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Study of free radicals in poly(diethylene glycol bis(allyl carbonate)) irradiated by γ rays

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Free radicals in poly(diethylene glycol bis(allyl carbonate)), commercially known as CR-39 resin, cured by radical mechanism with various amounts of diisopropyl peroxydicarbonate were studied by electron paramagnetic resonance (e.p.r.) spectroscopy. It was found that the radicals can survive in the unirradiated polymer network for at least 6 months after polymerization. The dependence of the amplitude of the e.p.r. signal on the dose for CR-39 polymer irradiated by ^{60}Co γ rays was found to show a maximum which increased in magnitude and shifted in position to higher doses for samples cured with lower initiator concentration. This behaviour is explained by examining the role of residual allyl groups present in the cured polymer and the scission of the network at the carbonate group. It was found that the refractive index increase observed in the irradiated polymer cannot be directly attributed to the presence of free radicals in the network.

(Keywords: irradiated polymer; e.p.r. signal; free radicals)

INTRODUCTION

It is known that the refractive index of some polymers, such as poly(diethylene glycol bis(allyl carbonate)), increases on irradiation with γ rays or ion beams. For ion beams, the increase can be sufficient to produce optical waveguides[1–3]. In order to control the properties of such waveguides, a thorough understanding of physical and chemical processes induced by the radiation in this material is essential. The work presented here is concerned with the study of free radical processes in CR-39 resin before and after irradiation with γ rays using electron paramagnetic resonance (e.p.r.) spectroscopy.

EXPERIMENTAL

Materials

Poly(diethylene glycol bis(allyl carbonate)), known as CR-39 resin, is a highly crosslinked network polymer with the repeat unit shown in *Figure 1*. It is prepared by chain-growth polymerization involving both allyl groups, and the polymerization is initiated by free radicals.

The samples used in this work were prepared by bulk polymerization of liquid monomer using diisopropyl peroxydicarbonate (IPP) as the initiator. The curing regime used by Ahmad and Stejny[4] (4 h at 45°C, 4 h at 49°C, 4 h at 56°C, 2 h at 65°C, 2 h at 85°C, in succession) was employed, with the initiator concentration ranging from 1.5 to 10%. Previous work[4] has shown that the initiator concentration controls the conversion of the monomer and the density of crosslinks of the network, the latter reaching a maximum at an initiator concentration of about 5%.

Irradiation

After the polymerization, the samples were irradiated by γ rays from a ^{60}Co source delivering 2 kGy h^{-1}, with doses ranging from 2 to 150 kGy.

E.p.r. measurements

A Brücker ER 200 and a Varian X-band spectrometer (range 8.2–12.4 GHz) were used to obtain the e.p.r. spectra. The 'peak-to-peak' amplitude S_{pp} of the derivative absorption curve was calculated for all samples, but the area under the absorption curve (related to the concentration of free radicals) was determined only for one set of samples (γ-irradiated CR-39/1.5% IPP).

RESULTS AND DISCUSSION

Figure 2 shows typical e.p.r. spectra of unirradiated samples taken 2 and 6 months after polymerization.

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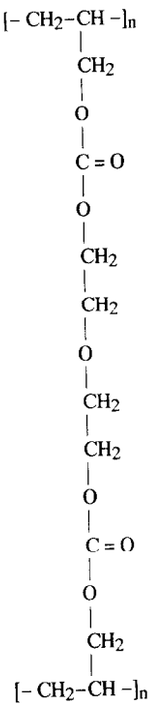

Figure 1 CR-39 polymer repeat unit

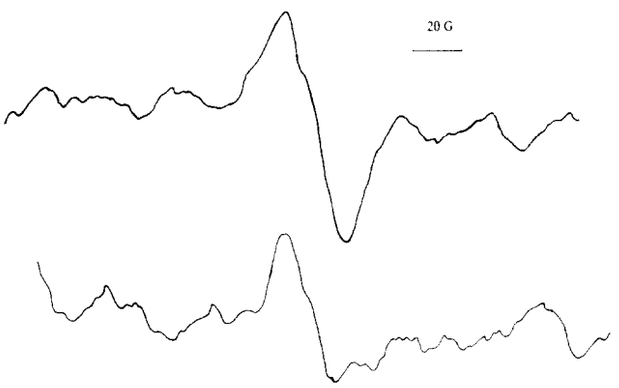

Figure 2 E.p.r. spectra of unirradiated CR-39 taken 2 and 6 months after polymerization

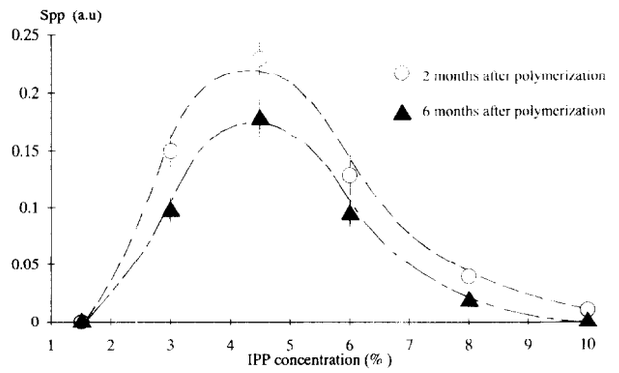

Figure 3 Dependence of the e.p.r. signal amplitude S_{pp} on the IPP concentration

They consist of a single peak, similar to the spectra observed previously for unirradiated[5] and γ-irradiated[6] CR-39. The dependence of amplitude S_{pp} on the initiator concentration is plotted in *Figure 3*.

We must recall here that the concentration of free radicals is proportional to the area under the e.p.r. absorption curve, with magnetic field as the abscissa. Therefore, the concentration of radicals cannot be related a priori to the amplitude S_{pp} of the derivative absorption curve and there is no linear relation between them. However, it can be concluded (*Figure 3*) that the dependence of the free radical concentration on the concentration of initiator is similar to the S_{pp} dependence, with the provision that the position of the maximum could be different.

It follows from *Figure 3* that the free radicals introduced by the initiator can survive for at least 6 months after the polymerization, and the highest concentration of preserved radicals survives in the polymer prepared with 4.5% of IPP initiator. As shown by Ahmad and Stejny[4] (*Table 1*), the dependence of the glass transition temperature on the concentration of IPP has a strong maximum at the same IPP concentration. It can therefore be concluded that the decay rate of the radicals in the polymer is inversely related to the glass transition temperature and is controlled by the mobility of the network. The radical most likely to survive is the resonance-stabilized allyl radical shown in *Figure 4*. Experiments are in progress at present to confirm the identification of this radical.

Figure 5 shows the dependence of the e.p.r. signal S_{pp} on the dose of γ radiation for samples polymerized with initiator concentrations of 1.5, 4.5, 6 and 10%. The samples were irradiated 2 months after polymerization and the spectra were taken within 2 days of the irradiation being completed.

Together with the S_{pp} measurements, we have also measured the concentration of free radicals using the area of the absorption curve for three samples of CR-39/1.5% IPP irradiated with 10, 20 and 50 kGy. In order to correlate S_{pp} with the concentration of free radicals, the dependence of both S_{pp} and the concentration of radicals on the dose is compared in *Figure 6*. This shows that both curves have similar shapes, hence the S_{pp} is directly

Table 1 Dependence of the glass transition temperature, T_g, and the concentration of residual allyl groups on the concentration of IPP initiator[4] in CR-39

IPP concentration (%)	Residual allyl group concentration (%)	Glass transition temperature (°C)
1.5	24.7	22
3.0	7.2	77
4.5	3.8	91
6.0	2.9	90
8.0	1.8	83
10.0	1.7	75

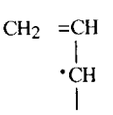

Figure 4 Allyl radical

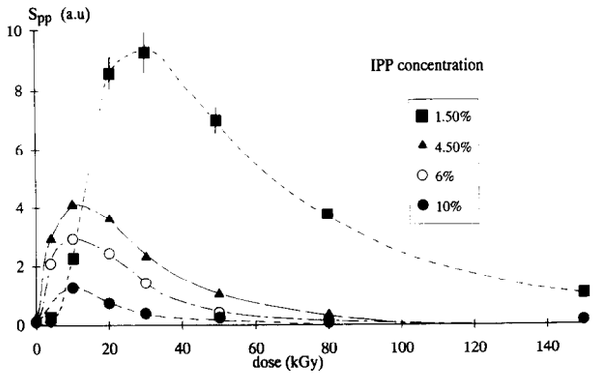

Figure 5 Dependence of the e.p.r. signal amplitude S_{pp} on the γ radiation dose

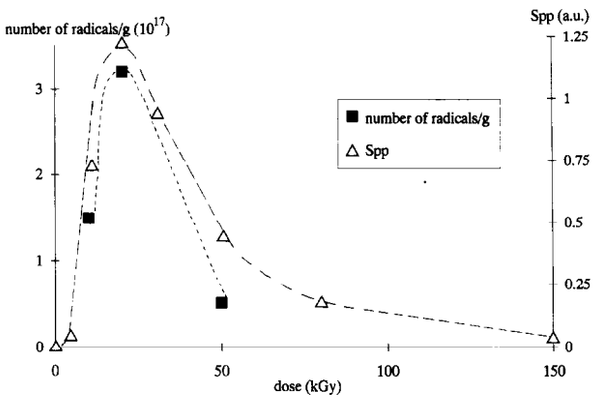

Figure 6 Dependence of the e.p.r. signal amplitude S_{pp} and the concentration of free radical in γ-irradiated CR-39/1.5% IPP on the γ radiation dose

related to the concentration of the radicals within the dose range used. We can therefore conclude that the dose dependence of S_{pp} and the radical concentration is similar. The characteristic feature is that the dependence passes through a maximum located at some critical dose; the height of the maximum and its position increase with decreasing initiator concentration. However, the positions of the maximum S_{pp} and the maximum of the radical concentration may not coincide.

We propose the following explanation of the observed behaviour of CR-39 polymer under γ radiation based on the experimental data so far obtained. It is known that the polymerization of allyl groups in the CR-39 monomer can be initiated by the radicals created by γ radiation[7], which results in the formation of CR-39 polymer network. However, it was found that the CR-39 polymer network undergoes scission[8], preferably at the carbonate group[9], when irradiated with γ radiation. The effect of these two opposing processes explains the observed results. As shown in *Table 1*, CR-39 polymers prepared with IPP initiator contain a significant amount of unpolymerized allyl groups[4] which decreases with increase in the initiator concentration. The γ radiation creates radicals which can either initiate further polymerization of the residual allyl groups (provided that there is enough mobility in the system for the polymerization to proceed) or can abstract hydrogen from them. Both these processes contribute to the survival of the radicals; the polymerization reduces the mobility of the network making the diffusion-controlled decay reactions slower, and the hydrogen abstraction converts the allyl groups into relatively stable allyl radicals incapable of initiating further polymerization[10]. The e.p.r. signal is therefore expected to increase with the dose. However, as the allyl groups are consumed, the increase of the signal should slow down with the dose. After reaching the critical dose and the consumption of available allyl groups, the radiation-induced scission of the network at the carbonate link becomes the dominant process. The scission increases the mobility of the network and therefore increases the decay rate of the radicals. This is responsible for the decrease of the e.p.r. signal observed above the critical dose.

The maximum in the dependence of the e.p.r. signal on the dose should be higher for samples polymerized with lower concentrations of initiator, as they have higher concentrations of residual allyl groups. Also, the position of the maximum for samples with higher concentrations of allyl groups should be reached at a higher dose, as more radiation is needed to convert larger amounts of allyl groups. Both these effects are observed experimentally, as shown in *Figure 5*. The repeat of the e.p.r. examination of the samples taken 4 months after the irradiation shows the same behaviour in the dependence of the e.p.r. signal on the dose; however, the signal is reduced by a factor of about eight owing to radical decay.

In order to relate the change in the properties of the CR-39 polymer to the radiation-induced processes in its network, the e.p.r. signal and the increase in the refractive index of the irradiated polymer as a function of the dose are both shown in *Figure 7*. As expected, the e.p.r. signal reaches a maximum at a dose of about 30 kGy and then decreases continuously to less than 10% of its maximum value at a dose of about 300 kGy. However, the refractive index starts increasing significantly only after the dose of the maximum e.p.r. signal is reached. Thereafter, it continues increasing rapidly in the whole high-dose range whilst the e.p.r. signal decreases to very low values. This shows that the increase in the refractive index cannot be attributed directly to the radicals. However, they can act as precursors to permanent chemical changes in the material which are responsible for

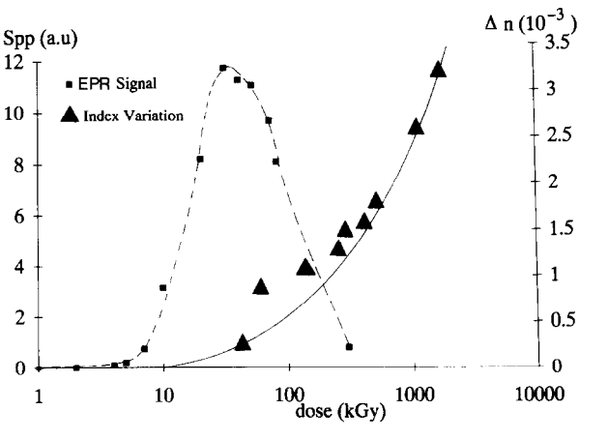

Figure 7 Dependence of the e.p.r. signal amplitude S_{pp} and the refractive index difference Δn on the γ radiation dose

the observed increase. This conclusion is also supported by the fact that the increase in the refractive index remained unchanged for over 1 year and does not decay with time.

CONCLUSIONS

This study shows that the free radicals created during polymerization or by γ radiation can survive in the CR-39 polymer for at least 6 months. The radical most likely to survive is the resonance-stabilized allyl radical. Two opposing processes affecting the density of crosslinks, and hence the decay rate of the radicals, can take place when CR-39 polymer containing residual allyl groups is irradiated with γ rays: (1) polymerization of allyl groups, which increases the density of crosslinks; (2) scission of the network at the carbonate group, which has the opposite effect. These processes, together with the formation of relatively stable allyl radicals, can explain the observed dependence of the radical concentration on the dose.

It was found that the increase in the refractive index of the polymer cannot be directly attributed to the increase in the concentration of free radicals, but is related to the permanent chemical changes in the polymer structure.

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