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ESR Studies on Poly(methyl acrylate) Radicals in the Frozen State

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Poly(methyl acrylate) radical and poly(methyl acrylate-α-*d*) radical, generated from the polymerization of methyl acrylate (MA) and methyl acrylate-α-*d* (MA-*d*) in the frozen (solid) state, have been investigated by Electron Spin Resonance (ESR). The α-position selective deuteration of poly(MA) radical made the shoulders of poly(MA) radical emerge as more clearly isolated peaks. Both ESR spectra of poly(MA) radicals and those of poly(MA-*d*) radicals were simulated for the conformational ratio 2.2 between a stable conformation and eclipsed conformations. The energy difference between the stable conformation and two eclipsed conformations was estimated to be 0.27 kcal mol^{-1} for poly(MA) radical in the thermal equilibrium solid state.

Polyacrylate radicals, resulting from the photopolymerization of acrylates monomers or the photodegradation of polyacrylate polymers, have been of interest with regard to industrial applications.[1,2] It is important to make clear the structure of poly(methyl acrylate) (MA) radical as a basic system for studying the structure and chemistry of polyacrylate radicals.

Compared with many Electron Spin Resonance (ESR) studies of poly(methyl methacrylate) (MMA) radicals,[3—5a)] there are few ESR studies of poly(MA) radicals,[6—11)] which contain ESR spectra of the mid-chain radical resulting from the C_α–H_α cleavage at the α-position of the polyacrylate chain, as pointed out by Best and Kasai.[12)]

In the previous letter,[13)] it was described that the propagating radicals have the chain-end (I) and not the mid-chain (II) structure (Chart 1), and the dominant (stable) conformation of poly(MA) radical was also determined. The present paper reports the detailed analysis of ESR spectra of poly(MA) radicals and poly(methyl acrylate-α-*d*) (MA-*d*) radicals in the solid state.

Experimental

Materials. Methyl acrylate-α-*d* (MA-*d*) was prepared according to the literature,[14)] and purified by preparative gas chromatography (GC) on a Shimadzu GC-9A with a 5-m glass column packed with Gaskuropack 54 (GL Sciences Inc.). The purity of MA-*d* was 99.2% by GC analysis. ^{1}H NMR chemical shifts (δ) referenced to TMS as internal standard and coupling constants (J) were $\delta_{\mathrm{OHC_3}} = 3.71$, $\delta_{\mathrm{H_a}}$ (*trans* H referenced to CO_2CH_3) = 5.77, $\delta_{\mathrm{H_b}}$ (*cis* H referenced to CO_2CH_3) = 6.34, and $J_{\mathrm{H_a-H_b}} = 1.4$, $J_{\mathrm{H_a-D}} = 1.4$, $J_{\mathrm{H_b-D}} = 2.5$ Hz, respectively, measured on a JEOL JNM-EX 400 NMR (400 MHz) spectrometer in carbon tetrachloride at ambient temperature. Isotope (D) purity was determined to be 97.9%, performed on a Shimadzu GCMS-QP1000EX (GC14A) GC-mass spectrometer, based on electron impact ionization and selected ion monitoring techniques, comparing MA and MA-*d*. MA was a commercial product (Tokyo Kasei Industry Co., Ltd.). Inhibitor was removed by simple distillation. Monomers were sealed, refrigerated at 5 °C and stored in the dark before use.

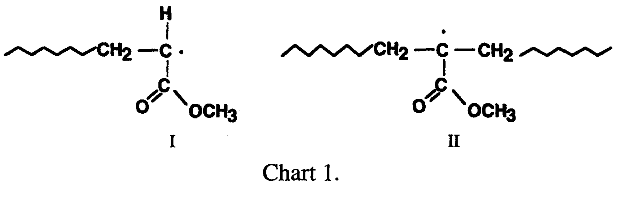
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Chart 1.

The photoinitiator was 1-hydroxycyclohexyl phenyl ketone, obtained from Ciba–Geigy, and used as received without further purification.

ESR Measurements. A solution of 2 wt% photoinitiator in monomer MA (or MA-*d*) was placed in a quartz tube, degassed on a vacuum line with a sufficient number of freeze-pump-thraw cycles, frozen in liquid nitrogen, and then sealed off under vacuum with a torch. Samples were placed in the resonant cylindrical mode cavity (ES-UCX2), which had a slotted opening for photoirradiation, of a JEOL JES - RE 2X ESR spectrometer equipped with an X-band microwave unit, 100-kHz field modulation, and a variable temperature accessory (ES-DVT2). The samples were irradiated with Xe arc lamp operated at 1000-W (ES-UXL10) in the ESR cavity. The lamp was outfitted with a mirror and two quartz collector lenses (ES-UVLL). After the definite time of irradiation started by opening the shutter placed between the light source and the two lenses, ESR spectra were measured under no irradiation at −100 °C. The sequence of irradiation times was 5s, 25s (30 s), 30s (1 min), 30s (1.5 min), 30s (2 min), 30s (2.5 min), 30s (3 min), and 30s (3.5 min). Here the accumulated irradiation times are shown in the parentheses.

Spectral integrations and simulations were carried out on a JEOL ES-PRIT 375 ESR data system. The relative radical concentrations were determined from double integrations of the spectra.

Results and Discussion

ESR Spectra. Figure 1 shows ESR spectra of poly(MA) radicals generated from the polymerization of MA with increasing irradiation time (as indicated by accumulated irradiation times) at −100 °C. No signal was observed in the absence of photoinitiator under the same conditions. Fig-

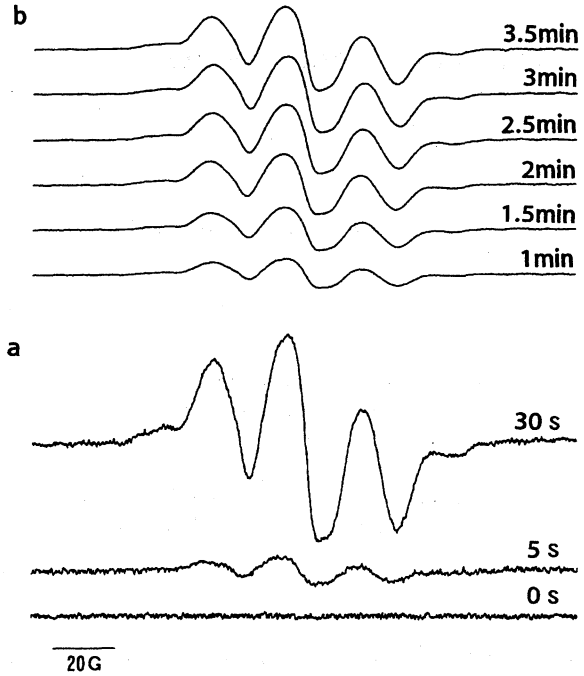

Fig. 1. ESR spectra of poly(MA) radicals with increasing irradiation time (as indicated by accumulated irradiation times) at −100 °C. Amplitude: (a) ×100, (b) ×20.

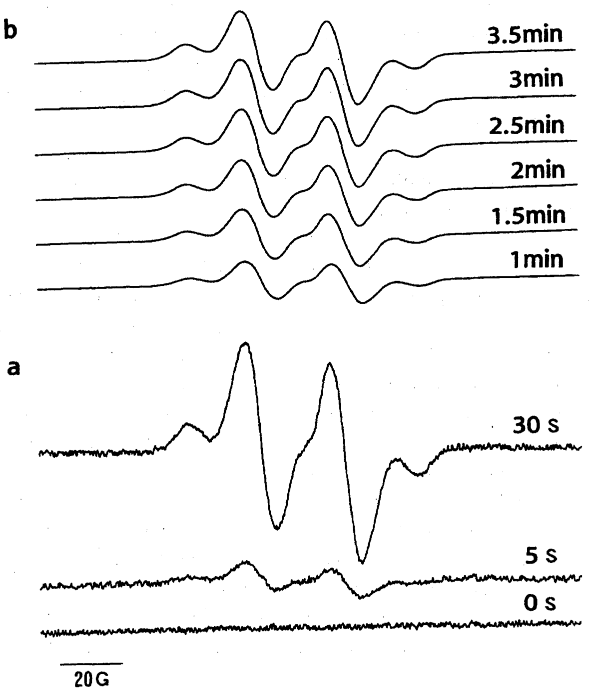

Fig. 2. ESR spectra of poly(MA-*d*) radicals with increasing irradiation time (as indicated by accumulated irradiation times) at −100 °C. Amplitude: (a) ×100, (b) ×20.

ure 2 shows ESR spectra of poly(MA-*d*) radicals generated similarly from the polymerization of MA-*d*. In Figs. 1 and 2, amplitudes of (a) and (b) are ×100 and ×20, respectively. In the preceding paper,[13] the ESR spectra of poly(MA) radicals (Fig. 1 of the earlier report[13]) and poly(MA-*d*) radicals (Fig. 2 of earlier report[13]) at the accumulated irradiation time 30s were shown and analyzed roughly.

Figure 3 presents the relation between the radical amount of poly(MA) radicals at −100 °C and the accumulated irradiation time. The radical amount at the accumulated irradiation time 2.5 min is the reference radical amount (1.0). The relative radical concentration increases monotonously with exposure time.

Figure 4 shows monotonous decay of the intensity of ESR spectra of poly(MA) radicals with warming by 5 degrees at a time from −100 to −75 °C. We cannot observe any other radicals than poly(MA) radicals, having three lines (1 : 2 : 1) with an equal spacing of ca. 24 G, during the radical decay process presented in Fig. 4. This reveals that only poly(MA) radicals were observed throughout the whole process from polymer radical formation (Fig. 1) to its decay (Fig. 4). The previous letter[13] reports that the propagating radicals have the chain-end (I) and not the mid-chain (II) structure of poly(MA) radicals on the basis of observing different ESR spectra from the photopolymerization of MA and MA-*d*. This con-

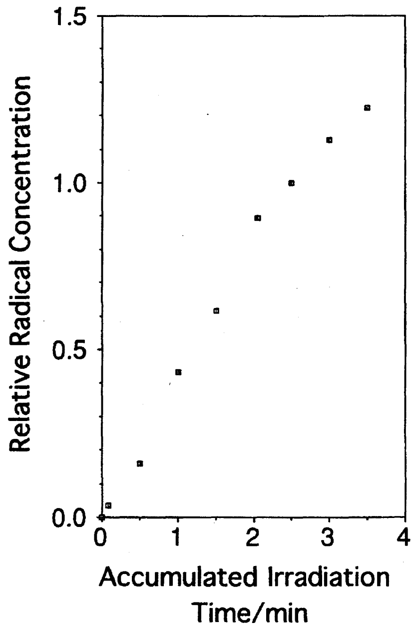

Fig. 3. Relation between radical amount and accumulated irradiation time for poly(MA) radicals at −100 °C.

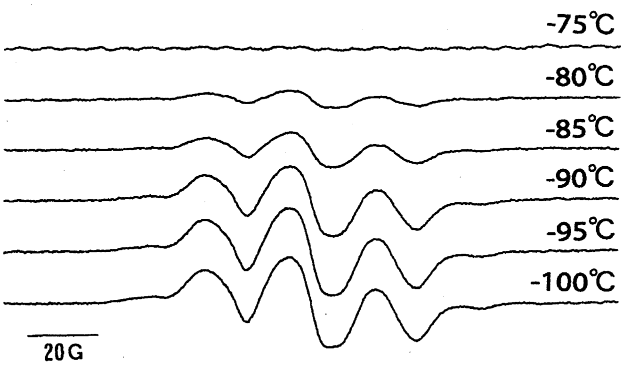

Fig. 4. Decay of ESR spectra of poly(MA) radicals with raising temperature from −100 to −75 °C.

clusion, i.e., that the propagating radicals have the chain-end structure (I), is also confirmed by the whole process observation of poly(MA) radicals. At the first accumulated irradiation time of 0.5 min within the total accumulated irradiation time of 3.5 min, it is more confirmed that both poly(MA) radicals shown at 30s of Fig. 1 and poly(MA-*d*) radicals shown at 30s of Fig. 2 have the chain-end structure (I).

Simulation. For the simulation of ESR spectra of both poly(MA) and poly(MA-*d*) radicals, a Gaussian line shape was assumed. Poly(MA) radicals have the α-protons (H_α) with anisotropic electron-nuclear dipolar interactions in the frozen state and completely random orientation in the magnetic field **H**. Principal values of g tensor were assumed to take those in $\dot{C}H_2(CO_2H)$,[15] with principal values of $g_x = 2.0034$ when **H** is parallel to C–H_α bond (*X* axis), $g_y = 2.0042$ when **H** is mutually perpendicular to the 2pπ (unpaired electron)-orbital axis and the C–H_α bond (*Y* axis), and $g_z = 2.0020$ when **H** is parallel to the 2pπ-orbital axis (*Z* axis). Principal values of the line width tensor were assumed to be $S_x = S_y = S_z = 9.4$ G. For the simulation of ESR spectrum of poly(MA) radicals, the electron–hydrogen hyperfine (isotropic + anisotropic) interactions were assumed to take the values of the α-proton in $CH_3\dot{C}H(CO_2H)$,[16] with principal values of $A_x(H) = -8.5$ G, $A_y(H) = -31.8$ G, and $A_z(H) = -24.2$ G. 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 $g_D/g_H = 0.1531$,[17a)] principal values of electron–deuteron hyperfine (isotropic + anisotropic) interactions were assumed to be $A_x(D) = -1.3$ G, $A_y(D) = -4.9$ G, and $A_z(D) = -3.7$ G for the simulation of ESR spectrum of poly(MA-*d*) radicals.

In the following discussions (in this paper), a stable conformation and eclipsed conformations of poly(MA) radical are those referenced to the unpaired electron orbital, as shown in Fig. 7. Figure 5a is the ESR spectrum of poly(MA) radicals computed for the conformational ratio 2.2 between a stable conformation (Fig. 5b) and eclipsed conformations (Fig. 5c). It has been well-established that, for an alkyl radical in which the unpaired electron resides in the 2pπ orbital of sp^2 hybridized α-carbon, the hyperfine coupling constant (hfc) of a β-proton depends on the dihedral angle (θ) as follows:[12,17b)]

$$a(H_\beta) = B\cos^2\theta \qquad B = 50\text{G}. \tag{1}$$

Here θ is the dihedral angle between the projections of the axes of the unpaired electron orbital and the C_β–H_β bond upon the plane perpendicular to the C_α–C_β bond. Figure 5b shows the ESR spectrum simulated for a stable conformation with a β-proton hfc $a(H_\beta)$=27.5 G (θ=42.1°).[13] Figure 5c is a computer-simulated ESR spectrum of eclipsed conformations with $a(H_\beta)$=50 G (θ=0°) and $a(H_\beta)$=12.5 G (θ=60°). The shoulders outside the main three lines (1 : 2 : 1) in Fig. 1 are attributed to the eclipsed conformations (Fig. 5c).

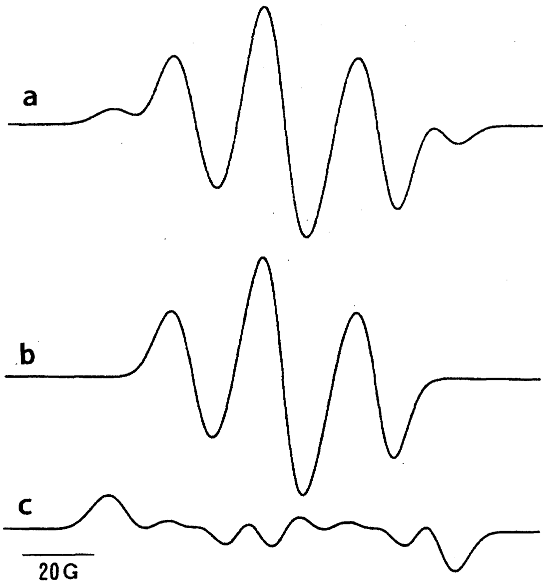

Fig. 5. Simulated ESR spectra of poly(MA) radicals. (a) ESR spectrum simulated for the conformational ratio 2.2 between a stable conformation (b) and eclipsed conformations (c), (b) ESR spectrum simulated for a stable conformation with $a(H_\beta)$=27.5 G (θ=42.1°), and (c) ESR spectrum simulated for eclipsed conformations with $a(H_\beta) = 50$ G ($\theta = 0°$) and $a(H_\beta) = 12.5$ G ($\theta = 60°$).

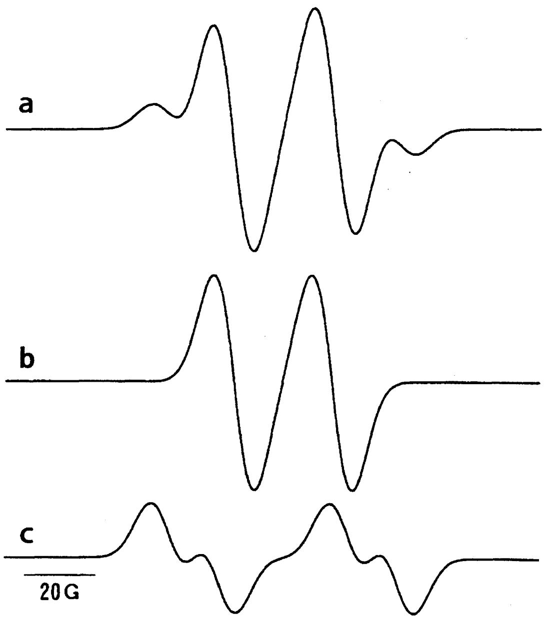

Fig. 6. Simulated ESR spectra of poly(MA-*d*) radicals. (a) ESR spectrum simulated for the conformational ratio 2.2 between a stable conformation (b) and eclipsed conformations (c), (b) ESR spectrum simulated for a stable conformation with $a(H_\beta) = 27.5$ G ($\theta = 42.1°$), and (c) ESR spectrum simulated for eclipsed conformations with $a(H_\beta) = 50$ G ($\theta = 0°$) and $a(H_\beta) = 12.5$ G ($\theta = 60°$).

Figure 6a shows the ESR spectrum of poly(MA-*d*) radicals simulated for the conformational ratio 2.2 between a stable conformation (Fig. 6b) and eclipsed conformations (Fig. 6c). Figure 6b shows a computer-simulated ESR spectrum of a stable conformation with $a(H_\beta)$=27.5 G (θ=42.1°). Figure 6c shows ESR spectrum simulated for eclipsed con-

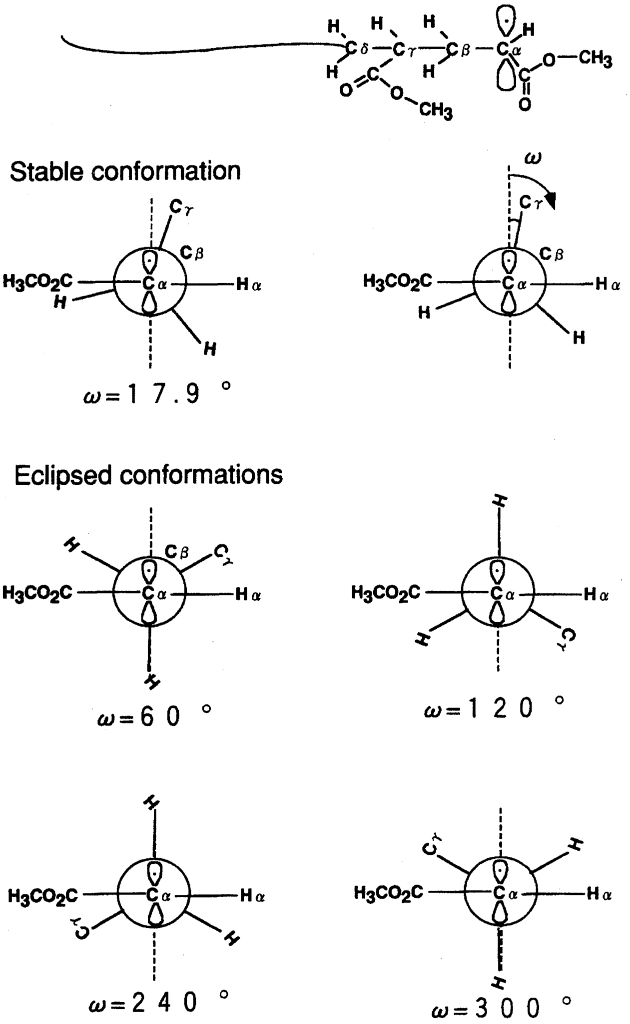

Fig. 7. Newman projection of a stable conformation and four eclipsed conformations of poly(MA) radical.

formations with $a(\mathrm{H}_\beta)=50$ G ($\theta=0°$) and $a(\mathrm{H}_\beta)=12.5$ G ($\theta=60°$). The isolated small peaks outside the main doublet in Fig. 2 are attributed to the eclipsed conformations (Fig. 6c). The exchange of principal values of g tensor, that is, $g_x=2.0042$ and $g_y=2.0034$,[15] doesn't have any significant change in the simulated ESR spectra of both poly(MA) and poly(MA-*d*) radicals. The agreement between the observed and simulated spectra Figs. 1a (30s) and 5a ; Figs. 2a (30s) and 6a is good.

Conformational Analysis. Figure 7 shows a Newman projection of a stable conformation ($\omega=17.9°$: $\theta=42.1°$) and four eclipsed conformations ($\omega=60°$, 120°, 240°, and 300°) of poly (MA) radical. Here ω is the dihedral (rotational) angle between the projections of the 2pπ-orbital axis and the C_β–C_γ bond upon the plane perpendicular to the C_α–C_β bond. Due to the steric hindrance between the $\mathrm{CO_2CH_3}$ group bonded to C_α and the polymer chain bonded to C_β, the former two eclipsed conformations ($\omega=60°$ and 120°) are dominant. Two eclipsed conformations ($\omega=60°$ and 120°) are symmetrical about the plane (H_α–C_α–C_β) and have the same potential (conformational) energy, so they have the same conformational ratio 0.5 : 0.5. The conformational ratio 2.2 between a stable conformation ($\omega=17.9°$) and the two eclipsed conformations ($\omega=60°$ and 120°) gives the stable/eclipsed energy difference 0.27 kcal mol^{-1} for poly(MA) radicals (and poly(MA-*d*) radicals) in the thermal equilibrium state, estimated from the Boltzmann factor.

Based on the conformational analysis of poly(MMA) radicals, Kamachi et al.[18] reported that the energy difference between the most stable conformation (B) and the next stable conformation (A) was 0.52 kcal mol^{-1}, calculated by the molecular mechanics (MM) method. It is interesting from the viewpoint of the substitution effect and/or the steric hindrance that the hydrogen atom substitution from the methyl group at carbon atom bonded to the $\mathrm{CO_2CH_3}$ group, i.e., poly(MA) radical ← poly(MMA) radical, results in the decrease of the energy difference between two stable conformations by a factor ca. 1/2, i.e., 0.27 kcal mol^{-1} ← 0.52 kcal mol^{-1}. Kamachi also discussed monomer (MMA) addition reaction to the poly(MMA) radical in the frozen state, i.e., isotactic (B) and syndiotactic (A) conformations.[5b] It would become important for elucidating of the stereoregularity and/or the chain propagation mechanismin[19] of polyacrylate radicals that poly(MA) radicals have the experimental conformation ratio 2.2 between a stable conformation and two eclipsed conformations in the frozen state.

Conclusions

The detailed analysis of ESR spectra of poly(MA) and poly(MA-*d*) radicals has been done. Poly(MA) radicals have the conformational ratio 2.2 between a stable conformation ($\omega=17.9°$) and two eclipsed conformations ($\omega=60°$ and 120°). The stable/eclipsed energy difference is 0.27 kcal mol^{-1} for poly(MA) radicals in the thermal equilibrium frozen state.

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