Mechanistic Study of Radiation-Induced Depolymerization of Poly(chloroacetaldehyde)

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ABSTRACT: The γ-radiolysis and deep ultraviolet photolysis of poly(chloroacetaldehyde) (PCA) resulted in depolymerization. Oxygen has a pronounced effect on the process. In air, the G(M) value (number of monomer molecules produced per 100 eV absorbed) is 11 000 and the G(S) yield (number of chain scission/100 eV) is 5.5. In the absence of air, the values of G(M) and G(S) are lowered to 1100 and 2.1, respectively. There is no cross-linking in either case. The depolymerization is retarded by 2,6-di-*tert*-butyl-*p*-cresol but is not affected by Bu_4NBr. The radicals produced by photolysis at −195 °C were identified by electron spin resonance. Irradiation of PCA containing diaryl iodonium salt caused efficient depolymerization initiated by protons generated from the onium salt. This process is insensitive to oxygen. The importance of radiation-induced depolymerization via free radicals and cationic species is discussed.

There is renewed interest in the radiation chemistry of polymers because of their applications in microelectronic lithography. Conventional positive resist systems,[5] of which poly(methyl methacrylate) (PMMA) is a prime example, are based upon radiation-induced chain scission. The latent image thus produced is developed by using a solvent mixture which maximizes the differential solubilities of the exposed and the unexposed materials. PMMA has a relatively low G(S) value of 1.2 main-chain scissions per 100 eV of energy deposited. The radiation sensitivity of a polymer can be enhanced by halogen atom substitution[1-8] to promote dissociative electron captures. We have systematically investigated the radiolysis of acrylate polymers having F, Cl, and Br atoms on the backbone and in the pendant group[9-11] and found polymers of trifluoroethyl- and hexafluoro-*n*-propyl-α-chloroacrylates to have G(S) values three times that of PMMA.[12]

A polymer would have very high radiation sensitivity if the primary radiative chain-scission process is followed by depropagation; the image thus formed needs no developing. Such direct imaging or self-developing systems have the obvious advantages of simplicity and economy.[13-17] Poly(alkylene sulfone)s have been studied in this regard because they have low ceiling temperatures (T_c). Maximum G(M) values (M = olefin, SO_2) were about 20 for irradiation temperatures of 60–70 °C.[20,21] These values are much smaller than the degree of polymerization, DP, indicating that only a small fraction of the polymer chain is depolymerized. The radiolysis yields are much lower when the copolymers were irradiated at room temperature and $G(\text{olefin}) \ll G(SO_2)$. There is both repolymerization and isomerization of olefins under these conditions. The low G(M) values and their temperature dependences may be partly attributable to the high T_c of polymerization for poly(olefin sulfone)s, which are 48 and 64 °C for poly(*trans*-2-butenyl sulfone) and poly(1-butenyl sulfone), respectively.[22] Therefore, other radiolysis pathways can compete with unzipping at moderate temperatures. For instance, bombardment of poly(1-butenyl sulfone) with 11-keV Cs^+ ions produces oligomeric fragments[23] of two to seven structural repeat units but no butene.

If one assumes that a high G(M) is associated with the propensity for depolymerization, then low T_c polymers should give large values of G(M). Poly(alkyl aldehyde)s have very low T_c's of −31 to −39 °C. Hatada et al.[24] had reported very high radiation sensitivities for copolymers of alkyl aldehydes, but the materials tend to depolymerize spontaneously and are deficient in mechanical and physical properties.

We have found that poly(chloroacetaldehyde) (PCA) which has both low T_c and contains halogen atom possesses extremely high radiation sensitivity for depolymerization. This process is promoted by oxygen. These results are presented here and the radiolysis mechanism discussed.

Experimental Section

Materials. Monochloroacetaldehyde was prepared according to the method of Iwata et al.[25] It has the correct elemental analysis and ^{1}H NMR; it is >99% pure according to GC. Iodonium salt, $(C_6H_5)_2I^+PF_6^-$, BHT, 2,6-di-*tert*-butyl-*p*-cresol, tetrabutylammonium bromide, and phenyl isocyanate were purchased from Aldrich Chemicals. Phenyl isocyanate was dried over P_2O_5 under nitrogen for 60 min and then distilled at 45–47 °C (10 Torr) immediately before use.

Polymerization. A toluene solution of monochloroacetaldehyde was polymerized at −78 °C with 1 mol % of $BF_3{\cdot}Et_2O$ initiator. Polymerization was quenched with methanol. This PCA has two hydroxyl termini as determined by $LiAlH_4$.[26] PCA was stabilized by dissolving in chloroform and end-capped by reaction with stoichiometric amount of phenyl isocyanate with dibutyltin dilaurate catalyst. The mixture was first stirred at room temperature for 2 h followed by heating at 70 °C for 10 min. The end-capped polymer was purified by reprecipitation with methanol.

Polymer Characterization. PCA has IR bands at 765 cm^{-1} from C—Cl stretching and 1150–1085 cm^{-1} from C—O—C stretching as reported.[25] The IR spectrum of end-capped PCA has additional bands at 3300–3500, 1735, and 1495 to 1530 cm^{-1} due to the N—H, C=O, and aromatic vibrations, respectively. ^{1}H NMR spectra of PCA has peaks at 3.67 ppm (br s, 2 H) and 5.1–5.5 ppm (m, 1 H). 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, determined by GPC, are 6.5×10^4 and 9.1×10^4, respectively, with a polydispersity index $\bar{M}_w/\bar{M}_n = 1.39$. Monodispersed α,ω-dihydroxypoly(propylene oxides) with $\bar{M}_n$'s of 1000, 2000, 3000, and 4000 were used for calibration.

Radiolysis. The γ-ray 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 to be 0.03–0.07 Mrad h^{-1}. Deep ultraviolet (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 s^{-1} cm^{-3} found with ferrioxalate actinometry.

Twenty to thirty milligrams of PCA was irradiated in weighed 5-mm-o.d. sample tubes 2 in. in length either open to air or sealed under vacuum. Following irradiation, the volatile products were removed by mechanical pumping for 24 h at 60 °C and analyzed by GC-MS (gas chromatography-mass spectrometry). The residue was weighed by difference and its IR and ^{1}H NMR spectra were taken. The molecular weights and distribution were determined by GPC; there is no insoluble polymer in irradiated samples. Samples were also photolyzed in vacuo and in air at −195 and 25 °C for ESR measurements.

Instrumentation. The instruments used in this work are the following: Varian XL-300 for ^{1}H NMR, IBM ESP-300 for ESR, Perkin-Elmer 283-B for IR, and Hewlett-Packard 5890 system

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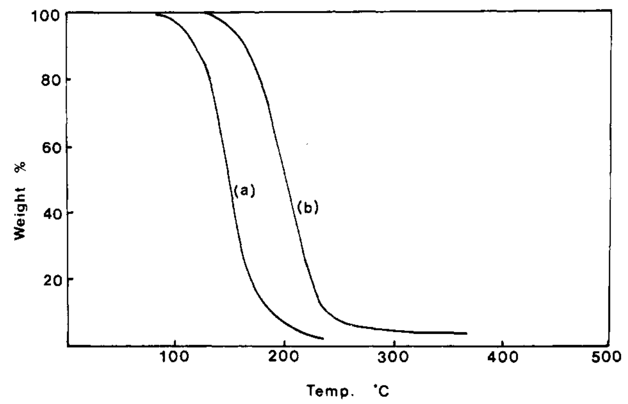


Figure 1. Thermogravimetric analysis of (a) PCA and (b) end-capped PCA.

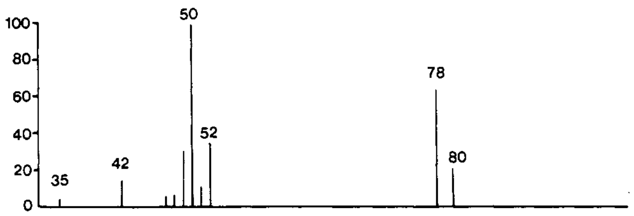


Figure 2. Mass spectrum of the volatile γ-radiolysis product of PCA which is identical with the mass spectrum of monochloroacetaldehyde.

for GC-MS. A Waters Associates 201 GPC equipped with five microstyragel columns was used to determine molecular weights of PCA in THF with α,ω-dihydroxypoly(propylene oxides) as the standards (vide supra). TGA of PCA was performed on a Perkin-Elmer TGS-2 system under N_2 with a heating rate of 20 deg min^{-1}.

Results

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

γ-Irradiation of PCA in air resulted in rapid weight loss. GC analysis showed only a single volatile product. The mass spectrum of which (Figure 2) is identical with 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 50, 52 and 49, 51 peaks are attributable to the isotopic CH_3Cl and CH_2Cl, respectively.

About 94 ± 1% of PCA was depolymerized by γ-radiolysis in air (Figure 3a). The residue is mostly low molecular weight oxidation products. The radiolysis yield of monomer or G value, G(M), is about 11 000. The IR spectra of irradiated PCA showed a new carbonyl absorption; in the case of end-capped PCA the carbonyl absorption is superimposed on the urethane group vibration. The ^{1}H NMR spectra of irradiated PCA showed additional resonances at 4.06 ppm (s, 0.2 H) and 9.62 ppm (s, 0.09 H), which may be attributed to residual monomer and/or oxidation products. There is no cross-linked polymer formed since the residue is completely soluble.

The G(S) and G(X) values can be calculated from the change of $\bar{M}_n$ and $\bar{M}_w$ with dose by the well-known relationships[1,27]

$$\bar{M}_{n,D}^{-1} = \bar{M}_{n,0}^{-1} + [G(S) - G(X)]\frac{D}{100N} \qquad (1)$$

$$\bar{M}_{w,D}^{-1} = \bar{M}_{w,0}^{-1} + [G(S) - 4G(X)]\frac{D}{200N} \qquad (2)$$

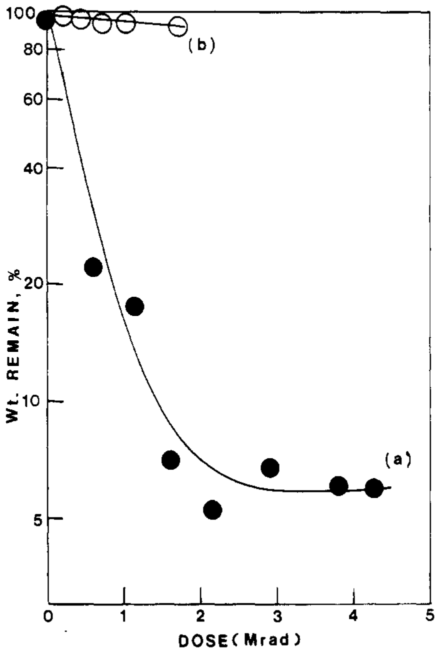


Figure 3. Weight percent of PCA remaining versus γ dose: (a) in air; (b) in vacuo.

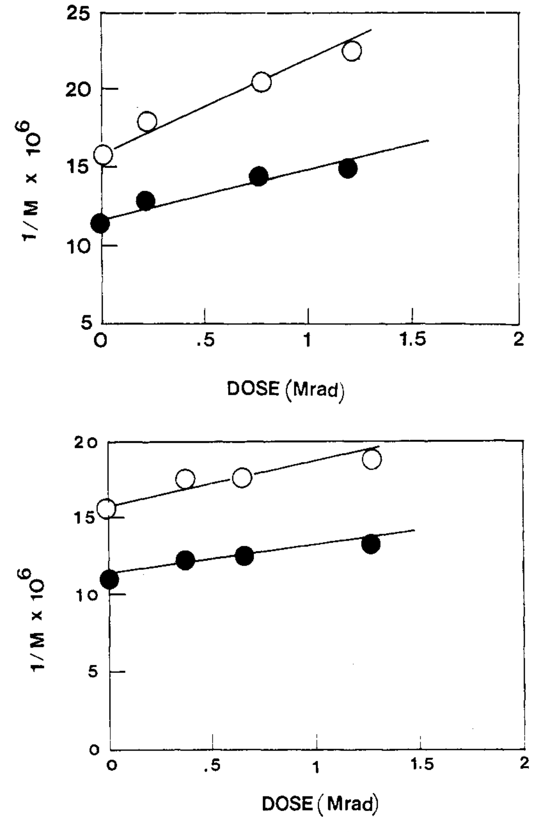


Figure 4. Variation of M_n^{-1} (○) and M_w^{-1} (●) of PCA with γ dose: (a, top) in air, (b, bottom) in vacuo.

where subscripts 0 and D designate molecular weight before and after D dose of γ-irradiation and N is Avogadro's 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.

Scavenger was added to PCA at a 2 wt % level. It was 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

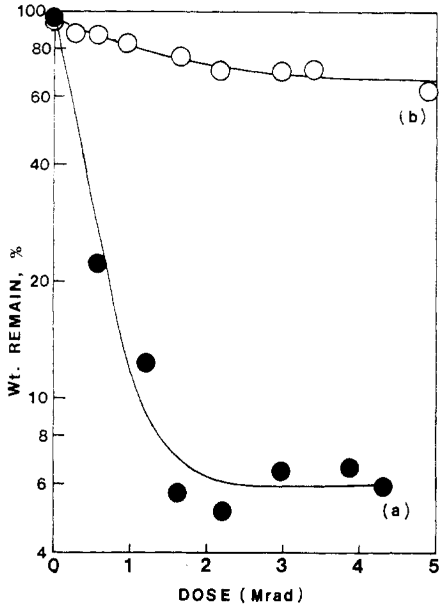


Figure 5. Effect of additives on the weight percent of PCA remaining as a function of γ dose: (a) 2% Bu_4NBr; (b) 2% of 2,6-di-*tert*-butyl-*p*-cresol.

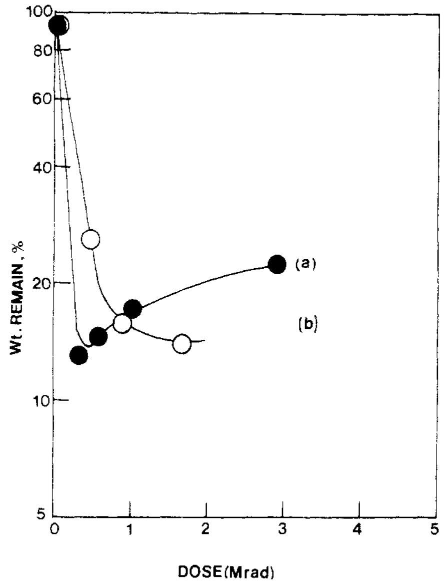


Figure 6. Variation of weight percent of PCA containing 10% $(C_6H_5)_2IPF_6$ with γ dose: (a) in air; (b) in vacuo.

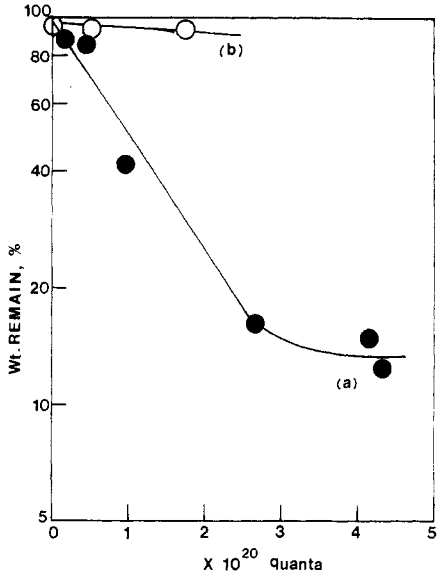


Figure 7. Weight percent of PCA remaining versus 254-nm photon intensity: (a) in air; (b) in vacuo.

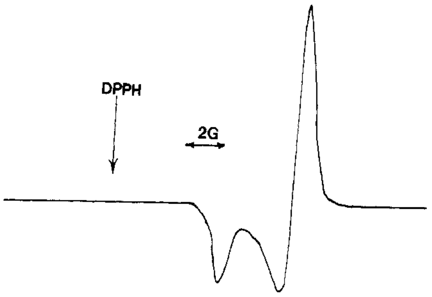


Figure 8. ESR spectra of PCA irradiated with γ-ray or DUV at room temperature in the presence of air.

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 Figures 5a and 3a are superimposable.

The γ-radiolysis of PCA in vacuo is much less efficient than in air (compare parts a and b of Figure 3). The value of $G(M)$ is only about 1100 in the absence of air which is one-tenth of that found in the presence of air. This discrepancy is only partly attributable to a decrease in the scission yield. The results of molecular weight change with dose (Figure 4b) gave $G(S) = 2.1$ and $G(X) = 0$; there is a slight increase of $\bar{M}_w/\bar{M}_n$ to 1.51.

Poly(phthalaldehyde) can be depolymerized by acid catalysis. Making use of the knowledge that UV photolysis of diaryliodonium salt produces a Brønsted acid,[28] Willson et al.[29] showed self-developing photoresist behaviors for the poly(phthalaldehyde)/onium salt system. It is thought likely that the radiolysis of onium salt can also produce a Brønsted acid to initiate depolymerizations. γ-Irradiation of PCA containing 10% of $(C_6H_5)_2IPF_6$ resulted in depolymerization of about 85% of the polymer by a dosage of about 1 Mrad. However, the weight loss versus dose curve (Figure 6a) showed reversal at high dosages, indicative of repolymerization of monomers produced by radiolysis. This cation-initiated depolymerization of PCA is insensitive to oxygen. Comparison of curves a and b of Figure 6 showed that only slightly higher γ dosage is required for 85% weight loss in vacuo than in air.

DUV irradiation of PCA also initiates depolymerization. GC-MS showed the volatile products to be monomers as in γ-radiolysis. A 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 as compared to only a few percent of PCA photolyzed in vacuo (Figure 7b).

For ESR measurements PCA was irradiated in supersil sample tubes. Due to the space limitation of the γ-source chamber, γ-irradiation of PCA was performed only at room temperature. No signal was detected for PCA γ-irradiated in vacuo. An intense ESR signal was observed for PCA irradiated in air (Figure 8) with $g_\perp = 1.998$ and $g_\parallel = 2.000$ attributable to peroxy radical. From the signal intensity, one estimates a yield of 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.

PCA was photolyzed at −195 °C to detect the primary radicals. The ESR spectra of Figure 9 may be analyzed as arising from two radicals. Radical I$^\bullet$ has $g = 2.002$ coupled to one proton with hyperfine splitting of 25 G and

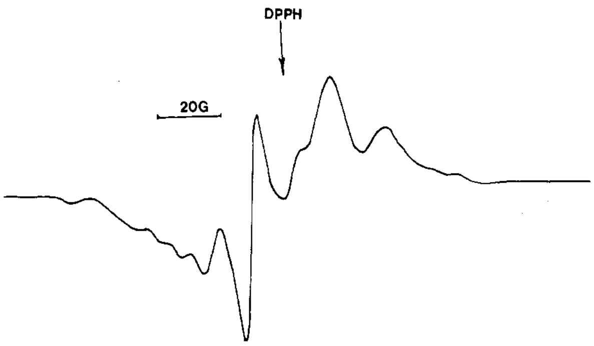


Figure 9. ESR spectra of DUV-photolyzed PCA in vacuo at −195 °C.

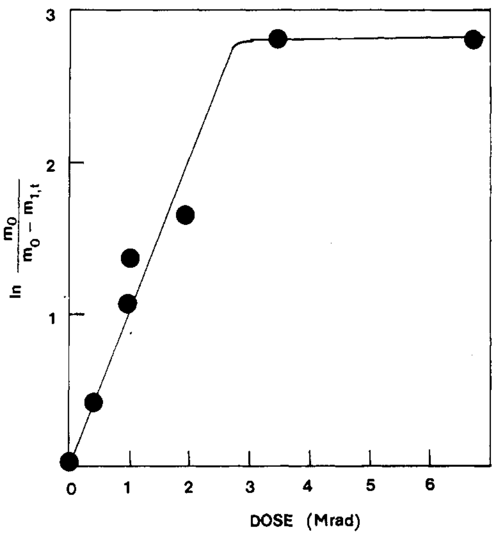


Figure 10. Variation of ln $(m_0/m_0 - m_{1,t})$ versus dose for the γ-radiolysis of PCA in air.

two equivalent protons with hyperfine splitting of 12.5 G. A second radical II• has $g = 2.025$ hyperfine coupled to two protons with a splitting of 25 G and to ^{35}Cl with a 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.

Discussion of Results

Cationic Depolymerization. Radiolysis of onium salt produces protons[28]

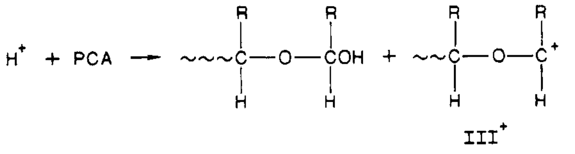
$$\mathrm{Ph_2I^+PF_6^-} \xrightarrow{\gamma} [\mathrm{Ph_2I^+PF_6^-}]^* \tag{3}$$

$$[\mathrm{Ph_2I^+PF_6^-}]^* \rightarrow \mathrm{PhI^{\bullet+}} + \mathrm{Ph^\bullet} + \mathrm{PF_6^-} \tag{4}$$

$$\mathrm{PhI^{\bullet+}} + \mathrm{PCA} \rightarrow \mathrm{PhI^+\text{-}H} + \mathrm{PCA^\bullet} \tag{5}$$

$$\mathrm{PhI^+\text{-}H} \rightarrow \mathrm{PhI} + \mathrm{H^+} \tag{6}$$

where Ph denotes a phenyl group. The proton catalyzes the depolymerization of PCA



$$\mathrm{H^+ + PCA} \longrightarrow \sim\sim\sim\overset{R}{\underset{H}{C}}\text{—O—}\overset{R}{\underset{H}{C}}\mathrm{OH} + \sim\sim\overset{R}{\underset{H}{C}}\text{—O—}\overset{R}{\underset{H}{C^+}} \tag{7}$$

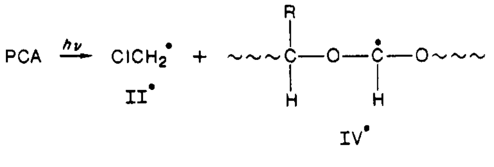
$$\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{III^+}$$

$$\mathrm{III^+} \longrightarrow \text{monomer} + \mathrm{III^+} \tag{8}$$

Reaction 8 is the depropagation step in the cationic equilibrium polymerization of monochloroacetaldehyde. The participation of alkoxy carbenium ion intermediate had been demonstrated in the acid-catalyzed depolymerization of 2-alkyl-1,3-dioxepane,[30] 2-alkyl-1,3,6-trioxocane,[31,32] and 4-methyl-1,3-dioxolane.[33] The fact that depolymerization stops at about 80% is best explained by repolymerization (reverse of eq 8) of the monomers accumulated during irradiation; in these experiments the monomer formed by radiolysis was removed by evacuation only at the end of an irradiation.

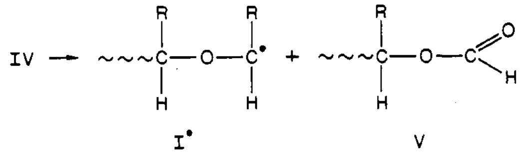
Free radicals were also produced by the radiolysis of the onium salt (eq 4 and 5) and of the PCA itself. The contribution of these radicals to the depolymerization of PCA can be estimated (vide infra).

Electron Spin Resonance. Photolysis of PCA at −195 °C produces two radicals whose ESR spectra are shown in Figure 9. The chloromethyl radical II• is produced by



$$\mathrm{PCA} \xrightarrow{h\nu} \underset{\mathrm{II^\bullet}}{\mathrm{ClCH_2^\bullet}} + \underset{\mathrm{IV^\bullet}}{\sim\sim\sim\overset{R}{\underset{H}{C}}\text{—O—}\overset{\bullet}{\underset{H}{C}}\text{—O}\sim\sim\sim} \tag{9}$$

The carbon terminal radical of PCA is most likely to be formed from IV.



$$\mathrm{IV} \longrightarrow \underset{\mathrm{I^\bullet}}{\sim\sim\sim\overset{R}{\underset{H}{C}}\text{—O—}\overset{R}{\underset{H}{C^\bullet}}} + \underset{\mathrm{V}}{\sim\sim\sim\overset{R}{\underset{H}{C}}\text{—O—C}\overset{\text{O}}{\underset{\text{H}}{\lessgtr}}} \tag{10}$$

Our γ-ray source did not have space to accommodate a Dewar so PCA cannot be γ-irradiated at −195 °C. But according to known radiation chemistry, γ-irradiation of PCA should produce excited-state molecules and radical ions (VII)

$$\mathrm{PCA} \xrightarrow{\gamma} \mathrm{PCA^*} + \mathrm{PCA^{\bullet+}} \tag{11}$$

The excited molecule undergoes the following bond scissions

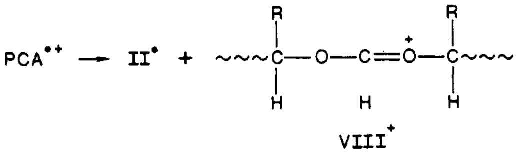
$$\mathrm{PCA^*} \rightarrow \underset{\mathrm{VI^\bullet}}{\sim\sim\sim\mathrm{CHR\text{—}O\text{—}CHR\text{—}O^\bullet}} + \mathrm{I^\bullet} \tag{12}$$

and

$$\mathrm{PCA^*} \rightarrow \mathrm{II^\bullet} + \mathrm{IV^\bullet} \tag{13}$$

The bond scission processes for PCA radical ion are

$$\mathrm{PCA^{\bullet+}} \longrightarrow \mathrm{III^+} + \mathrm{VI^\bullet} + \mathrm{I^\bullet} + \mathrm{VI^+} \tag{14}$$



$$\mathrm{PCA^{\bullet+}} \longrightarrow \mathrm{II^\bullet} + \underset{\mathrm{VIII^+}}{\sim\sim\sim\overset{R}{\underset{H}{C}}\text{—O—}\underset{H}{C}\text{=}\overset{+}{O}\text{—}\overset{R}{\underset{H}{C}}\sim\sim\sim} \tag{15}$$

The only new radical expected in the radiolysis of PCA is the terminal alkoxy radical of PCA VI•. Such radical would not be observed by ESR because it reacts rapidly by hydrogen atom abstraction. No authentic ESR evidence for alkoxy radical exists except by the matrix isolation technique.

Radicals I• and II• were not detected by ESR in PCA samples irradiated in vacuo with γ-ray or DUV at room temperature. In the presence of oxygen, they are transformed into the respective peroxy radicals observed by ESR.

Radiolysis Depolymerization Mechanism. Radiolysis of polymers should produce both radicals and ions as depicted by eq 11–15 for PCA, which will all lead to scission and depolymerization. The total yields of scission, G(S,total), and of depolymerization, G(M,total), are the sum of yields from the radicals and the ions:

$$G(\mathrm{S,total}) = G(\mathrm{S,radical}) + G(\mathrm{S,ion}) \quad (16)$$

$$G(\mathrm{M,total}) = G(\mathrm{M,radical}) + G(\mathrm{M,ion}) \quad (17)$$

O'Donnell and co-workers[20,12] had considered the roles played by radicals and cations in the radiolysis of poly(olefin sulfone)s. O'Donnell and co-workers[20,12] had considered the roles played by radicals and cations in the radiolysis of poly(olefin sulfone)s. The participation of a cationic intermediate is demonstrated by the effect of triethylamine on the radiolysis of poly(1-hexenyl sulfone). Et_3N caused a marked reduction of $G(SO_2)$ from 24.6 to 4.5 and G(hexene) from 19.2 to 5.5. It is not feasible to use Et_3N with PCA because it causes spontaneous degradation of PCA. Instead, Bu_4NBr was added as a scavenger for cations but had no effect on the radiolysis of PCA (Figure 5a). The result indicates that in this system the radical ions are efficiently neutralized by the secondary electrons in the proximity to form PCA* leading to radicals according to eq 12 and 13. On the other hand, BHT strongly retards the radiolytic depolymerization of PCA. Therefore, $G(\mathrm{M,radical}) \gg G(\mathrm{M,ion})$. In the case of DUV-induced depolymerization, it must proceed via free radicals. The 253-nm photon is energetically unable to cause ionization.

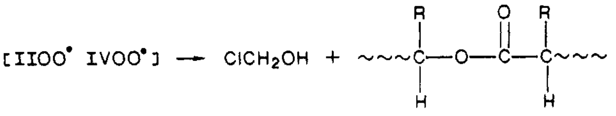
Effect of Oxygen. In the absence of oxygen, the radical pairs formed by eq 13 and 14 have high probabilities of primary cage recombination

$$[\mathrm{I^\bullet\ VI^\bullet}] \quad \text{or} \quad [\mathrm{I^\bullet\ IV^\bullet}] \rightarrow \mathrm{PCA} \quad (18)$$

where the bracket denotes the primary cage, and do not contribute to G(S). Also, those radicals which diffuse away from their partners and out of the cage can recombine to interrupt the depolymerizations to decrease G(M). When PCA is irradiated in air, oxygen reats with these radicals at diffusion-controlled rates. The conversion of I• to a peroxy radical, IOO•, effectively inhibits the recombination process.

$$[\mathrm{I^\bullet\ VI^\bullet}] \xrightarrow{O_2} [\mathrm{IOO^\bullet\ VI^\bullet}] \rightarrow \mathrm{IOO^\bullet} + \mathrm{VI^\bullet} \quad (19)$$

On the other hand, the oxygenation of the radicals II• and IV• in the second kind of cage would change their simple combination to the termination of the peroxy radicals

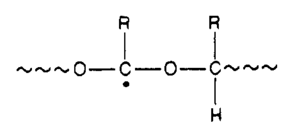


$$[\mathrm{IIOO^\bullet\ IVOO^\bullet}] \rightarrow \mathrm{ClCH_2OH} + \sim\!\sim\!\sim\mathrm{C(R)(H)}-\mathrm{O}-\mathrm{C(=O)}-\mathrm{C(R)(H)}\sim\!\sim\!\sim \quad (20)$$

According to this analysis oxygen can increase G(S) by 50% to 150%. The observed G(S) values are 5.5 and 2.1 with and without oxygen, respectively, which is not out of line with expectation.

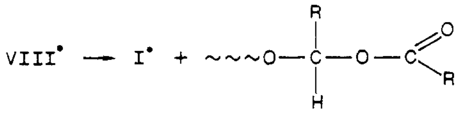
In the absence of oxygen there are 10 different termination reactions between alkyl radicals I•, II•, and IV• and the alkoxy radical VI•. Only the three reactions between the alkoxy radical and the three alkyl radicals are prevented to occur in analogy to eq 19. The other reactions between the peroxy radicals of I•, II•, and IV• still result in terminations like eq 20. Oxygen also has no effect on the self-termination of alkoxy radicals.

The G(M) yield in the presence of air is 10-fold of that without air. Taking into account the effect of oxygen on the primary cage recombinations (vide supra), the efficiency of depolymerization is about four times greater in the presence of air than without it. Outside of the primary cages only three terminations out of the total of 10 involving the alkoxy radical VI• are suppressed by oxygen. The results suggest other contributions from oxygen. For instance, the peroxy radical can abstract the tertiary protons of PCA which is the propagation process in autoxidations of polyolefins[34-37]



$$\mathrm{IOO^\bullet\ (IIOO^\bullet)} + \mathrm{PCA} \rightarrow \mathrm{IOOH\ (IIOOH)} + \sim\!\sim\!\sim\mathrm{O}-\mathrm{\dot{C}(R)}-\mathrm{O}-\mathrm{C(R)(H)}\sim\!\sim\!\sim \quad (21)$$

VIII



$$\mathrm{VIII^\bullet} \rightarrow \mathrm{I^\bullet} + \sim\!\sim\!\sim\mathrm{O}-\mathrm{C(R)(H)}-\mathrm{O}-\mathrm{C(=O)R} \quad (22)$$

Also, alkoxy radicals can be produced in the reactions between alkyl and peroxy radicals. In general, depolymerization by alkoxy radicals is more important than by alkyl radicals because of the longer kinetic lifetimes for the former.

The effect of oxygen observed in this work is much greater than the small effects reported for radiolysis of other polymers. 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.[38] However, air reduces cross-linking[39] because the oxygenation of the backbone radicals competes against their combination. Others polymers, such as poly(ethylene),[40,41] poly(propylene),[42] poly(styrene),[43,44] and poly(vinyl chloride),[45,46] which cross-link upon irradiation in vacuo, undergo predominantely main-chain scission upon irradiation in air. The radiation-induced main-chain scission of poly(tetrafluoroethylene) occurs in much higher yield in oxygen than in vacuo.[47]

Kinetic Chain Length. The kinetic chain length for depolymerization, ν, is

$$\nu = \frac{\text{rate of depropagation}}{\text{rate of initiation}} = \frac{G(\mathrm{M})}{nG(\mathrm{S})} \quad (23)$$

where n is the number of depropagating radicals per chain scission. In the presence of oxygen the main scission process is eq 19 and chain unzipping is mainly by alkoxy radical VI•. There is no unzipping from IOO• and $n \approx 1$ for this case. The value of ν for γ-radiolysis of PCA in air is 2000. Since PCA has an initial DP_0 of 800, each main-chain scission resulted the depolymerization of 2.5 PCA molecules per radical produced.

In γ-radiolysis of PCA, the initiation process is random and the termination is bimolecular. Jellinek[48] had analyzed the kinetics of such depolymerizations; the results for the special case of $\nu > DP_0$ is

$$\ln\left(\frac{m_0}{m_0 - m_{1,t}}\right) = (DP_0 - 1)k_i t \quad (24)$$

where m_0 is the moles of monomer in PCA at $t = 0$, $m_{1,t}$ is the moles of monomer produced by radiolysis at time t, and k_i is the rate constant of initiation. The data of γ-radiolysis in air are plotted in Figure 11. Using eq 24 one finds $k_i = 1.7 \times 10^{-8}\ \mathrm{s^{-1}}$.

The molecular weight distribution of PCA remains virtually unchanged during a γ-radiolysis experiment. This is consistent with the above analysis of $n \sim 1$. If the two primary radicals produced in a chain scission both initiate unzipping, i.e., $n = 2$, then the irradiated polymer should have either bimodal distribution or broadened MW distribution in contrast to the observed results.

The depolymerization process does not proceed to completion. The few percent of residue contains largely oxi-

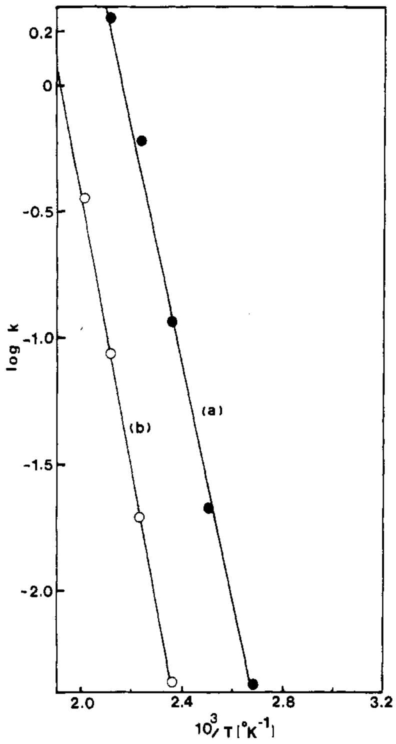


Figure 11. Arrhenius plot of the first-order rate constant of thermolysis of (a) PCA and (b) end-capped PCA.

Table I
Radiolysis Yields of PCA Containing Ph_2I^+

radiolysis	G(M,total)	G(M,Ph_2I^+,ion) + G(M,Ph_2I^+,radical)	G(M,PCA)
air	44 000	33 000	11 000
vac	15 000	14 000	1 000

dation products derived from the alkoxy radicals, peroxy radicals, and hydroperoxides.

In the absence of oxygen, the pair of radicals both initiate depolymerization. The value of n may be taken to be about 2 in eq 23, $\nu \approx 260$, and the radical initiates unzipping of about one-third of a polymer chain before termination.

γ-Radiolysis of PCA containing Ph_2I^+ resulted in much more depolymerization than without it. The total monomer yield is

$$G(\mathrm{M,total}) = G(\mathrm{M,Ph_2I^+,ion}) + G(\mathrm{M,Ph_2I^+,radical}) + G(\mathrm{M,PCA}) \tag{25}$$

where on the right-hand side the first two terms are due to ions and radicals generated by the radiolysis of Ph_2I^+ (eq 3–6) and the third for the radiolysis of PCA itself. From the experimental G(M) values, as given in Table I, one estimates G(M,Ph_2I^+,ion) = 12 000 and G(M,Ph_2I^+,radical) = 21 000.

Thermolysis. The TGA of PCA obeys a first-order kinetic plot according to the method of Freeman et al.[49,50] (Figure 11a)

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{AW}{RT}\exp(-E/RT) \tag{26}$$

where W is the sample weight and A and E are the frequency factor and activation energy, respectively. The activation energies are nearly the same for PCA and end-capped PCA having values of 23 and 24 kcal mol^{-1}, respectively. Thermolysis of other oxygen-containing low T_c polymers have similar activation energies, they are 31 kcal mol^{-1} for poly(1,3-dioxolane)[51] and 28 kcal mol^{-1} for poly(oxymethylene).[52] The rate of thermolysis of end-capped PCA is slower than that of PCA itself at the same temperature. This may be due to the presence of terminal urethane which tends to interrupt the chain-transfer process to propagate the unzipping reaction.

In conclusion, PCA has been found to possess extreme sensitivity to radiation-induced depolymerization. The kinetic chain length for depropagation is several hundred fold of that for poly(olefin sulfones). The PCA/onium salt system also undergoes extensive depolymerization upon irradiation. PCA shows good promise as a self-developing resist for microelectronic lithography.

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Registry No. PCA, 27577-42-0; O_2, 7782-44-7; Bu_4NBr, 1643-19-2; $(C_6H_5)_2IPF_6$, 58109-40-3; monochloroacetaldehyde, 107-20-0; 2,6-di-*tert*-butyl-*p*-cresol, 128-37-0.

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Synthesis and Characterization of Soluble Polymers Containing Electron- and Energy-Transfer Reagents

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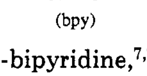
ABSTRACT: A series of monofunctional redox polymers containing a visible chromophore [tris(bipyridyl)ruthenium(II) derivatives] or an organic energy-transfer reagent (derivatized anthracenes) were synthesized by reaction of poly(*m*(*p*)-(chloromethyl)styrene-*stat*-styrene) with alkoxide or carboxylate nucleophiles. Bifunctional polymeric materials incorporating substituted anthracenes and a reductive organic electron-transfer quencher (phenothiazene) were prepared by analogous stepwise procedures. The degree of loading of the modified polystyrenes was controlled in a reproducible manner by variation of the ratio of the nucleophile to the starting copolymer as indicated by ^{1}H NMR, UV–visible spectroscopy, and elemental analysis. Results from cyclic voltammetry confirm the electroactivity of the pendant functionalities and are consistent with a hydrophobic environment surrounding the redox sites. Comparison of the steady-state emission spectra of the ruthenium(II) polymers with monomeric models indicates that the excited-state properties of the metal complex are maintained upon polymeric attachment.

Introduction

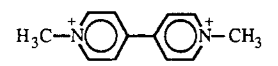
Soluble electroactive or photoactive polymers constitute unique excited-state redox reagents often enhancing energy migration[1] and attenuating charge recombination[2] of photoproduced transient intermediates. A number of homogeneous charge storage systems utilizing polymer-bound ruthenium(II) bipyridyl derivatives have been reported in aqueous[3–5] or organic[3b,6] media in response to their potential utility in the conversion and storage of solar energy. Our interests in this area include the assembly of mixed functional polymers containing a variety of chromophore–quencher combinations, with polymer-bound ruthenium(II) or osmium(II) tris(bipyridyl) derivatives serving as the primary chromophoric sites. One of our goals is to learn how to control intrapolymeric energy and electron-transfer events to effect efficient photochemically induced charge separation at the molecular level.

Typically, syntheses of polymeric ruthenium(II) bipyridyl complexes are based on vinylic derivatives of 2,2′-bipyridine (bpy) including 6-*p*-styryl-2,2′-bipyridine,[5a]

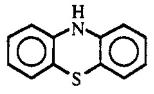


(bpy)

4-methyl-4′-vinyl-2,2′-bipyridine,[7,7a] and 6-vinyl-2,2′-bipyridine[7] as well as copolymeric combinations.[3b,3d,5b,6] Clearly, a more general synthetic approach is necessary for the attachment of a wide variety of potential photoredox reagents. We recently reported the preparation of soluble redox polymers containing controlled loadings of derivatives of a reductive quencher (phenothiazine, PTZ), an

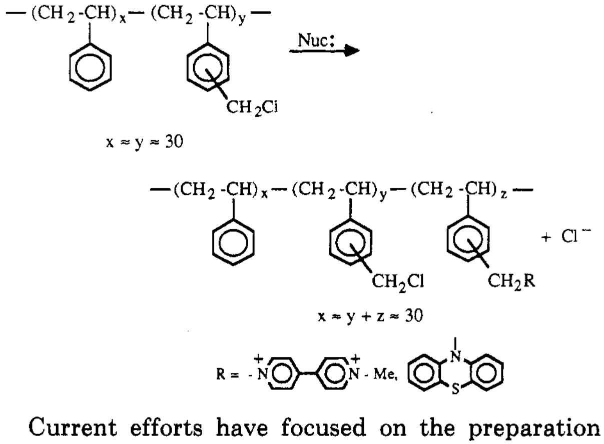


(PQ^{2+})



(PTZ)

oxidative quencher (paraquat, PQ^{2+}), and combinations of the two based on nucleophilic displacement of Cl^- in a 1:1 statistical copolymer of styrene and *m*(*p*)-(chloromethyl)styrene (reaction 1).[8]



(1)

Current efforts have focused on the preparation of polymer-bound derivatives of tris(bipyridyl)ruthenium(II),

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