ESR Studies on Poly(methyl acrylate) Radicals to Estimate Their Dominant Structure

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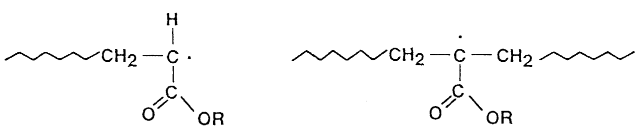
Electron Spin Resonance (ESR) examinations of the propagating radicals in the polymerization of methyl acrylate (MA) and methyl acrylate- α -d (MA-d) in the frozen state have been made. Selective deuteration of MA showed that the propagating radicals have the chain - end (I) and not the mid-chain (II) structure. The stable conformation of poly (methyl acrylate) (poly (MA)) radical was also determined.

In order to elucidate polymerization and degradation mechanisms of polyacrylate systems, it is important to clarify the structure of poly (MA) radical as a basic system.

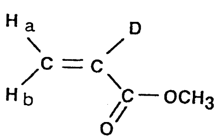
The stable free radical in photopolymerized diacrylate network, having the ESR spectrum of three lines (1:2:1) of ~25G (in unit of 1G = 0.1mT) spacing, was identified as the mid-chain radical (II) resulting from the $C\alpha$- $H\alpha$ cleavage at the α position of the polyacrylate chain.[1]

There are a lot of ESR studies in which ESR spectra of three lines (1: 2 : 1) of ~25G spacing , resembling ESR spectrum of mid-chain radical (II) [1], were attributed to the chain - end structure (I) of polyacrylate radicals.[2-6] However, as far as I know, there is no unambiguous evidence for observing the chain - end structure (I) of polyacrylate radicals.



I II

The present communication reports ESR observation of the propagating radicals in the polymerization of MA and MA-d under the same conditions. The deuteration at the α - proton of MA also makes it possible to estimate the stable conformation of poly (MA) radical, based on the β - proton hyperfine splitting constant (hfsc) of MA-d.



MA-d

MA-d[7] was prepared according to the literature.[8] A solution of 2 wt% photoinitiator (1-hydroxy cyclohexyl phenyl ketone) in monomer MA (or MA-d) was put into a quartz tube and sealed under vacuum. The samples were irradiated with a 1 kW Xe arc lamp in the ESR cavity at -100 ℃. After the irradiation for 30 s, ESR spectra were measured by a JEOL JES - RE 2X X-band spectrometer.

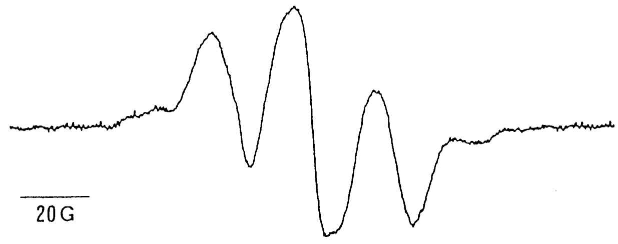


Figure 1. ESR spectrum of poly (MA) radicals at -100 ℃.

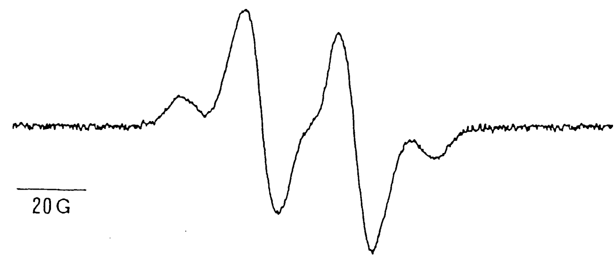


Figure 2. ESR spectrum of poly (MA-d) radicals at -100 ℃.

The ESR spectra obtained by the polymerization of MA and MA-d are shown in Figures 1 and 2, respectively. The former spectrum has three lines (1: 2: 1) with an equal spacing of 23.7 G and the peak to peak line width (ΔH_{pp}) 11.9 G. The latter spectrum has two lines (1:1) with a spacing of 27.5 G and ΔH_{pp} 10.2 G, containing additional shoulders outside the main doublet.

If the ESR spectrum of Figure 1 observed by the photopolymerization of MA were attributed to the mid-chain radical (II), the same spectrum should be observed by the photopolymerization of MA-d. But, the observed spectra shown in Figures 1 and 2 were different. Therefore, the author attributed the ESR spectrum of Figure 1 to the chain-end radical (I), and that of Figure 2 to the chain-end radical (I) having a deuterium atom (D) at the radical center carbon atom $C\alpha$.

It is reasonable to assign the hfsc of 27.5 G to $H\beta 1$ (one of the two β -protons) of the chain-end radical (I). Since the magnitude of interaction between the electron spin and the deuteron spin is less than that between the electron spin and the proton spin by a factor g_D / g_H = 0.1531, [9a] the hyperfine structure resulted from the former interaction would be involved in the line width. It is well known that the β-proton hfsc depends on the angle (θ) between the projections of the axis of the unpaired electron orbital ($\rho\pi$) and the $C\beta$-$H\beta$ bond upon the plane perpendicular to the $C\alpha$-$C\beta$ bond as follows:[9b,10]

$$a(H\beta) = B\cos^2\theta \qquad B = 50\,G$$

The β-proton ($H\beta 1$) hfsc (27.5 G) gives 42.1° to the dihedral angle (θ_1) between the axis of $\rho\pi$ and the $C\beta$-$H\beta 1$ bond. Assuming the three dihedral angles between the three planes ($C\alpha C\beta H\beta 1$, $C\alpha C\beta H\beta 2$, and $C\alpha C\beta C\gamma$) to be 120°, two dihedral angles θ_2 (between the axis of $\rho\pi$ and the $C\beta$-$H\beta 2$ bond) and θ_3 (between the axis of $\rho\pi$ and the $C\beta$-$H\beta 3$ bond) are resulted to be 77.9° and 17.9°, respectively.

Due to the steric hindrance between the $COOCH_3$ group bonded to $C\alpha$ and the polymer chain bonded to $C\beta$, the stable conformation of the propagating chain-end structure (I) is estimated as shown in Figure 3.

The shoulders outside the main doublet in Figure 2 would be attributed to the low polymerized radicals having the eclipsed conformation between the axis of $\rho\pi$ and the $C\beta$-$H\beta$ bond, the free rotating conformation about the $C\alpha$-$C\beta$ bond, etc. But, the details are under investigation.

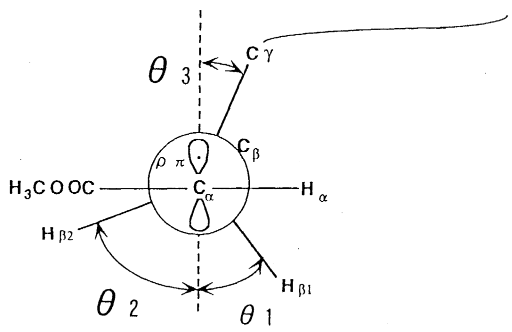


Figure 3. Newman projection of the chain-end structure of poly (MA) radical.

In conclution, the unambiguous ESR spectrum of the chain-end (I) structure of poly (MA) radical was observed, which dominant (stable) conformation was also determined.

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References and Notes

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7 Purity 99.2% by GC; ^{1}H NMR (440 MHz, CCl_4, relative to TMS) δ_{OCH_3} 3.71, δ_{Ha} 5.77, δ_{Hb} 6.34 ppm, $J_{Ha\text{-}Hb}$ 1.4, $J_{Ha\text{-}D}$ 1.4, $J_{Hb\text{-}D}$ 2.5 Hz; isotope (D) purity 97.9% by GC-mass, based on electron impact ioniization and selected ion monitoring techniques, comparing MA and MA-d.

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