

Study of γ -Irradiated Lithographic Polymers by Electron Spin Resonance and Electron Nuclear Double Resonance

SHULAMITH SCHLICK *Department of Chemistry, Wayne State University, Detroit, Michigan 48202* and LARRY KEVAN, *Department of Chemistry, University of Houston, Houston, Texas 77004*

Synopsis

The room temperature gamma irradiation degradation of the lithographic polymers, poly(methylmethacrylate) (PMMA), poly(methyl- α -chloroacrylate) (PMCA), poly(methyl- α -fluoroacrylate) (PMFA), and poly(methylacrylonitrile) (PMCN), have been studied by electron spin resonance and electron nuclear double resonance (ENDOR) to assess their molecular degradation processes of relevance to electron beam lithography. Two classes of radicals are found, chain radicals and chain scission radicals. PMMA and PMCA mainly form chain scission radicals consistent with degradation while for PMCN the resolution is poorer, and this is only probable. PMFA forms mainly chain radicals consistent with predominant crosslinking. The total radical yield is greatest in PMCA and PMCN. ENDOR is used to assess the compactness of the radiation degradation region for PMMA and PMCA and hence the potential resolution of the resist; this appears to be about the same for these methacrylate polymers.

INTRODUCTION

Poly(methylmethacrylate) (PMMA) has been extensively investigated as a positive resist in electron beam and X-ray lithography.¹⁻³ High energy irradiation results in polymer degradation, i.e., formation of smaller molecular units. The behavior is an example of the Miller rule,¹ which states that when each carbon atom of the main polymer chain is substituted by at least one hydrogen atom, the polymer crosslinks on irradiation and is therefore a negative resist. If this condition is not obeyed, the polymer degrades on irradiation and is a positive resist.

It has recently been shown^{4,5} that the sensitivity of the resist can be enhanced by substitution of a polar group such as Cl or CN in PMMA, as evident in poly(methyl- α -chloroacrylate) (PMCA), $[\text{CH}_2\text{C}(\text{Cl})(\text{CO}_2\text{CH}_3)]_n$, and in poly(methylacrylonitrile) (PMCN), $[\text{CH}_2\text{C}(\text{CH})\text{CH}_3]_n$.

The molecular details of the degradation process are of considerable interest and are frequently studied by electron spin resonance (ESR) for identification of the radical and for determination of the reaction kinetics. More recently the matrix electron nuclear double resonance (ENDOR) line has been studied in irradiated polymers⁶ in order to determine the average dipolar coupling of the radical to the matrix nuclei.

In this study we have applied ESR and ENDOR techniques in order to obtain information and to compare degradative processes in PMMA, PMCA, and PMCN. In addition we have studied poly(methyl- α -fluoroacrylate), $[\text{CH}_2\text{C}(\text{F})(\text{COOCH}_3)]_n$, (PMFA) which has recently been found to predominantly crosslink in opposition to the Miller rule.^{6b}

EXPERIMENTAL

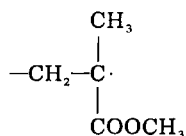
Samples of the polymers PMMA, PMFA, PMCA, and PMCN were kindly supplied to us by Dr. J. N. Helbert of the U.S. Army Electronics Technology and Devices Laboratory, Fort Monmouth, N.J. Polymer samples were sealed under vacuum ($\sim 10^{-5}$ torr) in quartz tubes. Irradiation was carried out at room temperature (290 K) in a ^{60}Co γ -source at a dose rate of ~ 0.1 Mrad/h to a typical total dose of 10 Mrads.

ESR spectra were taken with Varian E-4 and V-4500 instruments: ENDOR was detected by interfacing the V-4500 ESR spectrometer with a Varian E-700 ENDOR unit. The radio frequency (rf) field is pulsed at 6 kHz and the magnetic field is modulated at low frequency (40 Hz). Cold helium gas from liquid helium was used as the coolant for spectra taken in the temperature range 25–80 K.

RESULTS

PMMA

ESR spectra of γ -irradiated PMMA in vacuum at 290 K consist of the well-known⁷⁻¹⁰ nine-line spectrum due to the presence of the radical produced by



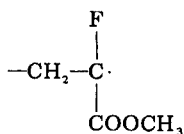
chain scission. A proton matrix ENDOR line at ~ 14 MHz was observed in the temperature range 40–70 K. Measurements were taken over the range of 2–10-mW microwave power and 4–10-G radio-frequency field. No systematic variation of the lineshape with these two parameters and with temperature in the above range was observed. The variation of the line width at half-intensity remained within experimental error and the average line width is 0.69 ± 0.06 MHz.

Figure 1 shows the ESR spectrum at 290 K and the matrix ENDOR spectrum at 50 K at the indicated microwave power level.

If the irradiation takes place in the presence of oxygen, an ESR spectrum consistent with axial g -anisotropy is observed and is shown in Figure 2. The calculated g -values are $g_{\parallel} = 2.034$, $g_{\perp} = 2.009$, with $g_{\text{average}} = 2.017$. These values for the g -components indicate the presence of a peroxy radical.¹¹

PMFA

The ESR spectrum of γ -irradiated PMFA at 290 K is shown in Figure 3(a). The separation between the two extreme weak shoulders as indicated by the two arrows is ~ 85 G. This spectral width suggests the formation of the radical



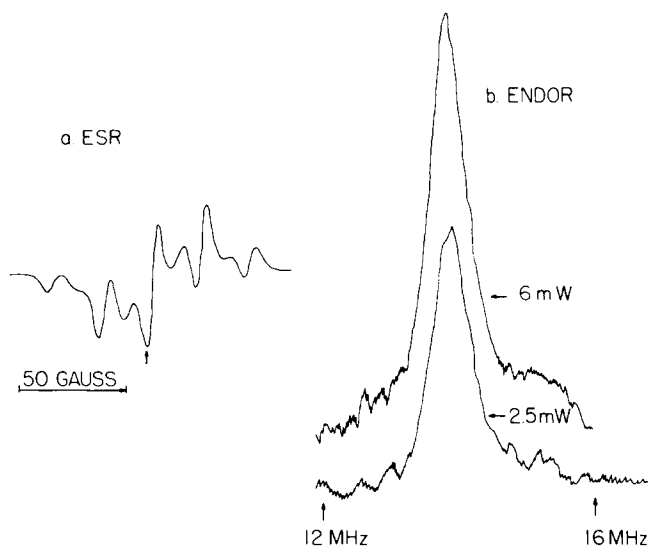


Fig. 1. (a) ESR spectrum of γ -irradiated PMMA at 50 K. The arrow denotes the observing position for ENDOR. (b) Proton matrix ENDOR line at 50 K at two microwave power levels.

by chain scission. In this radical the unpaired electron interacts with one α -fluorine nucleus and two β -protons. The β -proton splittings might be similar to those in the corresponding radical in γ -irradiated PMMA, or $\sim 11.5 \pm 3.5$ G. The fluorine splitting is obtained by subtracting $2a_{\beta}^H$, or ~ 20 G, from the total width, giving $a_{\alpha}^F \approx 65$ G. This value is not far from the value of 90 G assigned to the isotropic α -fluorine splitting of the chain radical $\{\text{CF}_2-\dot{\text{C}}\text{F}-\text{CH}_2\}_n$ obtained in γ -irradiated poly(tetrafluoroethylene), (PTFE).¹²⁻¹⁴ A value for the isotropic α -fluorine splitting can also be obtained from the hyperfine tensor elements as suggested by Iwasaki,¹⁵ with $A_{\parallel} = 189$ G and $A_{\perp} = 12$ G or by Siegel and Hedgepeth,¹² with $A_{\parallel} = 180$ G and $A_{\perp} = 20$ G. Both sets of tensor elements give $a_{\text{iso}}^{\alpha F} \approx 72$ G, which compares well with our estimated value of ~ 65 G.

The central strong lines in Figure 3(a), which form a barely resolved quintet are probably due to the presence of the chain radical $[\text{CH}_2-\dot{\text{C}}(\text{COOCH}_3)]_n\text{CH}_2$. In this radical the unpaired electron interacts with four β -protons, and, if again the assumption is made that the hyperfine splittings are ~ 11 G, the total width should be ~ 46 G for the dominant quintet in Figure 3(a).

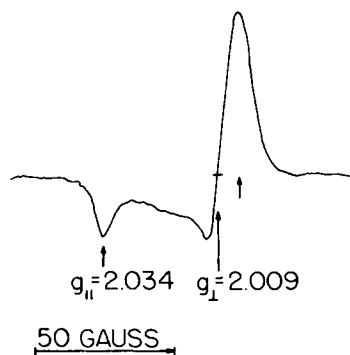


Fig. 2. ESR spectrum of γ -irradiated PMMA at 290 K in the presence of air. The arrow represents the position of DPPH. $g_{\text{average}} = 2.017$.

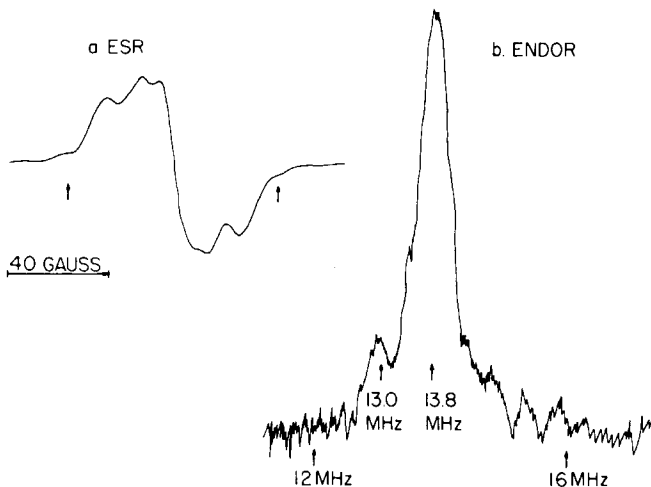


Fig. 3. (a) ESR spectrum of γ -irradiated PMFA at 290 K. The arrows indicate the extreme shoulders with a separation of 85 G. (b) Fluorine matrix ENDOR line at 13.0 MHz and proton matrix ENDOR line at 13.8 MHz at 30 K. The microwave power level is 2.5 mW.

Matrix ENDOR of γ -irradiated PMFA at 34 K is shown in Figure 3(b). The proton matrix ENDOR line appears at 13.8 MHz and the weaker (by factor of ~ 4.5) fluorine matrix ENDOR line appears at 13.0 MHz. The average proton matrix ENDOR linewidth at 34 K and 84 K and from 2 to 10-mW microwave power is 0.60 ± 0.05 MHz.

The ratio of the number of hydrogen to fluorine atoms in the undamaged polymer is 5 to 1. Assuming that the other factors determining the matrix ENDOR response are similar, the fluorine matrix ENDOR line should be weaker than the proton matrix ENDOR line by about 5. This is in reasonable agreement with the intensity factor of ~ 4.5 measured experimentally.

The radical yield in PMFA is less than in the other polymers studied by a factor of ~ 2.5 . Most matrix ENDOR spectra were measured on PMFA irradiated to a total dose of ~ 20 Mrad so that the radical concentration was similar to that in the other polymers.

PMCA

The ESR spectrum of γ -irradiated PMCA is shown in Figure 4. The total width as indicated by the arrows is ~ 80 G. The two outermost lines are not

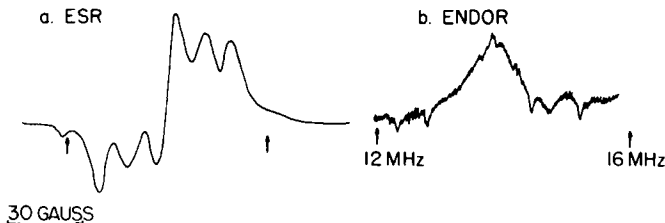


Fig. 4. (a) ESR spectrum of γ -irradiated PMCA at 290 K. The arrows indicate the extreme shoulders with a separation of 80 G. (b) Proton matrix ENDOR line at 80 K. The line width at half intensity is 0.75 ± 0.08 MHz.

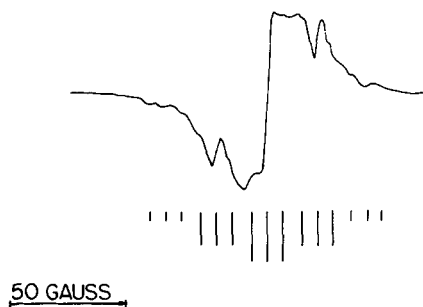
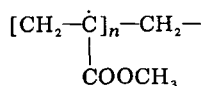
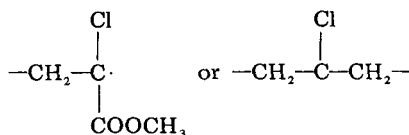


Fig. 5. ESR spectrum of γ -irradiated PMCN at 290 K. On spectral component is suggested by the stick diagram.

symmetric, suggesting anisotropy. Microwave power saturation measurements suggest the presence of more than one type of radical. The position, though not the relative intensities, of the central quintet with a total spectral width of 45 G suggests interaction with four equivalent protons. It is probable that the ESR spectrum is a mixture of the "chain" radical



and a chlorine-containing radical such as



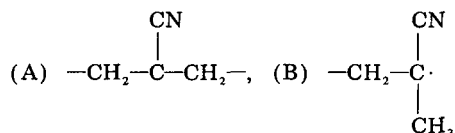
Such a situation would be similar to the mechanism of degradation in polyvinyl chloride $[\text{CH}_2-\text{CH Cl}]_n$ in which both C—H and C—Cl bond scissions occur.^{16,17} The proton matrix ENDOR in PMCA at 80 K with a poor signal-to-noise ratio is shown in Figure 4(b). The width at half-intensity is 0.75 ± 0.08 MHz.

In γ -irradiated PMCA, as well as in PMFA, the ESR resolution is reduced by ageing the sample at 290 K for several weeks in which case the spectrum consists of one broad line.

PMCN

The radical yield at 290 K is similar to that in γ -irradiated PMMA and PMCA.

The ESR spectrum of γ -irradiated PMCN is shown in Figure 5. The resolution is so poor that any identification is quite speculative. The spectrum could consist of five triplets with an intensity ratio close to 1:4:6:4:1, as shown in the stick diagram in Figure 5. This would indicate interaction with one nitrogen nucleus, $a_N \approx 6.5$ G and with four equivalent protons with $a_H = 20.8$ G and thus the radical A formed by methyl scission.



However, the spectrum is not inconsistent with six triplets with a smaller nitrogen coupling as would be predicted for radical B.

No matrix ENDOR spectrum was observed over the temperature range 25–290 K.

DISCUSSION

The ESR results indicate that PMFA is significantly less sensitive to irradiation than the other methacrylate polymers. This is consistent with a low yield of radiation-induced chain scission recently determined by molecular weight measurement.^{6(b)} In fact, it has very recently been shown that PMFA predominantly crosslinks, instead of degrading.^{6(b)} This is also consistent with our tentative radical assignments of a low yield of chain scission radical and a much higher yield of chain radical. It is the chain radicals that are most efficient at producing crosslinks.

In PMMA the predominant radical is a chain scission radical consistent with the known predominant radiation-induced degradation. In PMCA the probable identifications of the radicals are also chain scission radicals consistent with net radiation-induced degradation.¹⁸ In PMCN the radical identification is much more tentative. Either chain or chain scission radicals or a mixture of both are indicated. Based on the known radiation degradation of PMCN¹⁸ we favor the chain scission radical identification.

The presence of oxygen is very important to the degradative process, and in all the polymers reported here a peroxy type radical is formed when the irradiation takes place in air or when air is introduced to the system after the irradiation is completed.

Matrix ENDOR responses are due to nuclei situated at distances from the radical that usually exclude significant isotropic hyperfine interaction, the main interaction being electron–nuclear dipolar (END) interaction.¹⁹ These signals have frequently been analyzed^{6,20} in terms of two parameters: the nuclear spin-packet width α and the distance \bar{a} , where only an END interaction is considered. In terms of such a model with linewidths in PMFA, PMMA, and PMCA being 0.60, 0.69, and 0.75 MHz, respectively, the corresponding \bar{a} values decrease in this series but all values are within $4.0 \pm 0.2 \text{ \AA}$.

It is important to note that the line width of the proton matrix ENDOR line of $0.69 \pm 0.06 \text{ MHz}$ for PMMA in this study is considerably larger than the value of $0.44 \pm 0.08 \text{ MHz}$ reported previously⁶ for PMMA γ -irradiated to a dose of more than 200 Mrad. This discrepancy is understood in terms of a more efficient nuclear relaxation process in the high dose sample. The formulation of the matrix ENDOR response has been improved²¹ by describing the nuclear spin–lattice relaxation time T_{1n} in terms of paramagnetic and nuclear spin diffusion contributions.²² The conclusion pertinent to the results in this study is that the nuclear spin–lattice relaxation time due to spin diffusion, T_{1n}^{SD} , is inversely proportional to the radical concentration. In the heavily irradiated PMMA sample studied previously,⁶ the shorter T_{1n}^{SD} increases the relative contribution to the matrix ENDOR response of protons at large distances from and the interacting weakly with the radical. These nuclei have their ENDOR response close to the free nuclear frequency. The width in such a high dose situation is less than in the moderately irradiated samples studied here.

We comment that, due to the dependence of the matrix ENDOR response on several parameters of the system, comparison of line shapes and line widths of matrix ENDOR lines can be reliably made when the system and the experimental conditions are well defined. Attention must be paid to the nuclear spin-lattice relation mechanisms that dominate the matrix ENDOR response. These mechanisms and their experimental characterization have recently been elucidated in some detail.^{22,23}

We can summarize the radiation degradation of PMMA, PMCA, and PMCN as follows. Two classes of radicals can be formed, chain scission radicals in which the main carbon chain backbone is broken and chain radicals in which a side group is lost while the main chain remains intact. PMMA and PMCA mainly form chain scission radicals, while for PMCN the resolution is poor and consistent with either or both chain scission and chain radicals. The total radical yield is greatest, however, in PMCA and PMCN. It would seem that formation of chain scission radicals as well as high radical yield are the optimum degradation processes for efficient positive resists. The compactness of the radiation degradation region also should affect the resolution of resist. The ENDOR results suggest equally sharp radiation damage areas consistent with similar lithographic resolution for PMMA and PMCA.

The irradiation of PMFA forms mainly chain radicals and the total radical yield is at least two times lower than for the other methacrylate polymers. This is consistent with predominant crosslinking and negative resist behavior of this polymer.

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