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Dr. Kenneth Wynne	(202) 9696-4409	

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Radiolysis of Poly(acetaldehyde-co-chloral), A Positive E-beam Resist

X. Zhao, D.N. Khanna, B. Xu and James C.W. Chien*

Department of Polymer Science and Engineering
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003, USA

ABSTRACT

Acetaldehyde and chloral were copolymerized using triethyl aluminum catalyst. The copolymer (ACC) obtained with equimolar monomer feed is not alternating in structure as it was once thought to be; it is comprised of two fractions differing in MW and composition. ACC has good thermal stability which is further improved by endcapping. Radiolysis in vacuo caused depolymerization with a G(M) value (number of monomers produced per 100 eV) of about 4000 to 80% completion. The G(S) value for chain scission is 1.9. These processes are effectively inhibited by benzoquinone. Oxygen markedly increases G(M) to ca 18000 and >97% completion. Addition of tetrabutyl ammonium salt or tetramethyl urea has no effect on the depolymerization, whereas the addition of di-t-butyl-p-cresol causes an induction period after which normal unzipping ensues. Even UV photolysis of ACC in the presence of oxygen produces monomer with a quantum yield of 1.7 but very little photolysis occurs in the absence of oxygen. Gamma Radiolysis sensitized by $(C_6H_5)_2$ IPF$_6$ has G(M) value of 327000. These results are very similar to the radiolysis

and photolysis of the homopolymer of monochloroacetaldehyde and reinforce the mechanisms proposed for them. The E-beam sensitivity of ACC is about 3×10^{-6} C cm^{-2}.

INTRODUCTION

Basic study of the radiation chemistry of polymers is needed both for the understanding of interaction of radiation with matter and for various technological applications. In the context of microelectronic lithography, polymers which undergo radiation induced crosslinking or scission are useful as negative or positive resists, respectively. There is a natural amplification of the physical effects of a radiolytic event. In the former case the formation of crosslinks insolubilizes the macromolecules. In the latter case the occurrence of one main chain scission can render the macromolecule more soluble than the parent polymer. Latent images can be developed by these solubility changes.

Direct imaging is possible for positive acting resists if radiation causes complete degradation of the polymer into volatile products. Such system may be referred to as self-developing,[1] and has the distinct advantages of simplicity and economy. The obvious candidates are polymers with low ceiling temperatures. Ideally, radiolysis inititates the unzipping process to convert the entire macromolecule into its monomer without side reactions. Poly(alkylene sulfone)s[2] have been proposed for this application. Depolymerization of a poly(alkylene sulfone) should produce equal numbers of olefin and SO_2 molecules.[3] Experimentally, many more SO_2 molecules than olefin molecules are produced by radiolysis at room temperature. The side reactions are

the isomerizations and polymerization of the olefins. At elevated temperatures the radiolysis yield of olefin approaches that of SO_2. The highest radiolysis yields reported for poly(alkylene sulfone) is less than thirty structural units per 100 eV.

Poly(aldehydes) are also candidates for self-developing resists. A preliminary study on copolymers of alkyl aldehydes have been reported;[4] the copolymers are rather unstable toward spontaneous depolymerization.

Halogen atom sensitization in radiation chemistry is well recognized.[5] A systematic study has been made by us on the radiation sensitivities of polymers containing F, Cl and Br atoms on the backbone and in pendant groups. The results led to the postulation and experimental verification of high radiation sensitivity for polymers of trifluoroethyl- and hexafluoro-n-propyl-α-chloroacrylates; they have G(S) values about three times greater than that of PMMA.[7] Based on the above considerations, halogen containing polymers of aldehydes should be very effectively depolymerized by radiolysis. This was indeed found for poly(mono-chloroacetaldehyde), PCA.[8] Gamma radiolysis of PCA in the presence of air resulted in the unzipping of 11000 monomer units per 100 eV absorbed (G(M) = 11000). The G(S) yield (number of chain scission/100 eV) is 5.5, and there is no crosslinking. In the absence of air the values for G(M), G(S) and G(X) are 1100, 2.1 and 0, respectively. The depolymerization is retarded by 2,6-di-t-butyl-p-cresol but

is not affected by Bu_4NBr. The radicals produced by photolysis at -195°C have been identified by electron spin resonance. Irradiation of PCA containing a diaryliodonium salt caused efficient depolymerization catalyzed by the Bronsted acid generated from the onium salt; this photo-initiated cationic process is insensitive to oxygen.

PCA has certain shortcomings. It begins to decompose thermally at ca. 80°C. Endcapping with phenyl isocyanate raises the onset decomposition temperature to ca. 120°C. Therefore, PCA cannot survive baking processes used in the manufacturing of large scale integrated circuits. Also chloroacetaldehyde is a toxic substance.

The central purpose of this work is to find haloaldehyde polymers which are more thermally stable than PCA but still possess very high radiation sensitivity. Poly(chloral) is one of the more thermally stable aldehyde polymers, and the trichloromethyl group is readily dissociated by radiolysis.[6c,d] But poly(chloral) itself is insoluble in any organic solvent. Therefore, we have investigated the radiation chemistry of its copolymer with acetaldehyde; the results of this study are presented below.

EXPERIMENTAL

Materials. Acetaldehyde, phenyl isocyanate, acetic anhydride, diphenyliodonium hexafluorophosphate (a $(C_6H_5)_2IPF_6$), 2,6-di-t-butyl-p-cresol (BHT), and

tetrabutyl ammonium bromide were purchased from Aldrich Chemical. Triethylaluminum (TEA) was from Ethyl Corp., and chloral was from Crescent Chemical Co., Inc.

Acetaldehyde was treated either with sodium carbonate and calcium hydride or with anhydrous magnesium sulfate. It was distilled under N_2 in the presence of 0.1% of N,N'-di-β-naphthyl-p-phenylene diamine collecting the middle 50% fraction boiling between 20° and 21°C. It was used immediately.

Chloral was either refluxed with P_2O_5 for ten hrs. or heated with 2-5% sulfuric acid and calcium hydride. It was distilled under argon collecting the fraction boiling at 98°C, stored under argon, and used on the same day.

Toluene was washed with concentrated sulfuric acid and then water, dried over P_2O_5, distilled and stored under argon in a Schlenk tube. Acetic anhydride was distilled with P_2O_5 at 138-140°C. Pyridine was treated with either KOH or $LiAlH_4$ and distilled at 112°-114°C before use. Phenyl isocyanate was treated with P_2O_5 for one hr. and distilled at 45°-47°C/10 torr.

Polymerization. Copolymerizations of aldehydes and haloaldehydes had been studied,[9] and that of acetaldehyde and chloral had been reported by Iwata et al.[9a] Polymerization was carried out in crown-top pressure bottle, equipped with magnetic stir-bar. A metal cap with two holes was crimped over a butyl rubber liner sealing the bottle after it was first flame dried. Toluene, monomers, and TEA

(8.5 volume % toluene solution) were introduced in that order at -78°C. The amount of TEA corresponds to one mole % of total monomer. The polymerization was quenched with methanol after 72 hrs reaction. The copolymer was precipitated in methanol, filtered and redissolved in chloroform. Insoluble materials were removed by passage through a column of Celite 545 and glass fibre. Reprecipitation with methanol afforded a 20% yield of copolymers. The copolymer obtained with equimolar comonomer feed is designated as ACC.

ACC has sufficient stability so that it can be end-capped after it is polymerized and purified. Urethane end-capped copolymer (u-ACC) was obtained by reacting ACC with phenyl isocyanate in chloroform solution catalyzed with dibutyl tin dilaurate at room temperature for two hrs. and then at 70°C for 10 min. Copolymer was also endcapped by reaction with 8:1 acetic anhydride in pyridine solution under reflux for two hrs with argon blanket. The ester end-capped copolymers (e-ACC) were purified by reprecipitation with methanol.

Radiolysis. Twenty to thirty mg. of copolymer in a 5 mm o.d. high purity "supercel" quartz sample tube was irradiated either open to air with a ^{137}Cs gamma source or in dynamic vaccum with a ^{60}Co gamma source. The dose rate was determined by Fricke dosimetry. Following irradiation the volatile products were removed by mechanical pumping for 24 hrs at 60°C. The copolymer remaining was weighed and its

IR and H-NMR spectra taken. The molecular weights and distribution were determined by GPC. Additives were introduced by mixing with PAC in chloroform solution. The solution was then cast into film, followed by removal of the solvent by mechanical pumping at 60°C.

Instrumentation. The instruments used in this work were: Varian XL-300 for ^{1}H-NMR, Varian Aerograph for GC, and Perkin Elmer TGS-2 for thermogravimetric analysis. A Waters Associates 201 GPC equipped with five microstyrogel column was used to determine molecular weight of copolymers in chloroform with polystyrene standards. A JEOL JSM-35 CF scanning microscope was used for irradiation with 20 keV electrons.

RESULTS

Copolymerization

Acetaldehyde and chloral were copolymerized at a range of feed compositions. The resulting copolymers have compositions shown in Table I.

Table I. Copolymerizations of acetaldehyde and chloral

Chloral in feed, mol %	Elemental analysis % C	H	Cl	Chloral in PAC mol %
10	48.9	7.73	8.68	0.7
20	44.8	7.14	18.8	8.8
25	35.4	6.15	33.3	31
30	26.1	2.7	53.2	44
50	26.5	2.9	53.6	45

The copolymer obtained with 10% chloral in the feed contains largely acetaldehyde monomer. It is insoluble like the crystalline homopolymer of acetaldehyde. Copolymers obtained with 20 to 50 mol % of chloral in the feed are amorphous substances soluble in chloroform. Still higher percentages of chloral in the feed led to partially crystalline and incompletely soluble products.

The ACC obtained with 40 to 50 mol % of chloral in the feed was not an alternating copolymer as previously proposed.[9a-c] It is a mixture of two ACC fractions having different MW and composition. GPC of one copolymer ACC-a (Figure 1a) shows it to contain two fractions of MW 4.3×10^4 and 3.7×10^5. The peak areas of the low and high MW fractions are in the ratio of 54:46. It was not possible to separate the copolymers by solvent extraction; instead they were separated by preparative GPC. The low MW fraction

contains 40.1% Cl or 26% chloral. Since the total ACC-a has 54.0% Cl and 45% chloral, the high MW fraction is estimated to be a copolymer with 60% chloral.

Equimolar copolymerizations under identical conditions produced a slightly different product. Fig. 1b is the GPC trace of another preparation ACC-b. The low MW fraction has M_n=2.9x10^4, M_w=4.3x10^4 and M_w/M_n=1.48. The high MW fraction has M_n=3.1x10^5, M_w=3.6x10^5, and M_w/M_n=1.16. Their peak areas are in the ratio of 74:26. There is 43% of chloral in the total ACC-b material.

That the ACC is not an alternating copolymer[9a,c] is also shown by ^{13}C-NMR (Figure 2) which contains pentad information. The triad assignments are given in Table II.

All the experiments below were carried out on unfractionated PAC containing 43 to 45% chloral, which is completely soluble in CH_2Cl_2 and $CHCl_3$ and can be casted into strong films.

Table II. ^{13}C-NMR assigments

Assigment	Chemical Shift, ppm
Pentad CH_3	
AAA	20.1
AAC	20.8
CAC	22.1
Pentad CCl_3	
ACA	97.9
CCA	98.3
CCC	98.6
Backbone Carbon	
AAA	95.3
AAC	97.4
CAC	99.2
ACA	99.8
CCA	100.5
CCC	103.6

Thermal stability

The copolymers have a temperature onset of thermal decomposition higher than the homopolymers (Figure 3). However, fully stabilized polychloral has a weight loss onset near 200°C; complete thermolysis of polychloral requires heating to above 400°C. The nearly equimolar copolymer decomposes completely into its constituent monomers as shown by GC-MS. ACC not endcapped is thermally less stable than endcapped copolymers, and u-ACC is more stable than e-ACC (Figure 4). From the Arrhenius plots for the thermolysis data[10] (Figure 5), the activation energies were found to be 35.8, 55.1, and 63.6 kcal mol^{-1} for ACC, e-ACC, and u-ACC, respectively. In particular, the

onset temperature of decomposition is 200°C for end-capped PAC, which would enable these copolymers to survive baking treatments in electronic lithographic applications.

Radiolysis

Gamma radiolysis induced depolymerization and caused structural changes in the polymer which remained. The volatile products of radiolysis were shown by GC-MS to be acetaldehyde and chloral only. The weight change of ACC upon irradiation in an open sample tube is due to the loss of some of the acetaldehyde. But overnight heating under dynamic vacuum is necessary to completely eliminate the chloral liberated (Table III). Therefore, evacuation at 60°C to constant weight was used to determine the extent of depolymerization.

Table III. Weight loss in γ-radiolysis of e-PAC

Dose, Mrad	Weight loss, %: no evacuation	Weight loss, %: 60°C evacuation, 24 hrs
0.1	0	0.8
0.22	7.9	20
0.31	29	45
0.5	61	85

The structure of the ACC which remained after radiolysis was different from that of the unirradiated copolymer. The residue contains more chloral than

acetaldehyde. For instance, e-PAC γ-irradiated to 1.5 Mrad has increased chloral content of 65% as compared to 44% before irradiation. This effect was even greater for copolymers containing smaller amount of chloral. Irradiation of poly(91A-co-9C) to a dose of 4 Mrad increased the chloral content from 9% to 36%. Two factors are probably involved here. Firstly, the unzipping may tend to stop at a segment rich in chloral. Secondly, there is probably repolymerization of chloral as it accumulates, especially since the ceiling temperature for chloral polymerization is well above the irradiation temperature (room temperature). The lowered residual content of acetaldehyde is partly due to volatilization, but more importantly, repolymerization of acetaldehyde is inefficient because of its very low ceiling temperature.

The other consequence of radiolysis is the change in MW which will be presented below.

Gamma irradiation of ACC in air resulted in very efficient unzipping. From the slope of Figure 6 the G(M) value is estimated to be 17700. The same behavior was observed for e-ACC. However, urethane end-capped ACC is not depolymerized at irradiation levels up to 0.6 Mrad. At higher doses unzipping occurs with G(M)=16500 (Table IV, Figure 6). This induction behavior was seen repeatedly both in different samples from one preparation and of samples from different polymerizations. The unzipping of u-ACC

stops at 87% of completion as compared to >97% for both ACC without end-capping or with ester end-capping.

The effect of scavengers was investigated. The addition of 1.25% of Bu_4NBr to PAC has no effect on the radiolysis in air (Figure 7). On the other hand 1.25% of BHT inhibits depolymerization up to a radiation dose of ca. 3 Mrad. Above this dose, normal depolymerization occurs with G(M)=17000.

Table IV. Radiolysis of PAC

Copolymer	air/vac	additive	G(M)
ACC	air	none	17,700
e-ACC	air	none	17,700
u-ACC	air	none	16,500
ACC	air	Bu_4NBr[a]	17,700
ACC	air	BHT[a]	17,000
ACC	vac	none	3,900
ACC	vac	TMU[b]	3,900
ACC	vac	BHT[a]	2,400
ACC	vac	BQ[c]	250
ACC	vac	ϕ_2IPF_6[d]	32,700

[a]1.25%, [b]tetramethyl urea 1.5%, [c]benzoquinone, 0.7%; [d]diphenyl iodonium salt, 10%.

Gamma radiolysis of ACC in air leaves copolymers with progressively lower MW and having a broader distribution (Figure 8). The two MW fractions merge into a single broad one. It is not possible to obtain the chain scission yield

from this data. Such determination needs to be performed on isolated ACC fractions.

Radiolysis of ACC in vacuo is much less efficient than with air present (Figure 9). The G(M) value is only 3900 and unzipping stops at 80% conversion. Tetramethyl urea did not affect the radiolysis. Addition of BHT retards on the radiolysis to G(M) = 2400. Benzoquinone was a very efficient inhibitor for radiolysis of ACC in vacuum. Seven-tenths of a percent of BQ reduces the G(M) value to 250.

Addition of an iodonium salt resulted in very highly efficient radiolysis of ACC; G(M)=32700 even in vacuo. Apparently, radiolysis of this compound produces a different active species than that formed from the radiolysis of ACC itself, as indicated absence of effects by free radical scavengers and oxygen.

The MW of ACC decreases monotonically with radiation dose as shown by the GPC curves (Figure 10). The change of MW for the low MW peak of ACC-b is plotted according to the well known relationships[5a],

$$\bar{M}_{n,D}^{-1} = \bar{M}_{n,o}^{-1} + [G(S) - G(X)] \frac{D}{100N} \qquad (1)$$

$$M_{w,D}^{-1} = M_{w,o}^{-1} + [G(S) - 4G(X)] \frac{D}{200N} \qquad (2)$$

where subscripts o and D denote molecular weight before and after D dose of γ-irradiation and N is the Avogadro number Figure 11. The slopes of the plots gave G(S)=1.9 and G(X)=0.

Photolysis

ACC was also depolymerized by 253 nm photolysis in air (Figure 12). The copolymer has a molar extinction coefficient of 0.57 $(Mcm)^{-1}$. After an induction period of ca. 7 hrs, there is rapid weight loss with a maximum quantium yield of $\phi(M)=1.7$. There is also a very significant effect of oxygen because UV photolysis in vacuo resulted in negligible amount of monomer formation.

Electron-beam irradiation.

ACC film was irradiated with 20 keV electrons in vacuo. The decrease of film thickness versus dose (Figure 13) is slight. Developing with isopropanol gave a value of E-beam sensitivity for ACC of ca. $3x10^{-6}C\ cm^{-2}$.

DISCUSSION OF RESULTS

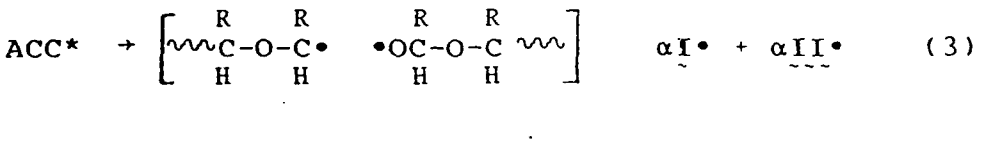
True alternating copolymerization would produce a 1:1 copolymer for a wide range of comonomer feed ratios. The results of Table I showed that the acetaldehyde and chloral contents in the copolymer vary with comonomer feed ratio.

The copolymers obtained at equimolar feed composition have bimodal distributions. The low MW fraction is rich in acetaldehyde while the high MW fraction is rich in chloral. The two fractions are probably produced by two different catalytic species such as the monomeric and dimeric TEA. Another possibility is that one of the active species is an ethyl aluminoxane, i.e. a reaction product of TEA with H_2O. Aluminoxanes have been used to polymerize alkylene oxides and as co-catalysts with metallocene compounds for olefin polymerizations.

Interaction of energetic electromagnetic radiation with ACC resulted in chain depropagation. Like all chain processes it is comprised of initiation, depropagation, transfer and termination. Let us consider the case of radiolysis in vacuo. The chain initiation is the consequence of excitation of PAC into excited states and radical ions. Both species are potential initiators for depolymerization, the effect of scavengers should reveal their relative importance. Cation scavengers, TMU and Bu_4NBr, have no effect on the radiolysis (Figures 7 and 8). On the other hand, free radical scavengers such as BHT and benzoquinone, BQ, are very effective inhibitors. Based on this and other evidence (vide infra) it is concluded that the ionic species are probably not important in the unzipping of ACC. They are probably neutralized by electrons and transformed to excited states. The same

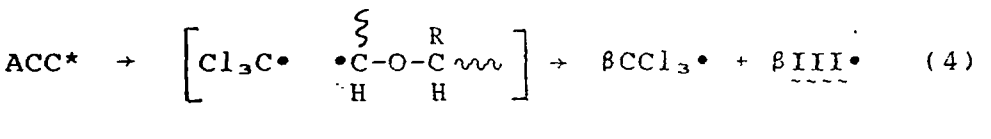
behavior was observed for the radiolysis of poly(chloroacetaldehyde).

The main chain initiation processes are the homolysis of weak bonds in the excited state molecule to produce radicals,



$$ACC^* \rightarrow \left[\sim C(R)(H)-O-C(R)(H)\bullet \quad \bullet O-C(R)(H)-C(R)(H)\sim\right] \rightarrow \alpha\underset{\sim}{I}\bullet + \alpha\underset{\sim\sim}{II}\bullet \qquad (3)$$

($\underset{\sim}{I}\cdot$) ($\underset{\sim\sim}{II}\cdot$)



$$ACC^* \rightarrow \left[Cl_3C\bullet \quad \bullet C(H)(H)-O-C(R)(H)\sim\right] \rightarrow \beta CCl_3\bullet + \beta\underset{\sim\sim\sim}{III}\bullet \qquad (4)$$

($\underset{\sim\sim\sim}{III}\cdot$)

where R is Me or CCl_3, and α and β are the fraction of radicals which did not recombine in the primary cage. Cleavage of the C-Cl bond also occurs but the process does not lead directly to main chain-scission. Radicals I• and $ClCH_2$• were observed in the low temperature photolysis of poly(chloroacetaldehyde) by process analogous to eqs. 3 and 4.

The chain propagation here is the depolymerization, i.e. unzipping, of I and II,

$$\underset{\sim}{I}\bullet \quad (\underset{\sim\sim}{II})\bullet \longrightarrow \text{monomer} + \underset{\sim}{I}\bullet \quad (\underset{\sim\sim}{II}\bullet) \qquad (5)$$

Radical III can also initiate depolymerization,

$$\underset{\sim\sim\sim}{III}\bullet \longrightarrow \sim\!\!\sim\!\!\sim\!\!\sim \overset{R}{\underset{H}{C}}\text{-O-C}\overset{O}{\underset{H}{}} + \underset{\sim\sim}{I}\bullet \qquad (6)$$

The dominant chain transfer process is that of hydrogen abstraction by the alkoxy radical

$$\underset{\sim\sim}{II}\bullet + ACC \rightarrow \sim\!\!\sim\!\!\sim\!\!\sim \overset{R}{\underset{H}{C}}\text{-OH} + \sim\!\!\sim\!\!\sim\!\!\sim \overset{R}{\underset{H}{C}}\text{-O-}\overset{R}{C}\text{-O}\sim\!\!\sim\!\!\sim \qquad (7)$$

$$(\underset{\sim\sim\sim}{IV}\bullet)$$

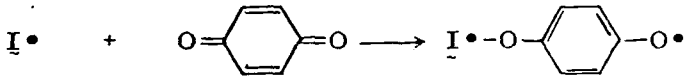
Combination and disapportionation of free radicals terminate the chain depolymerization. The fact that the irradiated copolymer is not crosslinked indicates that the termination of radicals $\underset{\sim\sim\sim\sim}{III}\bullet$ and $\underset{\sim\sim}{IV}\bullet$, having unpaired electrons in the backbone, are with the radicals $\underset{\sim}{I}\bullet$ and $\underset{\sim\sim\sim}{II}\bullet$, having unpaired electrons at its chain ends or $CCl_3\bullet$.

The alkoxy radical can be scavenged by BHT,

$$II\bullet + \text{BHT-OH} \longrightarrow \sim\!\!\sim\!\!\sim\!\!\sim \overset{R}{\underset{H}{C}}\text{-OH} + \text{BHT-O}\bullet \qquad (8)$$

The alkyl radical is not scavenged by BHT because the O-H bond is stronger than the CH bond. In contrast BQ is a much

more effective inhibitor against radiolysis, probably because it can scavenge both carbon radicals I and II



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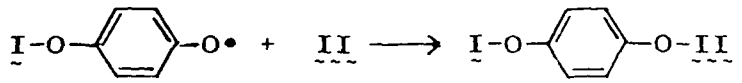
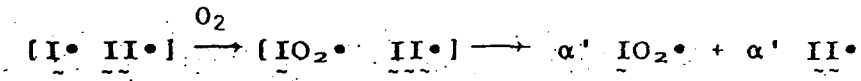
and



(10)

The induction period observed for u-ACC samples suggests a stabilizing effect of radicals of the urethane moiety.

Previously, only small effects have been reported on the radiolysis of polymers. For instance, the radiolytic degradation of poly(ethylene oxide) proceeds both in the presence and in the absence of air.[12] However, at low dosage air does reduce crosslinking.[13] This effect was attributed to the oxygenation of the backbone radicals in competition with their combination. The very large oxygen effect described above can be explained by its reactions with the alkyl radicals converting them into the respective peroxy radicals. The primary cage recombination efficiency of I• and II• is lowered and a large fraction (>α) of radicals diffuse out.



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The effect of oxygen on the other kind of cage is smaller because of competing termination of peroxy radicals in the cage

$$[Cl_3C\bullet\ \underset{\sim\sim\sim}{III}\bullet] \xrightarrow{O_2} [Cl_3COO\bullet\underset{\sim\sim\sim}{III}O_2\bullet] \rightarrow Cl_3CHO + \underset{\sim\sim\sim}{III}OH + O_2 + \beta' Cl_3COO\bullet + \beta'\ \underset{\sim\sim\sim\sim}{III}O_2\bullet \quad (12)$$

The actual unzipping efficiency is increased from G(M) in vacuo by air to G'(M). For irradiations at the same dose rate,

$$\frac{G'(M)}{G(M)} = \left[\alpha' \underline{k}_t \,/\, \alpha\, \underline{k}'_t\right]^{1/2} \quad (13)$$

where $\underline{k}_t$ are the rate constants of terminations in vacuo involving alkyl and alkoxy radicals and $\underline{k}'_t$ are the rate constants of termination in air involving peroxy and alkoxy radicals. In the case of radiolysis of poly(chloroacetaldehyde)[8], $\alpha'/\alpha \sim 2.6$. From the observed G(M) values, one can estimate $\underline{k}_t/\underline{k}'_t \sim 50$. Therefore, more depolymerization occurs in the presence of oxygen because of the slower terminations.

ACC has a molar extinction coefficient of 0.57 $(M\ cm)^{-1}$ at 254 nm which is the dissociative charge-transfer absorption of chlorine-containing aliphatic compounds. From the 50% weight loss during 1.25 hrs of photolysis following the induction period (Figure. 12), the quantum yield for mononomer formation is 1.2. Usually the quantum yield for

bond dissociation in solids is only a small fraction of a percent. The present results are consistent with photolytic initiation of ACC chain unzipping by,

$$\text{ACC} \xrightarrow{h\nu} 0.6\ CCl_3\bullet + 0.6\ \underset{\sim}{III}\bullet \qquad (14)$$

$$CCl_3\bullet + \text{ACC} \longrightarrow HCCl_3 + \underset{\sim}{III}\bullet \qquad (15)$$

followed by reaction 6 and depolymerization. There is also a large oxygen effect; photolysis in vacuo resulted in negligible weight loss. There is no contribution of ionic intermediates to the photolysis because the photon energy is insufficient to cause ionization.

Cationic unzipping can be initiated by protonic acid. Radiolysis of iodonium salt produces protons,[14]

$$(C_6H_5)_2I^+PF_6^- \xrightarrow{h\nu} [(C_6H_5)_2I^+PF_6^-]^* \qquad (16)$$

$$[(C_6H_5)_2I^+PF_6^-]^* \longrightarrow C_6H_5I^{+}\bullet + C_6H_5\bullet + PF_6^- \qquad (17)$$

$$C_6H_5I^{+}\bullet + \text{ACC} \longrightarrow C_6H_5I^+H + \underset{\sim}{IV}\bullet \qquad (18)$$

$$C_6H_5I^+H \rightarrow C_6H_5I + H^+ \qquad (19)$$

$$H^+ + \text{ACC} \rightarrow \sim\!\!\sim\!\!\underset{H}{\overset{R}{C}}\!\!-OH + \underset{\sim}{I}^+ \qquad (20)$$

followed by unzipping of $\underset{\sim}{I}^+$. The reason that oxygen has no effect on the process is that there is no radical pair formed in a cage in this system.

In conclusion, radiolysis and photolysis of ACC initiated efficient unzipping. The mechanisms and reaction yields are the same as found for PCA[8]. The radiolysis

efficiencies of the two systems are compared in Table I. Though the two polymers have the same G(S) values in vacuo

Table I. Radiolytic depolymerization of ACC and PCA[a]

Resist system	G(S)	G(M)	Number of polymer chains unzipped per 100eV	per radical
ACC(vac)	1.9	3900	13	6.6
ACC(air)	n.d.[b]	18000	60	n.d.
ACC (onium salt)[c]	n.d.	32700	110	n.d.
PCA(vac)	2.1	1100	1.2	0.3
PCA(air)	5.5	11000	13.5	3
PCA (onium salt)	n.d.	44000	54	n.d.

[a]Poly(chloroacetaldehyde); [b]not determined; [c]sensitized with ϕ_2IPF_6.

and probably also the same G(S) values in air, ACC depolymerizes three to ten times more than PCA. In addition, ACC is more thermally stable than PCA. Both polymers are useful as E-beam self-developing resist but ACC is superior to PCA.

Acknowledgement

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Figure Captions

Figure 1. GPC curves for ACC: (a) sample a; (b) sample b

Figure 2. ^{13}C-NMR spectra of ACC-a

Figure 3. TGA curves for: (1) poly(56A-co-44-c); (2) poly(70A-co-30-c); (3) polychloral; (4) polyacetaldehyde

Figure 4. TGA curves for: (a) ACC (———); (b) e-ACC(-·-·-·-); (c) u-ACC (-----).

Figure 5. Arrhenius plots of the first order rate constants of thermolysis: (a) ACC; (b) e-ACC; (c) u-ACC

Figure 6. Weight loss vs gamma dose in air of copolymer: (•) without endcapping; (□) endcapped with acetic anhydride; (▲) endcapped with phenylisocyanate

Figure 7. Weight loss vs gamma dose in air of copolymer: (•) no additive; (○) with 1.25% Bu_4NBr; (▼) with 1.25% BHT.

Figure 8. GPLC spectra of ACC γ-irradiated in Ar; (a) 0 Mrad; (b) 0.7 Mrad; (c) 0.29 Mrad; (4) 0.55 Mrad.

Figure 9. Weight loss vs γ dose (in vacuum) of ACC: (•) No additive; (○) 1.5% $Me_2N-\overset{O}{\overset{\|}{C}}-N-Me_2$; (■) 10% $(C_6H_5)_2IPF_6$; (▽) 1.25% BHT; (♦) 0.7% o=⟨⟩=o

Figure 10. GPL spectra of ACC γ-irradiation in vac: (a) 0 Mrad; (b) 0.2 Mrad; (c) 0.4 Mrad; (d) 0.6 Mrad.

Figure 11. Variation of $\bar{M}n^{-1}$, $\bar{M}w^{-1}$ of copolymer vs γ-dose in vacuum: (▼) $\bar{M}n$; (●) $\bar{M}w$.

Figure 12. Weight loss versus UV irradiation time of PAC: (•) in air; (o) in vacuo.

Figure 13. Normalized thickness vs electron-beam dose in copolymer exposure (in SEM); (■) before developing.

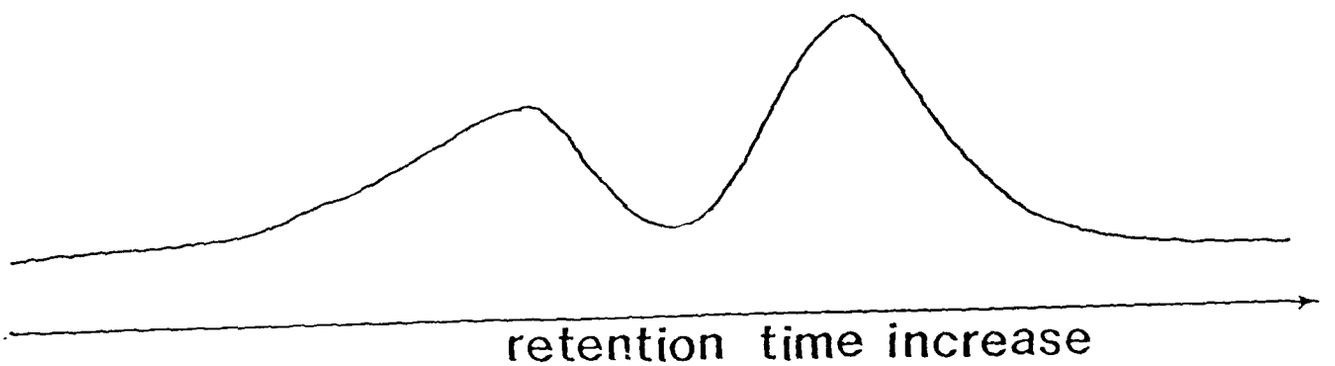
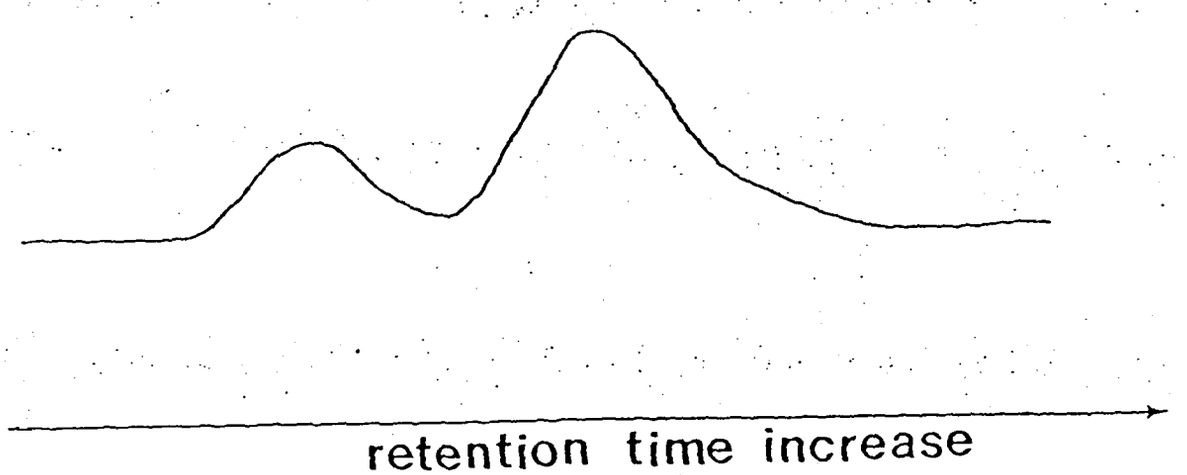


Fig. 1a



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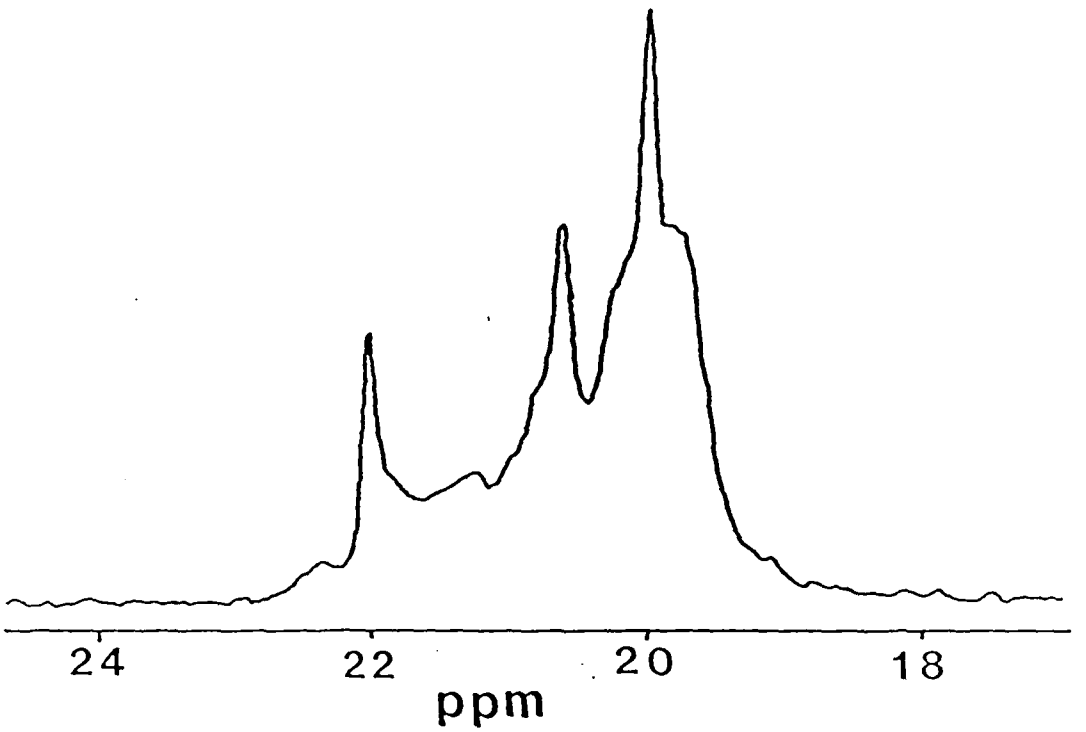


Fig. 2a

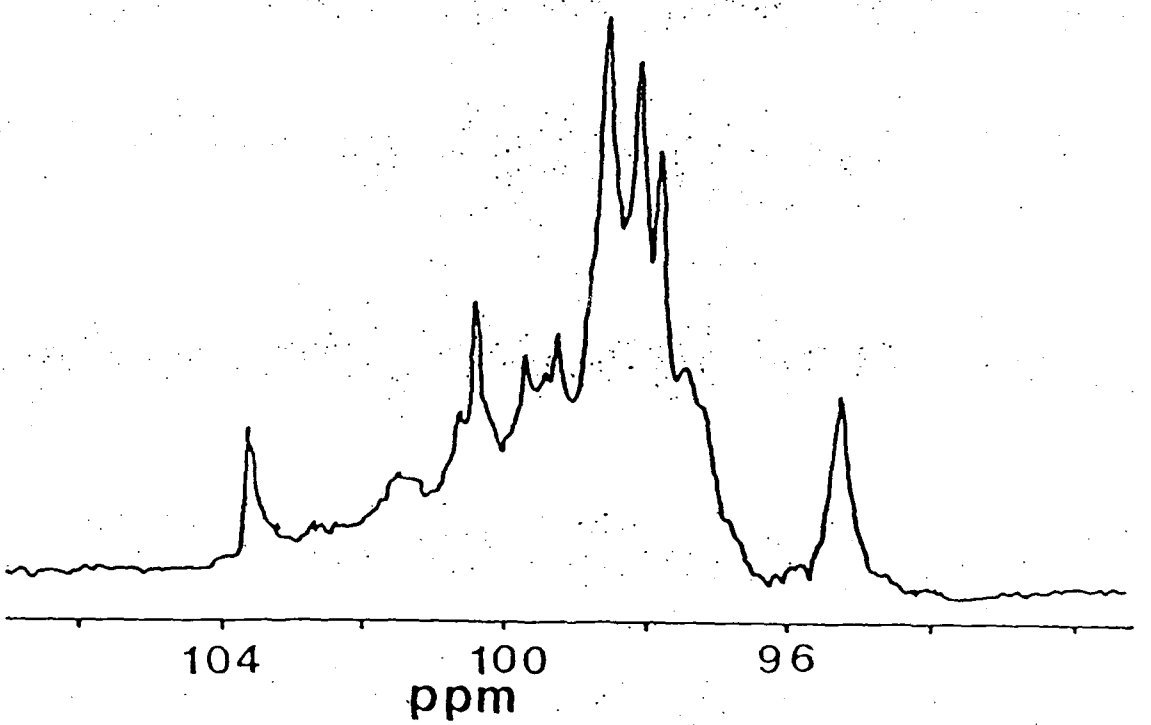


Fig. 2b

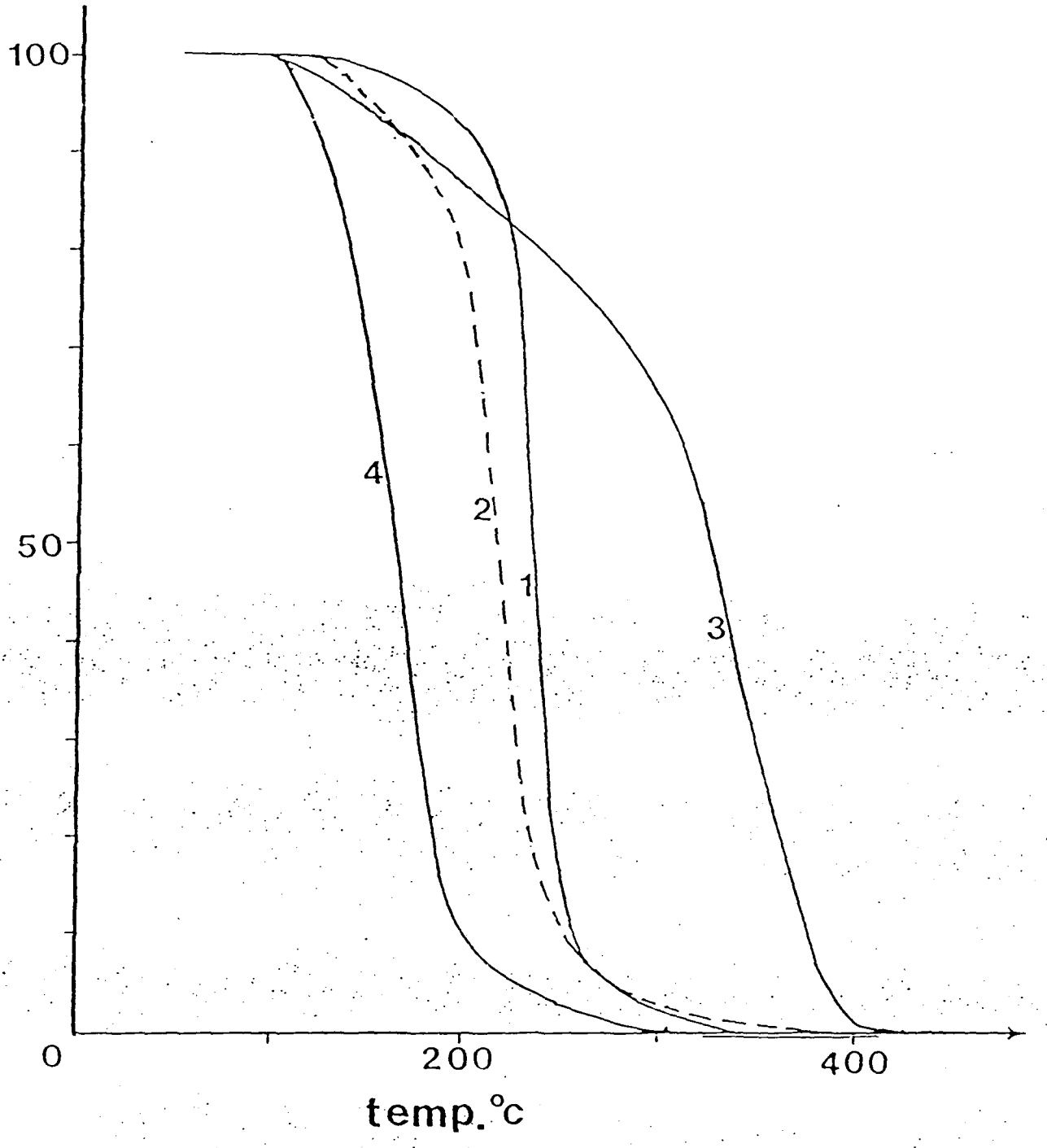


Fig. 3

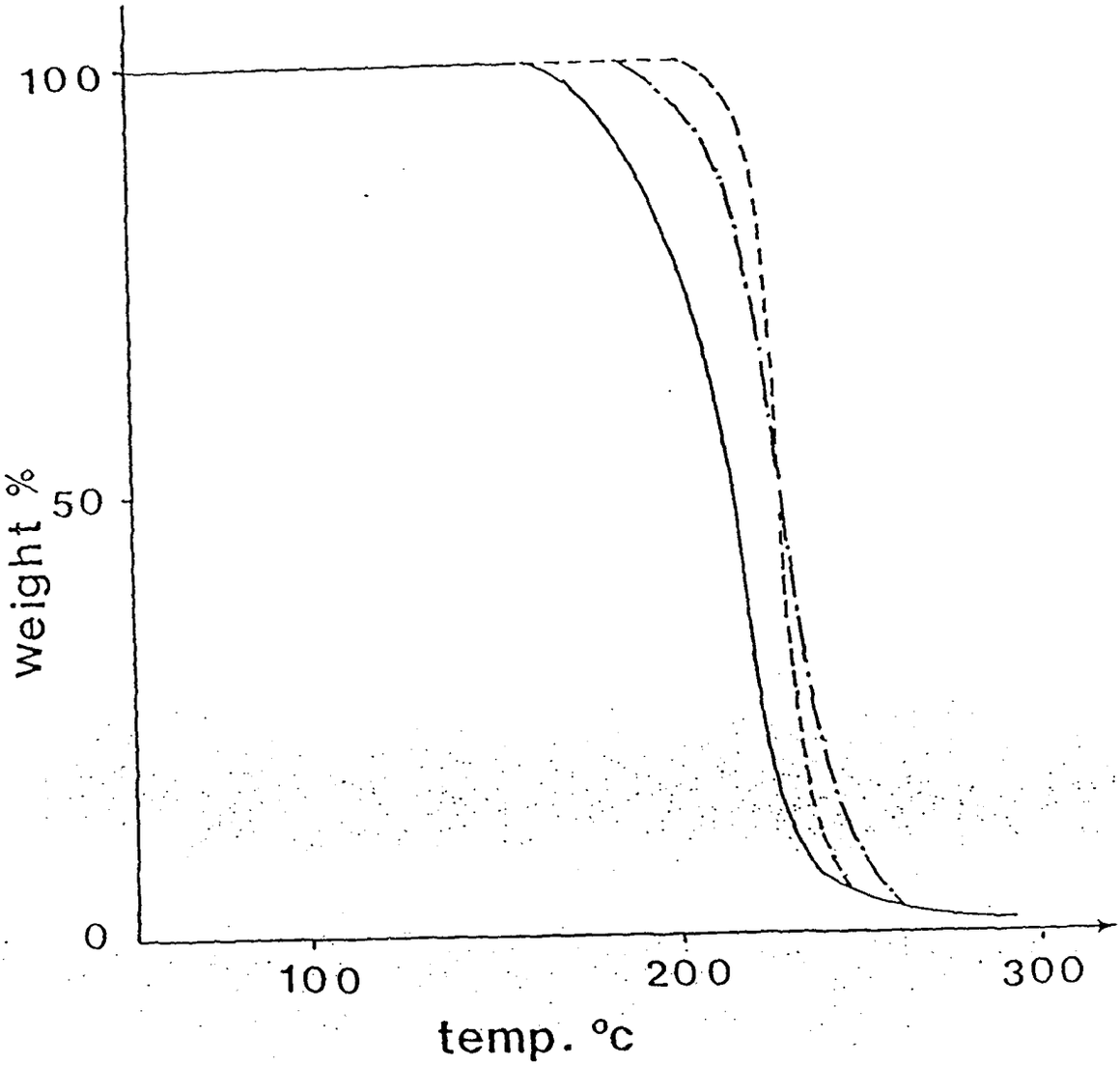
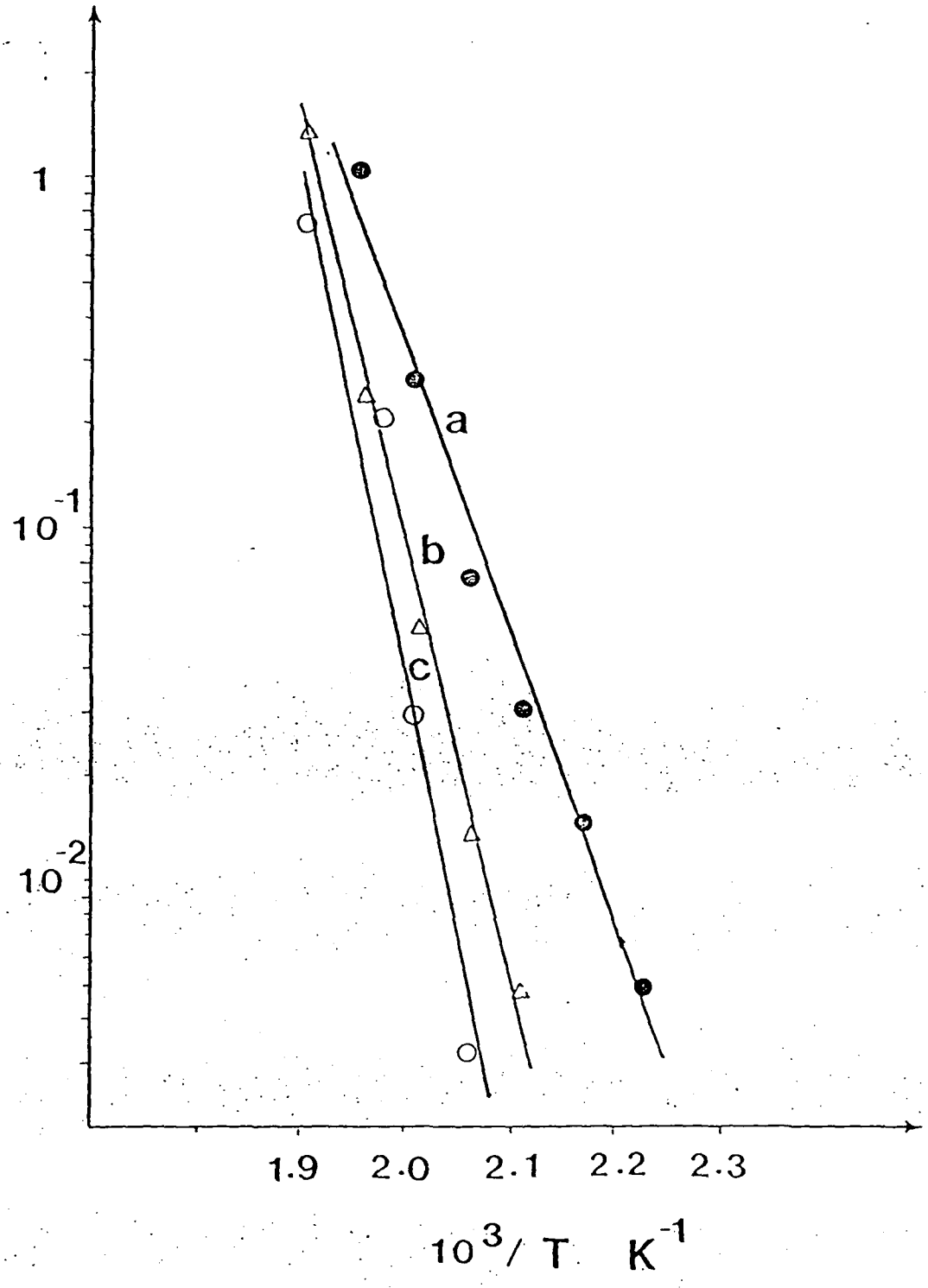


Fig. 4



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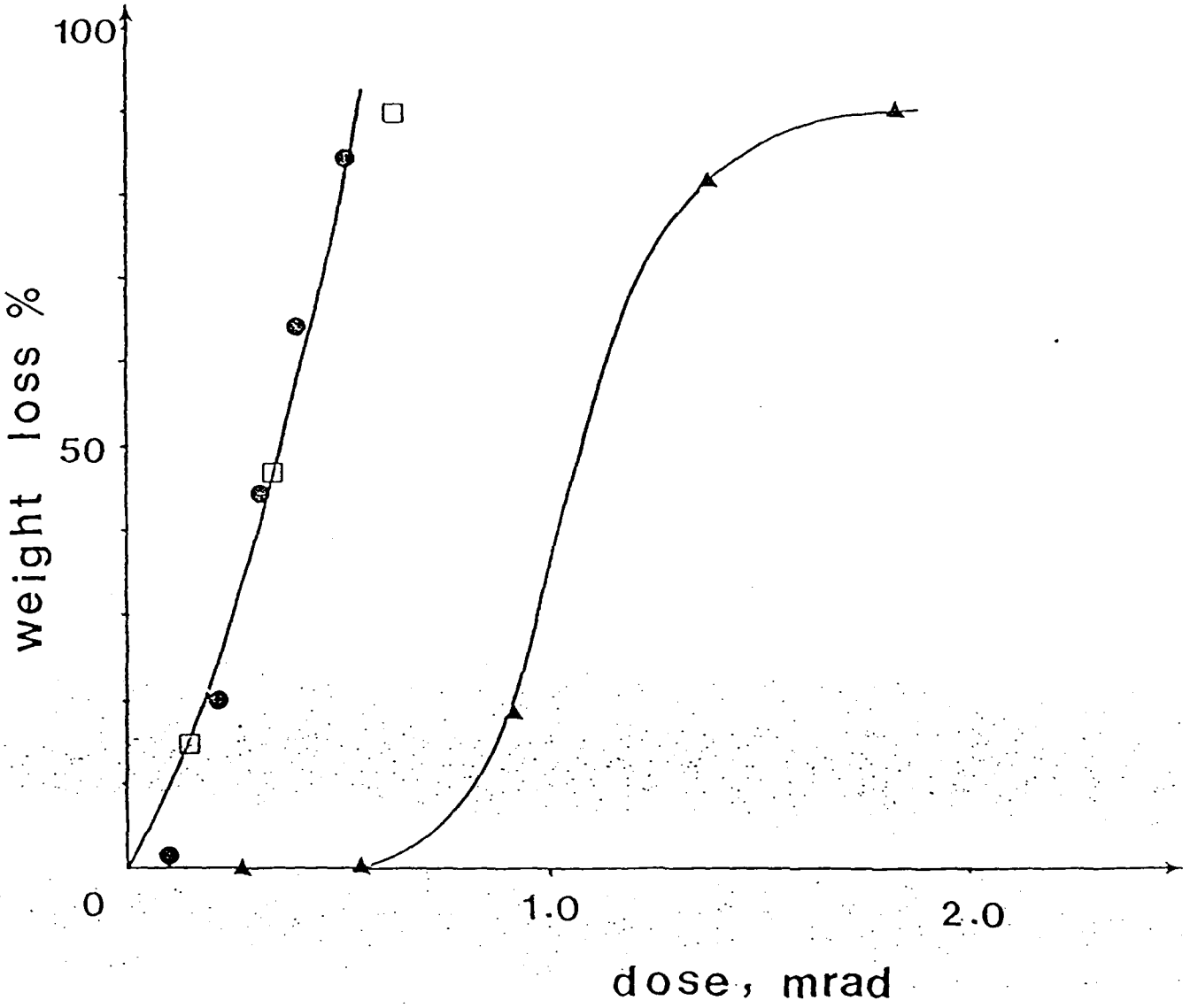

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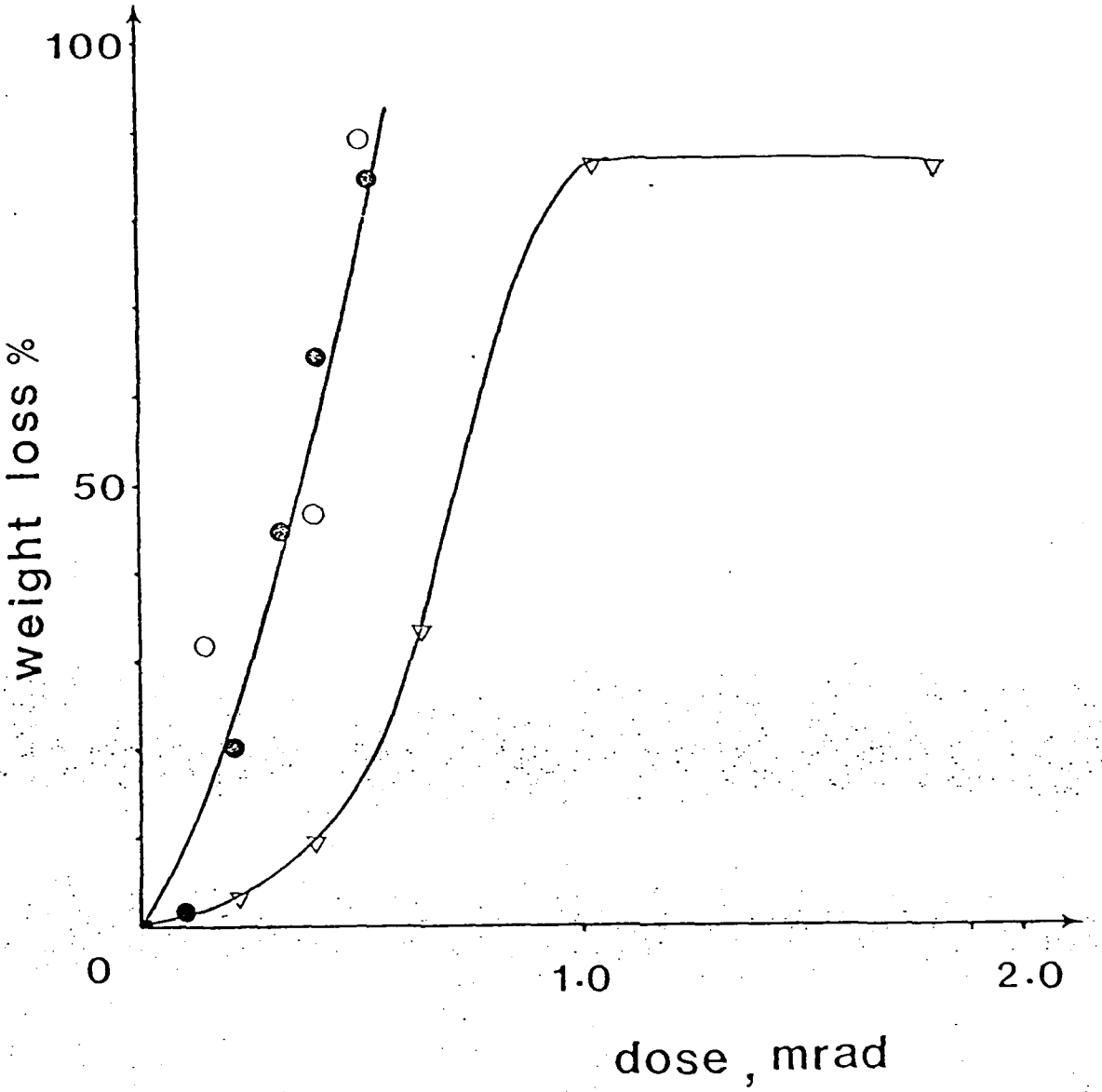

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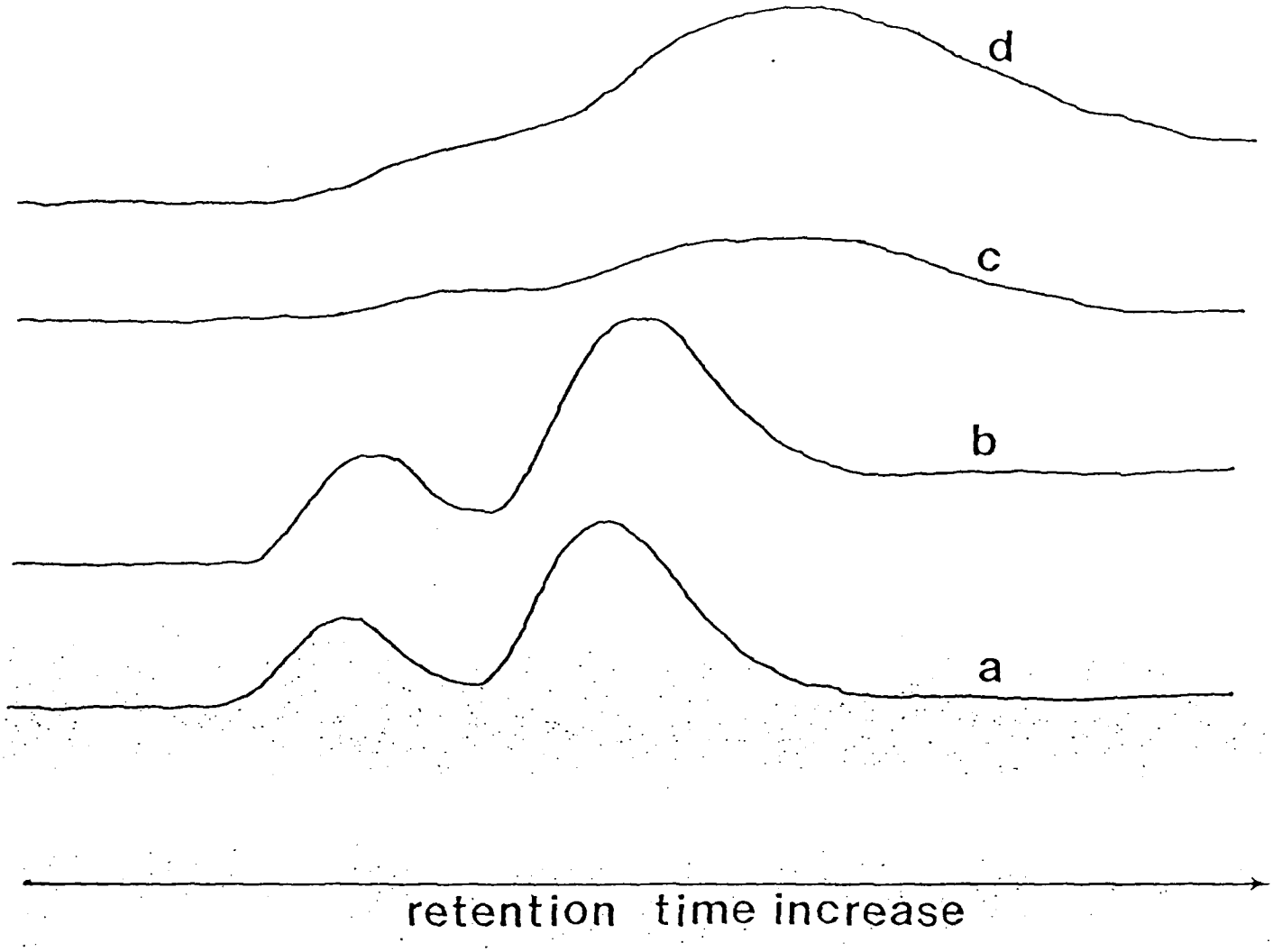


Fig. 8

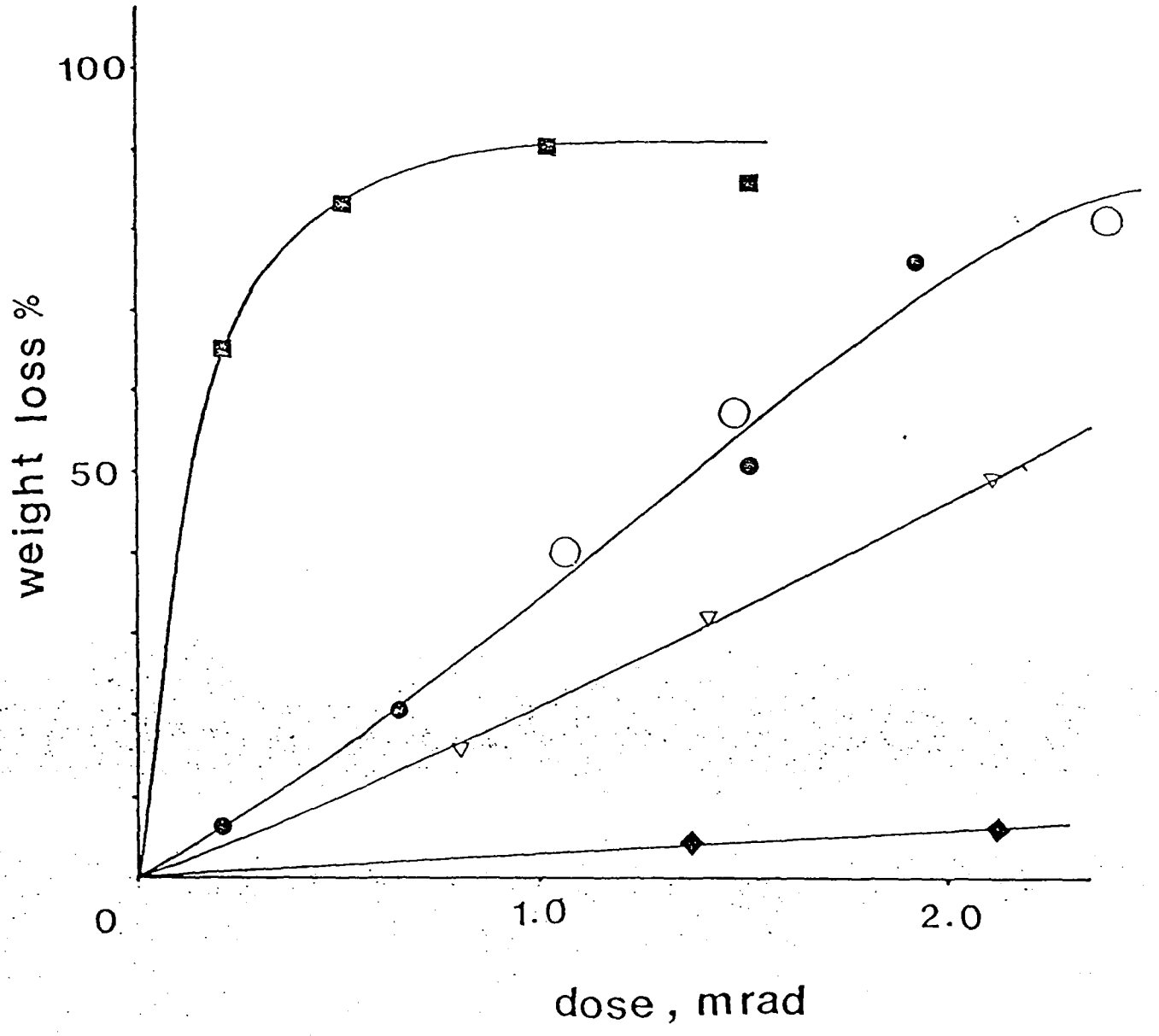


Fig 9

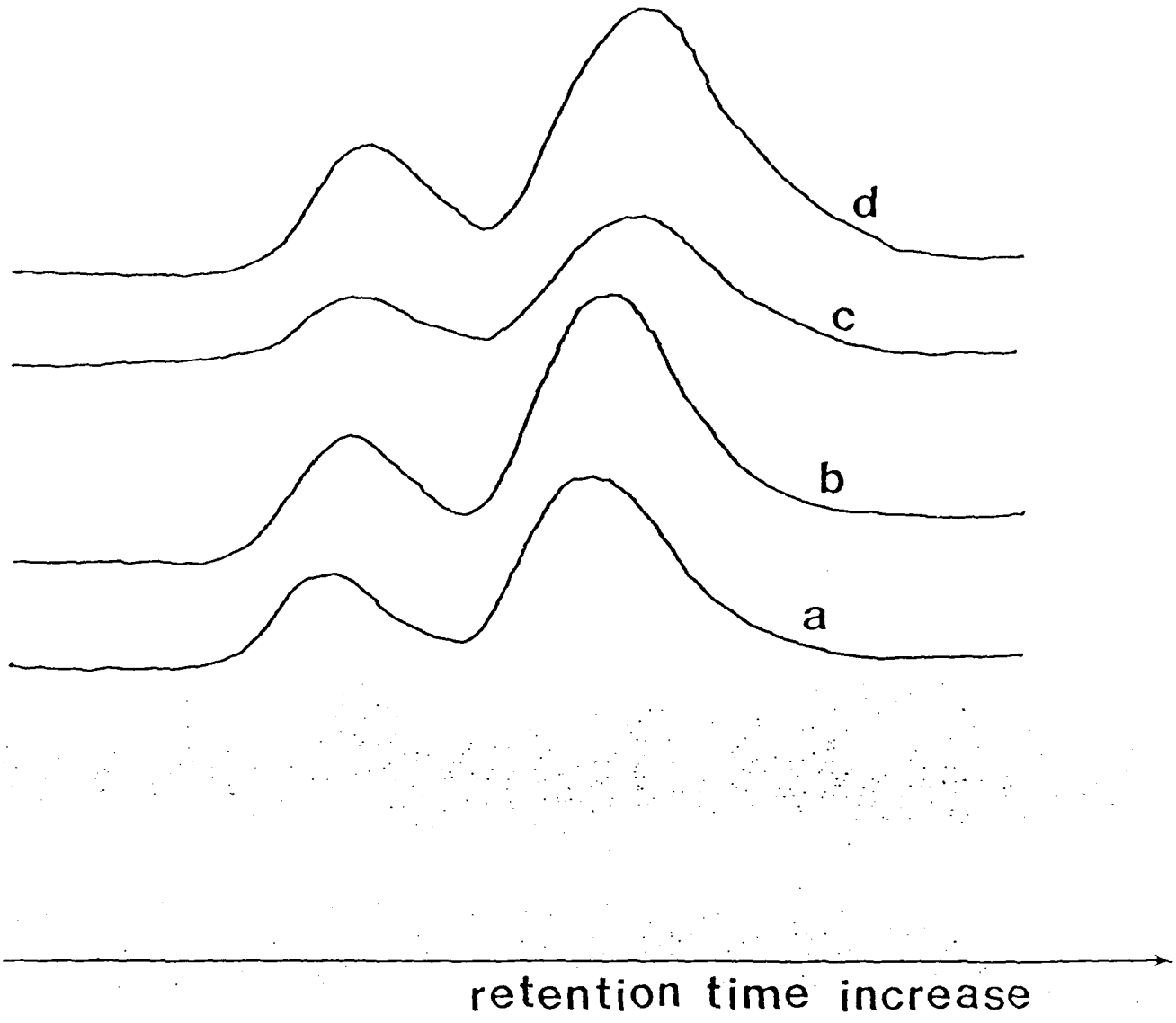
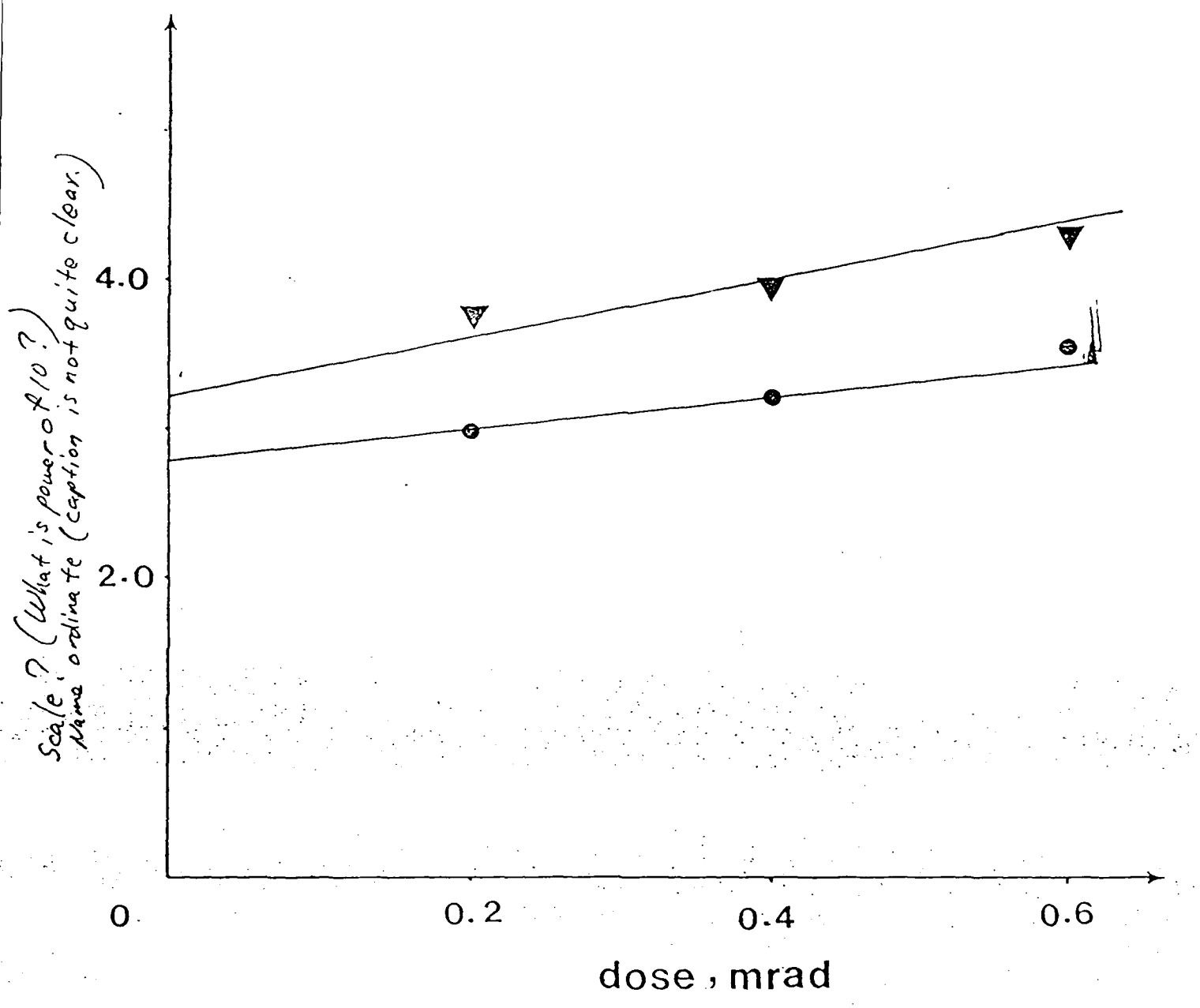


Fig. 10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Name ordinate (caption is not quite clear.)
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2.0
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dose , mrad

Fig. 11

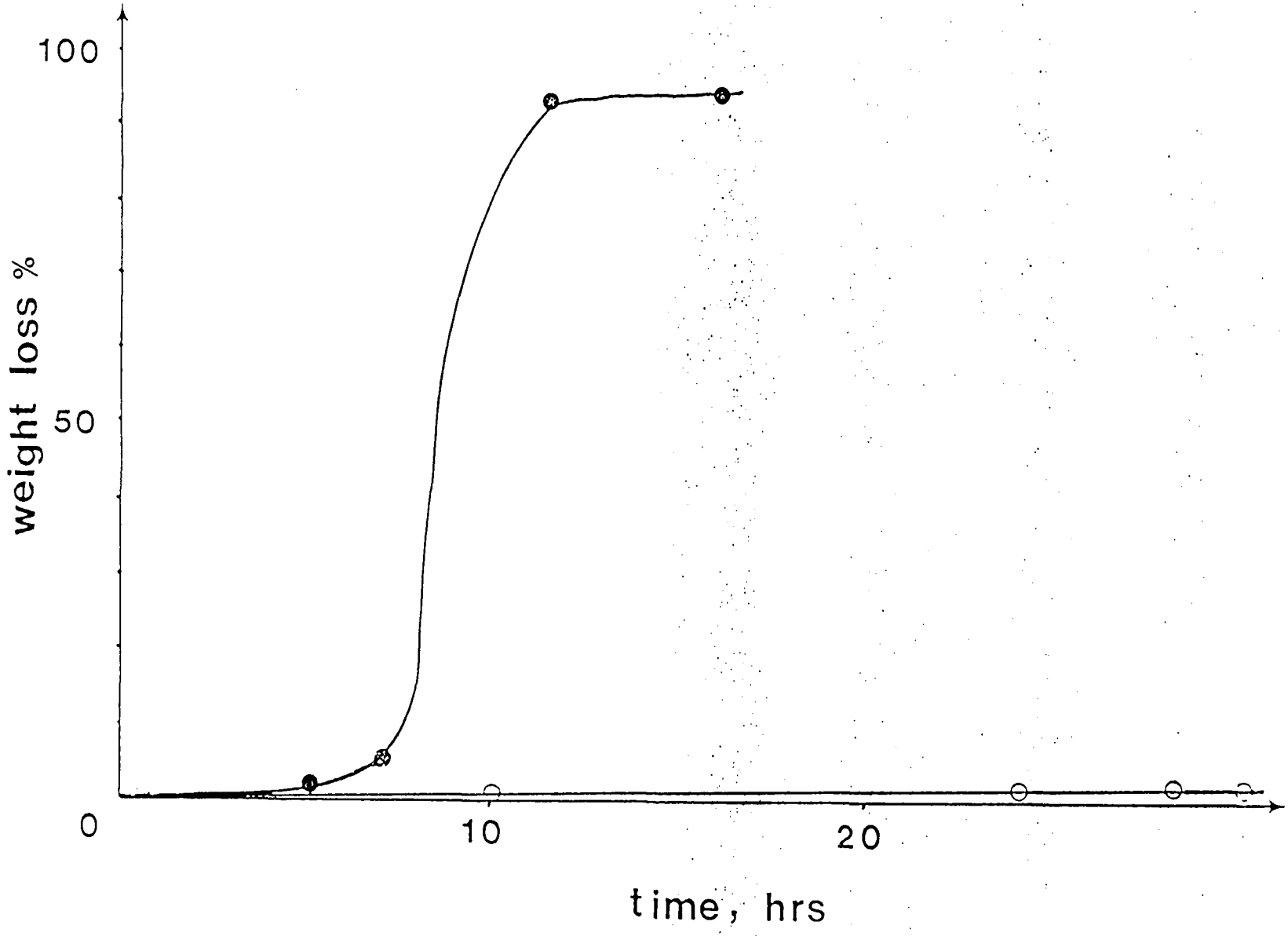

Fig. 12

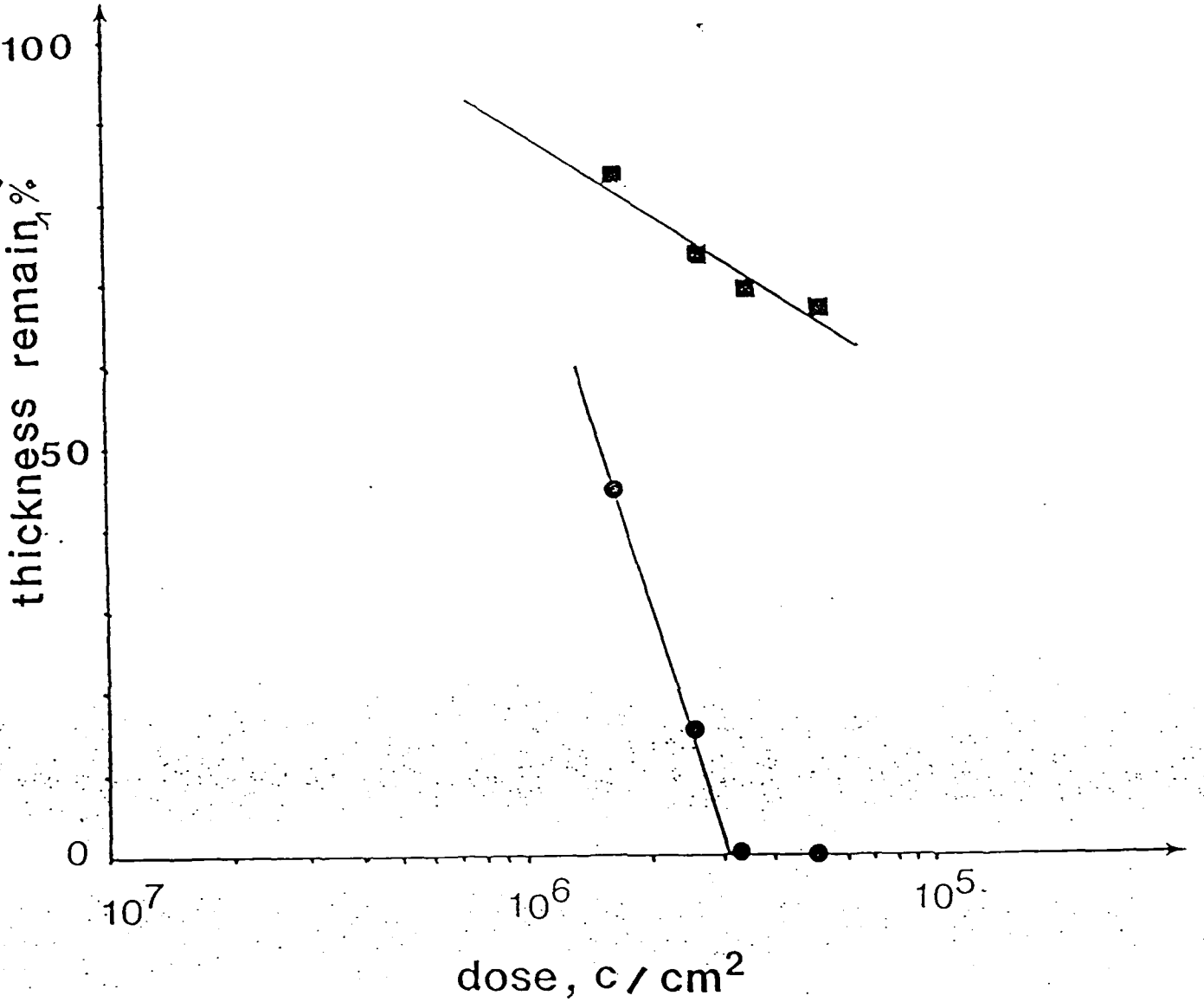

Fig. 13