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ESR Studies of γ-Irradiated Poly[3,3-bis(chloromethyl)oxetane]

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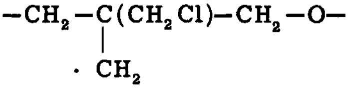
ABSTRACT

Poly[3,3-bis(chloromethyl)]oxetane in vacuo, after γ-irradiation at 77°K and room temperature, showed ESR spectra consisting of a triplet (hfs of 22.0G) and a doublet (hfs of 17.8G), respectively. The triplet ESR spectrum is attributed to the  $-CH_2-\underset{\cdot\,CH_2}{\underset{|}{C}}(CH_2Cl)-CH_2-O-$ radical and the doublet ESR spectrum is attributed to the $-CH_2-C(CH_2Cl)_2-CH-O-$ radical. The G values for formation of radicals are estimated to be 0.3 and 0.5 at 298 and 77°K, respectively.

INTRODUCTION

Extensive studies of radiation grafting to polymers for membrane materials have been carried out in these laboratories [1]. Membranes for reverse osmosis are used under various ranges of pH, pressure, and temperature. Consequently it is necessary to use polymers with high chemical and mechanical resistance. Poly[3,3-bis(chloromethyl)oxetane] (Poly-BCMO), which is characterized by excellent mechanical properties, high chemical, and thermal stability, appears to be a suitable polymer for such membranes although it does not have enough hydrophilic character for adequate fluxes. In attempts to impart the desired hydrophilicity, studies of the radiation grafting of poly-BCMO with hydrophilic monomers have been undertaken.

Previous studies [2] of radiation grafting to membranes have demonstrated the importance of controlling the kinetics to give the desired results. ESR studies of γ-irradiated poly-BCMO have been carried out to help understand the nature and yield of the free radicals formed. In this paper, ESR data of γ-irradiated poly-BCMO are presented together with discussions about a probable mechanism of radical formation. The ESR spectra obtained from poly-BCMO after γ-irradiation are found to be very similar to the reported [3] spectra of electron-beam irradiated poly-BCMO.

EXPERIMENTAL

Poly-BCMO in pellets was obtained from Hercules, Inc. and used without further purification. Two kinds of samples including pellets and films were used in the present ESR study. Films were made by casting a hot solution of poly-BCMO in dimethylformamide (DMF) on a glass surface at room temperature. Samples for the ESR studies were degassed to 10^{-5} Torr and sealed off in vacuo. ESR tubes were made from Suprasil tubing supplied by Amersil, Inc., Hillside, New Jersey. γ-Irradiation was carried out in a Gammacell-220 ^{60}Co source supplied by Atomic Energy of Canada Limited, and the dose rate of the source was 0.6 Mrad/hr. After γ-irradiation it was possible to anneal an ESR tube containing the sample by flaming after inverting the tube in liquid nitrogen. This treatment removed an impurity signal from quartz. ESR spectra were recorded with an X-band spectrometer with 100-Kc field modulation (Japan Electron Optics Laboratory Co., Model JES-ME-1X). The g-values were measured with reference to the spectrum of Mn^{2+} contained in MgO, and the g-value of the fourth spectrum of Mn^{2+} counted from the low magnetic field was used as 1.98.

RESULTS AND DISCUSSION

Since a γ-irradiated pellet of poly-BCMO gave the same ESR results as a γ-irradiated film, only the results obtained from the film will be presented to avoid duplication. Poly-BCMO in vacuo, after γ-irradiation at room temperature, showed a doublet ESR spectrum with 1:1 intensity ratio, and this ESR spectrum is shown in Fig. 1. The hyperfine splitting (hfs) and g-value of the doublet were determined as 17.8G and 2.003, respectively. The doublet hfs of 17.8G was ascribed to the nuclear hyperfine interaction with an α-proton. Accordingly the doublet ESR spectrum was assigned to the $-\dot{C}H-C(CH_2Cl)_2-CH_2-O-$ radical. This radical is very stable under vacuum at room temperature, and it is hereinafter referred to as Radical I for brevity.

On exposure of the γ-irradiated sample to air, the doublet ESR spectrum of Radical I changed slowly to give rise to an asymmetric ESR spectrum, as shown in Fig. 2. The asymmetric ESR spectrum was analyzed into the two components with $g_{\parallel} = 2.036$ and $g_{\perp} = 2.008$.

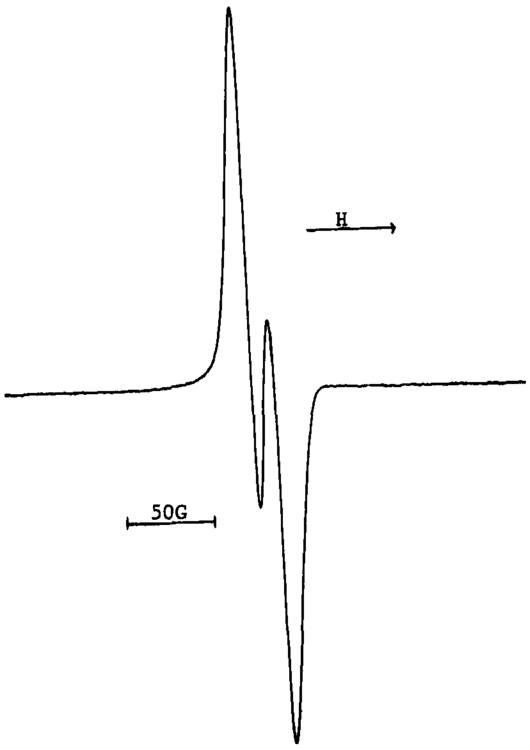


FIG. 1. ESR spectrum of poly-BCMO after γ-irradiation at room temperature.

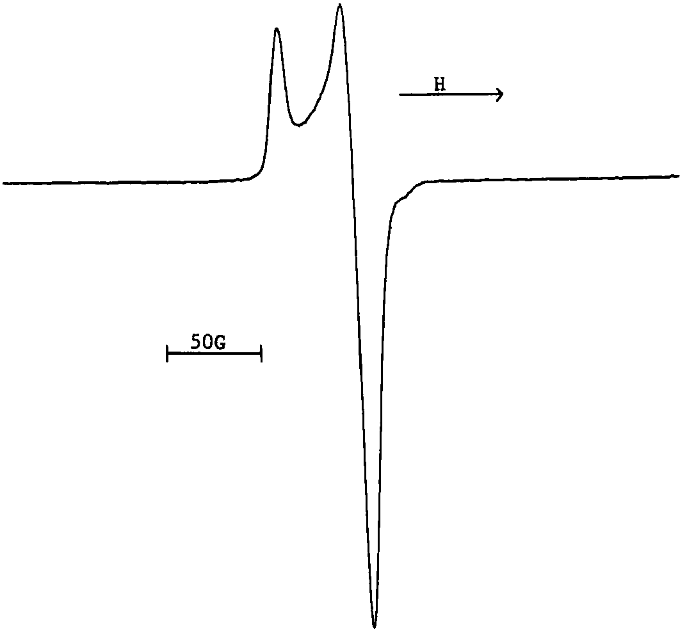


FIG. 2. ESR spectrum of poly-BCMO after γ-irradiation at room temperature and exposure to air.

These principal values of the g-tensor are in good agreement with those of the reported [4] g-tensor for a peroxy radical. Accordingly, the asymmetric ESR spectrum is attributed to the $-CH(OO\cdot)-C(CH_2Cl)_2-CH_2-O-$ radical. The peroxy radical in the pressure of air decayed at room temperature, and this radical is thermally less stable than the Radical I. Both the doublet ESR spectrum of Radical I and the asymmetric ESR spectrum of peroxy radical did not show any change as the temperatures of the samples were lowered from room temperature of 77°K.

The ESR spectrum of γ-irradiated poly-BCMO at room temperature in air consists of mainly a 1:1 doublet and partly an asymmetric singlet at lower magnetic field. The doublet ESR spectrum decayed gradually, giving rise to the asymmetric ESR spectrum characteristic of peroxy radicals. This result indicates that oxygen diffuses slowly into a site of the Radical I to form the peroxy radical in the poly-BCMO matrix. However, in the case of methyl methacrylate (MMA), preliminary results [5] of the preirradiation grafting of poly-BCMO with MMA showed that a swelling agent like DMF is required for MMA to diffuse into the site of Radical I.

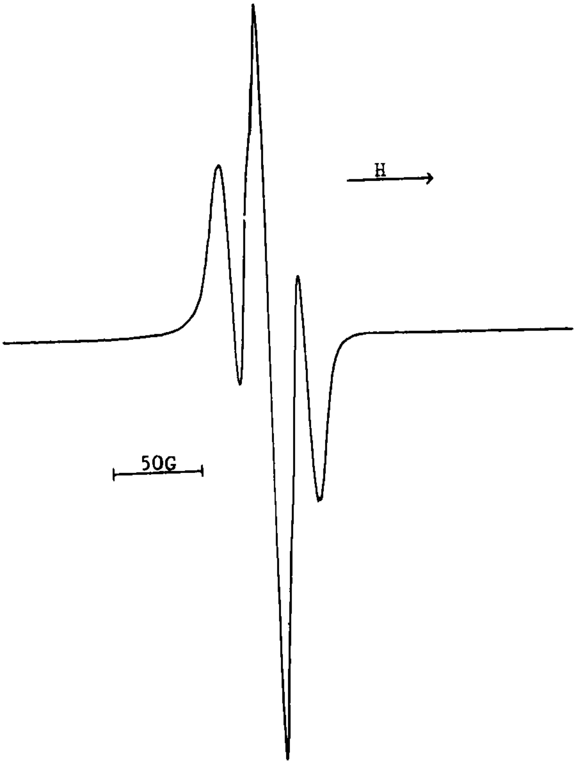
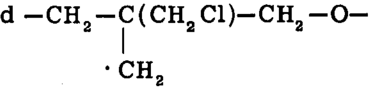


FIG. 3. ESR spectrum of poly-BCMO in vacuo at 77°K after γ-irradiation.

Figure 3 shows an ESR spectrum of γ-irradiated poly-BCMO in vacuo at 77°K. This ESR spectrum can be analyzed into three equally spaced lines with intensities in the ratios of 1:2:1. The triplet ($g = 2.004$) with hfs of 22.0G was ascribed to the nuclear hyperfine interactions with two magnetically equivalent protons which were bonded to an α-carbon, i.e., to a type of $-\dot{C}H_2$ radical. The probable species of the triplet ESR spectrum in the poly-BCMO matrix may be $-CH_2-C(CH_2Cl)_2-\dot{C}H_2$ (Radical II) and  $-CH_2-\underset{\substack{| \\ \cdot CH_2}}{C}(CH_2Cl)-CH_2-O-$ (Radical III). The assignment of the triplet ESR spectrum to one of these radicals may be feasible on the basis of radiation chemistry together with the ESR results. For this purpose, it is relevant to discuss whether Radicals II and III can be produced somehow in the γ-irradiated poly-BCMO. Possible processes for formation of the Radical II are an homolysis following geminate recombination

$$[-\mathrm{CH_2-C(CH_2Cl)_2-CH_2-O-CH_2-C(CH_2Cl)_2-CH_2-O-}]^{\dot{+}} + e^- \rightarrow$$

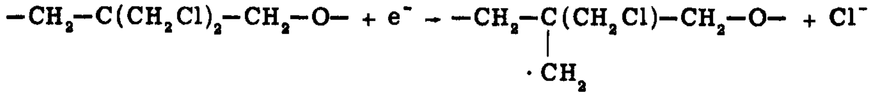
$$-\mathrm{CH_2-C(CH_2Cl)_2-\dot{C}H_2} + \cdot\mathrm{O-CH_2-C(CH_2Cl)_2-CH_2-O-}$$

and also by dissociative electron capture [6]

$$-\mathrm{CH_2-C(CH_2Cl)_2-CH_2-O-CH_2-C(CH_2Cl)_2-CH_2O-} + e^- \rightarrow$$

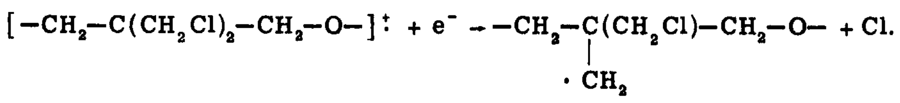
$$-\mathrm{CH_2-C(CH_2Cl)_2-\dot{C}H_2} + {}^-\mathrm{O-CH_2-C(CH_2Cl)_2-CH_2-O-}$$

Since the $\cdot\mathrm{O-CH_2-C(CH_2Cl)_2-CH_2-}$ radical has not been observed at 77°K in the present study, the formation of the Radical II through the homolysis may be negligible. In the radiation chemistry of the condensed state, dissociative electron capture is known [6] to occur efficiently for electrons of thermal energy whenever the electron affinity of X in the molecule AX is greater than the bond dissociation energy, D(A—X). In poly-BCMO the bond dissociation energy of a C—O bond and the electron affinity of the leaving group, $\cdot\mathrm{O-CH_2-C(CH_2Cl)_2-}$, can be approximated as 76 [7] and 60 kcal/mole [8], respectively, from the corresponding thermochemical data of the dimethyl ether. Based on the thermochemical consideration, the dissociative electron capture through the —C—O— bond in the poly-BCMO to produce the Radical II may presumably be neglected. This presumption is not inconsistent with the recent report [9] on the dissociative electron capture of dimethyl ether during photobleaching of trapped electrons in γ-irradiated 3-methylpentane glass. In contrast to the case of the Radical II, the Radical III is expected to be formed by the dissociative electron capture



$$-\mathrm{CH_2-C(CH_2Cl)_2-CH_2-O-} + e^- \rightarrow -\mathrm{CH_2-}\underset{\substack{|\\ \cdot\mathrm{CH_2}}}{\mathrm{C}}\mathrm{(CH_2Cl)-CH_2-O-} + \mathrm{Cl}^-$$

and a homolysis following geminate recombination



$$[-\mathrm{CH_2-C(CH_2Cl)_2-CH_2-O-}]^{\dot{+}} + e^- \rightarrow -\mathrm{CH_2-}\underset{\substack{|\\ \cdot\mathrm{CH_2}}}{\mathrm{C}}\mathrm{(CH_2Cl)-CH_2-O-} + \mathrm{Cl.}$$

Since the electron affinity of a chlorine atom (88 kcal/mole) is greater than the bond dissociation energy of a C—Cl bond (81 kcal/mole), dissociative electron capture by a C—Cl bond of the poly-BCMO molecule is a thermodynamically favorable process. Furthermore, in electron scavenging experiments using PVC as an electron scavenger in MTHF glass matrix, it has been shown [10] that primary PVC radical (—CH_2—CH—) has been produced by dissociative

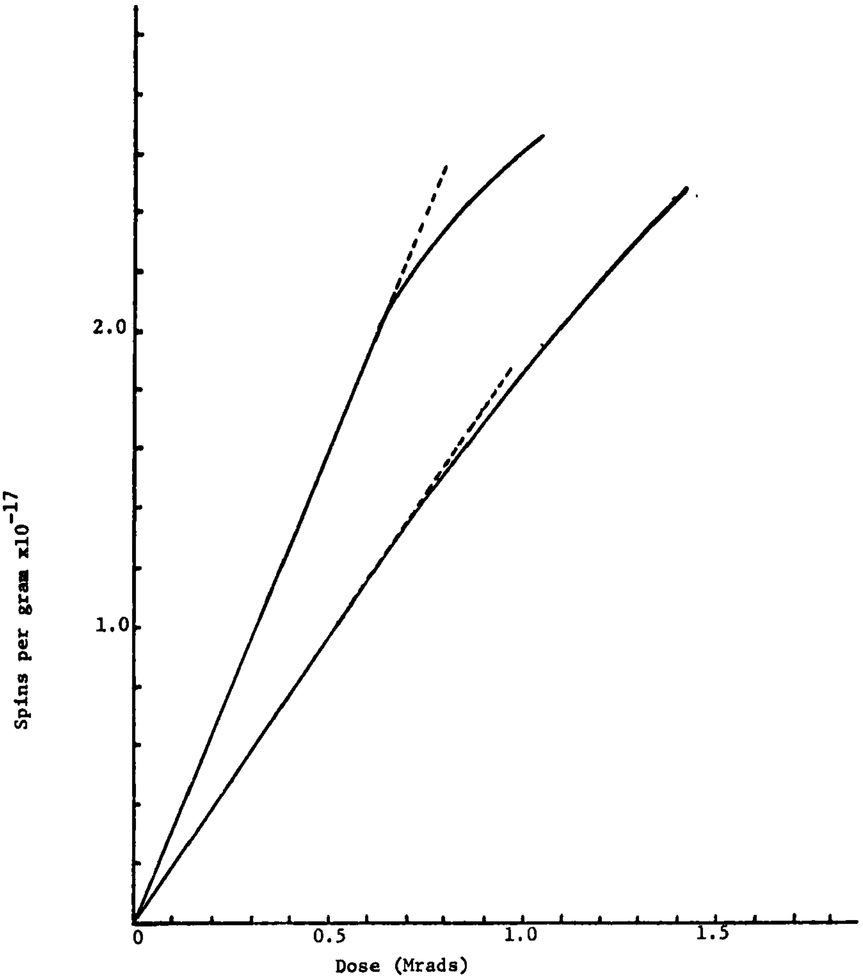
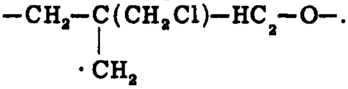


FIG. 4. The dose dependences of the radical concentrations. Upper curve, 77°K; lower curve, 25°C.

electron capture of a C—Cl bond. Similarly, in the bulk poly-BCMO matrix it is reasonable to assume that the dissociative electron capture by a C—Cl bond and the homolysis of a C—Cl bond may be important processes, giving rise to formation of the Radical III. On the basis of this discussion, it is tempting to assign the triplet ESR spectrum with hfs of 22.0G to the Radical III,



$$-\mathrm{CH_2}-\underset{\displaystyle \cdot\,\mathrm{CH_2}}{\underset{|}{\mathrm{C}}}(\mathrm{CH_2Cl})-\mathrm{HC_2}-\mathrm{O}-.$$

The concentrations of Radicals I and III, which have been produced in the γ-irradiated poly-BCMO under vacuum at room temperature and at 77°K, respectively, have been measured in various ranges of total irradiation doses. The dose dependences of the radical concentrations are shown in Fig. 4. From the initial slopes of the curves in Fig. 4, the G values for formation of the Radicals I and III are estimated to be 0.3 and 0.5, respectively. The G value of 0.5 at 77°K in the present study is lower than the corresponding G value [3] of 1.7 obtained from the electron-beam irradiated poly-BCMO at 77°K. This difference may qualitatively be expected from normal non-steady-state kinetic consideration, since the absolute concentration of radicals has been shown [11] to be proportional to the square root of dose-rate at steady-state. Alternatively, the polymer used by the two groups of investigators may be of a different crystallinity.

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