The Formation of Anion Radicals in Glassy *N*-Propyl and *N*-Benzyldimethacryloylamines γ-Irradiated at 77 K

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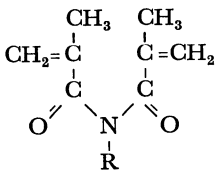
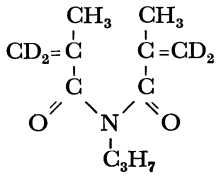
Synopsis. *N*-Propyl- and *N*-benzyldimethacryloylamines irradiated by γ-rays from ^{60}Co in their glassy state at 77 K yield anion radicals of their methacryloyl groups. These anion radicals afford a triplet with a coupling constant of 1.1 mT on measurement of the ESR and are bleached by a high-pressure mercury lamp at 77 K.

The primary effect of high-energy radiation is the excitation of the molecule, and ionization occurs subsequently. Electrons expelled are sometimes observed as trapped electrons in organic glasses, such as 2-methyltetrahydrofuran (MTHF)[1] and 3-methylpentane.[2] When electron-acceptors, for example, naphthalene or biphenyl, are added to organic glasses, the yield of the trapped electrons decreases and anion radicals of the solute electron-acceptors are formed through the reaction between the solute molecules and the electrons expelled from the solvent molecules.[3]

During the course of the studies of the solid-state cyclopolymerization of *N*-substituted dimethacryloylamines, *N*-propyl (DPA) and *N*-benzyl (DBA) derivatives were found to form a glassy state when they are quenched rapidly to the temperature of liquid nitrogen from above their melting points.[4] These results led us to ESR studies of these monomers in the glassy state, because the esters and amides of methacrylic acid trap electrons to form the anion radical of the methacryloyl group when they are exposed to ionizing radiation in such organic glasses as MTHF and 3-methylpentane.[5,6]



R = C_3H_7(DPA) or $CH_2C_6H_5$(DBA)



DPA-d_4

Experimental

DPA and DBA were synthesized as has been reported previously.[7,8] DPA deuterated at four methylene protons of methacryloyl groups(DPA-d_4) was prepared according to the procedure previously reported.[9] These monomers were dried over Drierite and distilled. The samples for ESR measurements were prepared in Suprasil tubes. The ESR spectra were recorded by means of a JEOL JES FE-1X X-Band spectrometer at a microwave power of 0.01 mW. The photobleach of the samples was carried out with a 100-watt high-pressure mercury lamp (Rikoh Scientific Industry Co., Ltd.) at a distance of 10 cm for 40 min at 77 K.

Results and Discussion

DPA and DBA subjected to γ-ray irradiation with a ^{60}Co source at 77 K in the dark afford the ESR spectra illustrated in Figs. 1a and 1d. After photobleaching, they changed to the spectral patterns depicted in Figs. 1c and 1f respectively. The 3-line spectra with a coupling constant of 1.1 mT were obtained by taking the difference between before and after the photobleaching of DPA and DBA irradiated at 77 K, as is shown in Figs. 1b and 1e. The spectra remaining after photobleaching at 77 K are mainly due to the 5-membered cyclic radical.[9] These results indicate that the active species which afford the 3-line spectra

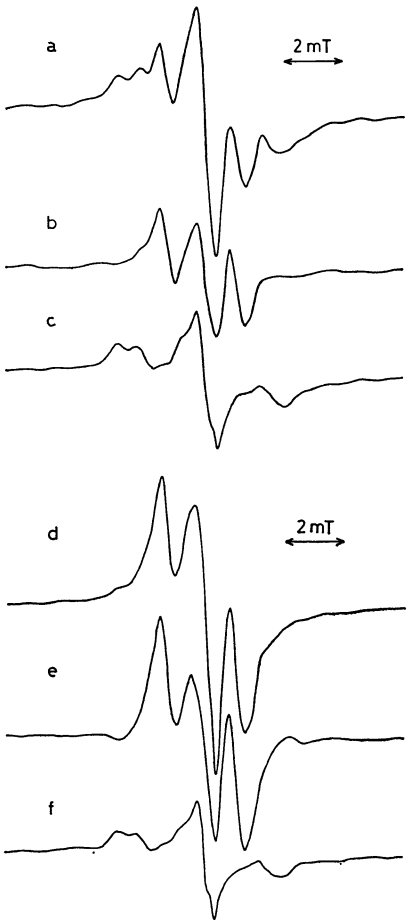


Fig. 1. ESR spectra of glassy DPA (a—c) and DBA (d—f) irradiated at 77 K for 2 h with a dose rate of 2.67×10^4 J/kg/h: (a,d) recorded at 77 K; (b,e) obtained by subtracting c from a and f from d, respectively; (c,f) measured at 77 K after photobleach.

with a coupling constant of 1.1 mT are formed on the γ-irradiation of glassy DPA and DBA at 77 K. The 3-line spectra with a separation of 1.1 mT observed on the ESR measurement of irradiated methacrylic acid derivatives in organic glasses have been ascribed to the anion radical of the methacryloyl groups.[5,6] The splitting was considered to be due to the methylene protons of the methacryloyl group, and the hyperfine splitting constant agreed well with the value obtained from theoretical calculations.[5] Accordingly, the triplets which disappeared during the photo-irradiation are attributable to the anion radicals of the methacryloyl groups of DPA and DBA.

To confirm the above identification, the ESR spectra of DPA-d_4 were measured. The spectrum illustrated by solid line in Fig. 2a was obtained when DPA-d_4 was γ-irradiated at 77 K. After photobleaching, it changed to the dotted spectrum depicted in Fig. 2a. The spectrum shown in Fig. 2b was obtained by subtracting the dotted line from the solid one. The large difference between the two spectra in Fig. 1b and Fig. 2b indicates that the methylene protons of the methacryloyl groups of DPA are responsible for the active species which yield the triplet with the coupling constant of 1.1 mT. In the case of DPA-d_4, a 5-line spectrum with an intensity ratio of 1:2:3:2:1 and with a coupling constant of about 0.17 mT should be observed if the photobleached spectrum is due to the anion radical of the methacryloyl group. The obtained spectrum (Fig. 2b) has a reasonable linewidth when we assume that it is a result of the line-broadening of the quintet. The 3-line spectra could not be detected when 14 mol% of CCl_4 known as a good electron-scavenger was added to the glasses of DPA and DBA. These results support the above conclusion that the triplets of 1.1 mT are due to the anion radicals of methacryloyl groups of DPA and DBA.

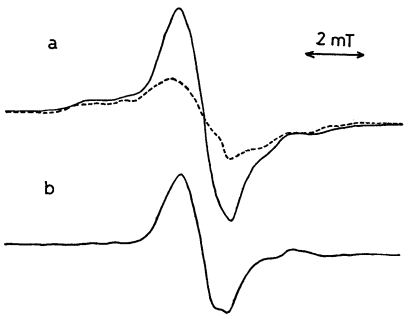


Fig. 2. ESR spectra of glassy DPA-d_4 irradiated at 77 K for 2 h with a dose rate of 2.67×10^4 J/kg/h: (a) solid line, recorded at 77 K; dotted line, measured at 77 K after photobleach; (b) obtained by subtracting dotted line from solid line in a.

When crystalline DPA and DBA were irradiated at 77 K, the anion radicals were not formed, and the main product was the 5-membered cyclic radical.[9]

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