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ESR Study of the Radical Polymerization of Styrene. 3. Assignments of Well-Resolved Spectra of Propagating Radicals of Styrene and Para-Substituted Styrene

Bunichiro Yamada,* Masakazu Kageoka, and Takayuki Otsu*

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

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Introduction. In free-radical-initiated polymerization free radicals are present in very low concentrations. Steady-state kinetics does not yield data on the radical reactivity from the overall rate of polymerization.[1] Direct observation of the propagating radical by ESR spectroscopy is the most promising technique for obtaining information on the polymer radical. However, the low concentration due to a short lifetime had allowed the spectroscopic detection of the polymer radical only under special conditions such as the frozen state.[2]

Several investigations have used ESR spectroscopy with enhanced sensitivities for the study on polymerization in homogeneous solution. Bresler et al.[3] determined the steady-state concentration of the polymer radical from methyl methacrylate (MMA) with a highly sensitive ESR spectrometer. Using a specially designed cavity, Kamachi[4] has studied the ESR spectra of the polymer radicals from methacrylic esters in relation to their conformations, and the concentrations of the polymethacrylate radicals have also been determined to evaluate the absolute rate constants of propagation (k_p) and termination (k_t).

During polymerization of vinyl acetate, the propagating radical was detected and the steady-state concentration of the polymer radical was determined to evaluate k_p and k_t.[3,4]

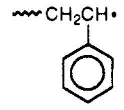
More recently radical polymerization of MMA in bulk up to high conversions has been studied in detail by ESR detection of the polymer radical.[5–9] Changes in the rate constants of the elementary reactions with progression of the polymerization have been discussed. Considerable decreases in termination, propagation, and initiation rates have been noted.

The polymerization and copolymerization of styrene (St), a versatile monomer, have been studied extensively, and these data have been accumulated and compiled.[10] However, only a few ESR studies on the propagating radical during St polymerization have been reported. A highly sensitive ESR spectrometer has been successfully employed to record the spectrum of the poly(St) radical by Bresler and co-workers,[11] who have reported a spectrum consisting of 12 broad lines. Shen and co-workers[12] have recently recorded a 12-line spectrum during St polymerization. However, details of the hyperfine structure have not been given by either Bresler et al.[11] or Shen et al.[12] because the linewidth of the spectra recorded was too broad for precise simulation. Smith and co-workers[13] have simultaneously detected the poly(St) radical and an initiator radical by means of a flow technique. Although they have estimated the hyperfine coupling constants (hfc's) for all the hydrogens of the poly(St) radical, the spectrum of the polymer radical has not been given separately.

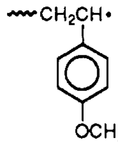
A computer-controlled ESR spectrometer being commercially available has allowed us to determine the concentration of the polymer radical throughout the polymerization of St under proper polymerization conditions.[14,15] It was noted that the nonpolar nature of St and poly(St) is advantageous over MMA and poly(MMA) for ESR measurement. The sensitivity of the ESR spectrometer remained constant throughout the polymerization, unlike the MMA polymerization studied by Carswell and co-workers,[8] as evidenced by the constancy of the sensitivity of the ESR spectrometer irrespective of conversion as confirmed by the same intensity of the signal of Mn^{2+}/MgO in a capillary tubing attached to the sample tube throughout the polymerization.

On the basis of the absolute rate constants at different conversions calculated from the instantaneous polymerization rate and the concentration of the poly(St) radical, we found that the k_p value remained constant over a wide conversion range (0–97%) while k_t decreased beyond 30% conversion.[14] In addition to the conversion dependence of the rate constants, we have reported the constancy of the k_p value irrespective of the chain length of the poly(St) radical.[15] In these experiments, the concentration of the poly(St) radical was determined by using its ESR spectrum of a broad linewidth at a relatively high modulation amplitude because an accurate determination of the intensity of the spectrum was preferred over a well-resolved spectrum.

In this paper, we report the detection and full assignment based on a well-resolved ESR spectra of the polymer radicals of St and *p*-methoxystyrene (*p*-MeOSt)[16] in bulk at room temperature:



poly (St) radical



poly (*p*-MeOSt) radical

To our knowledge, the well-resolved spectra of poly(St) and poly(substituted St) radicals have so far not been reported. Since the steady-state concentration is too low to be determined by not only conventional ESR spectroscopy but also any spectroscopic means in homogeneous solution, the direct detection of the polymer radical has been employed as a useful technique for kinetic analysis of the radical polymerization. Furthermore, a well-resolved ESR spectrum of the polymer radicals allows us to know delocalization of the unpaired electron and conformation of the polymer radicals during polymerization. Since the ESR data on the polymer radicals are expected to be correlated with their reactivities, an ESR study on radical polymerization using the modern instrument can proceed the understanding of radical polymerization in a quantitative and straightforward manner.

Experimental Section. St and *p*-MeOSt were commercially available and were distilled under reduced pressure before use. Commercial *tert*-butyl peroxide (TBP) was also distilled under reduced pressure. ESR spectra observed in the initial stage of polymerization were recorded on a Bruker ESP 300 spectrometer at X band (ca. 9.49 GHz) utilizing 100-kHz field modulation, and a microwave power of 20 mW was applied. A quartz 1-cm-o.d. tube filled with the monomer containing 1 mol/L of TBP was inserted into a TE102 cavity of the spectrometer. The polymer radical was generated by irradiation with a

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500-W xenon lamp to a distance of ca. 45 cm from the tube in the cavity at room temperature (ca. 22 °C).

The spectra were recorded over a magnetic field range of 15 mT divided into 1000 points, and the conversion time for each point was 40.92 ms, resulting in a sweep time of ca. 41 s for each scan. Fremy's salt (a_N = 13.0 G and g = 2.0055) was used as reference for measuring hyperfine splitting and g values, and the aqueous solution of the salt in 0.1-cm-o.d. quartz capillary tubing was attached to the sample tube containing the polymerization mixture. Computer simulation of the spectra was performed on Hitac M660-K by using a program based on the procedure originally reported by Stone and Maki,[17] and the line shape used is Lorentzian.

Results and Discussion. For determination of the radical concentration in our previous papers,[14,15] we measured the spectrum at a relatively high modulation amplitude, like 1.0 mT. Care was exercised to prevent the saturation of the spectrum and 4-line spectra with increasing linewidth with conversion were obtained. As a consequence of the search for optimum conditions to obtain a well-resolved spectrum,[18] we recorded the spectrum consisting of apparently more than 18 lines for the poly(St) radical as shown in Figure 1A. The spectrum was observed within a short period after turning on the xenon lamp, and the irradiation was continued during the period of the accumulation of the spectrum. At a lower modulation amplitude, the intensity of the spectrum decreased considerably and a higher modulation amplitude brought about a broader line. The conditions for the polymerization and ESR measurement in the present work seem to be suitable for obtaining the spectra with narrow line width.

The spectrum in Figure 1A can be satisfactorily reconstructed by using proper hfc's because of a sufficiently narrow linewidth. Since $a_{\alpha\text{-H}}$ = 1.625 mT for the benzyl radical and $a_{\alpha\text{-H}}$ = 1.625 and $a_{\beta\text{-H}}$ = 1.769 mT for the phenethyl radical have been tabulated by Arnold,[19] we started the simulation using hfc's similar to those of the low molecular weight radicals. However, hfc's evaluated for the α-hydrogens of the benzyl and phenethyl radicals were found to be too small for the poly(St) radical, which yielded $a_{\alpha\text{-H}}$ = 1.830 mT. The values of hfc's for the α-, β-, *o*-, *m*-, and *p*-hydrogens, which are summarized in Table I, were determined by the simulation. The simulated spectrum superimposable on the observed one is depicted in Figure 1B; linewidth = 0.140 mT and g = 2.0025 ± 0.0005. Since hfc for the *m*-hydrogens is similar to the linewidth, 0.14 mT, the splitting by the *m*-hydrogens does not appear clearly. Figure 1C exhibits a stick plot of all the signals arising from the splitting by the α-, β-, *o*-, *m*-, and *p*-hydrogens.

The spectrum of the poly(*p*-MeOSt) radical shown in Figure 2A is not as complicated as the spectrum of the poly(St) radical illustrated in Figure 1A, because the *p*-methoxy substitution excludes the splitting due to the *p*-hydrogen. The spectrum of the poly(*p*-MeOSt) radical was also observed just after the start of the irradiation, and the polymerization mixture was irradiated during the accumulation of the spectrum. Figure 2B is the simulated spectrum with linewidth = 0.150 mT and g = 2.0025 ± 0.0005, and Figure 2C depicts the stick plot of the simulated spectrum. hfc's used for the simulation are summarized in Table I. The spectrum of the poly(*p*-MeOSt) radical consists of a doublet of a triplet by α- and β-hydrogens further split into a triplet by the *o*-hydrogens while the splitting by the *m*-hydrogens and methoxy hydrogens was not observed definitely in the spectrum recorded. The splitting by the *p*-methoxy hydrogens which could contribute to an increase in the linewidth is not shown in Figure 2C.

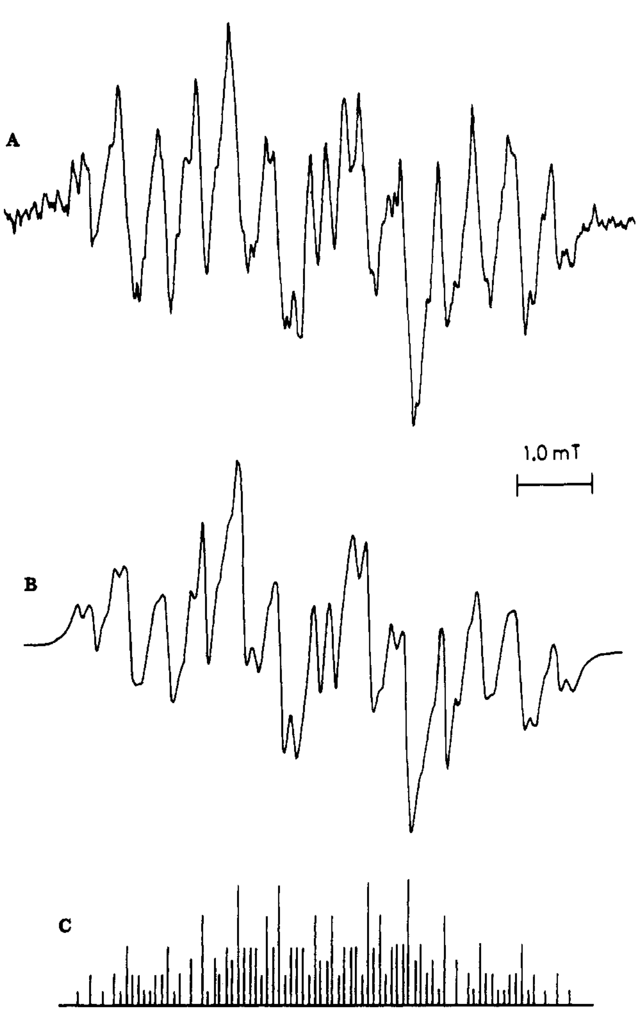

Figure 1. ESR spectrum of the poly(St) radical ($\sim\!\sim CH_2\dot{C}HC_6H_5$) observed during the polymerization sensitized with TBP by UV irradiation at a modulation amplitude of 0.1025 mT after 137 scans (A), a computer-simulated spectrum for A at a linewidth of 0.140 mT (B), and a stick plot for the simulated spectrum (C).

Inspecting the magnitudes of hfc's evaluated by the computer simulation, we found that hfc's for the poly(St) radical determined in the present study agree only qualitatively with those reported by Smith et al.[13] They estimated the same coupling constants for the α- and β-

Table I
hfc's for Poly(St), Poly(*p*-MeOSt), Benzyl, and *p*-Methoxybenzyl Type Radicals

radical	hfc (mT)						
	$a_{\alpha\text{-H}}$	$a_{\beta\text{-H}}$	$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{p\text{-H}}$	a_{CH_3O}	ref
poly(St)	1.830	1.590	0.495	0.170	0.595		this work
poly(*p*-MeOSt)	1.770	1.550	0.480	0.120		0.030	this work
benzyl	1.625		0.510	0.170	0.613		19
p-methoxybenzyl	1.595		0.502	0.160		0.075	19
phenethyl	1.625	1.769	0.495	0.165	0.590		19
p-methoxyphenethyl	1.560	1.725	0.495	0.150		0.070	19

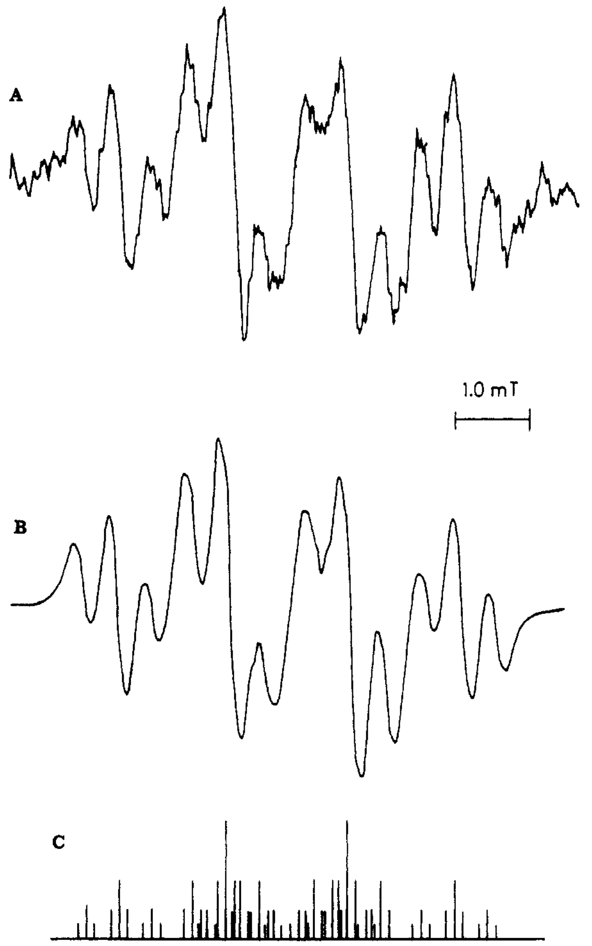

Figure 2. ESR spectrum of the poly(*p*-MeOSt) radical ($\sim CH_2\dot{C}HC_6H_4OCH_3$-*p*) observed during the polymerization sensitized with TBP by UV irradiation after 70 scans at a modulation amplitude of 0.2859 mT (A), a computer-simulated spectrum for A at a linewidth of 0.150 mT (B), and a stick plot for the simulated spectrum (C) in which the hyperfine coupling by the methoxy hydrogens is not shown.

hydrogens; $a_{\alpha\text{-H}}$ is apparently greater than $a_{\beta\text{-H}}$ as shown in Table I. A smaller $a_{\alpha\text{-H}}$ for the poly(*p*-MeOSt) radical as compared to that for the poly(St) radical is consistent with an increase in the resonance stabilization, leading to a lower spin density on the α-carbon as predicted from the larger *Q* value of the *Q*–*e* scheme for *p*-MeOSt, 1.53, than for St. 1.00.[20] A decrease in hfc's for the α-hydrogen by *p*-methoxy substitution has also been found in the benzyl and phenethyl radicals as shown in Table I.[19]

These findings indicate that the *p*-methoxy group affects the spin density of the benzyl and phenethyl type and poly(St) radicals in a quite similar manner. The greater $a_{\alpha\text{-H}}$ values for the polymer radicals compared to those for the small radicals might result from restriction of the resonance by interaction of the aromatic rings of the polymer radical to some extent.

The $a_{\alpha\text{-H}}$ value for both the poly(St) radical and the poly(*p*-MeOSt) radicals is less than that for the radicals from acrylic monomers. hfc's for the α-hydrogen of acrylic monomers have been evaluated to be ca. 2.0 mT,[21] showing that the phenyl and *p*-methoxyphenyl groups are capable of delocalizing the unpaired electron to a more significant extent than the carboxyl or cyano group of the acrylic monomers. Consistently, the *Q* values for St and *p*-MeOSt are greater than those for acrylic acid and acrylonitrile, 0.40 and 0.60, respectively.[20]

The same hfc for pairs of β-hydrogens were obtained for poly(St) and poly(*p*-MeOSt) radicals. The same hfc could be given by free rotation around the C_α–C_β bond or the same dihedral angle between the π-orbital and C–H bond, 60°. According to theory,[21] the β-hfc could be given by

$$a_{\beta\text{-H}} = B\rho \cos^2 \theta$$

where *B*, which has been estimated to be around 5.0 mT,[22] is a proportionality constant and ρ is the spin density. Adopting $B = 5.0$ mT and $\rho = 0.70$, we can obtain $\cos^2 \theta = 0.45$ for the poly(St) radical with $a_{\beta\text{-H}} = 1.59$ mT. The value of $\cos^2 \theta$ close to 0.5 implies that free rotation around the C_α–C_β bond leads to identical interaction of the two β-hydrogens with the unpaired electron as well as the poly(vinyl acetate) radical.[23] With the same dihedral angle for the two β-hydrogens, $a_{\beta\text{-H}} = 0.93$ mT, which is much smaller than evaluated by the computer simulation, could be obtained by using $B = 5.0$ mT and $\rho = 0.70$. The same hfc for the two β-hydrogens of the poly(*p*-MeOSt) radical was also interpreted as indicating free rotation around the C_α–C_β bond.

Full assignment of the well-resolved ESR spectra of poly(St) and poly(*p*-MeOSt) radicals allows us to characterize these. ESR spectra[11,12] with broad linewidths previously obtained under different conditions are also accounted for by the hfc's evaluated in the present study with increased linewidths.

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Registry No. (*p*-MeOSt) (homopolymer), 24936-44-5; PS, 9003-53-6.