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ESR study of radical polymerization of styrene
7. Hyperfine structures of ESR spectra of propagating radicals from substituted styrenes

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Abstract

Propagating radicals of *o*-, *m*-, and *p*-substituted styrenes were detected using ESR spectroscopy during their bulk or benzene solution polymerizations. The hyperfine coupling constants for the protons of the monomeric unit carrying an unpaired electron was determined. Similar to the benzyl-type small radicals, an increase in the resonance stabilization of the polymer radical only slightly decreases the coupling constants for the α- and β-protons (a_α and a_β, respectively). Plots of a_α and a_β of the polymer radicals versus $\sigma^{\cdot}_\alpha$ which has been defined as a substituent constant based on a_α of the nuclear substituted benzyl radicals gave linear relationships. A substituent of which $\sigma^{\cdot}_\alpha$ value is positively large indicating low spin density at benzyl positions resulted in a decreases in a_α and a_β. Plots of the a_α and a_β for the polymer radical versus the *Q* value for the substituted styrene showed that an increase in the *Q* value brings about a decrease in the coupling constants. The hyperfine coupling constants for the *m*-, *o*-, and *p*-protons were also evaluated. © 2000 Elsevier Science Ltd. All rights reserved.

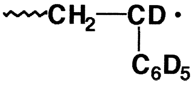
Keywords: Radical polymerization; ESR; Benzyl radical

1. Introduction

ESR spectroscopy is the only method to directly observe the propagating radical of the free radical polymerization in a homogeneous system [1,2]. The hyperfine coupling of the spectra of the radicals from a series of monomers could be related to spin delocalization and the polymerization reactivity. Polymer radicals of styrene (St) and nuclear-substituted Sts were thought to be conducive to such study because the effect of the substituent bound to the π-electron system can be reflected in the spectra of radicals. Further, the non-polar or weakly polar nature of St and substituted St are advantageous over polar monomers for ESR measurement.

We succeeded in recording the well-resolved spectra of the propagating radicals of St [3], *p*-methoxystyrene (*p*-MeO–St) [3], and the *p*-methylstyrene (*p*-Me–St) [2], which allowed evaluation of the hyperfine coupling constant (hfcs) for the α- and β-protons (a_α and a_β, respectively), and all other protons including the *p*-methoxy and *p*-methyl protons. These spectra of the propagating radicals of St and substituted Sts were obtained after the accumulation of scans. More recently, Kamachi and Kajiwara [4] have reported that the well-resolved spectrum of the poly(St) radical can be recorded by a single scan. The ESR spectra of the poly(St) radical recorded by Bresler et al. [5], Shen et al. [6], and Mao et al. [7] consisted of lines too broad to assign the hfcs for all the protons bound to the terminal monomeric unit.

For the unambiguous assignment of hfcs, the spectra of poly(α-2,3,4,5,6-hexadeuteriostyrene) radical (**1**) and poly (β,β,2,3,4,5,6-heptadeuteriostyrene) radical (**2**) were taken and assigned [8] because of a smaller hyperfine coupling for deuterium than proton by a factor of ca. 6.5. **1** yielded a broad three-line spectrum which could be two sets of doublets by the β-protons broaden by the coupling of the α-deuterium. Summation of hfcs was obtained: $a_{\beta1} + a_{\beta2} = 33.5$ G. **2** was detected as a broad doublet: $a_\alpha = 15.2$ G. Based on these results, hfcs for poly(St) radical have been assigned: $a_\alpha = 15.9$, $a_{\beta1} = 15.9$, and $a_{\beta2} = 18.3$ G.


$\sim\!\sim CH_2{-}CD\cdot(C_6D_5)$

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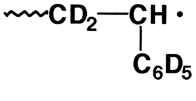
$\sim\!\sim CD_2{-}CH\cdot(C_6D_5)$

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The present work deals with evaluation of hfcs for the propagating radicals from nuclear-substituted St to consider the substituent effect on delocalization of an unpaired

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Table 1
Polymerization and ESR conditions for recording the spectra of propagating radicals from substituted Sts (microwave frequency = 9.48 GHz; conversion time = 41 ms; time constant = 655 ms; and sweep time = 41.9 s/scan)

Nuclear substituent	[M] (mol/l)[a]	[TBP] (mol/l)	Modulation amplitude (G)	Microwave power (mW)	Number of scan
m-Cl	3.51	0.54	1.4	16	200
o-Cl	3.39	0.72	2.0	20	141
p-Cl	3.23	0.67	2.0	20	150
m-MeO	3.18	0.75	2.0	20	200
o-MeO	3.44	0.76	2.0	20	53
p-F	7.04 (neat)	0.81	3.6	5.0	200

[a] Benzene solution.

electron. The hfc values determined for the poly(St) radical are not in agreement with those reported by Kamachi and Kajiwara, $a_\alpha = 17.8$ G, $a_{\beta1} = 17.5$ G, and $a_{\beta2} = 16.3$ G [4]. However, hfcs evaluated under comparable conditions using the same instrument could be employed for a discussion on the substituent effect.

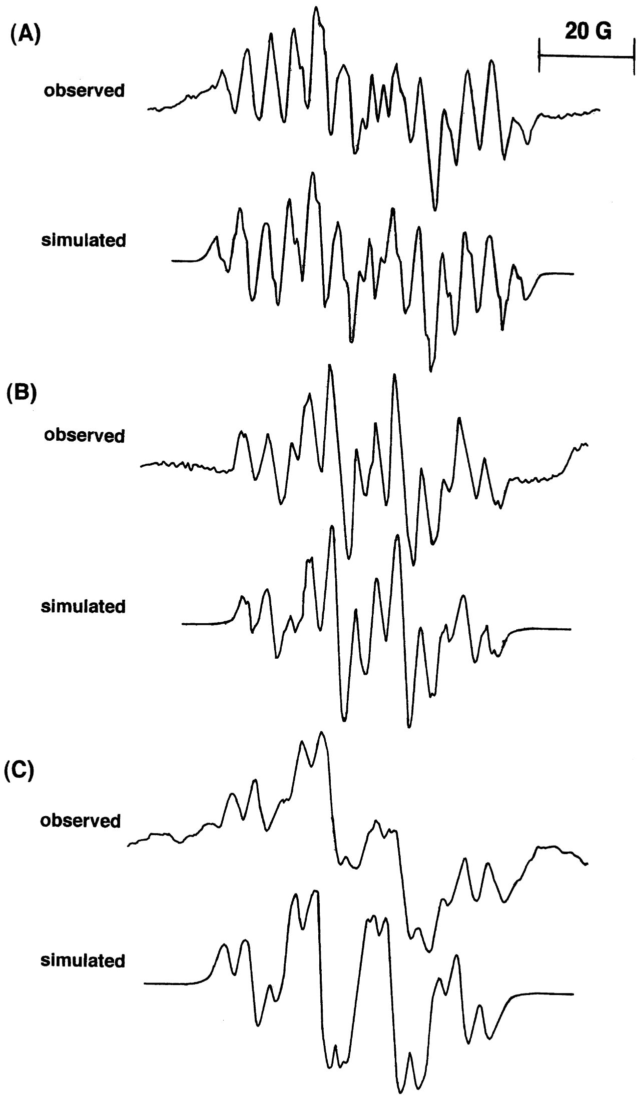

Fig. 1. (A) Observed and simulated ESR spectra of propagating radicals from *m*-Cl–St; (B) *o*-Cl–St; and (C) *p*-Cl–St.

2. Experimental

Commercially available *p*-chlorostyrene (*p*-Cl–St) and *p*-fluorostyrene (*p*-F–St) were distilled under reduced pressure before use. *o*-Chlorostyrene (*o*-Cl–St), *m*-chlorostyrene (*m*-Cl–St), *m*-methoxystyrene (*m*-MeO–St), and *o*-methoxystyrene (*o*-MeO–St) were prepared by the dehydration of the corresponding substituted 1-phenylethanols which were synthesized by the reactions of the Grignard reagents of the substituted bromobenzenes with acetaldehyde. 2,3,4,5,6-Pentadeuteriostyrene (St-d_5) was prepared as described in our previous paper [8]. The structures of all the synthesized monomers were verified by ^{1}H and ^{13}C NMR spectroscopies. *tert*-Butyl peroxide (TBP) was commercially obtained and distilled under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol.

The copolymerizations were carried out in benzene at 60°C using AIBN as the initiator, and the copolymers obtained from different comonomer compositions were isolated at conversions of less than 5%. The compositions of the copolymers of the methoxystyrenes were calculated from the intensity ratios of the ^{1}H NMR resonance due to the methoxy protons to those due to the aromatic protons or the methylene and methine protons. The copolymer compositions of the St/St-d_5 copolymers were calculated from the intensity ratios of the resonance due to the aromatic protons of the St unit to those in the range of 0–3 ppm. The copolymers of St-d_5 with *p*-F–St were determined by ^{1}H NMR spectroscopy using the resonances of the methylene and methine protons, and the aromatic protons. The monomer reactivity ratios, r_1 and r_2, were determined by a non-linear least squares procedure [9] and were used for calculation of the *Q* and *e* values.

ESR spectra were recorded on a Bruker ESP 300 spectrometer at X band with a 100 kHz field modulation. A benzene solution of the substituted St or neat and TBP in a 0.5 cm outer diameter quartz tube sealed under vacuum in the cavity was irradiated by a 500 W xenon lamp from a

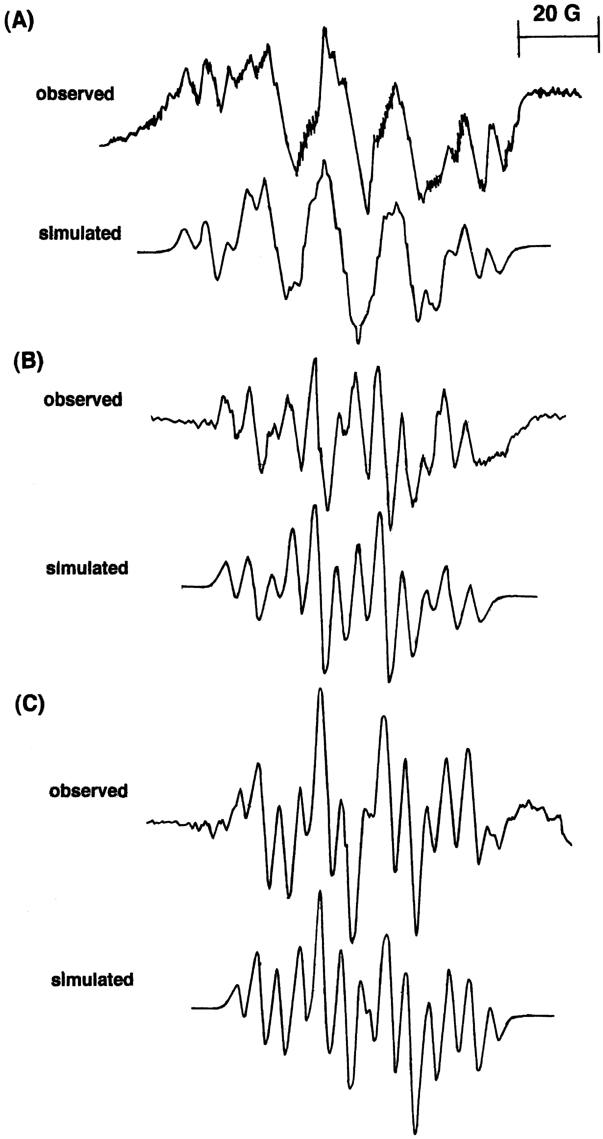

Fig. 2. (A) Observed and simulated ESR spectra of propagating radicals from *p*-F–St; (B) *m*-MeO–St; and (C) *o*-MeO–St.

distance of ca 45 cm at room temperature. The conditions of polymerization and ESR measurement are summarized in Table 1. The hfc values were calibrated by a microwave counter (Advantec R5372) and an NMR field meter (Echo Electronics EFM 2000AX). The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GX400 spectrometer. Deuteriochloroform and tetramethylsilane were used as the solvent and the internal standard, respectively, for the NMR measurements.

3. Results and discussion

3.1. ESR spectra of propagating radicals

The spectra of the polymer radicals from chlorostyrenes are illustrated in Fig. 1. The spectrum of the poly(*m*-Cl–St) radical can be explained by splitting it into a doublet due to one of the β-protons, a triplet due to the α- and another β-protons, a triplet due to the *o*-protons, and doublets due to the *p*-proton and the *m*-proton. The splitting by the *m*-protons was too small to be visually confirmed in any of the spectra. The poly(*o*-Cl–St) radical yielded a well-resolved spectrum which is accounted for by the splitting due to the α-, β-, *m*-, *o*-, and *p*-protons. In this case, the splitting by a single *o*-proton into a doublet was confirmed by simulation. The poly(*p*-Cl–St) radical gave the observed spectrum consisting of broad lines as well as the spectrum of the poly(*p*-F–St) radical (Fig. 2A). The relevant hfcs of the respective protons of the radicals from the halostyrenes are summarized in Table 2. Fig. 2 illustrates the spectra of the poly(*m*-MeO–St) and poly(*o*-MeO–St) radicals, and the hfcs for the protons of these radicals are tabulated in Table 2 where hfcs for poly(St), poly(*p*-MeO–St), and poly(*p*-Me–St) radicals used for further discussion are also quoted [2,3].

3.2. Comparison of substituent effects

To compare the effect of the nuclear substituent, Fig. 3 shows plots of a_α for the poly(St), benzyl [10], and phenethyl radicals [10], and a_β for the phenethyl and cumyl radicals [10] versus a_β for the poly(St) radical. Table 2 shows that each polymer radical has two of hfcs for β-protons. For further discussion of the substituent effect on a_β, the larger a_β values were adopted because the smaller a_β value is equal to the a_α value. The a_α value for the poly(substituted St) radical tends to increase as the a_β value for the radical increases: $15.5\ \mathrm{G} < a_\alpha < 16.4\ \mathrm{G}$ and $17.5\ \mathrm{G} < a_\beta < 18.4\ \mathrm{G}$. These trends seem to be reasonable because of the proportionalities of the a_α and a_β values to the spin density on the α-carbon (Eqs. (1) and (2)) [11]:

$$a_\alpha = Q_\alpha \rho \qquad (1)$$

$$a_\beta = Q_\beta \rho \qquad (2)$$

where Q_α and Q_β, and ρ are the empirical factors for a_α and a_β, and the π spin density at the α-carbon, respectively. Noteworthy is that most of the points of a_α for the poly(St), benzyl, and phenethyl radicals except for the *o*-substituted St radicals are in a narrow range in Fig. 3.

Small changes in the a_α and a_β values for the benzylic radicals by nuclear substitution are known [10], and the ranges of the a_α and a_β values suggest a similar delocalization of the spin of the polymer radicals. The exceptionally small a_β for the poly(*o*-substituted St) radicals could be explained by the steric effect of the substituent on the dihedral angle between the orbital of the unpaired electron and the C_β–H_β bond. A plot of a_β for the phenethyl radicals versus a_β for the poly(St) radical did exhibit quite different tendency from a_β for other radicals as can be seen in Fig. 3.

Table 2
Hfc values of the protons of poly(St) and poly(substituted St) radicals

Radical	hfc(G)					Reference
	a_α	a_β	a_m	a_o	a_p	
m-Cl–St	15.9	15.9, 18.4	1.6	5.0	6.1	This work
m-MeO–St	16.5	16.5, 18.4	1.2	4.7	6.2	This work
St[a]	15.90	15.90, 18.30	1.70	4.05	5.95	[3]
p-Cl–St	15.9	15.9, 18.2	1.6	4.8	–	This work
p-Me–St	15.90	15.90, 18.00	1.30	4.95	6.00[b]	[2]
p-F–St	15.9	15.9, 17.9	1.4	4.9	14.2[c]	This work
p-MeO–St[a]	15.50	15.50, 17.70	1.60	4.80	0.30[d]	[3]
o-Cl–St	15.9	15.9, 16.9	1.6	4.8	5.8	This work
o-MeO–St	15.7	15.7, 16.7	1.2	4.7, 0.3[d]	6.1	This work

[a] Although a_α for poly(St) and poly(*p*-MeOSt) radical were tentatively assigned in our previous paper (Ref. [3]), the deuterated radicals indicated that the greater coupling constants should be a_β.
[b] hfc for *p*-methyl protons.
[c] hfc for *p*-fluoro substituent.
[d] hfc for methoxy protons.

3.4. Correlation of hfc with $\sigma^{\cdot}_{\alpha}$

An increase in the resonance stabilization of the poly(St) radical could decrease the spin density of the α-carbon resulting in smaller a_α and a_β. Although a_α may be proportional to the spin density of the α-carbon, dependence of the a_α value on the substituent of the polymer radicals are still unknown. Arnold has defined a substituent parameter scale, $\sigma^{\cdot}_{\alpha}$, based on the a_α value of substituted benzyl radicals using Eq. (3) [10]:

$$\sigma^{\cdot}_{\alpha} = 1 - (a_\alpha)_X/(a_\alpha)_H \tag{3}$$

where the subscripts X and H denote the substituted and unsubstituted benzyl radical, respectively. A substituent with a smaller $\sigma^{\cdot}_{\alpha}$ value would result in a greater a_α value due to a smaller spin delocalization. The $\sigma^{\cdot}_{\alpha}$ values do not correlate with Hammett's polar substituent constants, and the electron withdrawing and donating characters of the nuclear substituents have been shown to decrease and increase, respectively, the a_α value [10,12].

Table 3
$\sigma^{\cdot}_{\alpha}$ for the nuclear substituent, and *Q* and *e* values for monomeric St and substituted St

Substituent	$\sigma^{\cdot}_{\alpha}$ [a]	*Q*	*e*	Reference
m-Cl	−0.007	1.03	−0.36	[13]
m-MeO	−0.001	0.92	−0.58	This work
H	0.000	1.00	−0.80	[13]
p-Cl	0.011	1.33	−0.64	[13]
p-Me	0.015	1.10	−0.63	[13]
p-F	−0.011	1.01	−0.86	This work
p-MeO	0.018	1.53	−1.40	[14]
o-Cl	–	1.28	−0.36	[13]
o-MeO	–	2.57	−1.72	This work

[a] Ref. [10].

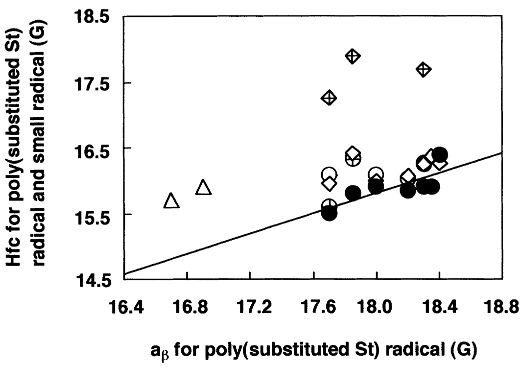

Fig. 3. Plot of a_α or a_β for various radicals versus a_β for polymer radicals from St and substituted styrene: ●, a_α for poly(*m*-substituted St) and poly(*p*-substituted St) radicals; △, a_α for poly(*o*-substituted St) radical; ◇, a_α for benzyl radical; ⊕, a_α for phenethyl radical; ◈, a_β for phenethyl radical; and ○, a_β for cumyl radical. A linear relationship is obtained by plotting a_α versus a_β of polymer radicals from *m*- and *p*-substituted styrenes.

Table 3 lists the values of $\sigma^{\cdot}_{\alpha}$ for the substituents of St. Linear relationships of a_α and a_β for the polymer radical versus $\sigma^{\cdot}_{\alpha}$ in Fig. 4 show that an increase in $\sigma^{\cdot}_{\alpha}$ apparently brings about decreases in a_α and a_β. However, difference between the largest and smallest $\sigma^{\cdot}_{\alpha}$ values is only 0.018, and more significant changes are observed for a_α and a_β values. The polar effects of the *m*-MeO, *p*-MeO, and *p*-F group seem to be responsible for the deviation from the linear relationship.

3.5. Correlation of hfc with *Q*

Q, which is a parameter concerning a monomer based on the *Q*–*e* scheme, could be employed as a measure of resonance stabilization of the radical derived. Although the *Q* values of various nuclear substituted Sts have been compiled [13,14], those of *m*-MeO–St and *o*-MeO–St were not available. The copolymerizations of these monomers with St were carried out to obtain the *Q* and *e* values as shown in Table 3. The values of *Q* and *e* for *p*-F–St were recalculated because too large *e* value has been reported [13].

Fig. 5A shows plots of a_α and a_β versus *Q*. Difference in

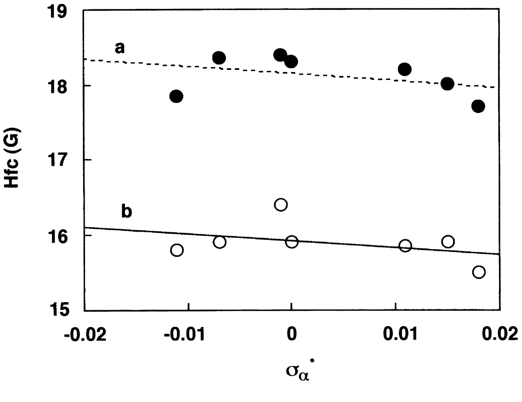

Fig. 4. Plot of: (a) a_α; and (b) a_β for polymer radicals from St and substitute styrenes versus $\sigma^{\cdot}_{\alpha}$. Straight lines are drawn as visual guides.

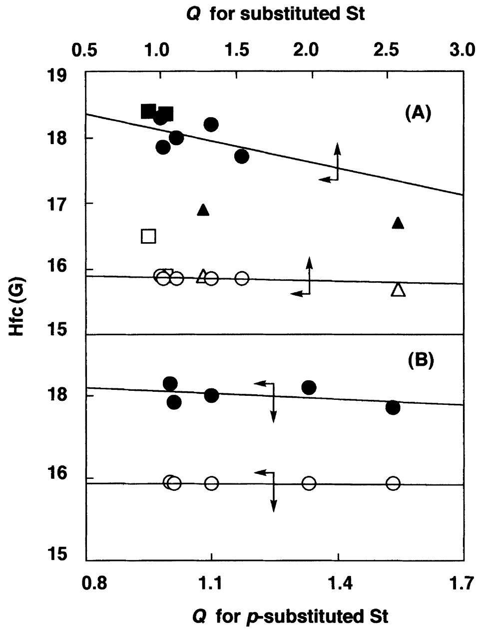

Fig. 5. Plot of a_β for polymer radicals of St and substituted St versus Q (A) and a_β for poly(p-substituted St) radical versus Q (B): ○, a_α for radical from St and p-substituted St; ●, a_β for radical from St and p-substituted St, □, a_α of radical from m-substituted St; ■, a_α for radical from m-substituted St; △, a_α for radical from o-substituted St; ▲, a_β for radical from o-substituted St. Straight lines are drawn as visual guides.

a_α and a_β between the polymer radicals from the monomers of the largest and smallest Q values, 0.35 (Fig. 5A) and 0.15 (Fig. 5B), are comparable to the largest changes in a_α and a_β. Although for the *p*- and *m*-substitued radicals and also for the *o*-substituted radicals fit to the linear relationship as shown in Fig. 5A, a considerable deviation of a_β for the *o*-substituents is noted. While an increase in Q value decreases the a_α and a_β values, the change in a_α value is quite small.

4. Conclusion

The ESR spectra of the propagating radical from nuclear substituted styrenes were recorded in homogeneous systems. It was found that a_α and a_β for the polymer radicals are changed with the type of substituent in limited ranges as well as for structurally similar small radicals. Linear relationships between $\sigma_\alpha^{\cdot}$ and a_α and a_β were obtained. Reasonable correlations between the Q value and a_α an a_β was also found. No prediction of hfcs for the *o*-substituted St radicals based on the substituent constant and the Q value was not available.

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