ESR Spectrum of the γ-Irradiated Copolymer of Methyl Methacrylate and Ethylene Dimethacrylate

INTRODUCTION

A great number of papers[1] have been concerned with the ESR spectra of irradiated poly(methyl methacrylate) and poly(glycol methacrylate). The nine-line spectrum was analyzed by using the simulation on a computer. The existence of an end radical and three types of chain radicals was confirmed.[2] At low temperatures the presence of other lines beyond the boundary of the nine-line spectrum has been reported.[3,4]

A spectrum analogous to that mentioned in several papers on PMMA and PGMA was expected for the copolymers of methyl methacrylate and ethylene dimethacrylate studied here. However, at room temperature we find an intense doublet at the extremes of the nine-line spectrum in the samples with high degree of crosslinking.

EXPERIMENTAL

The copolymers of methyl methacrylate (MMA) and ethylene dimethyl methacrylate (EDMA) were prepared by bulk copolymerization of fresh monomers redistilled in a nitrogen atmosphere under reduced pressure. Dibenzoyl peroxide (0.5 wt%) crystallized from a mixture of methanol and chloroform was used for initiation. The mixture of monomers containing 80 wt% of EDMA was filled into ampoules and deprived of oxygen by bubbling with nitrogen. Then the ampoules were sealed. The polymerization proceeded 5 h at 65°C and 3 h at 85°C. Then the temperature was raised to 125–130°C, and the samples were allowed to stand for 3 days at this temperature. After slow cooling to room temperature, the samples were taken from the ampoules.

Cylindrical samples (6 mm in length and 6 mm in diameter) were turned, out of the MMA–EDMA copolymers and were γ-irradiated for 18 h with a total dose of 4 Mrad at −78°C. The initial concentration of free radicals was determined on an ESR spectrometer (VARIAN E4). Then the sample was transferred to a pressure device where it was annealed by rapid heating under 200 MPa pressure to 130°C and after 20 min cooled to room temperature.[5]

RESULTS AND DISCUSSION

The ESR spectra of the irradiated MMA–EDMA copolymer recorded at room temperature before and after annealing are presented in Figure 1. The spectrum in Figure 1(a) recorded before annealing the sample corresponds to a total concentration of free radicals of 2×10^{18} spin g^{-1}. The second spectrum [Fig. 1(b)] was recorded 20 min after annealing the sample at 200 MPa and 130°C and corresponds to a total concentration of free radicals of 8×10^{17} spin g^{-1}. In addition to the known nine-line spectrum, these spectra contain another two lines at the extremes with a splitting of 12.8 mT. During free radical decay the intensity of the outer doublet increases by twofold.

Central nine-line part of the spectrum is assigned to an end radical and three types of chain radicals as previously discussed.[1,2,6,7]

The outer lines of the spectrum are assigned to the doublet of another radical. By analogy to papers [3,4] this doublet with a splitting of 12.8 mT might be attributed to the presence of the HĊO radical.

We do not know to what extent the high degree of crosslinking to the sample produces convenient conditions for stabilization of the HĊO radical. Crosslinking enhances steric hindrances and retards molecular motion. Pressure contributes to stabilization of the radicals to a lesser degree than the crosslinking. Pressure considerably affects the stability of the free radicals in noncrosslinked or poorly crosslinked polymer.[8] The fact that the concentration of radicals belonging to this doublet increases during free radical decay indicates that these radicals might be formed in a secondary reaction.

Journal of Applied Polymer Science, Vol. 32, 5673–5674(1986)

CCC 0021-8995/86/065673-02$04.00

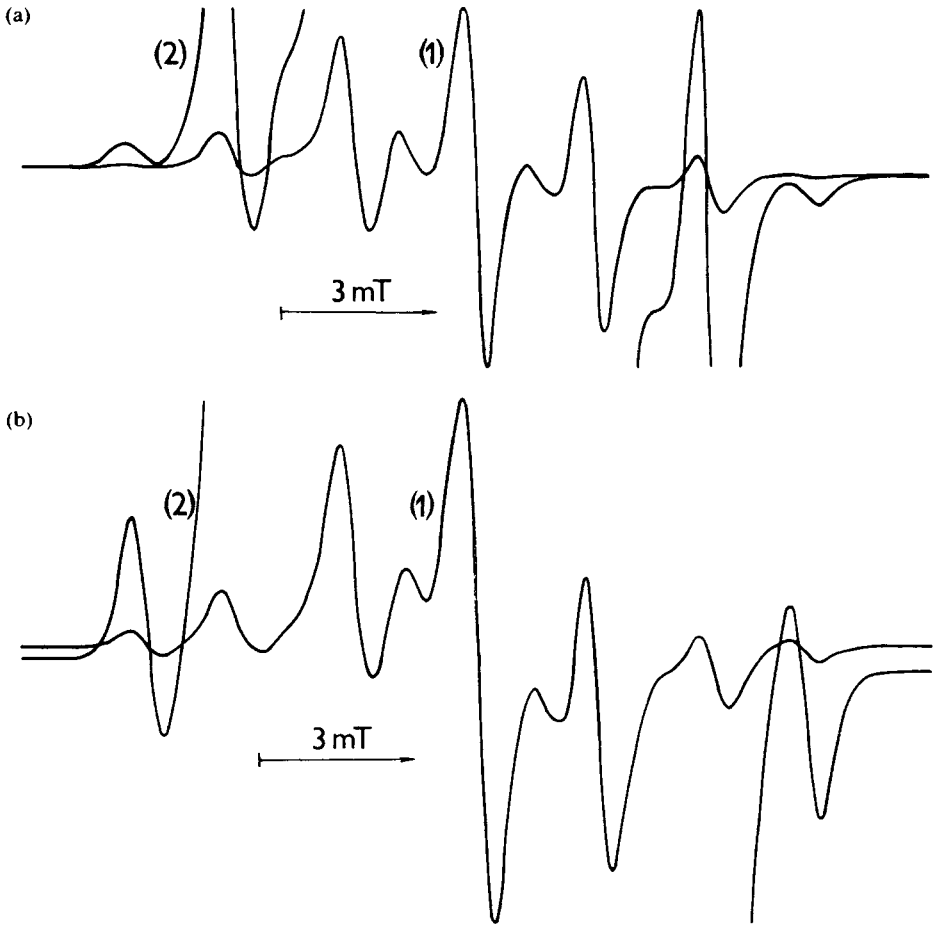

Fig. 1. ESR spectrum of the irradiated copolymer of methyl methacrylate and ethylene dimethacrylate: (a) before annealing the sample; (b) after annealing the sample for 20 min at 200 MPa and 130°C. The gain for a(1) = 12.5,a(2) = 125, b(1) = 50, b(2) = 500.

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Received January 22, 1986
Accepted February 26, 1986