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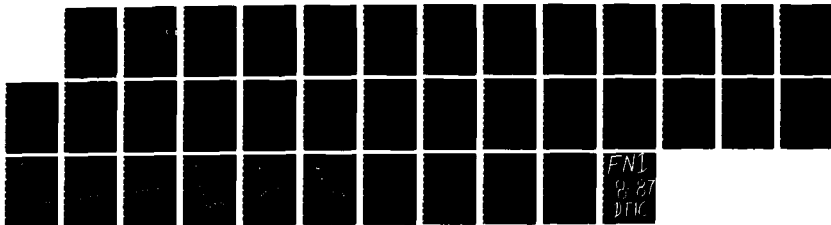
RADIOLYSIS OF POLY(CHLOROACETALDEHYDE) A POSITIVE
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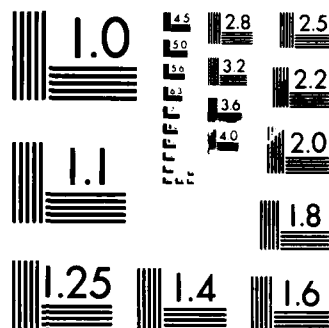
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Radiolysis of Poly(chloroacetaldehyde), A Positive

E-Beam Resist

by

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Radiolysis of Poly(chloroacetaldehyde), A Positive

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ABSTRACT

The gamma radiolysis and deep ultraviolet photolysis of poly(chloroacetaldehyde), PCA, caused efficient depolymerizations at ambient temperature. The processes are promoted by oxygen; the G_m value (number of monomer produced per 100 eV absorbed) is 11,000 in the presence of air. The chain scission yield is also high ($G_s = 5.5$) without crosslinking ($G_x = 0$). These processes are much less efficient in vacuo; $G_m = 1,100$, $G_s = 2.1$, $G_x = 0$. Depolymerizations stop short of completion due to repolymerization of monomer formed. Bu_4NBr has no effect on the γ -induced depolymerization but 2,6-di-*t*-butyl-*p*-cresol retards it suggesting the participation of free radicals rather than ionic species in the processes. This interpretation is supported by electron spin resonance evidences. PCA is highly susceptible to degradation by plasma. However, this susceptibility can be suppressed by DUV crosslinking of PCA with bis(azidoformates) prior to plasma exposure. Halogen containing polymers possessing low ceiling temperature may find usages as self-developing plasma etchable positive resists.



INTRODUCTION

Research on radiation chemistry of polymers have been rejuvenated to meet the technological needs of microelectronic lithography. Conventional positive resist system, of which poly(methyl methacrylate) (PMMA) is a prime example, is based upon radiation induced chain scission. The latent image is developed using solvent mixture which maximizes the differential solubilities of the degraded and the unexposed materials. PMMA has a relatively low G_s value of 1.2 main chain scission per 100 eV. Higher radiation sensitivity can be achieved by taking advantage of dissociative electron capture by halogen atoms.¹ A systematic study² has been made of the effects of the type of halogen atom and of its position of substitution on radiation sensitivity. The results led to the postulation and experimental verification of high radiation sensitivity for polymers of trifluoroethyl- and hexafluoro-*n*-propyl- α -chloroacrylates with G_s values three times that of PMMA.³

Polymers, which degrade upon irradiation to volatile products, are potentially capable of direct imaging and is therefore self-developing.⁴ Such systems have the obvious advantages of simplicity and economy. Polymers with low ceiling temperature (T_c) which undergoes depolymerization upon irradiation at temperatures above T_c are likely candidates for self-developing resists. A well known example is the alternating copolymers of olefin and SO_2 (poly(alkylene sulfone)s).⁵

However, its radiation chemistry is not as simple as expected. Only irradiations above 60 - 70°C are the yields of olefin and SO₂ the same consistent with depolymerization. At room temperature the yield of SO₂ is four to seven times greater than the yields of olefins which may be partly attributable to repolymerization of olefins. Olefin isomerizations also were observed. In fact bombardment of poly(1-butene sulfone) with 11-keV (C_s⁺ ion produces only oligomeric fragments⁶ comprised of two to seven structural repeat units.

Preliminary study on copolymers of alkyl aldehydes had been reported;⁷ the materials tend to depolymerize spontaneously. The central purpose of this research is to study the radiation chemistry of poly(monochloroacetaldehyde) (PCA). Based on the known enhancement of radiolysis efficiency^{1,2} by halogen atoms, PCA should exhibit very high radiation sensitivity for depolymerization. The results of γ -radiolysis and deep ultraviolet (DUV) photolysis of PCA and the effects of oxygen and scavengers for radicals and ions on the depolymerization are reported.

EXPERIMENTAL

Materials. Monochloroacetaldehyde was prepared according to the method of Iwata et al.⁸ It has the correct elemental analysis and ¹H-NMR; it is > 99% pure according to GC. Iodonium salt, (C₆H₅)₂I⁺PF₆⁻, BHT, 2,6-di-t-butyl-p-cresol, tetrabutyl ammonium

bromide, and phenyl isocyanate were purchased from Aldrich Chemicals. Phenyl isocyanate was dried over P_2O_5 under nitrogen for 60 min. then distilled at 45 - 47°/10 torr immediately before use.

Polymerization. Toluene solution of monochloroacetaldehyde was polymerized at -78°C using 1 mole % of $BF_3 \cdot Et_2O$ initiator. Polymerization was quenched with methanol. The PCA thus obtained has two hydroxyl termini as determined by $LiAlH_4$. PCA was stabilized by dissolution in chloroform and endcapped by reaction with stoichiometric amount of phenyl isocyanate (reaction catalyzed with dibutyl tin dilaurate at room temperature for 2 hrs then at 70° for 10 min). The end-capped polymer was purified by reprecipitation with methanol.

Polymer Characterization. PCA has IR bands at 765 cm^{-1} for C-Cl stretching and 1150 to 1085 cm^{-1} associated with C-O-C stretching as reported.⁸ The IR spectrum of end-capped PCA has additional bands at 3300 to 3500 cm^{-1} , 1735 cm^{-1} , and 1495 to 1530 cm^{-1} due to the N-H, C=O, and aromatic vibrations, respectively. 1H -NMR spectra of PCA has peaks at 3.67 ppm (broad s, 2H); 5.1 - 5.5 ppm (m, 1H). In addition there are signals at 4.06 ppm (d, 0.019H) and at 9.63 ppm (s, 0.008H), they may be attributable to the methylene and aldehyde proton of residual monomer and/or its oxidation product. PCA is soluble in tetrahydrofuran, THF,

chloroform, cyclohexanone and probably many other common solvents. The $\bar{M}_n$ and $\bar{M}_w$ values for PCA are 6.5×10^4 and 9.1×10^4 , respectively, with a polydispersity index $\bar{M}_w/\bar{M}_n = 1.39$.

Radiolysis. The gamma source was ^{137}Cs with a radioactivity of 400 Ci in August of 1968. The dose rate at individual sample position was determined by Fricke dosimetry. DUV irradiation was performed in a Rayonet Photochemical Reactor equipped with four RPR-1849 lamps emitting 253.7 nm radiation with an intensity of 1.65×10^{16} photons $\text{sec}^{-1} \text{ cm}^{-3}$ found with ferrioxalate actinometry.

Twenty to thirty mg of PCA was irradiated in weighed 5 mm o.d. sample tube 2" in length either open to air or sealed under vacuum. Following irradiation the volatile products were removed by mechanical pumping for 24 hrs at 60°C and analyzed by GC-MS (gas chromatography - mass spectrometry). The residue was weighed by difference and its IR and ^1H -NMR spectra taken. The molecular weights and distribution were determined.

Samples were also irradiated in vacuo and in air at -195°C and 25°C for ESR measurements.

Plasma Etching. Plasma etching at room temperature was performed in a tubular plasma reactor operating at 100 watts with 0.5 torr of CF_4 . PCA films were exposed to plasma¹ for 5, 10 or 20 min and weighed afterwards with a SARTORIUS Microbalance to 1 μg .

Instrumentation. The instruments used in this work are: Varian XL-300 for ^1H -NMR, IBM ESP-300 for ESR, for IR, Perkin Elmer TGS-2 for thermogravimetric analysis (TGA), and Hewlett Packard Model for MS. Waters Associates 201 GPC equipped with five microstyrogel column was used to determine molecular weights of PCA in THF with polystyrenes as the standards.

RESULTS

PCA begins to decompose thermally at ca. 80°C (Figure 1) reaching completion at about 210°C . The end-capped PCA is more thermally stable having a temperature for 50% decomposition which is 40°C higher than PCA itself. All experiments below were performed on end-capped PCA.

Gamma irradiation of PCA in air resulted in rapid weight loss. GC analysis showed only a single volatile product. Figure 2 is a mass spectrum of the radiolysis product which is identical to that of the monomer. The $m/e = 80$ and 78 peaks are due to the monomer molecular ions having the ^{37}Cl and ^{35}Cl isotopes, respectively. The m/e 51, 49 and 50, 51 peaks are attributable to the isotopic CH_3Cl and CH_2Cl , respectively.

About $94 \pm 1\%$ of PCA were depolymerized by γ -radiolysis in air (Figure 3a). The residue is mostly low molecular weight oligomers. The IR spectra of irradiated PCA showed a new carbonyl absorption; in the case of end-capped PCA the carbonyl absorption is superposed on the urethane group vibration. The

^1H -NMR spectra of irradiated have resonances at: 3.67 ppm (broad d, 2H), 5.1 - 5.5 ppm (m, 1H), 4.06 ppm (s, 0.2H) and 9.62 ppm (s, 0.09H). Therefore, there is an increase of dissolved monomer and/or its oxidation products in the irradiated polymer.

The G_s values can be calculated from the change of $\bar{M}_n$ and $\bar{M}_w$ with does by the well known relationships.^{1a,10}

$$\bar{M}_{n,D}^{-1} = \bar{M}_{n,0}^{-1} + [G_s - G_x] \frac{D}{100N} \quad (1)$$

$$\bar{M}_{w,D}^{-1} = \bar{M}_{w,0}^{-1} + [G_s - 4G_x] \frac{D}{200N} \quad (2)$$

where subscripts 0 and D designate molecular weight before and after D dose of γ -irradiation and N is the Avogadro number. The results for radiolysis in air (Figure 4a) gave $G_s = 5.5$ and $G_x = 0$. There is virtually no change in molecular weight distribution. The value of $\bar{M}_w/\bar{M}_n$ after 1.27 Mrad of irradiation in air was 1.41 as compared to 1.39 before irradiation. Therefore, there is no appreciable equilibration between the depropagation chains with PCA, otherwise the value should shift toward the most probable distribution with increasing irradiation.

The radiolysis yield of monomer, G_m , in air is found from weight loss versus dose data to be about 11,000. The G_m and G_s results indicate the depolymerization of 2.4 PCA chains per

scission which is slightly larger than the theoretical value of 2.0. However, it will be shown below that this may be a low estimate.

Scavengers were added to PCA at 2 wt. % level. They were incorporated by codissolving PCA and the additive in chloroform solution followed by evaporation to dryness. Figure 5 showed the effects of scavengers on the γ -ray induced depolymerization of PCA in air. Radiolysis is significantly retarded by BHT; about 70% of PCA remained after long irradiation. On the other hand Bu_4NBr had virtually no effect on the radiolysis as Figure 5a and 3a are superposable.

Poly(phthalaldehyde) can be depolymerized by acid catalysis. Photolysis of diaryliodonium salts have been shown¹¹ to generate protons cationic polymerizations by the formation of H^+ with photolysis. Therefore, the poly(phthalaldehyde)/onium salt system had been used as self-developing photoresist.¹² It is thought likely that radiolysis of cationic initiator may also produce protons to initiate depolymerizations. Ten percent of $(\text{C}_6\text{H}_5)_2\text{IPF}_6$ was added to PCA and γ -irradiated. There was rapid initial depolymerization of about 85% of the polymer with about one Mrad. However, the wt. loss vs. dose curve (Figure 6a) showed reversal at higher dosages indicative of repolymerizations. In other words, the monomer produced was repolymerized so that less monomer was removable by evacuation following radiolysis. Comparison of Fig. 6a with Fig. 3a showed clearly

that both depolymerization and repolymerization were promoted by the proton initiator.

The γ -radiolysis of PCA in vacuo is much less efficient than in air (compare figure 3b with 3a). The value of G_m is only about 1,100. This ten-fold smaller value of G_m in the absence of air is only partly attributable to a decrease in the scission yield. The molecular weight change with dose for irradiation in vacuo (Figure 4b) gave $G_s = 2.1$ and $G_x = 0$. Therefore, only about 0.56 PCA chains were depolymerized per scission in the absence of air. There is a noticeable increase of $\bar{m}_w/\bar{M}_n$ of PCA to 1.51 when irradiated in vacuo. In contrast, the cationic polymerization equilibria is not very sensitive to oxygen; as the same extent of depolymerization in vacuum requires larger doses of γ -radiation than in air (Figure 6b) and there is no marked reversal of the wt vs. dose curve in the former.

DUV irradiation of PCA also initiates depolymerization. GC-MS showed the volatile products to be the monomer as it was in γ -radiolysis. Very large effect of oxygen was also seen in DUV photolysis. Figure 7a showed that more than 86% of PCA was depolymerized by 254 nm irradiation in the presence of air, while only a few percent of PCA was photolyzed in vacuo (Figure 7b).

For ESR measurements PCA was irradiated in suprasil sample tubes. Because the space limitation of the γ -source chamber γ -irradiation of PCA was performed only at room temperature. No signal was detected for BEC γ -irradiated in vacuo. An intense

esr signal was observed for PCA irradiated in air (Figure 8) with $g_{\perp} = 1.998$ and $g_{||} = 2.000$ attributable to peroxy radical. The signal intensity corresponds to 0.013 radicals per 100 eV.

DUV photolysis of PCA gave similar results as radiolysis. No radical was detected in vacuo, peroxy radical was seen for photolysis in air albeit at a much reduced concentration than by radiolysis.

To observe the radicals produced initially by irradiation, PCA was photolyzed at -195°C . The esr spectra of Figure 9 may be analyzed as arising from two radicals. Radical A with $g_r = 2.002$ coupled to one proton with hyperfine splitting of 25 G, and two equivalent protons with hyperfine splitting of 12.5 G. A second radical B has $g = 2.025$ hyperfine coupled to two protons with splitting of 25 G and to ^{35}Cl with splitting of 7 G. Coupling to the less abundant ^{37}Cl , which should have hyperfine interaction within 20% of that for ^{35}Cl , was not resolved.

The SiO_2 layer on the silicon wafer surface can be etched away with hydrofluoric acid after development of the image. However, dry etching with plasma of fluorine containing gas is preferred. The energetic species in a plasma are ions and radicals. Therefore, a polymer sensitive to γ -ray, electron beam, or x-ray is also susceptible to degradation in a plasma environment. Figure 10 compares the etching resistance of PCA and poly(methyl methacrylate) (PMMA) toward CF_4 plasma which shows the former to be about twice more sensitive than the latter

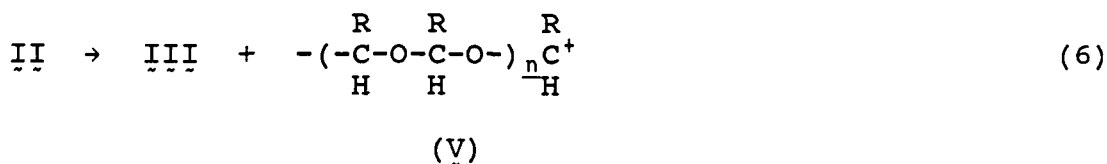
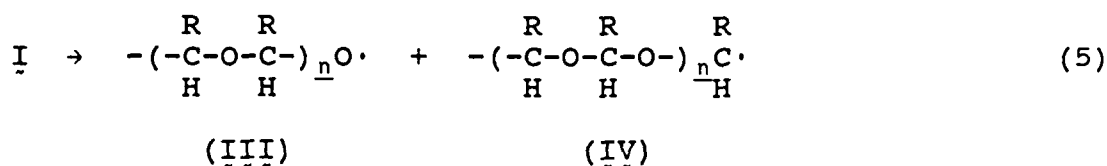
in degradation by plasma. However, a crosslinked polymer should possess greater plasma stability than the uncrosslinked material. Crosslinking can be achieved by photolysis of a substance such as a bis(azidoformate). A viable strategy to introduce plasma etching resistance to a self-developing resist is through the incorporation of a photo-crosslinking agent.

A bis(azidoformate), Hercules crosslinker S 3060, was incorporated into PCA at two and ten weight percent by casting a chloroform solution on Teflon sheet. The dried film was exposed to 254 nm light to photolyze the azido group to nitrene for insertion and crosslinking of PCA. The duration of irradiation was determined by the complete disappearance of the 2120 cm^{-1} stretching band of the azide group. Figure 10 showed that PCA crosslinked with 2% of bis(azidoformate) significantly reduces its plasma sensitivity. With 10% of crosslinker PCA has much better plasma etching resistance than PMMA and comparable to that of copolymers of trifluoroethyl methacrylate and N-p-methoxyphenyl citroconic malide or polyimides.¹³

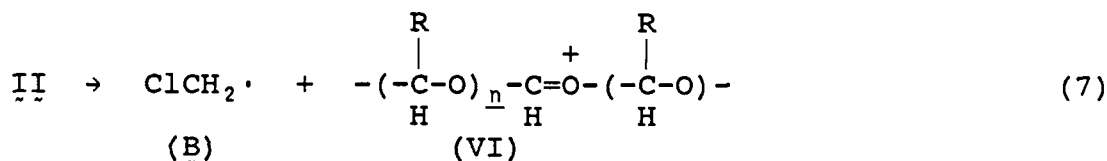
The presence of crosslinker tend to reduce the radiolysis yield of depolymerization. The G_m values are lowered to 5,300 and 1,300 for PCA containing 2% and 10% crosslinker, respectively.

DISCUSSION OF RESULTS

The TGA of PCA obeys first order kinetics plot according to

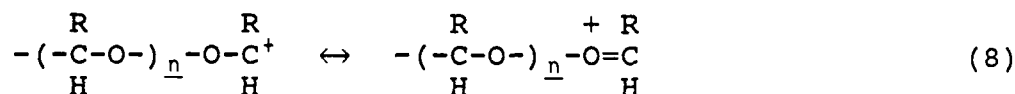


In addition, there is also scission of $\text{ClCH}_2\cdot$ group,



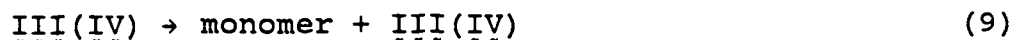
Radicals IV and $\text{ClCH}_2\cdot$ both observed their esr spectra A and B, respectively, -195°C DUV photolyzed PCA. The alkoxyl radical III reacts rapidly by abstracting hydrogen atom. No authentic esr evidence for alkoxyl radical exists except by matrix isolation techniques.

Ion V is stabilized by resonance

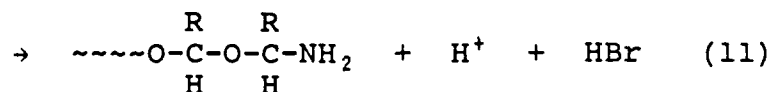
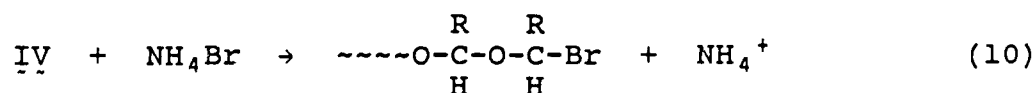


Dissociation of II to oxonium ion and radical III is much less favorable. Depolymerizations occur largely through the

unzipping of III or IV



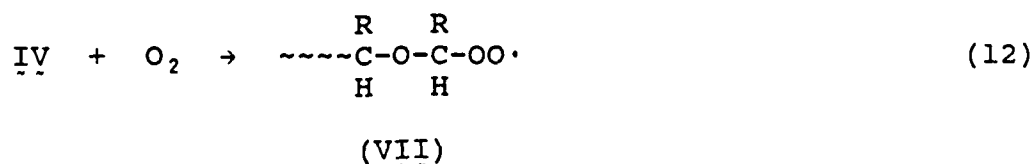
Though depolymerization of V probably also occurs to a small extent, it is limited by neutralization in this media of low dielectric constant to maintain electric neutrality. It is a common practice to ascribe chemical consequences of radiolysis of organic substances to radical reactions. The fact that the addition of NH_4Br had no observable effect on the radiolysis of PCA argues against the participation of ions V in the depolymerization. The following reactions,



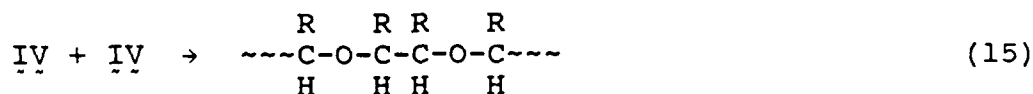
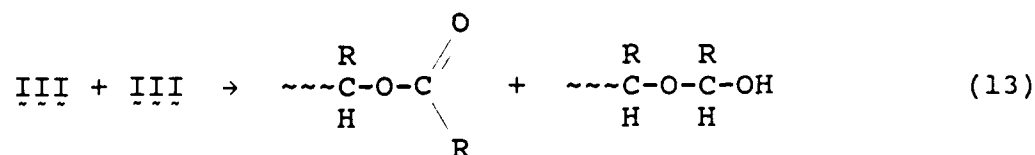
would have inhibited or retarded the processes. In contrast, the radiolysis of poly(1-hexene sulfone) is suppressed by triethylamine.^{5a} The amine causes a decrease in $G(\text{SO})_2$ from 24.6 to 4.5 and $G(\text{hexene})$ from 19.2 to 5.5. But triethylamine cannot be used here as it catalyzes spontaneous depolymerization of PCA.

The effect of oxygen on the radiolysis and photolysis of PCA cannot be attributed to some reactions of oxygen with ionic

species such as $\dot{\text{V}}$ because the effect is observed with both types of radiation and DUV is not sufficiently energetic to cause ionizations. The most probable explanation is that oxygen converts the carbon radical $\dot{\text{IV}}$ to a peroxy radical ($\dot{\text{VI}}$),



In the absence of air, termination can occur via combination of $\dot{\text{III}}$ and $\dot{\text{IV}}$



In the presence of O_2 and to the extent of conversion of radicals $\dot{\text{IV}}$ to $\dot{\text{VII}}$, reactions 14 and 15 are replaced by the slower processes involving tetroxide and trioxide molecules.¹⁷ The fact that G_s is twice greater in air than in vacuo indicates that reaction 12 even occurs in the spur to decrease the probability of primary cage recombination.

Small oxygen effects had been observed in radiolysis of polymers which are usually different in nature. For instance the radiolytic degradation of poly(ethylene oxide), which is without tendency to depolymerize, proceeds both in the presence and in the absence of air.¹⁸ However, at low dosage air does reduce crosslinking¹⁹ attributed to the oxygenation of the backbone radicals in competition with their combination.

If the above interpretation of the oxygen effect is correct then in the limiting case all radicals IV were converted to VII. If furthermore radical VII does not depropagate, then the number of PCA chain depolymerized per scission can be twice as great as estimated above. This consideration also applies to the photolysis in air but not to those results obtained in vacuo.

The depolymerizations of PCA stops at certain conversion short of completion depending upon experimental conditions. This is best attributed to repolymerization of the monomers formed by radiolysis and photolysis. This repolymerization is probably also free radical in nature because NH_4Br has no effect on the conversion whereas BHT greatly reduces it. Also the process is not as efficient as the cationic repolymerization caused by the radiolysis of onium salt.

The kinetics of depolymerization of polymer, P, involves the initiation



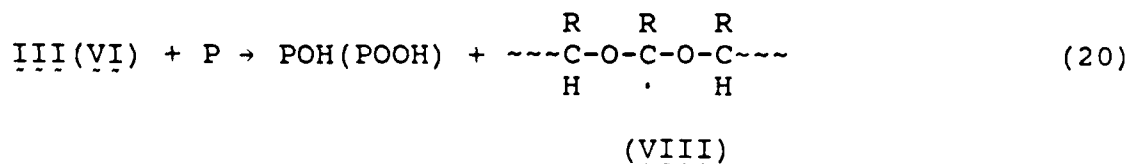
This rate for radiolysis is $G_s E_a$ where E_a is energy absorbed in 100 eV. It is ϕI_a the DUV photolysis where ϕ is the quantum yield and I_a is the light intensity absorbed. The radical $P_n\cdot$ participates in the polymerization equilibrium



If one assumes the chain termination to be the combinations of those radicals described above with an average rate constant k_t , then the solution obtained for steady state of $P_n\cdot$ is

$$\ln \left[\frac{1 + \sqrt{P_t/nK}}{1 - \sqrt{P_t/nK}} \right] - \ln \left[\frac{1 + \sqrt{P_0/nK}}{1 - \sqrt{P_0/nK}} \right] = k_{-1} \left(\frac{KG_s nE}{k_t} \right)^{1/2} t \quad (19)$$

Because of the very high radiation sensitivity, there is insufficient data at low dose to verify eq. 19. Furthermore, the propagation processes (eqs. 17 and 18) are complicated by chain transfer process due to hydrogen abstractions,



where POH(POOH) are hydroxyl(hydroperoxyl) terminated polymer chains. Radical VII can participate in reaction 18 but not reaction 17.

In conclusion, the γ -radiolysis and DUV photolysis of PCA showed very high tendency toward depolymerization. Repolymerization may be avoided and complete depolymerization may be attainable by continuous removal of monomers formed. The processes are aided by oxygen and retarded by alkoxyl radical scavenger. Halogen containing polymers of low T_g are good candidates for self-developing and plasma etchable positive resist together with a UV crosslinker.

Acknowledgement

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Figure Captions

- Figure 1. Thermogravimetric analysis of (a) PCA and (b) end-capped PCA.
- Figure 2. Mass spectrum of volatile γ -radiolysis product of PCA which is identical to the mass spectrum of monochloroacetaldehyde.
- Figure 3. Weight percent of PCA remained versus gamma dose (a) in air; (b) in vacuo.
- Figure 4. Variation of M_n^{-1} (O) and M_w^{-1} (●) of PCA with gamma dose: (a) in air, (b) in vacuo.
- Figure 5. Effect of additives on the weight percent of PCA remained as a function of gamma dose: (a) 2% Bu_4NBr ; (b) 2% of 2,6-di-t-butyl-p-cresol.
- Figure 6. Variation of weight percent of PCA containing 10% of $(\text{C}_6\text{H}_5)_2\text{IPF}_6$ with gamma dose: (a) in air; (b) in vacuo.
- Figure 7. Weight percent of PCA remained versus 254 nm photon intensity: (a) in air; (b) in vacuo.

Figure 8. ESR spectra of PCA irradiated with γ -ray or DUV at room temperature in the presence of air.

Figure 9. ESR spectra of DUV photolyzed PCA in vacuo at -195°C .

Figure 10. Percent weight loss of PCA versus plasma etching time:
($\square$) PCA; ($\bullet$) PMMA; (O) PCA containing 2% of bis(azidoformate); ($\blacktriangle$) PCA containing 10% of bis(azidoformate).

Figure 11. Arrhenius plot of the first order rate constant of thermolysis of: (a) PCA; (b) end-capped PCA.

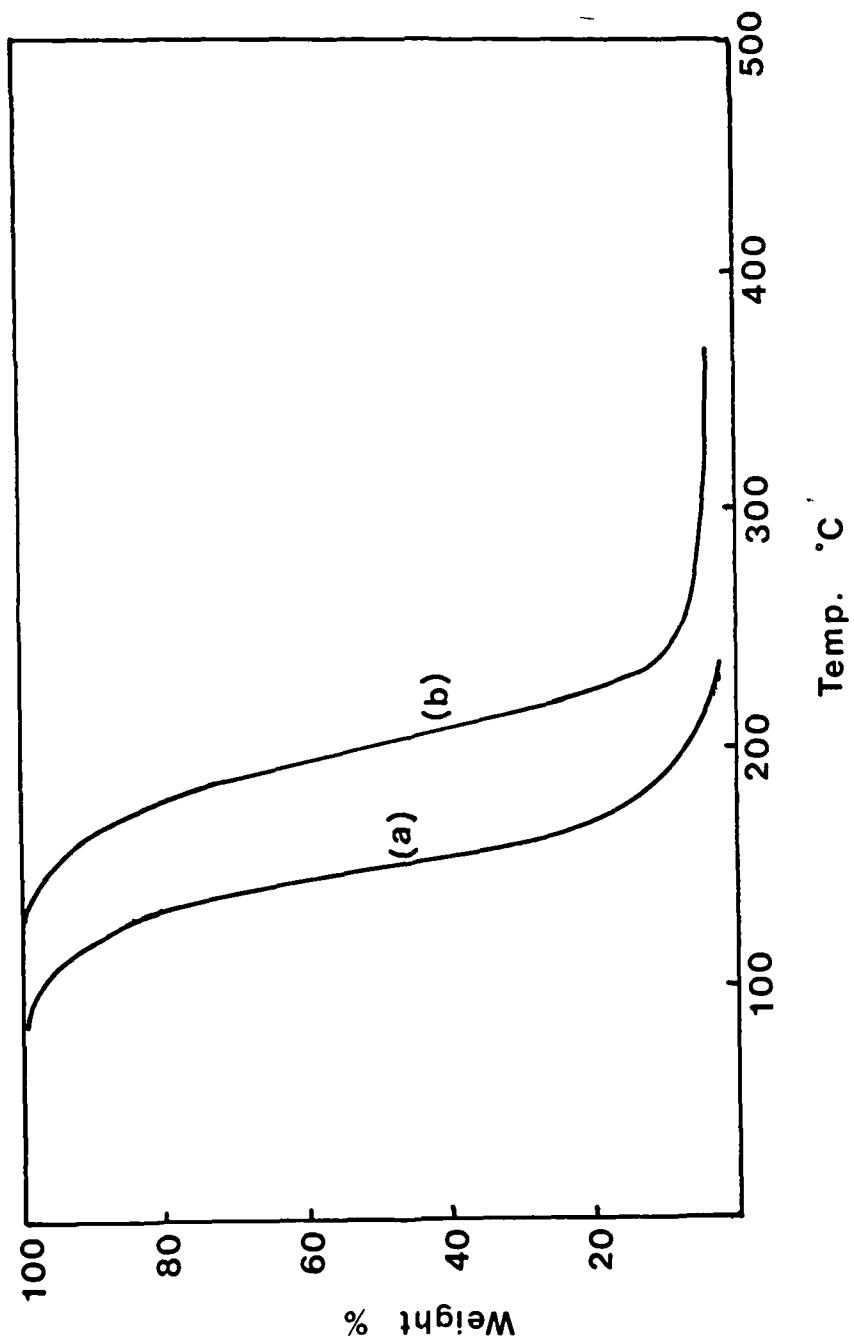


Fig. 1

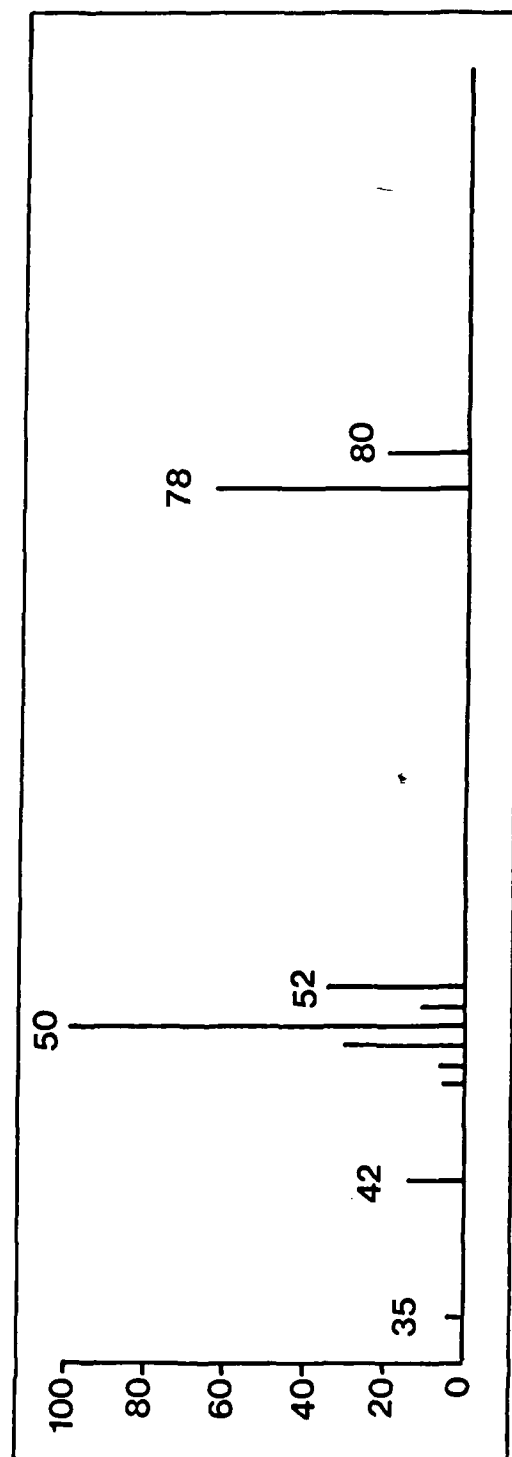


Fig. 2

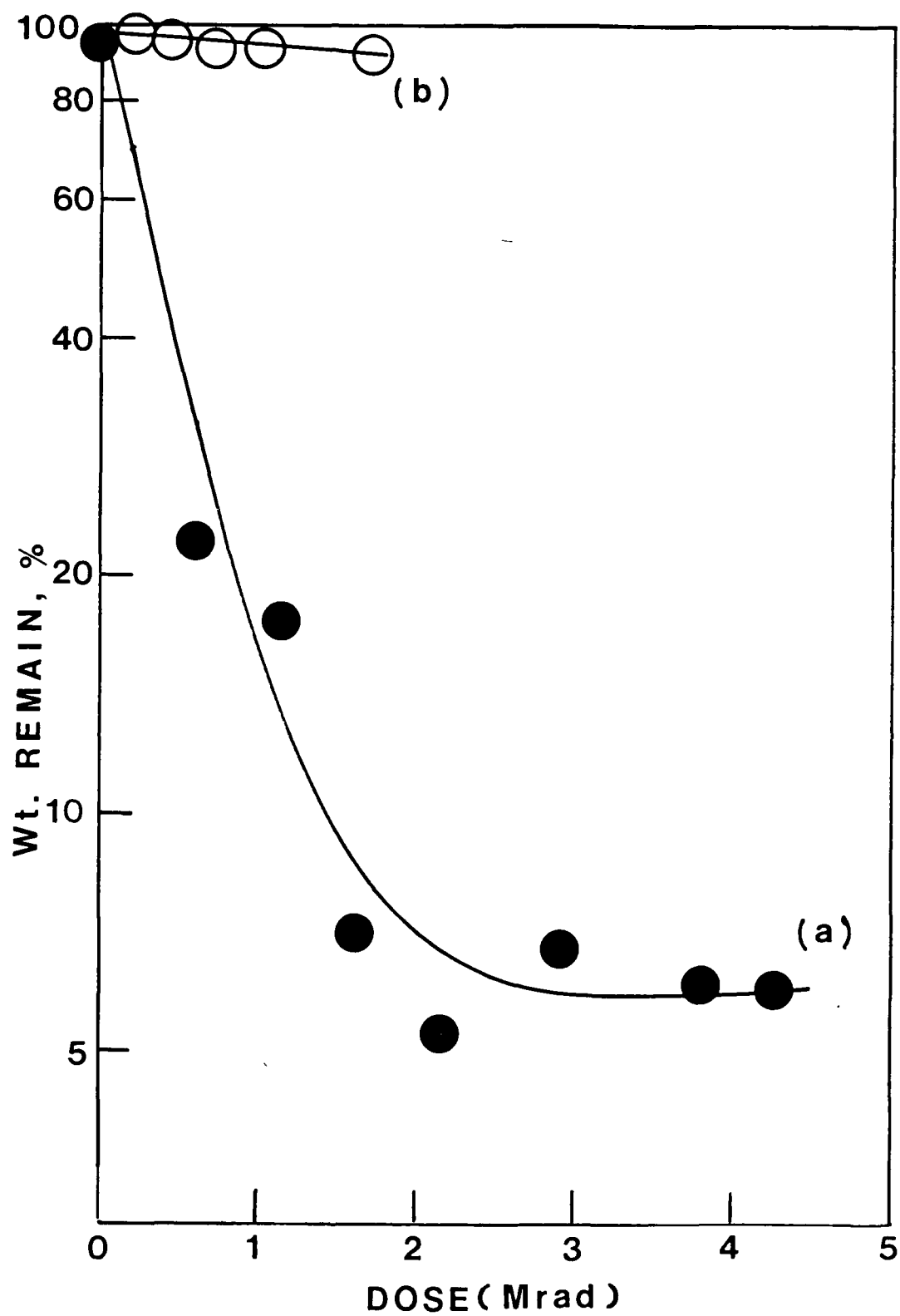


Fig. 3

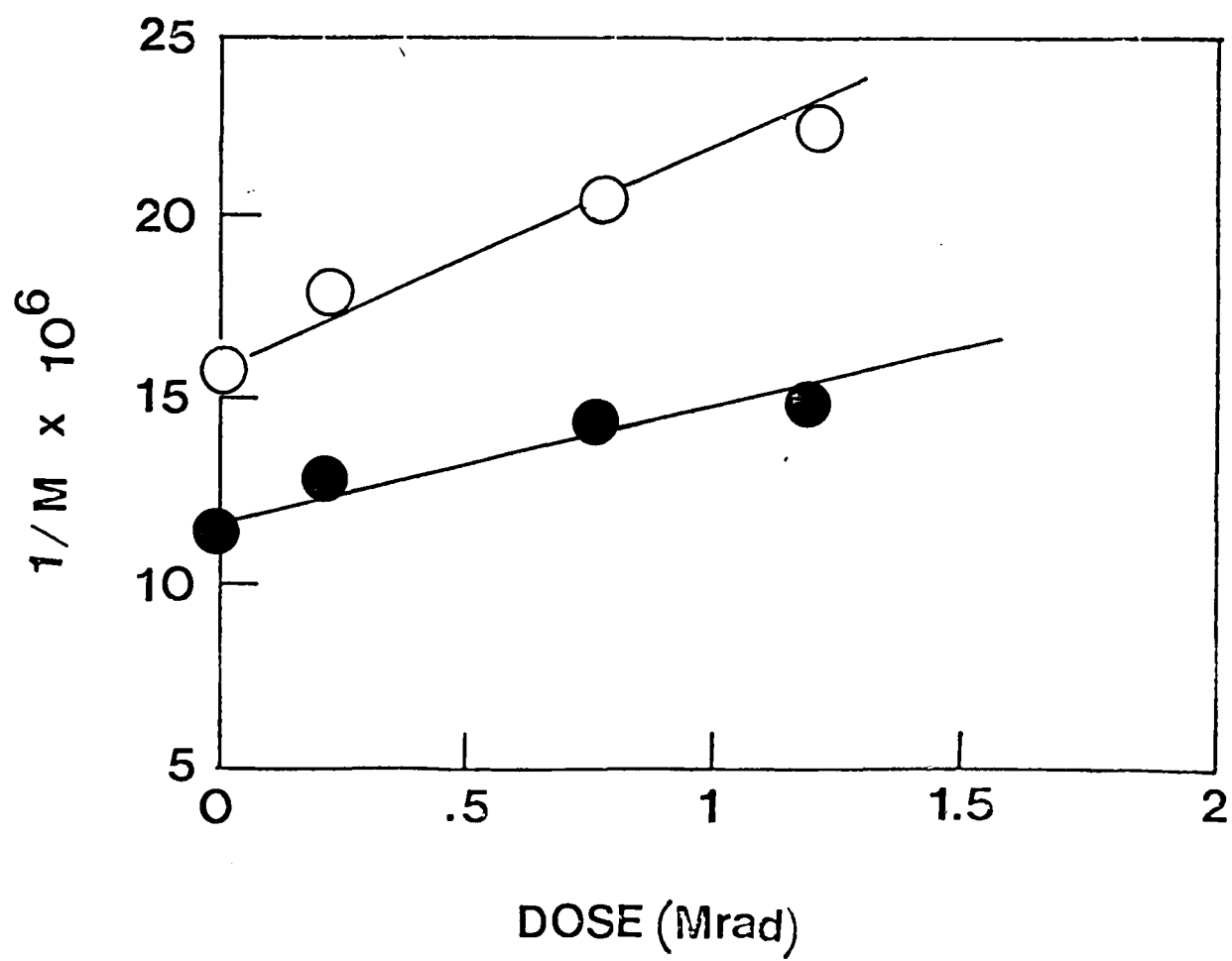


Fig. 4a

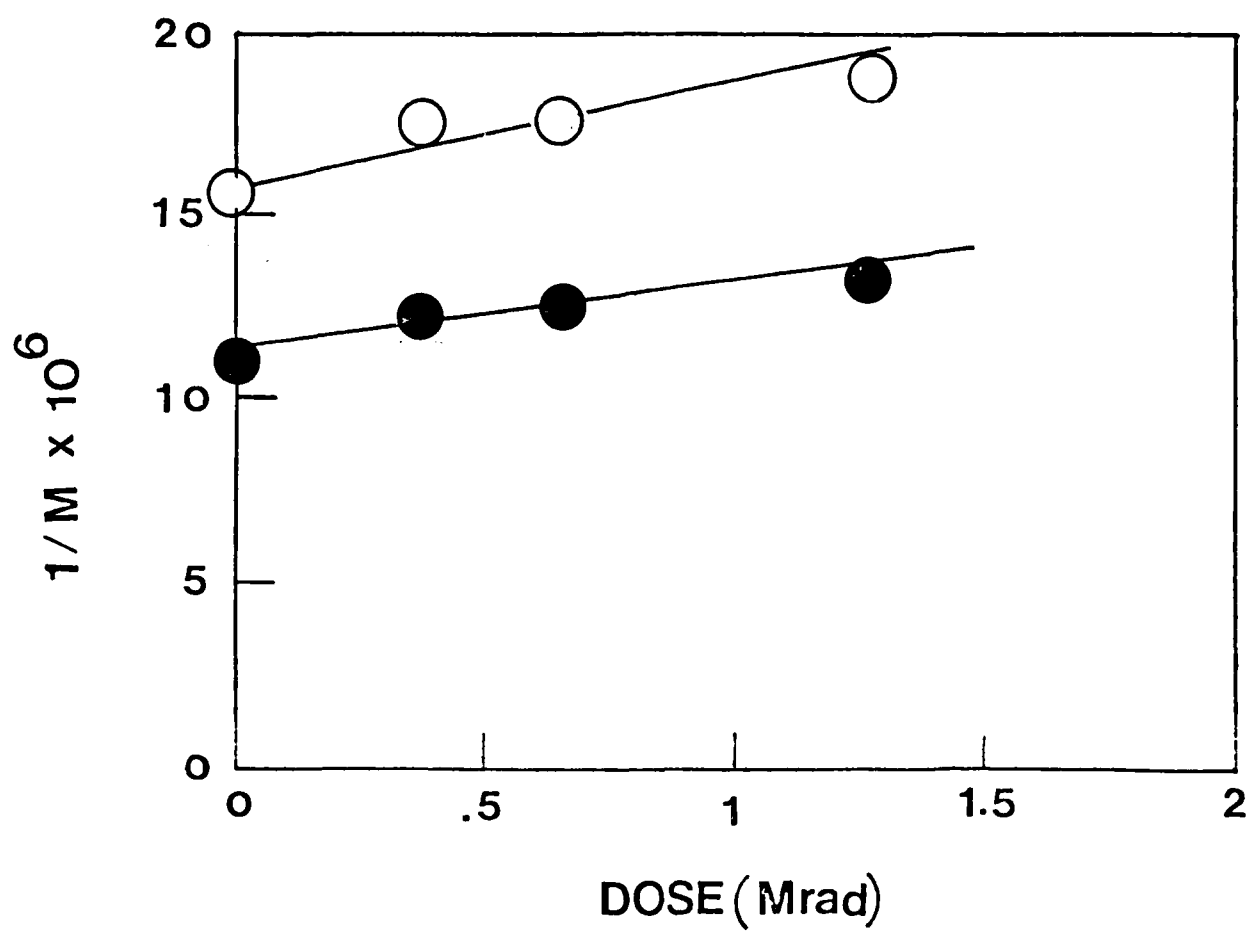


Fig.4b

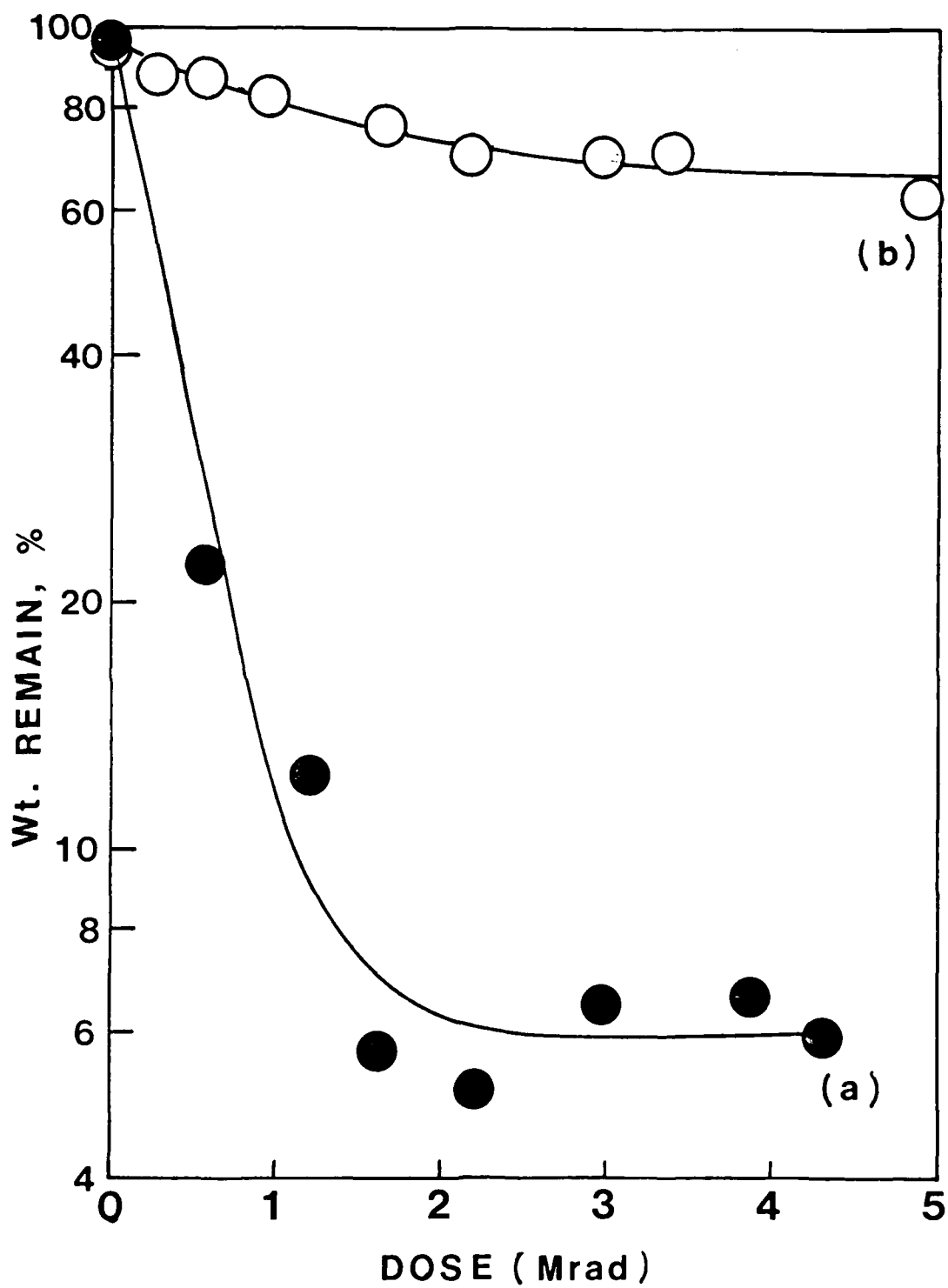


Fig. 5

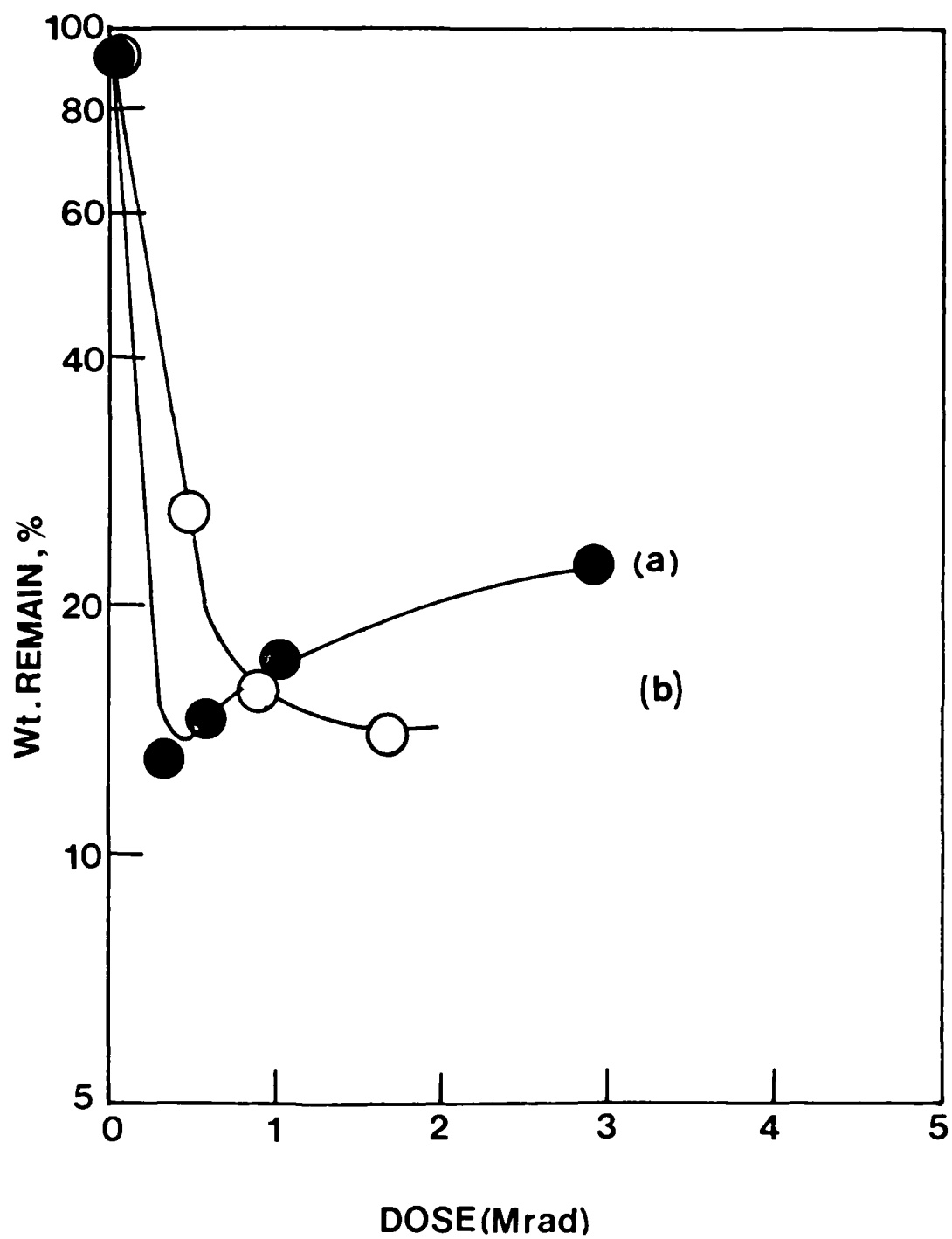


Fig.6

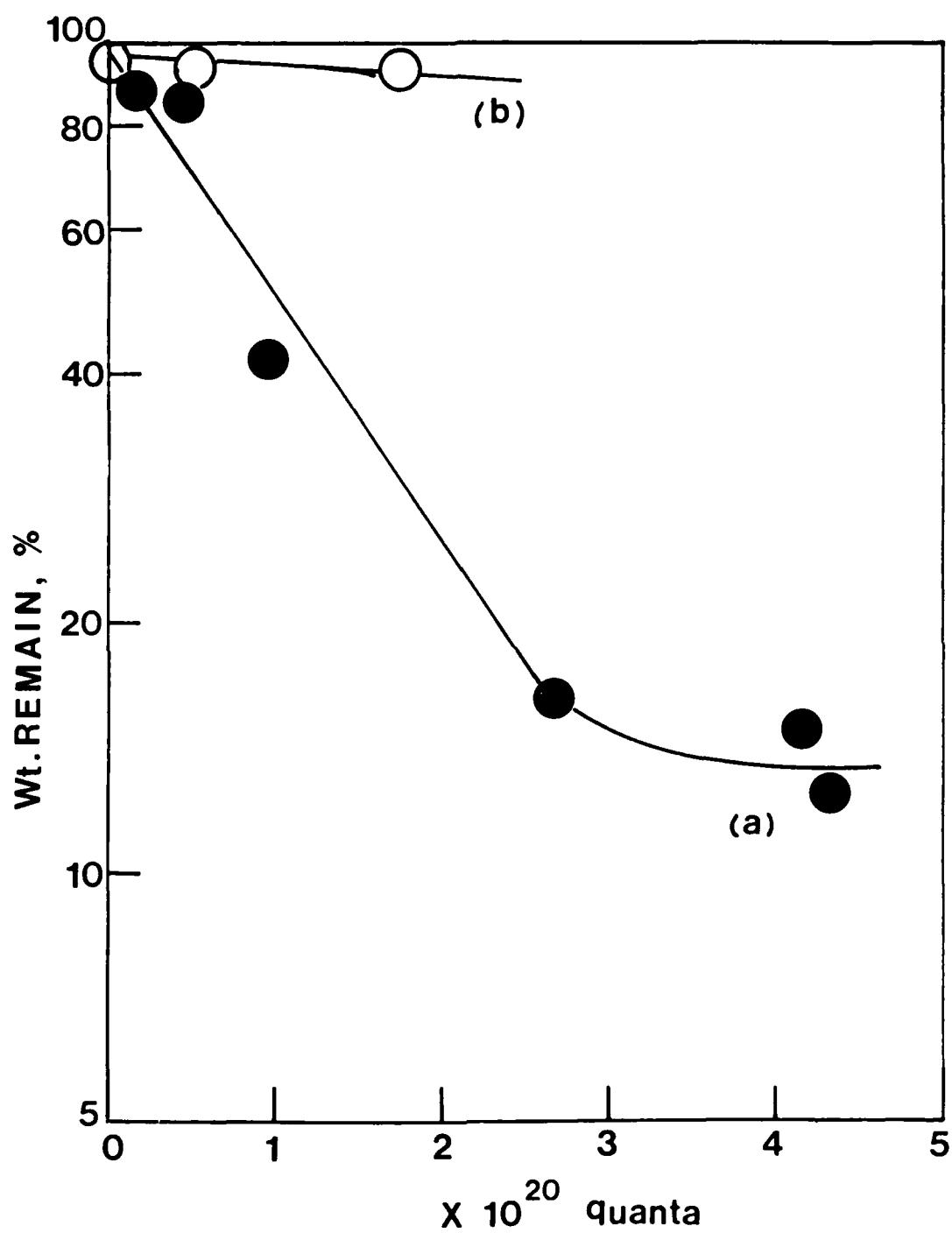


Fig.7

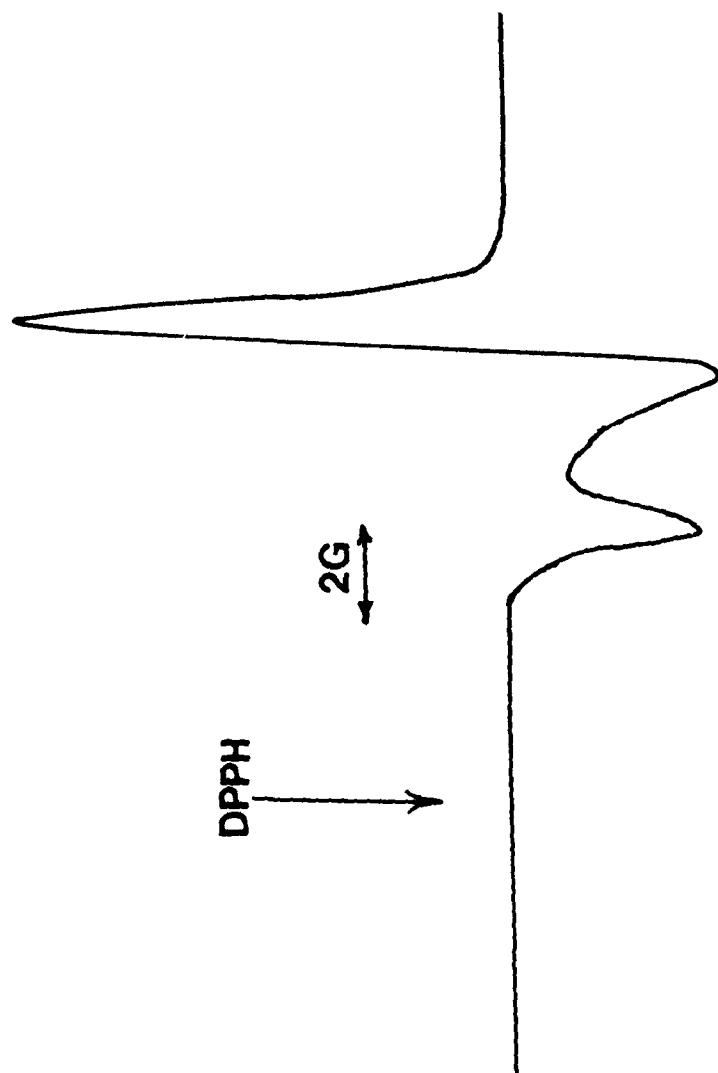


Fig. 8

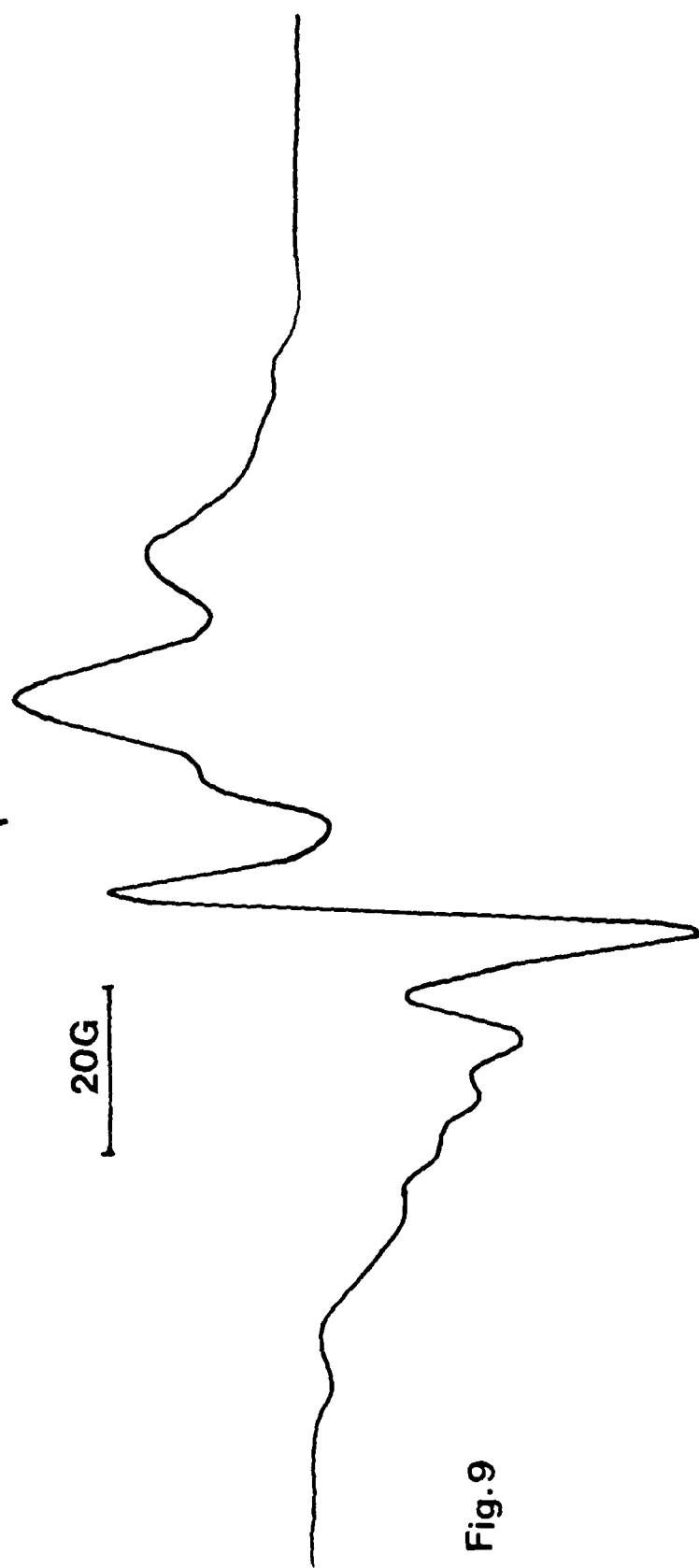
DPPH



20G



Fig.9



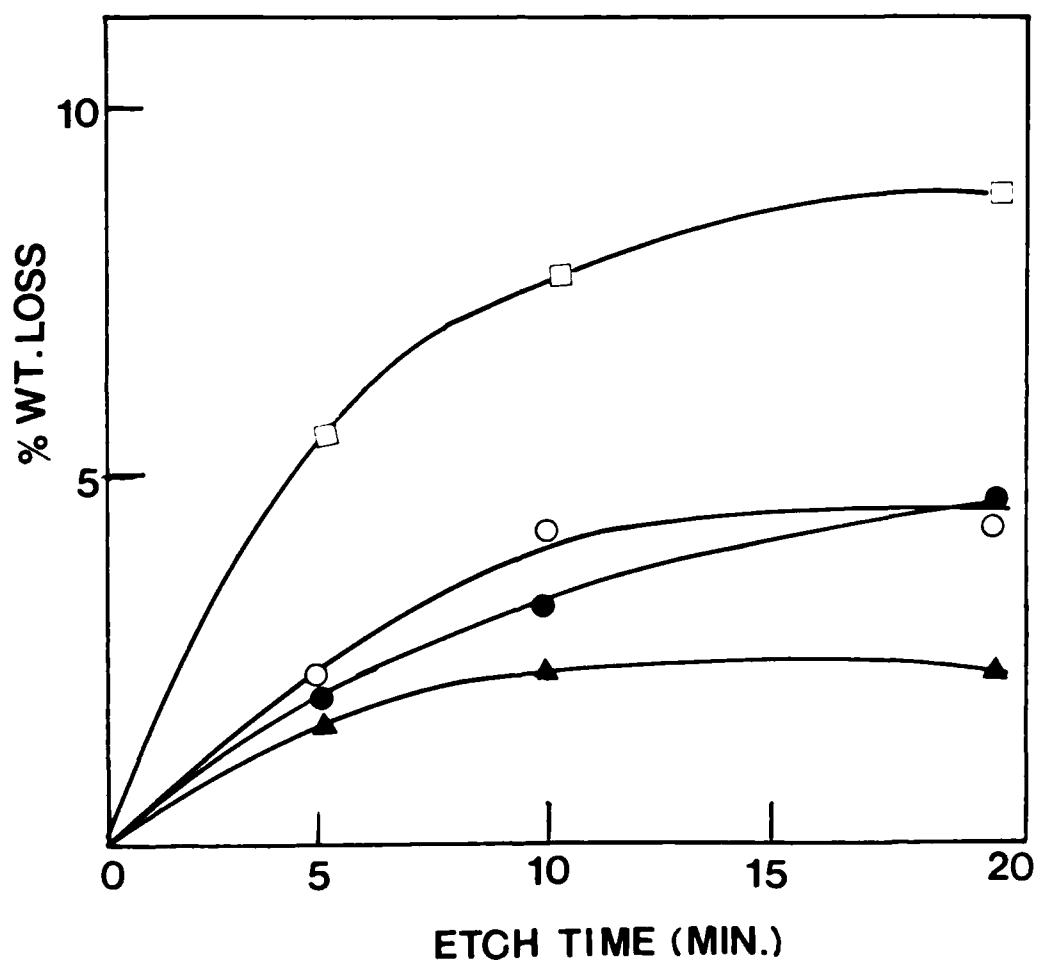


Fig.10

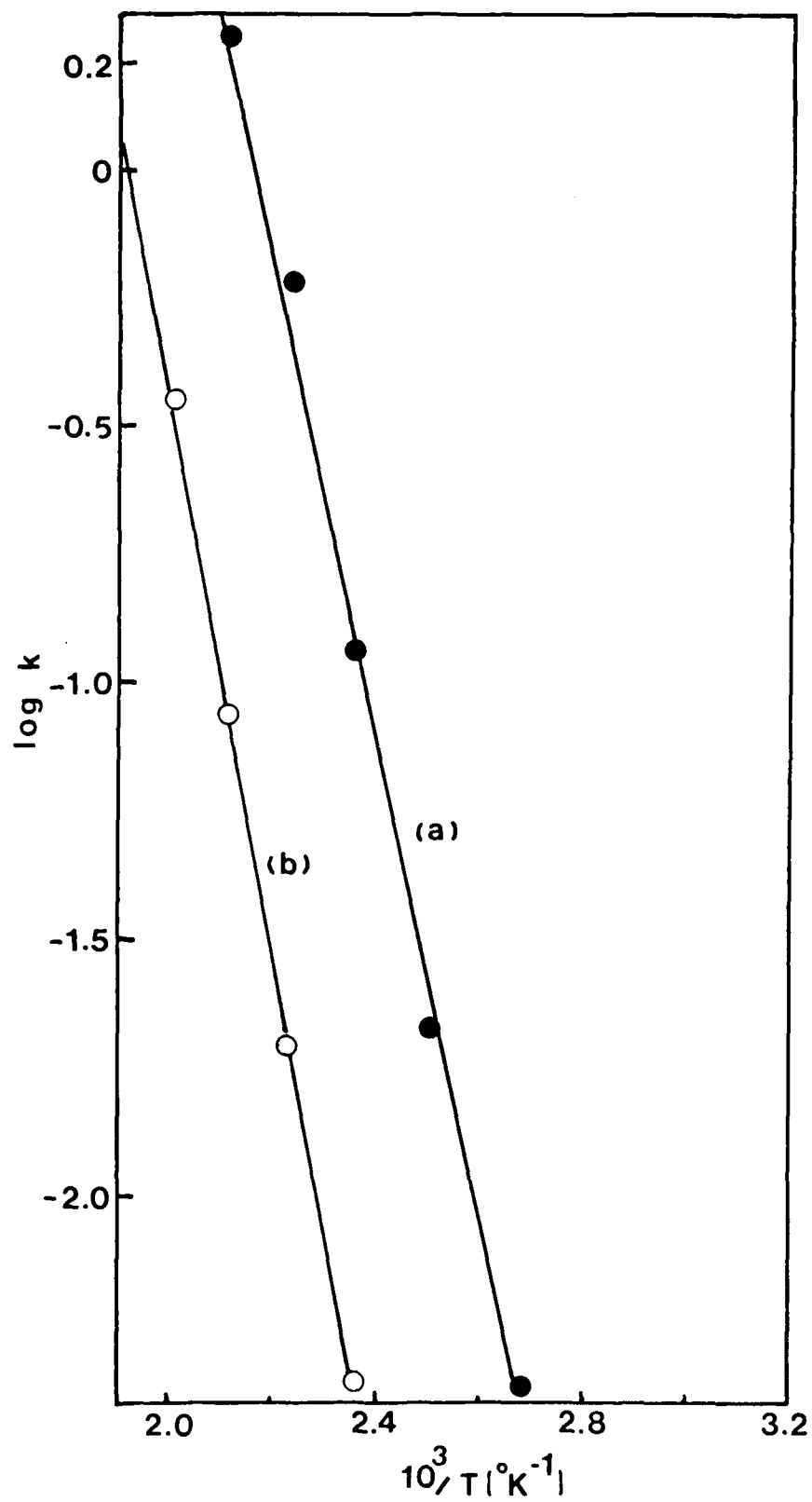


Fig.11

END

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