Identification of ESR Spectra of the Propagating Radical for Polystyrene and Their Changes with Medium Environment

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ABSTRACT: Reported here is the study on various types of ESR spectra of the propagating radical in polystyrene. Spectrum simulation, analysis of the hyperfine coupling constant, and calculations of the conformation energy show that the propagating radical of styrene has two stable inner-rotation conformations R1 and R2. R1 corresponds to a 6-line spectrum which, in some special conditions, can appear as a 4-line or 3-line spectrum. R2 corresponds to an 8-line spectrum which, in some special conditions, appears as a 6-line spectrum. All the ESR spectra observed in the polymerization process can be regarded as the superposition of some of these spectra. The concentration ratio of R1 to R2 is affected by rotational interchange between R1 and R2, as well as the propagating reaction. The rotational interchange between R1 and R2 favors the formation of R1, and the propagating reaction favors the formation of R2. At the beginning stage of polymerization (low monomer inversion stage), the rotational interchange between R1 and R2 is dominated and the value of the concentration ratio of R1 to R2 is consistent with the one given by the Boltzmann distribution. However, in the middle to end stage of the reaction (high monomer inversion stage), the propagating reaction dominates. Therefore, R2 is the major conformer at last. Furthermore, when the radical is in the solid matrix in which the monomer has almost been exhausted and the propagating reaction is close to stopping, the rotational interchange between R1 and R2 dominates again. Therefore R1 returns as the major conformer in the solid matrix.

Introduction

Although the concentration of the propagating radical of polystyrene (PSt) yielded in polymerization is very low, a few of the ESR spectra, the 3-line,[1,2] 12-line, 4-line, and 6-line ones,[3,4] have been observed. The origins of these spectra are, however, still confusing and open to question. Bresler et al. ascribed the 12-line spectrum to the superposition of the two spectra from two species of radicals having the same β-proton conformation,[3] but different phenyl orientations. However it is difficult to evaluate the differences between his 12-line and the 12-line[4] spectra reported by others in bulk polymerization. Tino et al. obtained the 3-line spectrum of the growing[2] radical and analyzed its conformation, but this is the radical trapped in mechanically degraded polystyrene, not in the real polymerization process. It is therefore difficult to use it to explain the ESR spectra for the polymerization of polystyrene. Except for the above-mentioned papers about the analysis of the conformations of the growing radical in polystyrene, no other ones have been reported.

The purpose of this paper is to find the β-proton conformations of growing radical in polystyrene that can explain all the ESR spectra observed in the polymerization process so far. Therefore, the calculations of the conformation energy of the radical of PSt were carried out and used in the analysis of different types of ESR spectra and their changes with the environment.

Experimental Section

The ESR spectra of the propagating radical of PSt in bulk polymerization observed in this study are the same as reported in ref 4. Samples of styrene (St) monomer and initiator, benzoyl peroperoxide (BPO), were purified as usual and both were introduced to a glass tube with o.d. = 4.5 mm. The concentration of BPO in the tube was about 0.455 mol/L. The occluded air was removed by repeated freezing and melting in vacuo, and the tube was then filled with argon and sealed.

Specimens in the tube prepared as described above were put into the TE102 cavity on a Bruker ER200D ESR spectrometer with the temperature controlled at 75-90 °C by a Bruker ER4111-VT variable temperature accessory. The equipment parameters used in measurement are a microwave frequency and power of 9.45 GHz and 4.1 mW, respectively, and a modulation frequency of 100 kHz. The ESR spectra were recorded at various times and the accumulation-scan method was used to promote the signal-to-noise ratio. When the signal was weak, the spectrum was accumulated 20 times at most. No change in the shape of the spectrum was found during every period of the accumulation scan. The real spectra (Figure 1) were obtained by deducting the background from the measured spectra.[4] The radical concentration was obtained by double integration of the real spectra and calibration with the known solution of diphenylpicrylhydrazyl (DPPH) in St.

The other spectra were quoted directly from the papers.[1,3]

Calculation

The conformation energy calculations were carried out by taking into account the internal rotation, the van der Waals nonbonded interaction and the conformation of a short sequence consisting of the radical end unit and a penultimate monomer unit.[5-7] The bond lengths and the bond angles were taken from the work of Kamachi.[5,8] Two phenyl rings and a $-CH_2-$ in the penultimate monomer unit were respectively considered as a unit, and additivity was assumed for the atomic polarizability α and the effective number of outer shell electrons N_{eff}.[8] The van der Waals parameters used in the calculations are listed in Table 1. The computer program was written in Fortran 77 by the authors. The calculations were made by varying the parameters of internal rotation angles as shown in Figure 2. τ_1, τ_4, and τ_5 were keep constant; τ_2 varied at 1° and τ_3 at 30°. $\tau_1 = \tau_2 = \tau_3 = \tau_4 = \tau_5 = 180°$ defines the planar zigzag conformation (Figure 2).

Results and Discussion

1. Spectra in the Bulk Polymerization of PSt. 1.1. 12-Line Spectra at the Beginning Stage of the Reaction. The experimental ESR spectra of the St radical are

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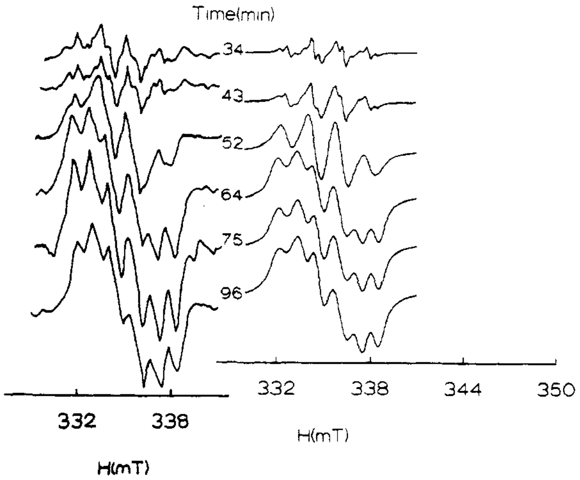

Figure 1. Spectra of the St radical in bulk polymerization: (left) experimental; (right) simulated.

Table 1. Parameters for Calculating the Potentials for Nonbonded Interactions

atoms or group	van der Waals radius (10^{-8} cm)	$10^{24}\alpha$ (cm^3)	N_{eff}
H	1.20	0.42	0.9
C	1.70	0.93	5.2
CH_2	2.0	2.91	7.9
benzene	1.8	7.68	35.7

shown in Figure 1. The spectra change from the 12-line spectrum at the beginning, through the 4-line spectrum in the middle stage, to the 6-line spectrum at the end. The 12-line spectrum can be simulated with two groups of hfs parameters, R1 (1.95, 1.58, 1.58 mT) (6-lines) and R2 (3.55, 1.58, 0.95 mT) (8-lines), a g value (g = 2.0027, from the experiment), and a proper concentration ratio of R1 and R2 (R1/R2 = 3.0). The hfs constants of the radical of PSt are derived from both the interaction between the unpaired electron and two β-protons and the interaction between unpaired electron and one α-proton.[3] The relation between the β-proton hfs value A_β and its tilt angle from the half-filled p-orbital to the C_β–H bond θ can be expressed as[9]

$$A_\beta = B\cos^2\theta \qquad (1)$$

$$B = B_0\rho \qquad (2)$$

where ρ is the spin density in the α-carbon atom and B_0 = 5.88 mT,[9] a constant. According to eqs 1 and 2, in R1 a value of 1.95 mT should be assigned to the α-proton hfs constant A_α. In R2 both values of 3.55 and 1.58 mT can be assigned to A_α. However, the value of 3.55 mT is too large when it is regarded as A_α since the spin density in C_α is obtained by an indirect (spin polarization) mechanism.

The final results are listed in Table 2 and shown in Figures 3 and 4. It is noted that R1 belongs to type I while R2 belongs to type II. The 12-line spectrum in the beginning stage of the reaction is the superposition of a 6-line spectrum of R1 and an 8-line spectrum for R2 according to a concentration ratio of R1/R2 = 3.0 (Figure 4a). From the ρ values, we can also conclude that the phenyl ring plane makes an angle of 90° with the sp^2 plane in R1 and a smaller angle in R2. These indicate that the unpaired electron is completely localized in C_α for R1 and partly delocalized on the phenyl ring for R2.

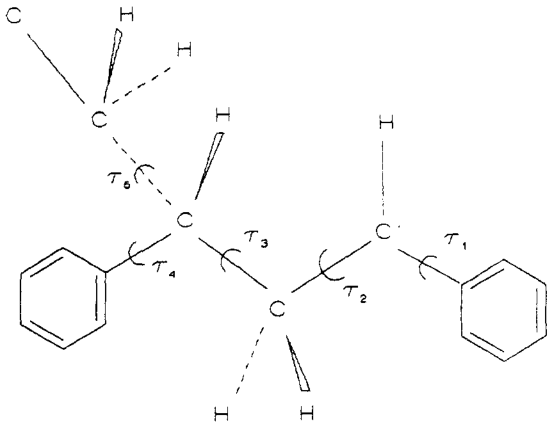

Figure 2. Schematic diagram of the poly(St) radical. $\tau_1 = \tau_2 = \tau_3 = \tau_4 = \tau_5$ = 180° defines the planar zigzag conformation.

Table 2. Structure Parameters of the Propagating Radical for Styrene from Experimental Spectra

radical	g	$A\alpha$ (mT)	$A_{\beta1}$	$A_{\beta2}$	θ_1 (deg)	θ_2 (deg)	B (mT)	ρ
R1 (I^1)	2.0027	1.95	1.58	1.58	60	60	6.32	1.08
R2 (II^2)	2.0027	1.58–1.38	3.55	0.95	–1.1	61.1	3.55	0.60

In order to understand the conformation of the polystyrene radical end, calculations of conformation energy were carried out, taking into consideration the conformations of the last two monomer units. The calculation results indicate that the propagating radical has two stable conformations I^1 (τ_3 = 60°, τ_2 = 85°) and II^2 (τ_3 = 60°, τ_2 = 147°) (see Figures 5 and 6). Dihedral angles (θ_1, θ_2) of β-protons with the π-orbital of unpaired electrons were calculated from the value of τ_2 for the two stable conformations (see Figure 6 and Table 3). For I^1 the dihedral angles are θ_1 = 65° and θ_2 = 55°; hence I^1 should be R1 ($\theta_1 = \theta_2$ = 60°). For II^2 the dihedral angles are θ_1 = –3° and θ_2 = 63°; therefore II^2 should be R2 (θ_1 = –1°, θ_2 = 61°). Some of the differences of dihedral angles between the energy calculational and experimental results are possibly due to the fact that, in the calculations, the intermolecular interactions with solvent and polymer molecules were not considered.

Another interesting problem is the concentration ratio of I^1 to I^2 (I^1/II^2). If I^1/II^2 obeys the rule of the Boltzmann distribution, it can be calculated from the conformation energy given in Figure 5. The calculated value of I^1/II^2 is 2.9 (see Table 3), which is consistent with the value of R1/R2 = 3.0 from the simulation of the 12-line spectrum. This suggests that the concentration ratio of R1 to R2 is thermodynamically dominated at the beginning stage of the reaction. In order to consider this, the propagating reaction was examined. As already shown above, since ρ of R1 is larger than that of R2, the activity of R1 (I^1) must be larger than that of R2 (II^2); that is, from the dynamics point of view, the formation of R2 is favored by the propagating reaction. Therefore, if R1/R2 is dynamically dominated, the value of it must be less than 1, which is not consistent with the experimental results. Therefore, the concentration ratio of R1 to R2 (R1/R2) is determined by their rotational interchange in the beginning stage of the reaction.

1.2. Spectra at the Middle and End Stages of Reaction. The more reasonable 4-line and 6-line simulated spectra can be obtained by adjusting the line width and concentration ratio of R1 to R2. The hfs constants, except that of the α-proton for R2 which varies from 1.58 mT at the beginning to 1.38 mT at the end, remain unchanged. The change of the hfs constant for the α-proton of R2 may be ascribed to the induction effect of the substitute phenyl group.[10] This is because the induction effect of the substitute phenyl group may change with the increase of monomer inversion. It is noted that

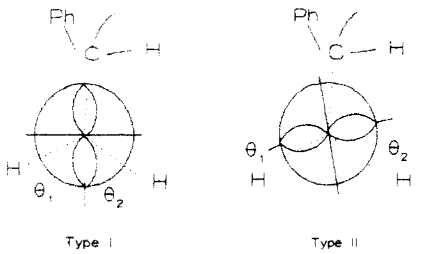

Figure 3. Two conformations for the styrene radical obtained from the experimental spectra. $\theta_1 < 90°$, $\theta_2 < 90°$. R1 (type I): $\theta_1 + \theta_2 = 120°$. R2 (type II): $\theta_1 + \theta_2 = 60°$.

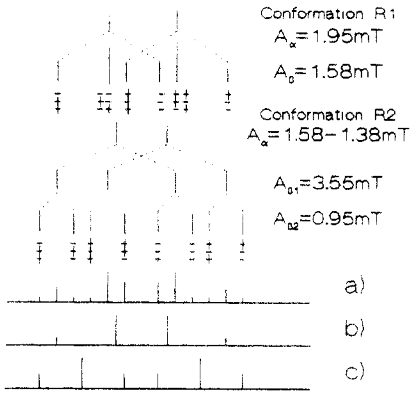

Figure 4. Theoretical ESR stick spectra for the propagating radical of styrene. (a) The 12-line spectrum in the beginning stage of reaction is the superposition of a 6-line spectrum for R1 and an 8-line spectrum for R2 with a concentration ratio of R1/R2 = 3.0. (b) The Experimental 4-line spectrum in the middle stage of the reaction is mainly ascribed to the R1 (6-line) spectrum which appears as a 4-line spectrum because of the broadened coalescence of line 2 with line 3 in the R1 (6-lines) spectrum, as well as line 4 with line 5. (c) The Experimental 6-line spectrum in the end stage of the reaction is mainly ascribed to the R2 (8-line) spectrum which appears as a 6-line because of the broadened coalescence of line 2 with line 3 in the R2 (8-line) spectrum, as well as line 6 with line 7.

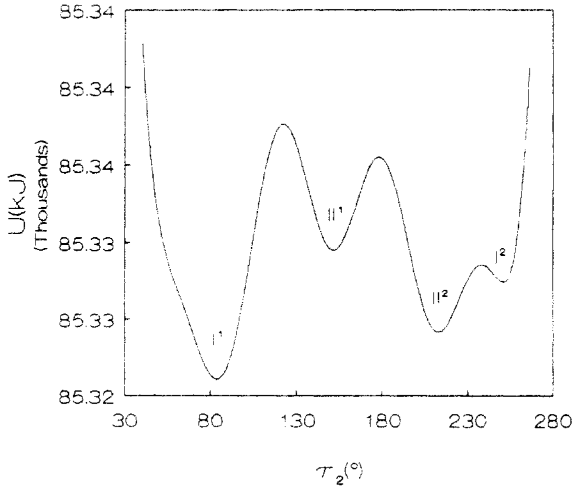

Figure 5. Calculated conformation energy for the polystyrene radical.

there is always a much broader single line with an intensity much higher than the sum of the intensities of R1 and R2 at the end stage of the reaction, which we called R3. Since R3 remains unchanged when the temperature is lowered at room temperature, at which point the reaction almost stops, R3 must be the propagating or chain radical wrapping by the polystyrene matrix.[2,4,11] This phenomenon also suggests that the radical was wrapped by the chain of polymer when the local viscosity of the radical is large enough.

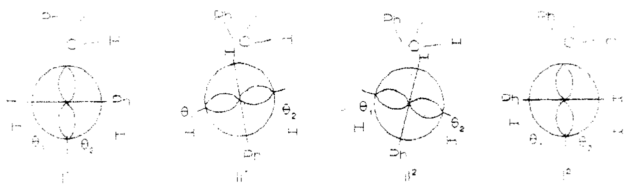

Figure 6. Conformations obtained from the energy calculation.

Table 3. Angles of Conformers from Conformational Energy Calculations and Their Relative Content Calculated by the Boltzmann Distribution

conformation	I^1 (R1)	II^1	II^2 (R2)	I^2
content (%)	65.9	3.8	22.9	7.4
θ_{1e} (deg)	65	1	-3	43
θ_{2e} (deg)	55	59	63	77

Table 4. Time Dependence of the Ratio (R1/R2)

time (min)	34	43	52	64	75	86	96
ratio of R1 to R2	3.0	3.0	1.41	0.6	0.5	0.3	0.25

In order to be able to simulate the experimental 6-line spectrum,[12] we generated the spectra of R3 by lowering the temperature of the sample. The simulated spectra were obtained by superposing the spectra of R1, R2, and R3.[12] The treatment does not influence the analysis of conformations of R1 and R2 and their concentration ratio since there is no hfs structure in the R3 spectra.

As shown in Figures 1 and 4, the conformations corresponding to the experimental 4- and 6-line spectra in the middle and end stages of the reaction are the same as that for the 12-line spectrum in the beginning stage, but the line widths and the concentration ratios of R1 to R2 are different. The experimental 4-line spectrum in the middle stage of the reaction is mainly ascribed to the R1 (6-line) spectrum which appears as a 4-line spectrum because of the broadened coalescence of line 2 with line 3, as well as that of line 4 with line 5. The experimental 6-line spectrum in the final stage of the reaction is mainly ascribed to the R2 (8-line) spectrum which appears as a 6-line spectrum also because of the broadened coalescence of line 2 with line 3, as well as that of line 6 with line 7.

The variation of the concentration ratio (R1/R2) is interesting for it decreases monotonously with the progress of the reaction from 3 corresponding to a 12-line spectrum at the beginning stage, through 2 corresponding to a 4-line spectrum in the middle stage, to 0.25 corresponding to a 6-line spectrum at the end. This shows that the concentration ratio of R1 to R2 is governed by thermodynamics at the beginning and by dynamics at the end since the rotational interchange favors the formation of R1 and the propagating reaction favors the formation of R2. The reason for this is that, with the increasing viscosity of the reaction system, the rate of the rotational interchange between R1 and R2 decreases much more rapidly than that of the propagating reaction since the former is controlled by the macromolecule relaxation and the latter by the small molecule (monomer) relaxation. Therefore the concentration ratio of R1 to R2 depends on the process of the propagating reaction at the end stage of the reaction.

2. 3-Line Spectra of Styrene in the Solid State. Ballard et al. observed the 3-line ESR spectrum at 100 K of samples taken 60 min after the addition of styrene (25% (w/w) of polymer) to a fully polymerized (>99%) seeded MMA emulsion polymerization 165 min after initiation.[1] The spectrum appears as a broad triplet with a hyperfine splitting of ca. 2.6 mT and a width at half-height of 1.4 mT. If the 3-line spectrum is compared with the 6-line spectrum of R1 and the broadening of the ESR spectra is taken into consideration, it leads to the conclusion that

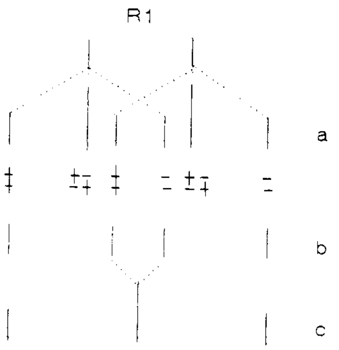

Figure 7. Identification of the 3-line ESR spectra of the styrene radical in the solid state: (a) shows the 6-line spectrum of R1. (b) Isotropic broadening of hf components (alternative broadening) caused by the hindered oscillation of the β-proton causes lines with $\Sigma M_I = 0$ in the 6-line spectrum[11] of R1 to disappear. (c) Anisotropic broadening of hf components caused by the α-proton leads to the 2 central lines in the 6-line spectrum of R1 coalescing into a single line.

the 3-line spectrum is derived from R1. The isotropic broadening of hf components (alternative broadening) caused by the hindered oscillation of the β-proton causes the lines with $\Sigma M_I = 0$ in the 6-line spectrum[11] of R1 to disappear. The anisotropic broadening of hf components caused by the α-proton causes the two central lines in the 6-line spectrum of R1 to coalesce into a single line (see Figure 7). From the point mentioned above, the hfs constant of the 3-line spectrum from R1 is 1.58 + 1.95/2 = 2.56 mT, that is comparable with the 2.6 mT from Ballard's 3-line spectrum. This result also suggests that the R1 is the major conformation of the propagating radical; i.e. the concentration ratio of R1 to R2 is determined by the rotational interchange between R1 and R2 in the irregular environment of the polymer matrix. This is a matter of course since, in this case, the monomer is almost exhausted and the propagating reaction is close to stopping but the rotational interchange between R1 and R2 is still in progress.

3. Bresler's 12-Line Spectra. Bresler et al.[3] observed an alternate type of 12-line spectra and ascribed it to the two overlapping series of 6-line spectra, each falling between the lines of the other. Both 6-line spectra have the same hfs constant (1.2 mT), i.e the same β-proton conformations, but they have different g factors (see Figure 8) because of the two possible configurations of the end group, isotactic and syndiotactic. We have found that the 6-line spectra in Bresler's 12-line spectrum are very similar to those we observed in the end stage of the bulk polymerization process. Therefore, it is possible that each of Bresler's two overlapping series of 6-line spectra originates from conformation R2; i.e. the 6-line spectra is actually the 8-line spectrum from R2. The analysis of theoretical stick spectra for R2 shows the same conclusion.

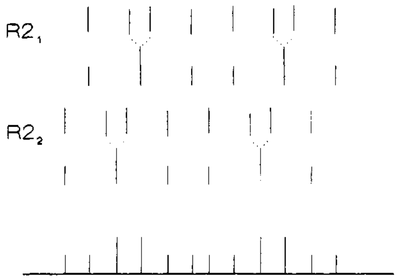

Figure 8. Identification of Bresler's 12-line spectrum. The distance of the 1st–2nd, 2nd–3rd, 4th–5th, and 5th–6th lines for the 6-line spectrum of R2 is 0.95 + (1.38 − 0.95)/2 = 1.16 mT ≈ 1.2 mT. The distance between the 3rd and 4th lines for the 6-line spectrum of R2 is 3.55 − 1.38 − 0.95 = 1.22 mT.

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