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ESR Studies on Irreversible Reactions of Poly(methyl methacrylate) Radicals and on Structures of Stable Polymer Radicals in the Frozen State

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Irreversible reactions of poly(methyl methacrylate) radicals generated from the polymerization of methyl methacrylate (MMA) and structures of the produced stable polymer radicals in the frozen state have been investigated by Electron Spin Resonance (ESR). The stable polymer radicals were produced through disproportionation and addition reactions of poly(MMA) radicals. The structure of stable polymer radicals was also determined by the simulation of the ESR spectrum.

Poly(methyl methacrylate) radicals, resulting from the photopolymerization of methyl methacrylate (MMA) monomers or the radiolysis of poly(methyl methacrylate) (PMMA) polymers, have been of interest with regard to industrial applications.[1,2] Electron Spin Resonance (ESR) studies of poly(methyl acrylate) radicals in the frozen state have already been done.[3] Methyl group substitution from the α-proton bonded to the radical-center carbon atom of poly(methyl acrylate) radical gives a poly(MMA) radical.

ESR studies of poly(MMA) radicals have been made from various points of view since as long as ca. 40 years ago.[4—6] But, as far as I know, the irreversible reaction of poly(MMA) radical in the frozen(solid) state has never been reported.

The present paper reports the irreversible reaction of the poly(MMA) radical with the temperature variation and the structure of the produced stable polymer radicals in the solid state.

Experimental

Materials. MMA (mp −48 °C) was a commercial product (Tokyo Kasei Industry Co., Ltd.). Inhibitor was removed by simple distillation. Monomers (MMA) were sealed, refrigerated at 5 °C, and stored in the dark before use.

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

ESR Measurements. Methods of sample preparations and ESR measurements were similar to those described previously.[3] Samples for the ESR measurements were made from a solution of 2.5 wt% photoinitiator in MMA. The samples, placed in a quartz tube under vacuum, were irradiated with Xe arc lamp operated at 1000 W in the ESR cavity. After the predetermined time of irradiation, ESR spectra were measured under no irradiation at −75 °C. The following ESR measurements were also done under no irradiation at various temperatures. ESR measuments were carried out on a JEOL JES-RE 2X ESR spectrometer equipped with an X-band microwave unit, 100-kHz field modulation, and a variable temperature accessory. Spectral integrations, multiplications, and simulations were performed on an ESR data system. The relative radical concentrations were determined from double integrations of the spectra.

Results and Discussion

ESR Spectra. Irradiation of the photoinitiator in MMA monomers forms poly(MMA) radicals as depicted in Chart 1, where P denotes a polymer chain consisting of MMA monomer units. Figure 1 shows ESR spectra of poly(MMA) radicals with increasing irradiation time (as indicated by accumulated irradiation times) at −75 °C. This ESR spectrum is a typical 9 line spectrum, having strong 5 lines with an equal spacing of 22.7 G and weak 4 lines, of poly(MMA)

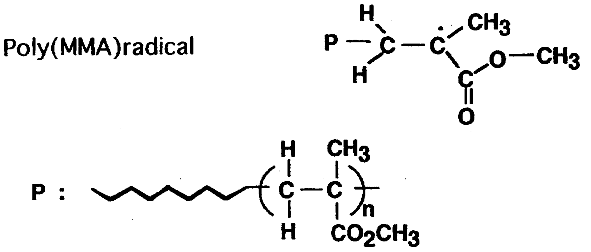


Chart 1.

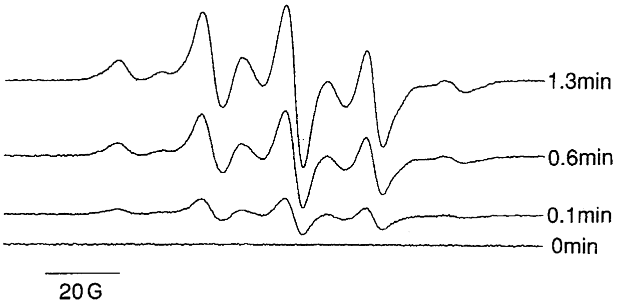


Fig. 1. ESR spectra of poly(MMA) radicals with increasing irradiation time (0 → 0.1 → 0.6 → 1.3 min), as indicated by accumulated irradiation times, at −75 °C.

radicals. The 9 line spectrum is well interpreted by assuming a Gaussian distribution (half-height width of 5—6°) around the most probable conformation where the conformational angles of the two $\mathrm{C{-}H}_\beta$ bonds to the half-filled p-orbital are 55° and 65°.4,5) No signal was observed in the absence of photoinitiator under the same condition. Figure 2 presents the relationship between the radical amount of poly(MMA) radicals at −75 °C and the accumulated irradiation time. The radical amount at the accumulated irradiation time of 1.3 min is the reference radical amount (1.0). The relative radical concentration increases monotonously with exposure time.

The ESR spectrum of poly(MMA) radicals at −160 °C, cooled from −75 °C, is shown at the top of Fig. 3. Figure 3 also shows ESR spectra of poly(MMA) radicals as the temperature was raised from −160 to −75 °C (−160 → −135 → −115 → −95 → −75 °C). Temperature variation doesn't produce any significant change in the line shapes of ESR spectra of poly(MMA) radicals in the temperature range −160 to −75 °C.

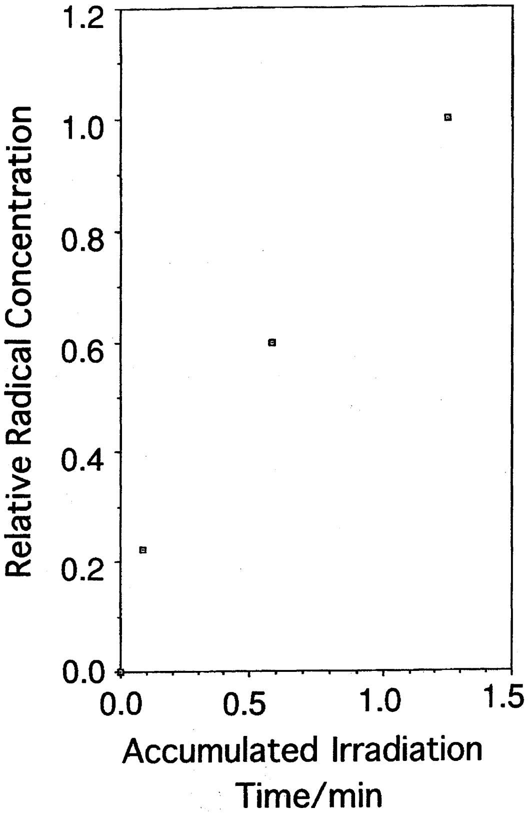


Fig. 2. Relationship between radical amount and accumulated irradiation time for poly(MMA) radicals at −75 °C.

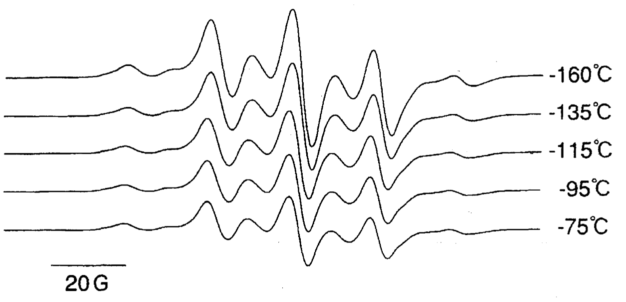


Fig. 3. ESR spectra of poly(MMA) radicals with raising temperature from −160 to −75 °C (−160 → −135 → −115 → −95 → −75 °C).

Figure 4 shows ESR spectrum changes with raising temperature from −75 to −60 °C (−75 → −65 → −60 °C), and holding at −60 °C for 22.8 min (0 → 3.5 → 6.8 → 13.2 → 22.8 min). Upon the raise of the temperature from −75 to −60 °C, a new 5 line ESR spectrum grew up at the sacrifice of the intensity of spectrum of poly(MMA) radicals. During the holding time of 22.8 mm at −60 °C, the intensity of ESR spectra decayed monotonously.

Figure 5 shows the temperature dependence of ESR spectra, observed with higher amplitude than that in Fig. 4, with cooling from −60 to −160 °C (−60 → −75 → −120 → −140 → −160 °C) and heating from −160 to −60 °C (−160 → −75 → −60 °C). The 5 line ESR spectra were observed throughout the cooling (−60 → −160 °C) and the raising (−160 → −60 °C) processes. Two ESR spectra observed at −60 °C are the same. Figure 6 shows the temperature dependence of ESR spectra, observed with higher amplitude than that in Fig. 5, with raising from −60 to −55 °C, and holding at −55 °C for 26.8 min (0 → 3.3 → 6.0 → 26.8 min). The ESR spectra at −55 °C and holding time above 3.3 min (3.3, 6.0, 26.8 min), didn't have the small and broad peaks which remained above and below the highest and lowest field extremes in the spectra at −60 °C (Figs. 4, 5,

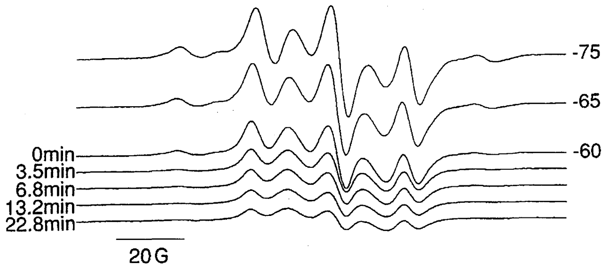


Fig. 4. ESR spectrum change of poly(MMA) radicals with raising temperature from −75 to −60 °C, and holding at −60 °C for 22.8 min (0 → 3.5 → 6.8 → 13.2 → 22.8 min).

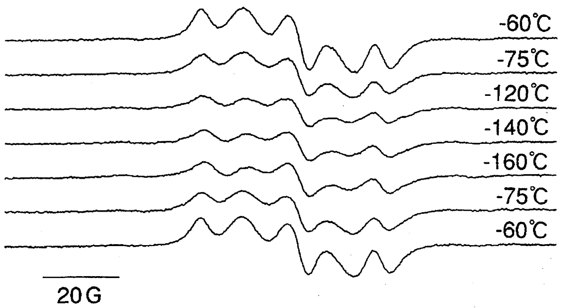


Fig. 5. Temperature dependence of ESR spectra of the stable polymer radicals (S) with cooling temperature from −60 to −160 °C (−60 → −75 → −120 → −140 → −160 °C) and raising temperature from −160 to −60 °C (−160 → −75 → −60 °C).

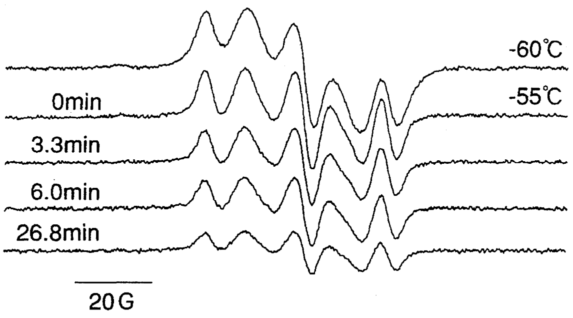


Fig. 6. Temperature dependence of ESR spectra of the stable polymer radicals (S) with raising temperature from −60 to −55 °C, and holding at −55 °C for 26.8 min (0 → 3.3 → 6.0 → 26.8 min).

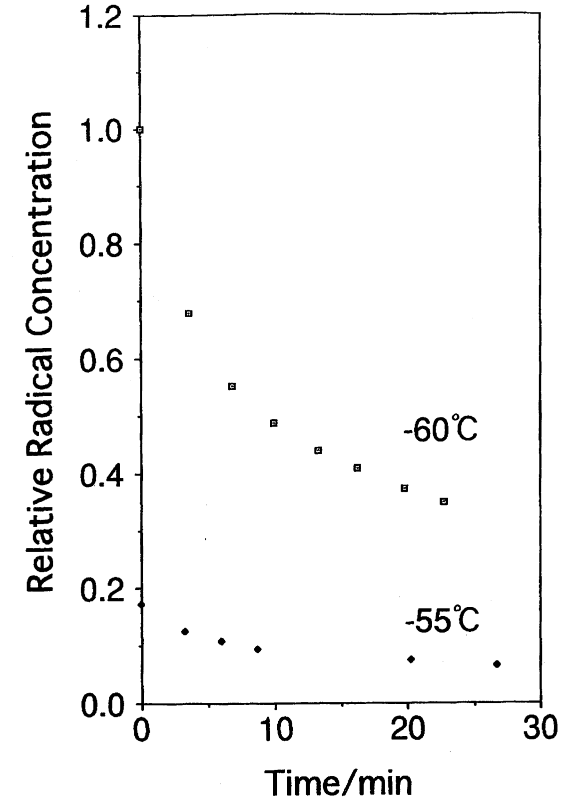
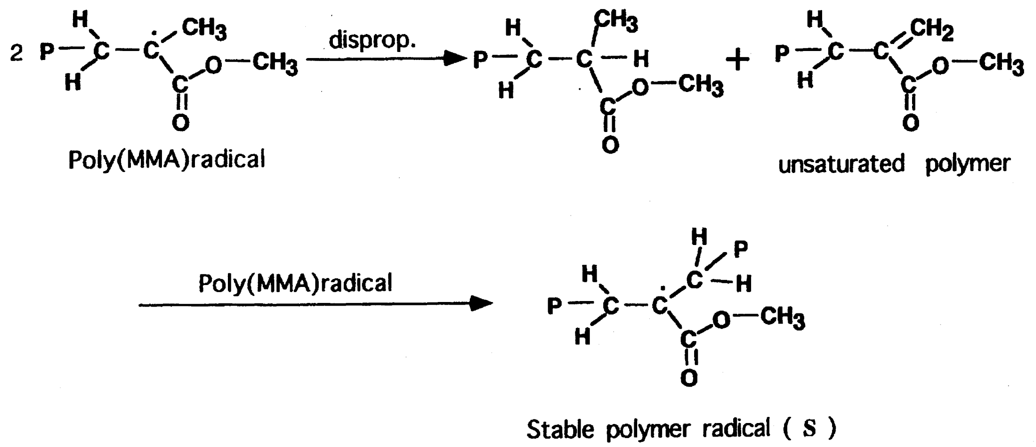


Fig. 7. Time dependence of radical amount of the stable radicals (S) in the dark.

and 6) and at −55 °C and holding time 0 min (Fig. 6). These small and broad peaks may be attributed to the remaining poly(MMA)radicals. During the holding time of 26.8 min at −55 °C, the intensity of ESR spectra decayed monotonously. The ESR spectrum multiplied by 1.166 (1.858) in intensity of the ESR spectrum at 6.0 min (26.8 min) was in good agreement with the ESR spectrum at 3.3 min in Fig. 6. These results indicated that the newly formed 5 line ESR spectrum consisted of one radical species.

Figure 7 presents the time dependence of the radical amount at −60 °C in Fig. 4 and −55 °C in Fig. 6. The radical amount at −60 °C and 0 min in Fig. 4 is the reference radical amount (1.0). The relative radical concentration decreases monotonously with the time in the dark. After leaving for ca. 30 min in the dark place at −60 and −55 °C, the radicals having 5 line ESR spectrum didn't vanish, which indicated that the newly formed radicals were very stable. Contrary to the conventional expectation of the faster decay at the elevated temperature, the radical decay rate at −60 °C was faster than that at −55 °C. This result was confirmed by overlapping of the radical decay curve made from multiplication of that at −55 °C in Fig. 7 by the factor 5.848 (= 1/0.171), where 0.171 was the relative radical concentration at −55 °C and 0 min in Fig. 7. The ratios of the remaining relative radical concentration at 20 min, −60 and −55 °C, were 37 and 44%, respectively. Probably the increasing viscosity of the matrix (monomer MMA + polymer PMMA et al.) caused the slower radical decay at −55 °C than that at −60 °C.

Irreversible Reaction of Poly(MMA) Radicals. The 9 line ESR spectra of poly (MMA) radicals produced at −75 °C (Fig. 1), changed reversibly over the temperature range −75 to −160 °C, as shown in Fig. 3. The raise of the temperature from −75 to −60 °C resulted in a 5 line ESR spectrum (Fig. 4), which remained unchanged upon the cooling between −75 and −160 °C (Fig. 5). This spectrum change reveals that irreversible reaction of poly(MMA) radicals took place upon the warming from −75 to −60 °C.



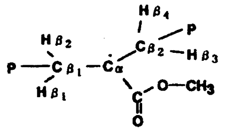
Scheme 1.

Fig. 8. Simulated ESR spectrum of the stable polymer radical (S) with $a(\mathrm{H}_\beta)=15.1$ G. $a(\mathrm{H}_\beta)=12.7$ G, $a(\mathrm{H}_\beta)=10.0$ G, and $a(\mathrm{H}_\beta)=8.0$ G.

The stable polymer radical (S) was probably produced according to the mechanism previously proposed by Tanaka et al.[7] and Matsumoto and Giese.[8] (Scheme 1). In this mechanism, an unsaturated polymer that is produced by disproportionation reaction of two poly(MMA) radicals reacts with another poly(MMA) radical (addition reaction); this results in a stable polymer radical (S). For the formation of one stable polymer radical (S), three poly(MMA) radicals are consumed. The high stability (low reactivity) of the newly formed radicals of the 5 line ESR spectrum is consistent with the fact that the stable polymer radical (S) has the sterically hindered structure having two polymer chains around the radical-center carbon atom (C_α) hearing an unpaired electron, as shown in Scheme 1. It also assists the assignment of 5 line ESR spectrum to the stable polymer radicals (S) that 5 lines ESR spectra presented in Fig. 6 resemble those observed during the bulk polymerization of methyl 2-[2-(methoxycarbonyl)ethyl]acrylate,[9a] methyl 2-[2,2-bis(methoxycarbonyl)ethyl)]acrylate,[9b] and so on.[9c]

It is interesting that the 9 line ESR spectrum of poly(MMA) radicals was reversible between −160 and −75 °C and changed irreversibly to a 5 line ESR spectrum of the stable polymer radicals (S) upon the warming from −75 to −60 (−55) °C, compared with the fact that the 9 line ESR spectrum of poly(MMA) radicals generated from γ-irradiated PMMA at +25 °C was reversible between −196 and +25 °C.[4] In the author's experiment, poly(MMA) radicals were in MMA monomer solid matrix. The reversible change was observed between −160 and −75 °C in the rigid solid MMA matrix. The irreversible change was observed upon the warming from −75 to −60 (−55 °C), near the mp (−48 °C) of MMA monomer, in the loose solid MMA matrix. On the other hand, in Iwasaki and Sakai's experiment, poly(MMA) radicals were in PMMA solid matrix. Therefore, a reversible change was observed between −196 and +25 °C

Simulation and Structure of the Stable Polymer Radical (S). ESR spectra observed at −60 and −55 °C (0 min) have small broad peaks outside the main 5 line ESR spectra (Fig. 6). So, for the simulation of ESR spectrum of the stable polymer radicals (S) in the frozen state, ESR spectrum observed at −55 °C and holding time 3.3 min (Fig. 6) was selected, and a Gaussian line shape was assumed. The stable polymer radical (S) has four β-protons. It has been well established that, for an alkyl radical in which the unpaired


Stable polymer radical (S)

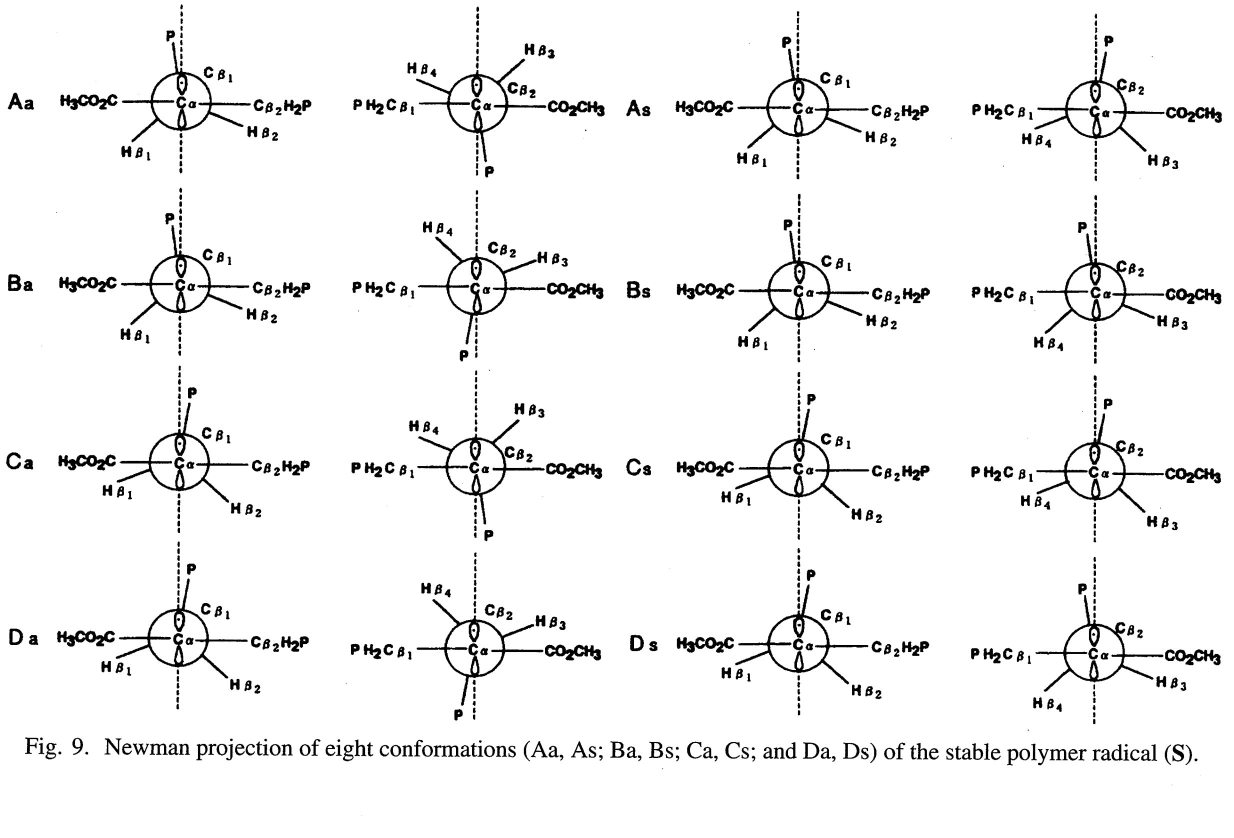


Fig. 9. Newman projection of eight conformations (Aa, As; Ba, Bs; Ca, Cs; and Da, Ds) of the stable polymer radical (S).

electron resides in the $2p_\pi$ orbital of sp^2 hybridized α-carbon, the hyperfine coupling constant (hfc) of a β-proton depends on the dihedral angle (θ) as follows:[10,11]

$$a(\mathrm{H}_\beta) = B\cos^2\theta \qquad B = 50\ \mathrm{G} \qquad (1)$$

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 8 shows the ESR spectrum simulated for the stable polymer radical (**S**) with $a(\mathrm{H}_\beta)=15.1$ G ($\theta=57°$), $a(\mathrm{H}_\beta)=12.7$ G ($\theta=60°$), $a(\mathrm{H}_\beta)=10.0$ G ($\theta=63°$), $a(\mathrm{H}_\beta)=8.0$ G ($\theta=66°$), and a line width=6.3 G. Here, the obtained θ values are those derived from the above approximate equation of $a(\mathrm{H}_\beta)$, not those derived from the absolute conformational determination. The agreement between the observed and simulated spectra is good.

It is reasonable that the stable polymer radical (**S**) has the planar structure around the radical-center carbon atom (C_α), that is, four carbons (C_α, C_α, $\mathrm{C}_{\beta 1}$, $\mathrm{C}_{\beta 2}$, and C (=0)) make one plane. Figure 9 shows a Newman projection of ESR spectrum which explains the eight conformations (Aa, As; Ba, Bs; Ca, Cs; and Da, Ds) of the stable polymer radical (**S**). In four cases (Aa, Ba, Ca, and Da), two polymer chains (**P**) are antarafacial. On the contrary, in four cases (As, Bs, Cs, and Ds), two polymer chains are suprafacial. In eight cases (Aa, As; Ba, Bs; Ca, Cs; and Da, Ds), four β-protons have the hfc's:

Aa and As : $a(\mathrm{H}_{\beta 1}) = 15.1$ G, $a(\mathrm{H}_{\beta 2}) = 8.0$ G,
$a(\mathrm{H}_{\beta 3}) = 12.7$ G, $a(\mathrm{H}_{\beta 4}) = 10.0$ G
or $a(\mathrm{H}_{\beta 1}) = 12.7$ G, $a(\mathrm{H}_{\beta 2}) = 10.0$ G,
$a(\mathrm{H}_{\beta 3}) = 15.1$ G, $a(\mathrm{H}_{\beta 4}) = 8.0$ G
Ba and Bs : $a(\mathrm{H}_{\beta 1}) = 15.1$ G, $a(\mathrm{H}_{\beta 2}) = 8.0$ G,
$a(\mathrm{H}_{\beta 3}) = 10.0$ G, $a(\mathrm{H}_{\beta 4}) = 12.7$ G
or $a(\mathrm{H}_{\beta 1}) = 12.7$ G, $a(\mathrm{H}_{\beta 2}) = 10.0$ G,
$a(\mathrm{H}_{\beta 3}) = 8.0$ G, $a(\mathrm{H}_{\beta 4}) = 15.1$ G
Ca and Cs : $a(\mathrm{H}_{\beta 1}) = 8.0$ G, $a(\mathrm{H}_{\beta 2}) = 15.1$ G,
$a(\mathrm{H}_{\beta 3}) = 12.7$ G, $a(\mathrm{H}_{\beta 4}) = 10.0$ G
or $a(\mathrm{H}_{\beta 1}) = 10.0$ G, $a(\mathrm{H}_{\beta 2}) = 12.7$ G,
$a(\mathrm{H}_{\beta 3}) = 15.1$ G, $a(\mathrm{H}_{\beta 4}) = 8.0$ G
Da and Ds : $a(\mathrm{H}_{\beta 1}) = 8.0$ G, $a(\mathrm{H}_{\beta 2}) = 15.1$ G,
$a(\mathrm{H}_{\beta 3}) = 10.0$ G, $a(\mathrm{H}_{\beta 4}) = 12.7$ G
or $a(\mathrm{H}_{\beta 1}) = 10.0$ G, $a(\mathrm{H}_{\beta 2}) = 12.7$ G,
$a(\mathrm{H}_{\beta 3}) = 8.0$ G, $a(\mathrm{H}_{\beta 4}) = 15.1$ G

respectively. Due to the steric hindrance between two polymer chains, four conformations (Aa, Ba, Ca, and Da) are estimated to be more stable than four others (As, Bs, Cs, and Ds), and the conformation Aa is expected to be the most stable one in these four conformation (Aa, Ba, Ca, and Da). But, several other conformations may make some contribution to the observed 5 line ESR spectrum at −55 °C and 3.3 min in Fig. 6, due to the flexibility of polymer chains.

Conclusions

The 9 line ESR spectrum of poly(MMA) radicals changed irreversibly to a 5 line ESR spectrum of the stable polymer radicals (**S**) upon the warming from −75 to −60 (−55) °C. It is reasonable to consider that the stable polymer radicals (**S**) were produced through disproportionation and addition reactions of poly(MMA) radicals. Based on the hfc's ($a(\mathrm{H}_\beta)=15.1$ G, $a(\mathrm{H}_\beta)=12.7$ G, $a(\mathrm{H}_\beta)=10.0$ G, $a(\mathrm{H}_\beta)=8.0$ G) of the 5 line ESR spectrum and the steric hindrance between two polymer chaines, the stable polymer radicals (**S**) are estimated to have the most stable conformation (Aa) with the dihedral angles ($\theta_1(\mathrm{H}_{\beta 1})=57°$, $\theta_2(\mathrm{H}_{\beta 2})=66°$, $\theta_3(\mathrm{H}_{\beta 3})=60°$, and $\theta_4(\mathrm{H}_{\beta 4})=63°$ or $\theta_1(\mathrm{H}_{\beta 1})=60°$, $\theta_2(\mathrm{H}_{\beta 2})=63°$, $\theta_3(\mathrm{H}_{\beta 3})=57°$, and $\theta_4(\mathrm{H}_{\beta 4})=66°$).

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