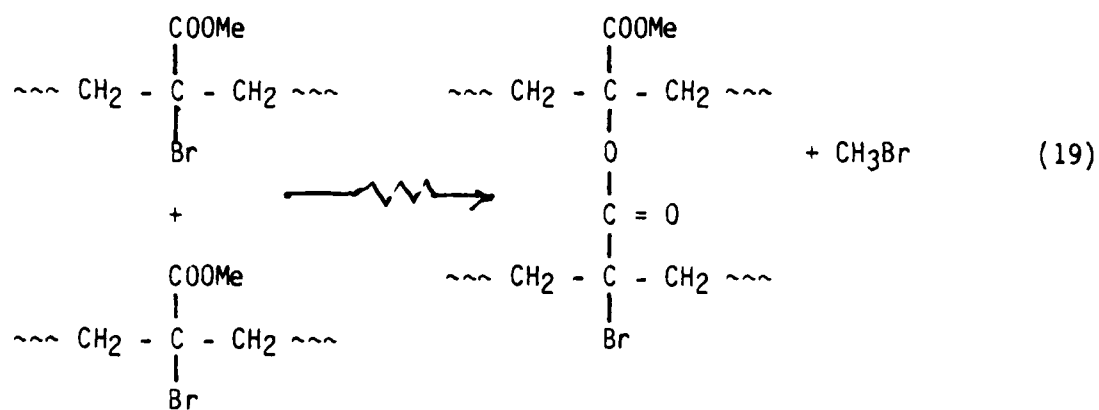
Herbert et al.<sup>3</sup> irradiated poly(MCA) and observed the ESR spectra at  $-195^\circ$ . They propose the formation of  $-\{\text{CH}_2\text{CCl}(\text{CO}_2\dot{\text{C}}\text{H}_2)\}-$  and  $\cdot\text{CH}_2\text{-CCl}(\text{COOMe})\cdot$  radicals. The former calls for the abstraction of the least labile hydrogen in the polymer and the latter would require the intermediacy of a vinyl chloride species. Both these species do not follow naturally from the initial dissociative electron capture event. Perhaps at very low temperatures, the cage effect facilitate the formation and trapping of unstable radicals, which disappear upon warming to room temperature as observed by these workers. In contrast, the radicals produced at room temperature irradiation led to more stable radicals. The radiation chemistry of bulk polymers can be very different at  $-195^\circ$  and ambient temperature, the latter should be more relevant than the former in the context of application as resist materials.

The radiolysis of homo- and co-polymers of MBA led to extensive crosslinking even though the efficiency of radical formation is comparable to those of MCA.  $\text{CH}_3\text{Br}$  and  $\text{HBr}$  are the dominant products. The

results may be rationalized assuming that in addition to the analogous reactions described above for MCA polymers, there are strong tendencies for MBA polymers to undergo intramolecular elimination of HBr,



and intermolecular elimination of CH<sub>3</sub>Br,



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

#### 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.

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#### 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.

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Figure Captions

- Figure 1. Plot of mole fraction of MCA ( $M_2$ ) in copolymer versus mole fraction ( $M_2$ ) in feed: (O) experimental values; (—) curve calculated from copolymer equation.
- Figure 2. Variation of  $\bar{M}_n$  ( $\Delta$ ) and  $\bar{M}_w$  ( $\Delta$ ) with  $\gamma$  dose, solid lines are least square fit of experimental data:  
(a) poly(84MMA-co-16MCA); (b) poly(81MMA-co-19MCA);  
(c) poly(62MMA-co-38MCA); (d) poly(57MMA-co-43MCA).
- Figure 3. ESR of polymers irradiated at ambient temperature:  
(a) PMCA; (b) poly(57MMA-co-43MCA);  
(c) poly(81MMA-co-19MCA); (d) poly(84MMA-co-16MCA). Marker is DPPH.
- Figure 4. Effect of microwave power on the ESR spectra of  $\gamma$ -irradiated PMCA. The peaks correspond to those indicated in Figure 3a.
- Figure 5. Effect of heating on the ESR spectra of  $\gamma$ -irradiated PMCA. The peaks correspond to those indicated in Figure 3a.
- Figure 6. ESR spectrum of  $\gamma$ -irradiated (a) poly(97MMA-co-3MBA), (b) PMBA.

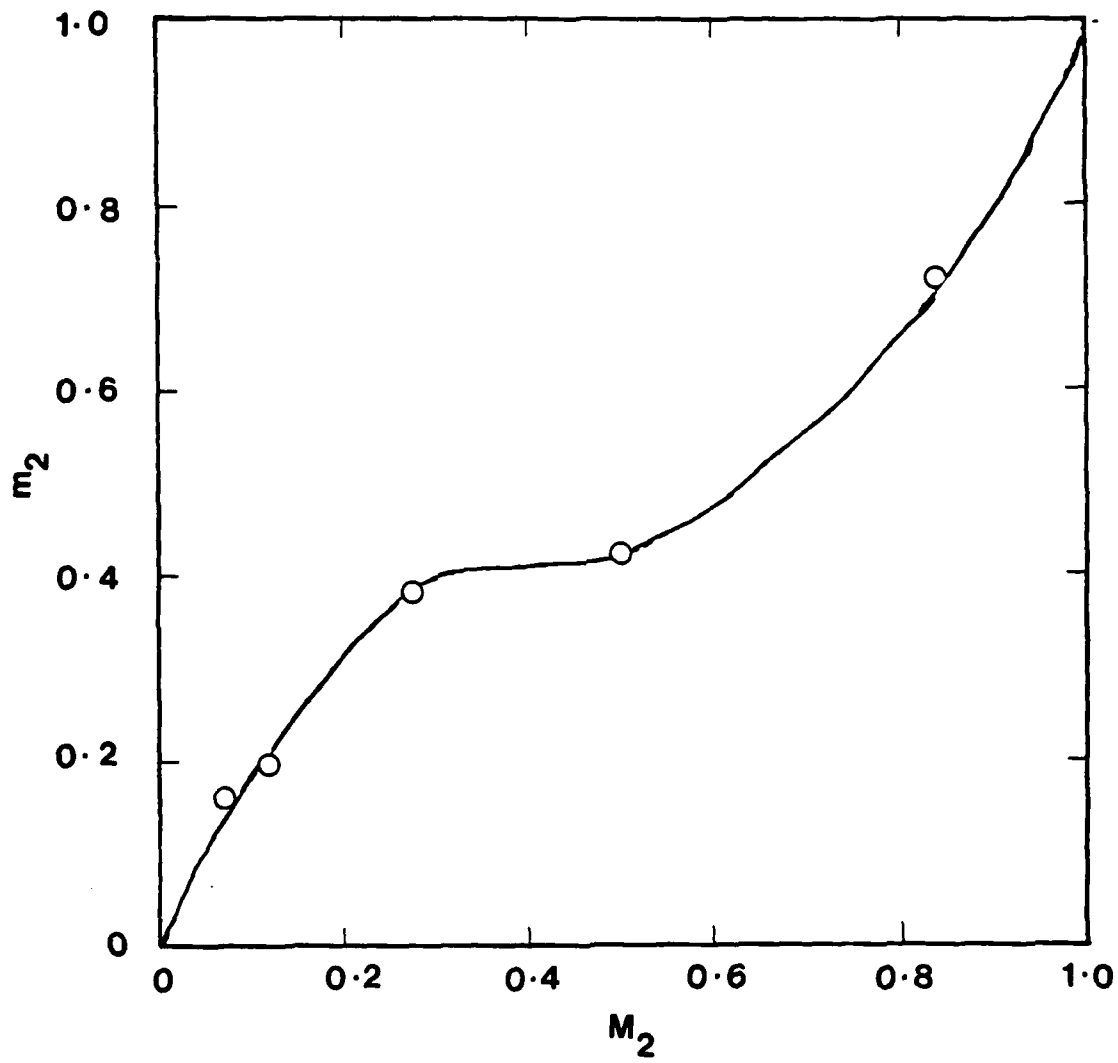


Fig. 1

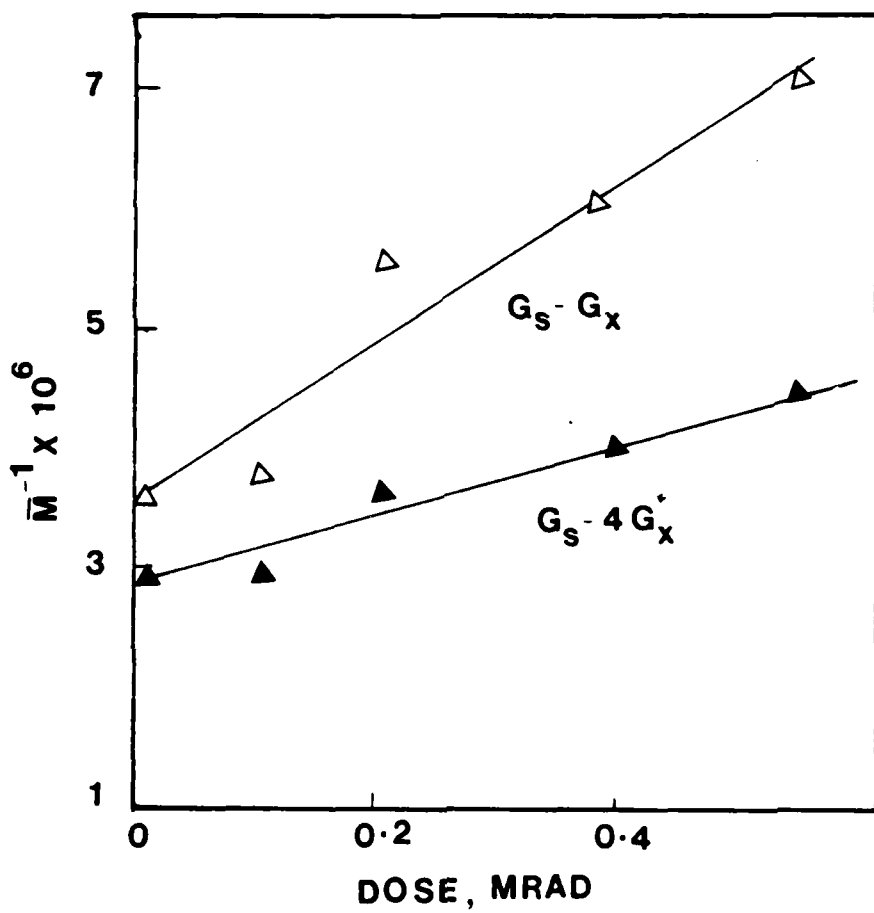


Fig. 2a

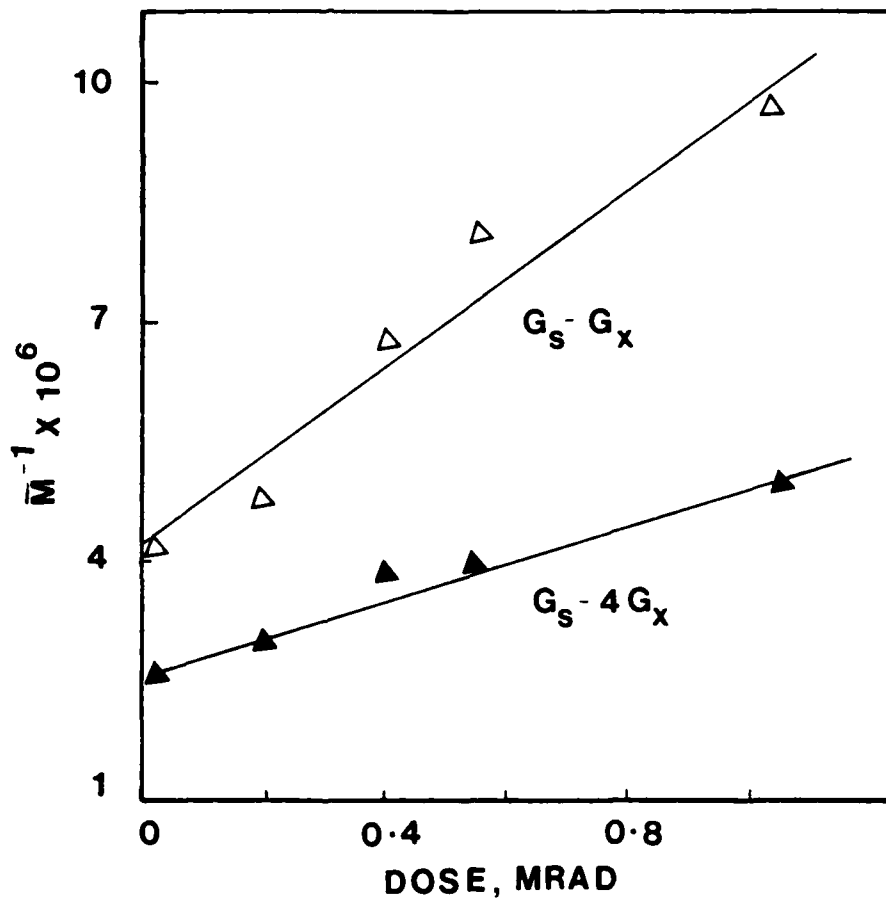


Fig. 2b

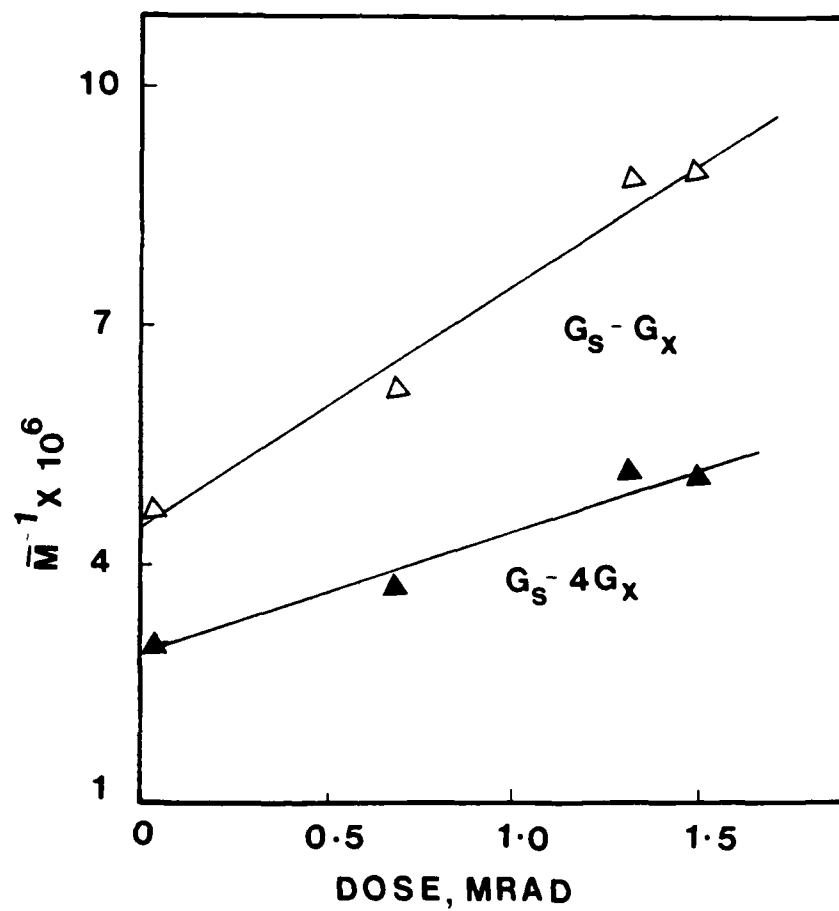


Fig. 2c

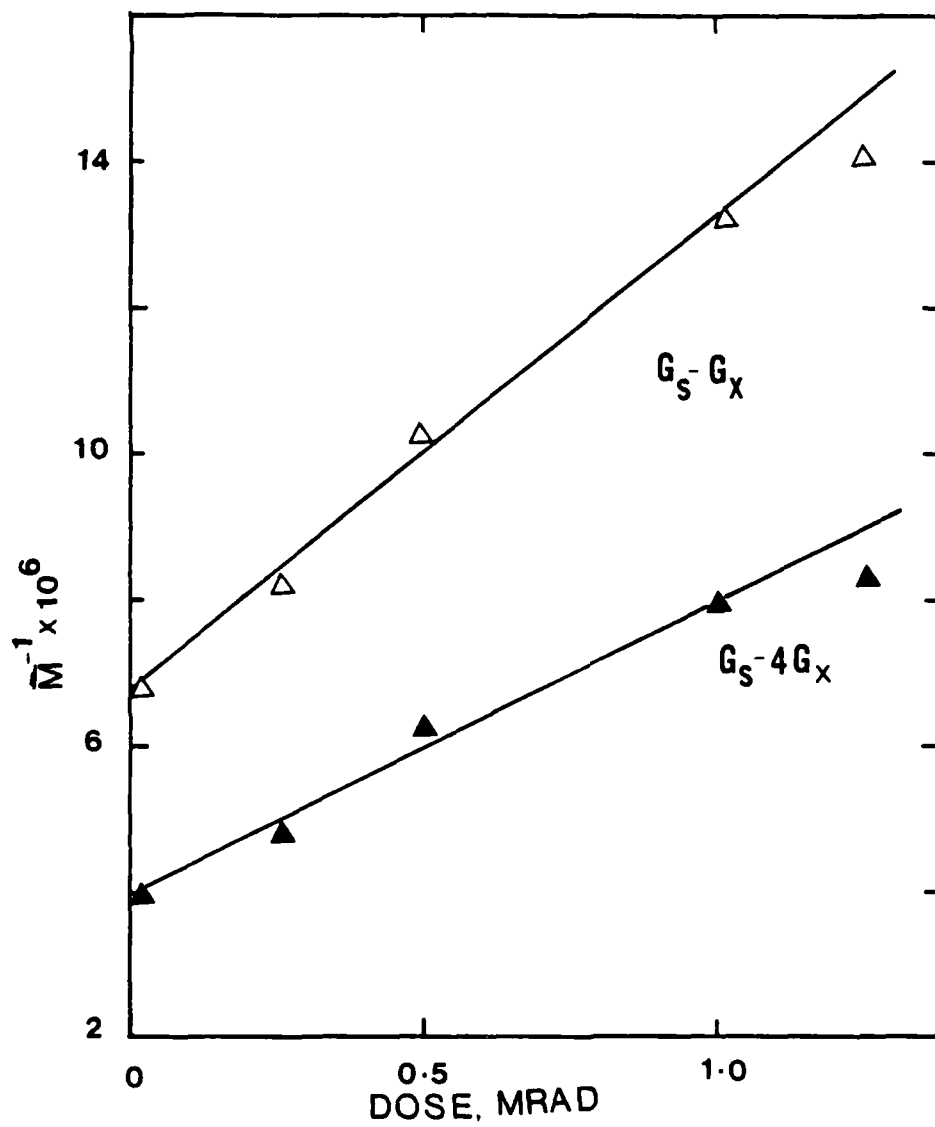


Fig.2d

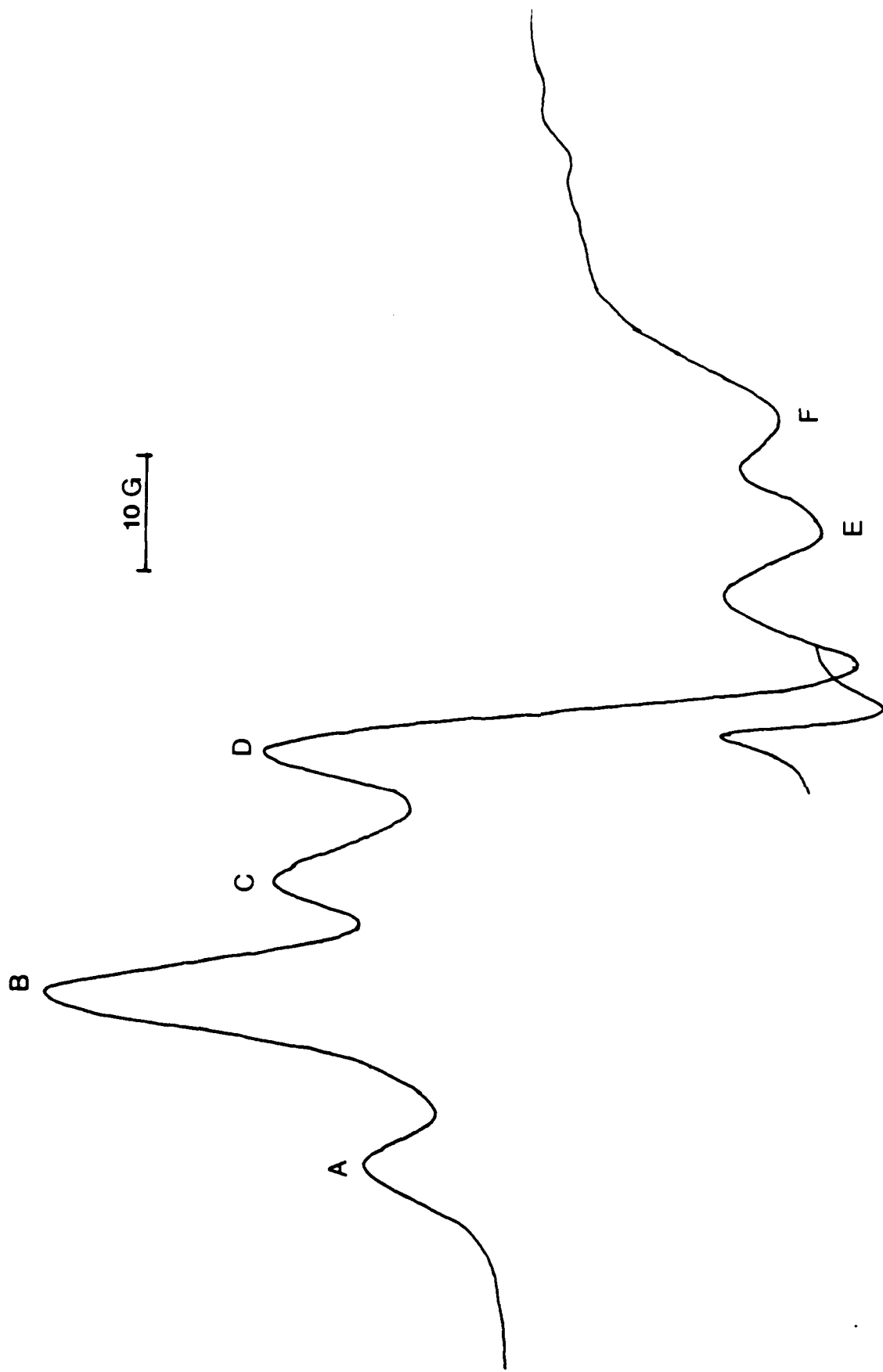


FIG 3a

10 G

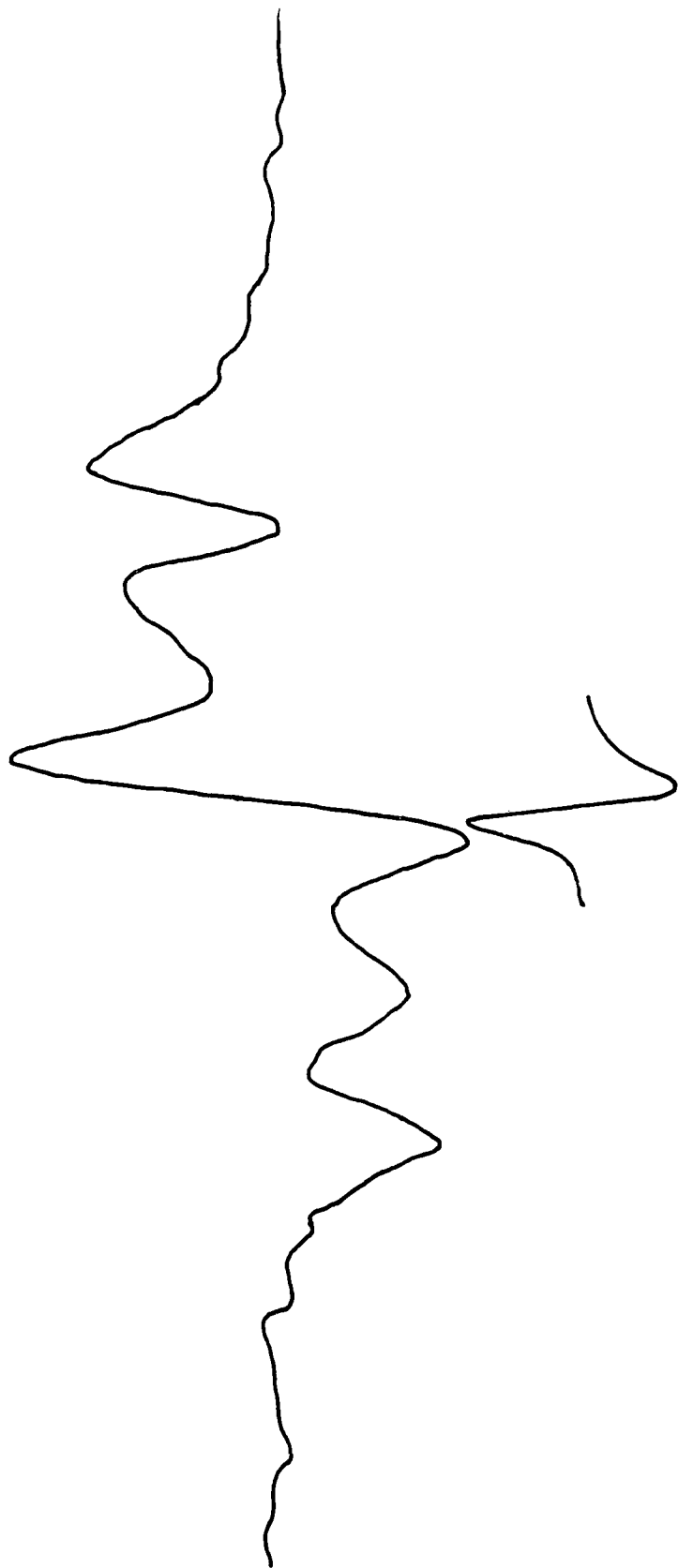


Fig 3b

10G

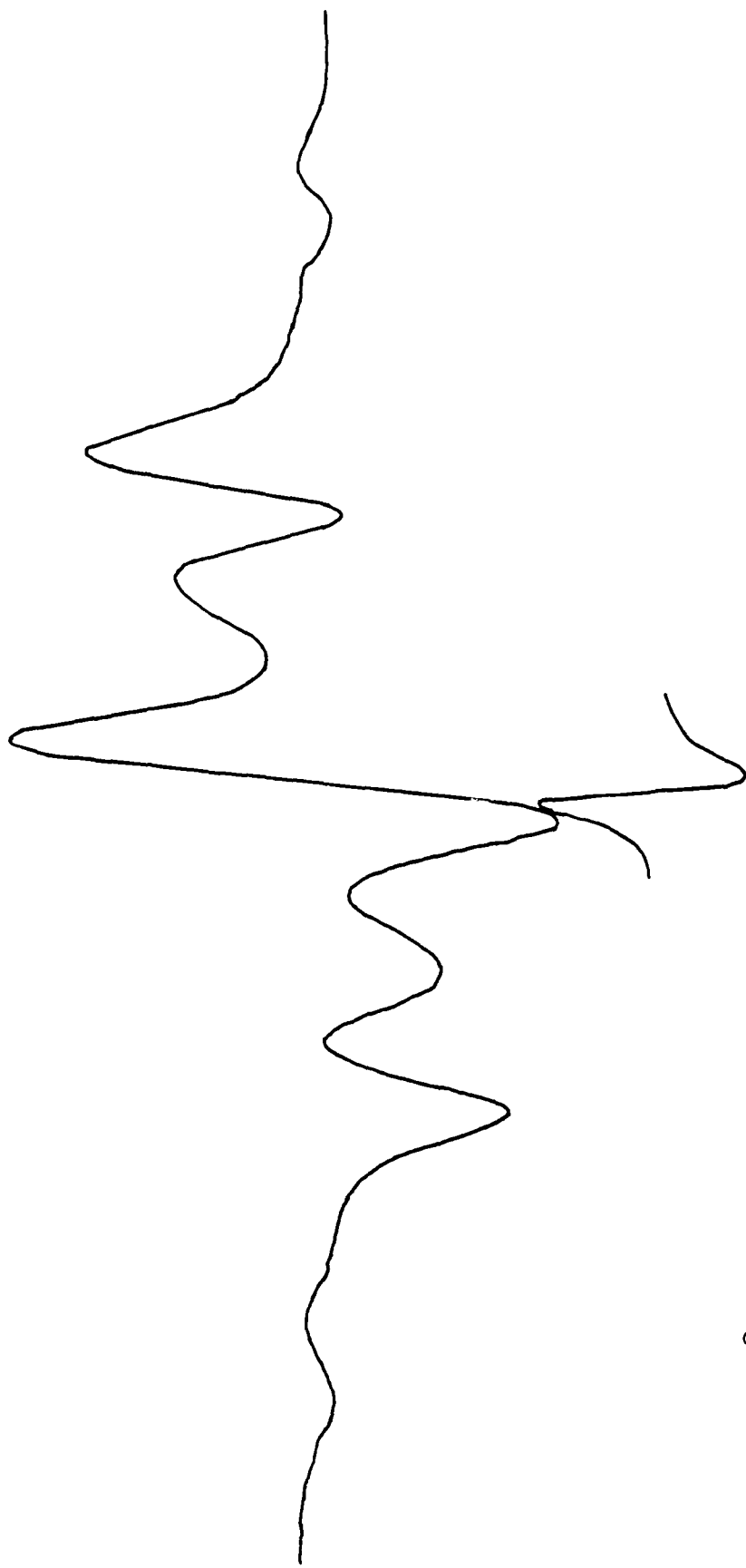


FIG 3c

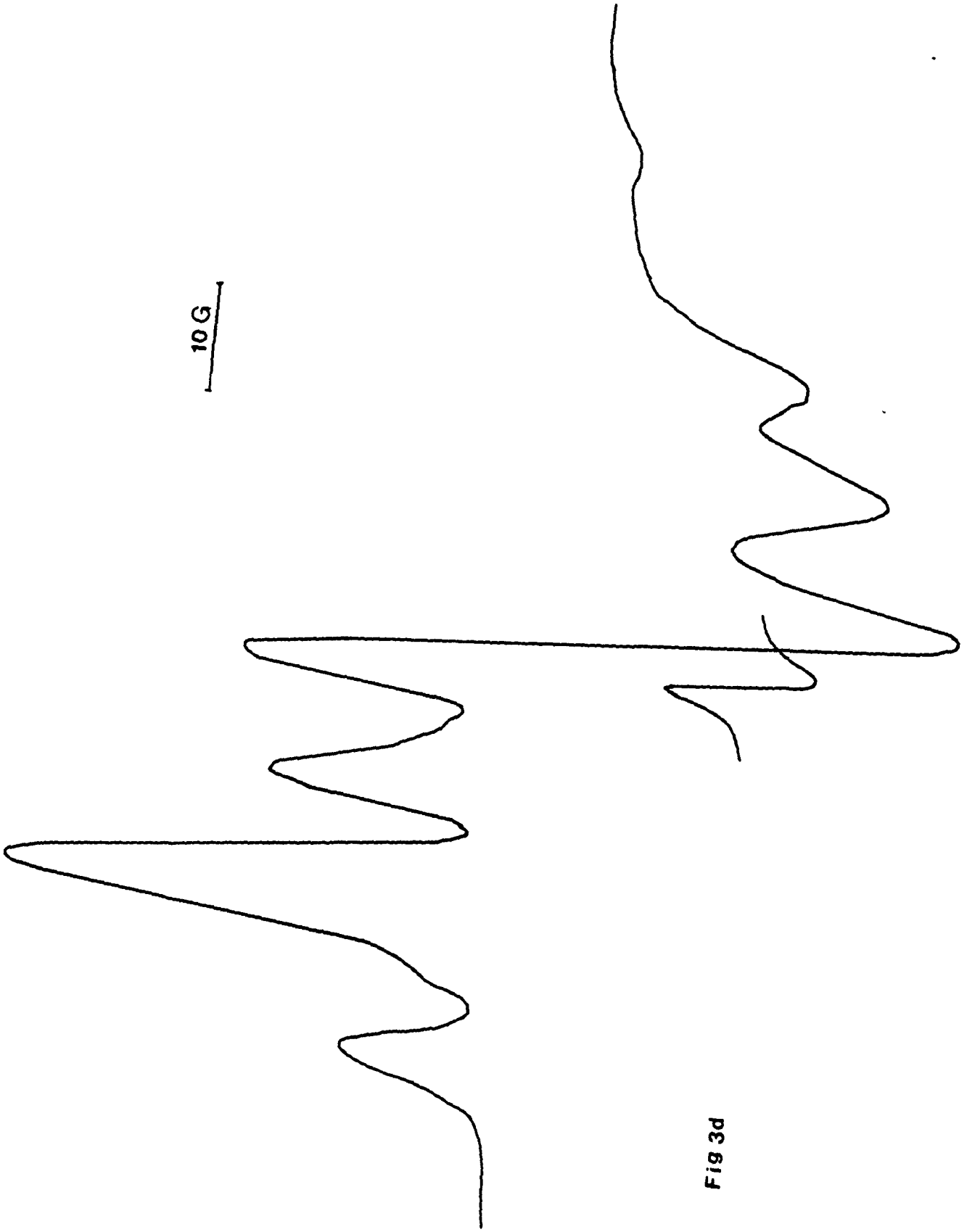


Fig 3d

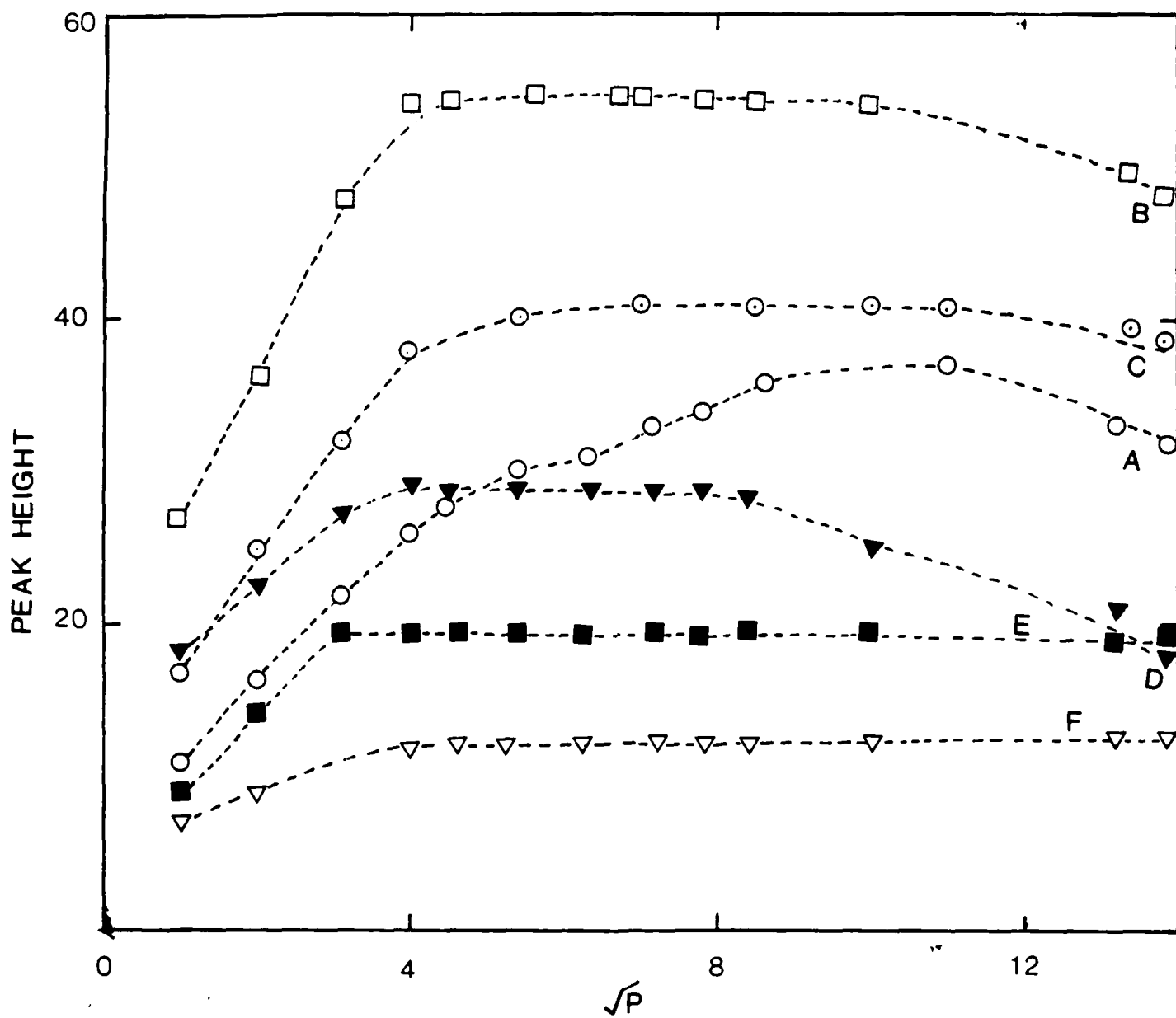


Fig. 4

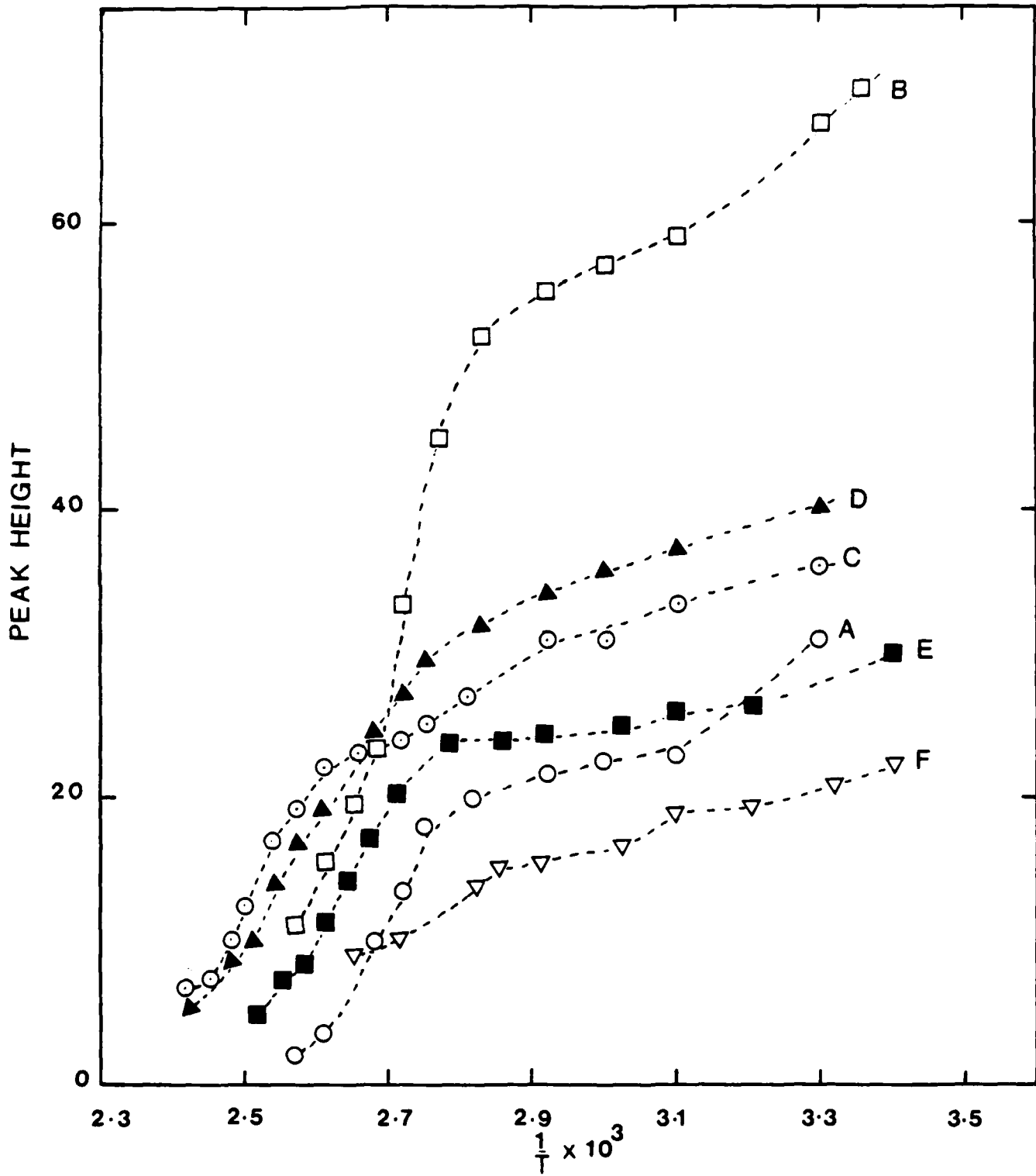


Fig. 5

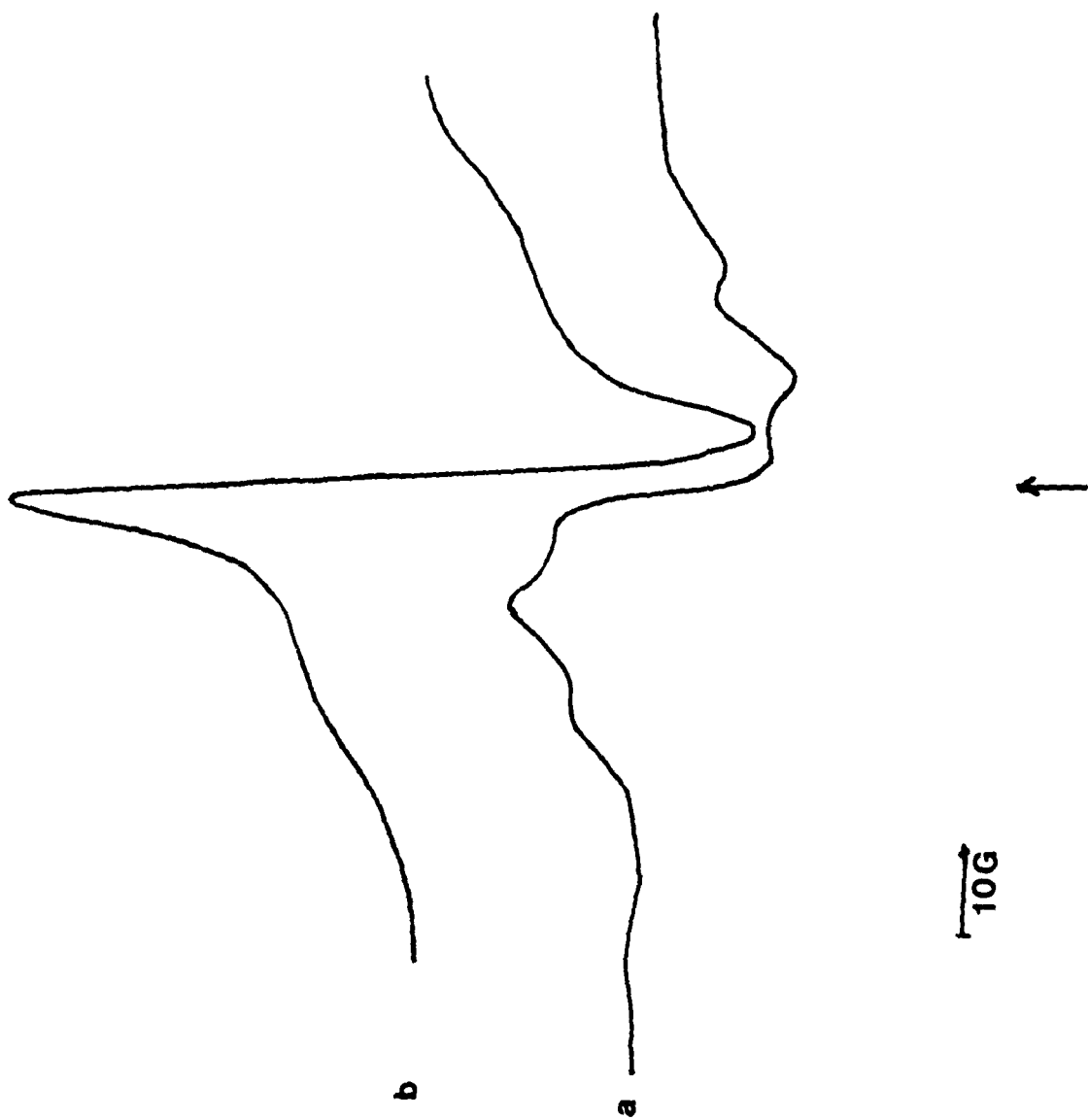


Fig 6

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