Macromolecules **1984**, *17*, 1139–1145

whether the observed anisotropy in T_{2L} for the poled material is real or whether it is an artifact of the decomposition procedure.

To summarize, NMR data for poled PVDF/TrFE (52/48 mol %) taken in conjunction with earlier results for the poled material give rise to the following conclusions:

(a) The shift to higher temperatures by 10–15 °C of the "ferroelectric" transition upon poling is confirmed. Additionally, the transition becomes sharper.

(b) In the poled material there is improved crystallographic packing in the ordered regions and there is a weak indication that the average ordered domain size is greater. These observations are consistent with the simple notion that the more compact structures are stabilized upon poling.

(c) Molecular motions in the amorphous regions are probably more constrained below the "ferroelectric" transition temperature in the poled sample.

(d) Chain rotation in the ordered regions is activated as the temperature is increased and this may be intimately associated with the onset of the "ferroelectric" transition.

Acknowledgment. We are grateful to A. J. Lovinger for X-ray data on the copolymer sample.

Registry No. (Vinylidene fluoride)·(trifluoroethylene) (copolymer), 28960-88-5.

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ESR Study on Local Conformations of Polystyrene Spin Adducts Produced by Chlorinated Nitrosobenzene as a Chain-Scission Inducer

O. Watanabe, M. Tabata,* and J. Sohma

Faculty of Engineering, Hokkaido University, Sapporo 060, Japan. *Received June 10, 1983*

ABSTRACT: Polystyrene (PSt) free radicals were produced in benzene solution by addition of 2,4,6-trichloronitrosobenzene (TCNB) followed by slight warming to 35 °C, and the radicals were trapped by TCNB to form spin adducts, from which ESR spectra were observed. On the basis of analysis of the observed ESR spectra, the spin adducts of three different species of PSt radicals, (A) $\sim CH_2-\dot{C}PhCH_2\sim$, (B) $\sim CHPh-\dot{C}H-CHPh\sim$, and (C) $\sim CH_2-\dot{C}HPh$, were identified. The assignments were confirmed by experiments using α-deuterated PSt. A spectral component observed as a double triplet was attributed to the spin adduct of the radical species B and the component was clearly split further into a quintet with small separation of 0.63 G. This quintet was assigned to the coupling with two meta protons in the trichlorobenzene and two additional δ-protons bonded to the carbon separated by three chemical bonds from the nitrogen having the unpaired electron. That is, long-range coupling was demonstrated in this spin adduct. It was found that an oligomer of styrene (St) showed a spectrum which lacked one component and had a different value for the long-range coupling. On the basis of both the McConnell equation and the Barfield equation for the δ-proton coupling, the local conformation of the spin adduct of the radical B, $\sim CHPh-\dot{C}H-CHPh\sim$, is discussed. It is concluded from the analysis of the observed quintet caused by the long-range coupling that the conformation of the TCNB referred to the main chain was fixed but the δ-protons as well as the main-chain carbon at the δ-site undergo hindered rotation among the three fixed positions.

Introduction

It was found recently that 2,4,6-trichloronitrosobenzene (TCNB) as a radical generator induced main-chain scission of poly(methyl methacrylate) (PMMA) in solution.[1] TCNB has two interesting functions; one is homolytic scission of its C–N bond caused by slight warming to produce a chlorinated phenyl radical, which abstracts a hydrogen from a molecule nearby, and the other is to serve as a spin-trapping reagent, which traps radicals to form nitroxide radicals as spin adducts. In the case of PMMA the spin adduct from primary carbon radical, $\cdot CH_2-C(CH_3)(COOCH)_3CH_2\sim$, was identified. This spectral assignment was confirmed by using α-methyl and ester methyl deuterated PMMA and with the aid of computer simulation. The evidence of main-chain scission of PMMA was provided by the observed decrease of molecular weight after addition of TCNB to the PMMA benzene solution. These facts mean that under relatively mild condition, around 40 °C, chemical degradation is induced by the addition of TCNB to break the main chain of polymers in solution to a substantial extent.

Polystyrene (PSt) is a particularly interesting polymer since it is known to undergo typical cross-linking, unlike PMMA, when γ-irradiated;[2] this is important from the viewpoint of industrial application. Therefore, it is worthwhile to investigate the degradation of PSt induced by addition of TCNB in comparison with degradation of PMMA by identifying the species of radicals produced. Analysis of the ESR spectra observed after the addition of TCNB to PSt in benzene solution provided positive evidence for formation of nitroxide radicals (spin adducts) of PSt radicals, (A) $\sim CH_2-\dot{C}Ph-CH_2\sim$, (B) $\sim CHPh-\dot{C}H-CHPh\sim$, and (C) $\sim\dot{C}HPh$.[3] Formation of radicals A and B, which are not direct products of main-chain scis-

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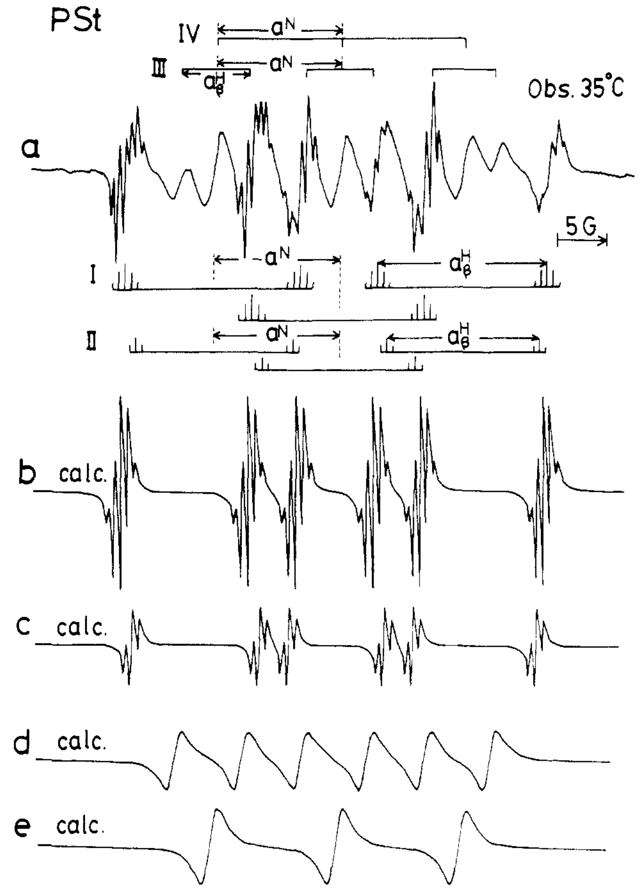


Figure 1. ESR spectrum of PSt radical adduct to TCNB in benzene solution at 35 °C. (b–e) Spectra simulated to those of the spin adducts I, II, III, and IV, respectively, shown in a. The parameters used and the corresponding spin adducts are given in the text and also in Table I.

sion, are in contrast to the behavior of PMMA under the same conditions. Details of the mechanism of PSt degradation induced by added TCNB are described in another report.[3] In this communication, we confine ourselves to finding long-range coupling in ESR spectra of the spin adducts of PSt radicals as well as discussion of the local conformation of PSt radicals deduced from a quantitative analysis of the long-range coupling. The long-range coupling was found in the ESR spectra of the spin adduct of PMMA radical produced by the similar addition of TCNB to the system.[1] In the case of PMMA radicals, multiplets caused by long-range coupling were so complex that quantitative analysis of the multiplets could not be done.

Experimental Section

The PSt sample used in this experiment was a commercial material, manufactured by Wako Pure Chemical Co. Ltd. The molecular weight was determined to be 177 000 by viscosity measurements using benzene as solvent. A sample of α-deuterated styrene monomer was synthesized according to the method of Wall et al.[4] The deuterated monomers were polymerized by using benzoyl peroxide as a radical initiator and the resultant polymer was precipitated twice for benzene–methanol solution in order to eliminate residual monomers and initiator. The 2,4,6-trichloronitrosobenzene (TCNB) was prepared by oxidation of the corresponding aniline by using a conventional oxidation method, followed by sublimation.[5]

Benzene solution of PSt containing TCNB at a known concentration was introduced in the bottom of the ESR sample tube for ESR measurements. Before mixing TCNB powder with the solution, air from the solution was carefully removed by repeated thawing and freezing under high vacuum (ca. 1×10^{-4} Torr) and then sealed off. Details of the experimental procedure are described in the previous paper.[1] ESR spectra were obtained on

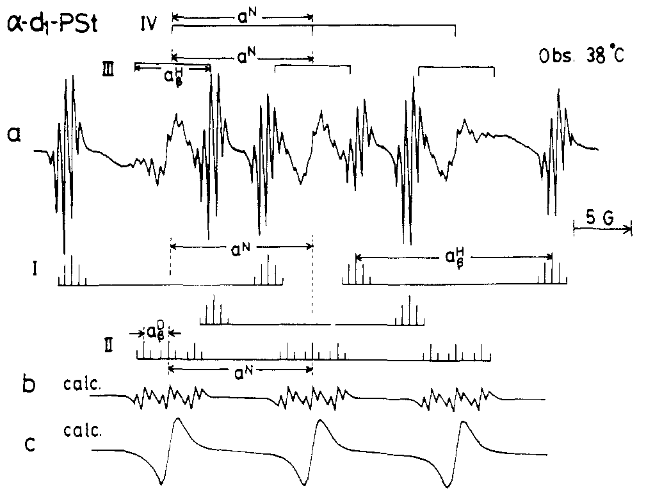


Figure 2. (a) ESR spectrum of PSt-α-d_1 radical adduct to TCNB in benzene solution at 38 °C. (b,c) Spectra stimulated to those of spin adducts I and IIα, respectively, shown in a. The parameters used and the corresponding spin adducts are given in the text and also in Table I.

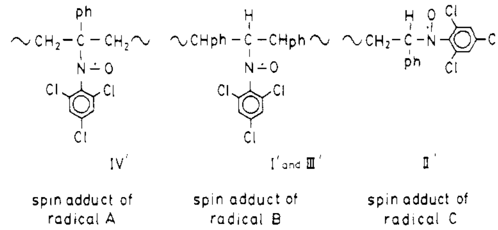


Figure 3. Molecular structures of spin adducts I′, II′, III′, and IV′.

a JEOL-JES-PE ESR spectrometer with 100-kHz modulation. The temperature was controlled by the JEOL temperature control unit and was found to vary no more than ±2 °C. Simulations were carried out by using a modified version of Maruani's program.[6]

Results and Identification of Radicals

A spectrum of negligible intensity was observed from a benzene–TCNB solution (0.12 mol L^{-1}) after slight warming for half an hour. The spectrum shown in Figure 1a was observed at 35 °C from the benzene solution of PSt (50 mg/mL) and TCNB (0.12 mol L^{-1}) after warming to 35 °C for 20 min. No ESR spectrum was observed from the same sample without warming. This observed spectrum consists of four different components represented by stick digrams I, II, III, and IV as shown in Figure 1a. On warming up to 50 °C, component II decayed first and this disappearance provided good evidence that the spectrum was a mixture of components. Simulations of observed spectral components, I, II, III, and IV were carried out. The best fit spectra of I and II are shown in Figure 1b,c. The best simulation of spectrum I was carried out by use of the following constants: isotropic hyperfine coupling of 12.5 G for one nitrogen (1 N) with $I = 1$, 17.3 G for one β-proton, which corresponds to a proton bonded to a β-carbon separated by one chemical bond from the nitrogen having the unpaired electron (see Figure 5), and 0.63 G for four protons and a Lorentzian line width of $\Delta H_{\mathrm{msl}} = 0.33$ G. The agreement between experimental and simulated spectra is satisfactory. Since the coupling with one β-proton was observed in addition to the nitrogen coupling, component I was assigned to a spin adduct formed by trapping a secondary carbon radical, $\sim\dot{C}H\sim$. Each peak of the double triplet of component I is split into a quintet having a small separation of 0.63 G and relative intensities, 1:4:6:4:1, as shown in both the stick diagram and simulated

Table I
Summary ESR Data on Polystyrene Nitroxide Radicals

compd[a]	a_N^H	a_β^H	a_m^H	a_δ^H	g	ΔH_{msl}	ϕ, deg	ϕ', deg	θ_1, deg	θ_2, deg
RN(–O·)CH< (I)	12.46	17.25	0.63	0.63	2.0066	0.33	37	157	51	291
RN(–O·)CH< (II)	12.46	15.45	0.63		2.0066	0.33	41			
RN(–O·)CH< $(\mathrm{II})_\alpha$	12.46		0.63		2.0067	0.33				
RN(–O·)CH< (III)	12.46	6.58			2.0066	1.5	60			
RN(–O·)C< (IV)	12.46				2.0067	1.5				
RN(–O·)CH< (I_8)	12.40	17.92	0.63	0.42	2.0071	0.7	35	155	57	297
RN(–O·)CH< (III_8)	12.20	6.47			2.0071	2.0	61			
RN(–O·)C< (IV_8)	12.40		0.63	0.42	2.0072	0.4				

[a] R = 2,4,6-trichlorophenyl.

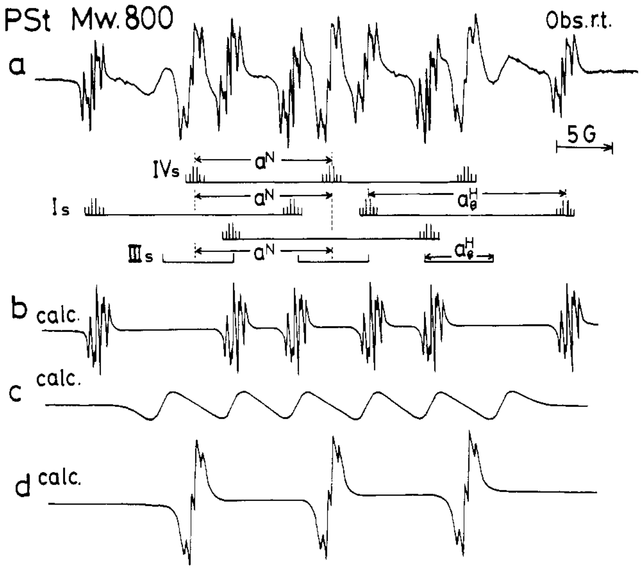


Figure 4. (a) ESR spectrum of polystyrene oligomer (n = 8) adduct to TCNB in benzene solution at room temperature. (b–d) Spectra simulated to those of spin adducts I_8, III_8, and IV_8, respectively, shown in a. The parameters used are given in Table I.

spectra. The relative intensities indicate an equal coupling with four protons, two of which are the meta protons in the chlorinated phenyl ring because of their known coupling constant.[7] The assignment of the other two protons will be discussed later. The simulated spectrum for the component II was calculated by using an isotropic hyperfine coupling of 12.5 G (one nitrogen, N), 15.5 G (one β proton, H_β), 0.63 G (two meta protons), and a Lorentzian line width of ΔH_{msl} = 0.33 G. This spectrum, Figure 1c, fits satisfactorily with component II in the observed spectrum. Component II was attributed to a spin adduct of another radical of the secondary carbon type, $\sim\dot{\mathrm{C}}\mathrm{H}\sim$, since this spin adduct shows coupling with one H_β. Component III is a broad double (6.6 G) triplet (12.5 G), which was also attributed to a spin adduct of another radical of secondary carbon type showing different coupling constants and no multiplicity with small separation. The simulated spectrum for this component is in Figure 1d. Component IV is a simple triplet (12.5 G), for which an adduct of a tertiary carbon radical having no β proton is responsible, and the best simulated spectrum is shown in Figure 1e. The tertiary carbon radical produced from PSt is the species (A) $\sim\mathrm{CH_2}\text{–}\dot{\mathrm{C}}\mathrm{Ph}\text{–}\mathrm{CH_2}\sim$. The ESR parameters used for the simulations are listed in Table I. In the assignments described above the spectral components I, II, and III are attributed to the different spin adducts of the same type of radicals, namely the secondary carbon radical, $\sim\dot{\mathrm{C}}\mathrm{H}\sim$. Two different radical species of the same type, the secondary carbon radical, could be produced from the mother molecule of PSt, that is, $\sim\mathrm{CHPh}\text{–}\dot{\mathrm{C}}\mathrm{H}\text{–}\mathrm{CHPh}\sim$ (B) and $\sim\mathrm{CH_2}\text{–}\dot{\mathrm{C}}\mathrm{HPh}$ (C). In order to make unique attribution of the spectral components I, II, and III to radical species α-deuterated polystyrene was used under the same experimental conditions. The spectrum shown in Figure 2a was observed when a benzene solution of the α-deuterated PSt, $\text{–(–CDPh–CH}_2\text{–)–}_n$, added to TCNB was warmed up to 38 °C. A comparison between the two spectra, Figures 1a and 2a, indicates that component II was changed but no other components were affected by replacement of the α-proton in PSt with deuterium, as illustrated with stick diagrams. The spectral simulation was carried out by assuming the ESR parameters listed in Table I, and the calculated spectrum for components II is shown in Figure 2c. The agreement between the observed and calculated spectra was satisfactory. The drastic change in component II by α-deuteration of the PSt leads us to conclude that the spin adducts responsible for component II involve the α-proton in PSt, as H_β, and the secondary carbon radical including the α-proton in PSt is the radical species C, $\sim\mathrm{CH_2}\text{–}\dot{\mathrm{C}}\mathrm{HPh}$, which is generated by chain scission. The corresponding spin adduct is II′, shown in Figure 3. On the other hand, the fact that no changes of the components I and III were caused by the α-deuteration indicates that these components originate not from species II′ but from species I′ and III′, as illustrated in Figure 3. Although two different double triplets, namely, the double-triplet quintet I and the broad double triplet III, were produced, we attributed them to the same type of spin adduct I′ and III′. The differences in the coupling constant a_β^H of the two components as well as spectral structures of small separation suggest some variation in the structure of the two radicals classified as the same type B.

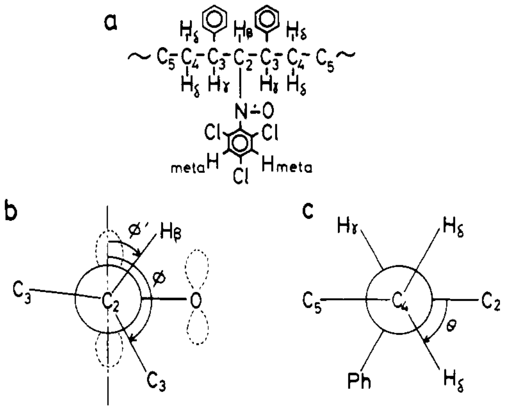


Figure 5. (a) Molecular structure of spin adduct I′. Molecular projections on a plane perpendicular to the C_2–N bond (b), and C_3–C_4 bond (c).

Styrene oligomer (degree of polymerization n = 8) was employed in order to study the molecular weight dependence of the coupling constants. PSt of low molecular weight, M_W = 800, was warmed with TCNB in benzene solution under the same experimental condition. The resultant spectrum is shown in Figure 4. This spectrum can be decomposed into the three components, I_s, III_s, and IV_s, as shown in Figure 4. The spectral parameters were obtained by computer simulation assuming data tabulated in Table I. The main structure of the component I_s is a double triplet, in which the separations of one nitrogen as well as one proton are nearly the same as in component I. However, the multiplet structure, a small double triplet of each peak of the double triplet, is different from the other large double triplet, and the small triplet with a separation of 0.63 G originating from coupling with two meta protons and one more proton causes an additional splitting of the doublet, as shown by stick diagram I_s in Figure 4. On the other hand, the broad double-triplet III_s is almost the same as component III, which is attributed to the spin adducts of the secondary carbon radical B. The simple triplet component IV_s can be assigned to the spin adduct due to tertiary carbon radical A. However, it is worthy of notice that each peak of the triplet splits into a double triplet with smaller separation as illustrated by stick diagram III_s in Figure 4. The smallest splitting observed, namely, 0.42 G for component I_s and III_s, are attributable to the same origin—long-range coupling—which causes the quintet with a separation of 0.63 G in component I of normal PSt. Thus, one may summarize the effect of low molecular weight as follows: (i) similar components to those of the normal PSt, I_s, III_s, and IV_s, appear, (ii) component II is negligibly small, and (iii) the multiplets with small separation of I_s and IV_s, which are caused by the long-range coupling, are different from those of normal PSt.

Origin of the Multiplets with Small Separations

One of the characteristics of ESR spectra from the TCNB spin adducts was appearance of the multiplets having smaller separations, either 0.63 G or 0.42 G. The multiplets appeared as a quintet for normal PSt, a double triplet for St oligomer, and complex structures for PMMA.[1] The two meta protons in the chlorinated phenyl of TCNB are certainly one origin of the multiplet because the observed coupling constants are close to the literature values.[7] The quintet requires coupling with two other equivalent protons, which gives a separation equal to that of the meta protons. For the double triplet in the oligomer a coupling with one more proton is required to give the smaller separation of 0.42 G. The small separation, less than 1 G, indicates a coupling with protons bonded with the carbons separated by two or more chemical bonds, that is, either γ or δ protons, because the β protons show a separation larger than 6 G, as shown in Table I. The ESR spectrum observed from the α-deuterated PSt showed an identical multiplet structure, that is, the quintent in component I, as shown in Figure 2. This fact indicates that the α-hydrogen in PSt, which is the proton at the γ-site from the unpaired electron at the nitrogen in spin adduct I′ in Figure 3, has no effect on the quintet with the separation of 0.63 G. Thus, it is most reasonable to attribute the quintet to the two protons at the δ-site in addition to the coupling to the meta protons in the chlorinated phenyl of TCNB. Such long-range coupling was reported for the propagating radicals of vinyl monomers by Fischer[9] and Yoshida and Rånby.[8] The separation of the multiplets found in the spin adduct of radical B is nearly the same as the values of the separation caused by the coupling with the δ-protons in their reports. Based on these facts it was concluded that the quintet with a separation of 0.63 G was caused by the coupling of the two meta protons and two δ-protons in spin adduct I′, which is the adduct of the radical species B of PSt. The origin of the double triplet due to the long-range coupling observed from the styrene oligomer was not clear, although one other proton at the δ-site is presumably responsible for the doublet with the separation of 0.42 G. Quantitative analysis of the spectrum was then performed not for the St oligomer but for the normal PSt of high molecular weight, and this quantitative analysis provides information on the local conformation of spin adduct I′ of PSt.

Conformation of Spin Adduct I′ of PSt Radical B Deduced from the Quantitative Analysis of the ESR Spectrum

Spectral component I (see Figure 1a,b) of the observed ESR spectrum of PSt, which was chemically degraded by TCNB, was attributed to the spin adduct I′ of the radical species B, $\sim$CHPh–$\dot{\mathrm{C}}$H–CHPh$\sim$ (see Figure 3). The doublet with separation 17.3 G was believed to be caused by coupling of the β proton with the unpaired electron. The quintet with the small separation was assigned to the coupling of the two δ-protons as well as the two meta protons, which showed equal coupling within experimental error. The relation between the conformation and the splitting with a β-proton is well described by the Heller–McConnel equation,[11] that is,

$$a_\beta{}^{\mathrm{H}} = A + B\cos^2\phi' \qquad (1)$$

where $A \cong 0$ and $B \cong 26.8$ G[12] and ϕ' is the angle between the projection of both the C_2–H_β bond and the P_π orbital of the unpaired electron on a plane perpendicular to the N–C_2 bond, as shown in the Newman projection in Figure 5b. For the observed value of 17.3 G for $a_\beta{}^{\mathrm{H}}$ of the component the angle ϕ' was determined as 37°. Since the C_2–C_3 bond deviates by either 120° or 240° from the C_2–H_β bond on the projection plane, the directions of the main-chain in this spin adduct are determined as either 157° or 277°, as shown in Figure 5b. This means that the local conformation of the main chain in the vicinity of the unpaired electron is now established with regard to the C_2–C_3 directions.

The splitting caused by the long-range coupling was studied in detail for both the aliphatic radicals and the nitroxide radicals by Barfield.[13] He assumed a spin polarization mechanism for the long-range coupling and proposed equations connecting the conformation and the long-range couplings due to the γ-proton (H_γ) and δ-proton (H_δ) which are bonded to the carbons separated by either two or three bonds, respectively, from the site of unpaired electron. The expressions for $a_\delta{}^{\mathrm{H}}$ are described as

$$a_\delta{}^{\mathrm{H}} = -8.42K(\theta)\cos^2\phi \qquad (2)$$

$$K(\theta) = -0.287\cos^2\theta + 0.016\cos\theta + 0.015 \qquad (3)$$

where the angles ϕ and θ are defined as those of the projections shown in Figure 5b,c. It is reasonably assumed that these equations are applicable to spin adduct I′, because there are no great differences in the chemical bond in this spin adduct from those in the aliphatic radicals and cyclohexyliminoxyl radical. On the basis of these assumptions, the angle ϕ in eq 2 is taken as either one of the angles of the C_2–C_3 bonds with regard to the P_π orbital of the unpaired electron, as shown in Figure 5b. The angle ϕ was determined as either 157° (=37° + 120°) or 277° (=157° + 120°) from the observed value $a_\beta{}^{\mathrm{H}}$, as discussed above.

Let us first consider the angle ϕ to be 277°. Both this value of ϕ and the observed value $a_\delta{}^{\mathrm{H}} = 0.63$ G were inserted into eq 2 and then $K(\theta)$ was determined. But the

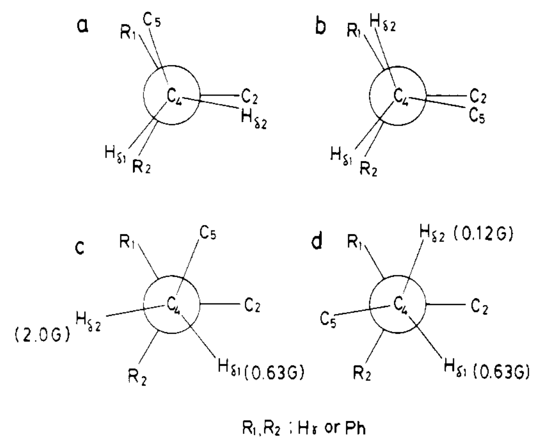


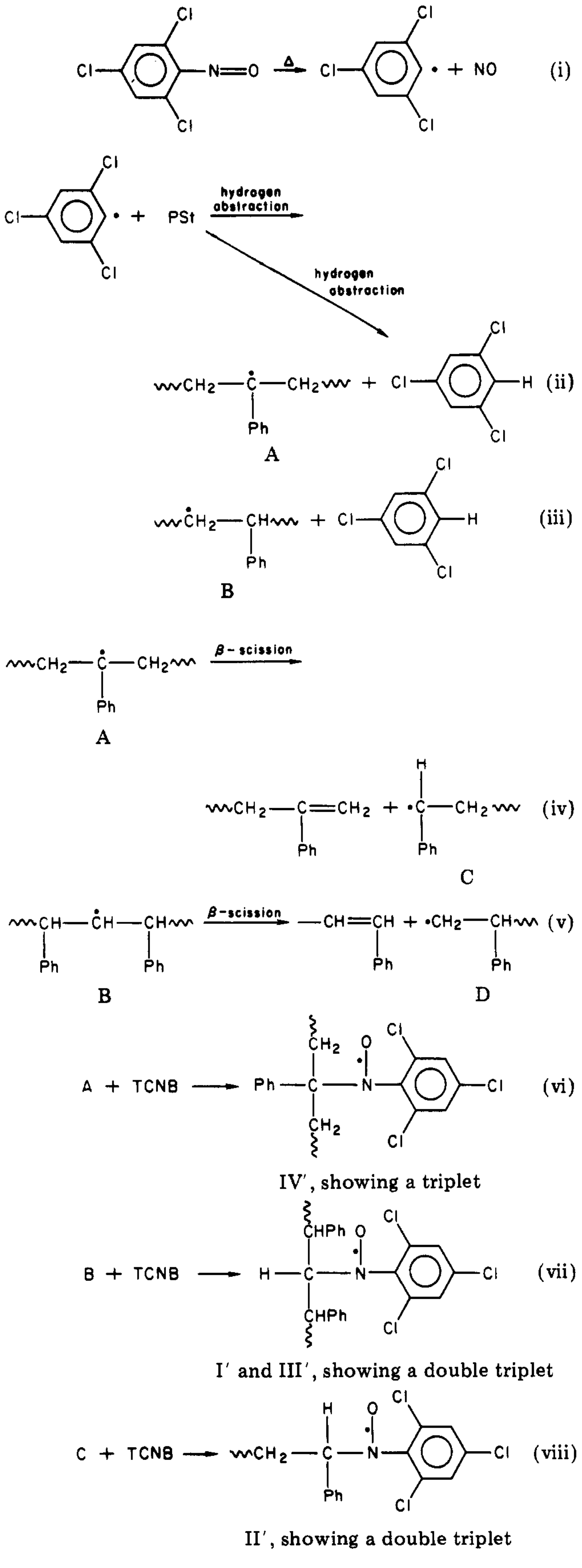
Figure 6. Various conformations of the spin adduct I′.

obtained value of $K(\theta)$ gives us an imaginary value for the angle θ. Since the imaginary value has no physical meaning this possibility of $\phi = 277°$ was ruled out. This conclusion means that of the four δ-protons shown in Figure 5a two of them, which are bonded to carbon C_4 connecting to carbon C_3 in the direction of $\phi = 277°$, do not have the observed value of $a_\delta^H = 0.63$ G. Thus we may direct our attention only to the δ-protons of the PSt main chain making a projection angle of 157°.

By insertion of $\phi = 157°$ and the observed value 0.63 G as a_δ^H into eq 2, the angles were determined as 51° and 125°, as solutions of eq 3. There are two conformations corresponding to the two values 51° and 125° for the angle between the bond C_4–H_{δ_1} and the bond C_3–C_2 on the projection plane perpendicular to the bond C_3–C_4, where H_{δ_1} means one of the δ protons, which is bonded with carbon C_4 and produces a coupling of 0.63 G. As shown in Figure 6a,b, one of the two δ protons is situated very close to the adjacent phenyl (either R_1 or R_2 in Figure 6a,b), and steric interaction must be larger in such an eclipsed conformations. For this reason it is very unlikely that these conformations are more stable than the other one corresponding to $\theta = 51°$. Thus, the conformations corresponding to $\theta = 51°$ (Figure 6c,d) are reasonably assumed to be favorable from the viewpoint of steric hindrance.

The experimental results demonstrate that the two δ-protons produce an equal splitting, as $a_\delta^H = 0.63$ G. The steric situation derived from the analysis based on the eq 1–3 was determined as either of the two conformations shown as Figure 6c,d in which the H_{δ_1} is the δ proton producing the splitting of 0.63 G. In these conformations the other δ proton, H_{δ_2}, orients in a fixed direction described as θ_2 from the directions C_3–C_2. θ_2 is either 171° (=51° + 120°) (Figure 6c) or 291° (=171° + 120°) (Figure 6d). The splitting caused by the H_{δ_2} was estimated as either 2.0 G for $\theta_2 = 171°$ or 0.12 G for $\theta_2 = 291°$. Neither value exactly equals the observed value of 0.63 G. In other words, two of the δ-protons do not produce an equal coupling, which was concluded from the analysis of the experimental data, exactly speaking. However, the estimated value of 0.12 G is on the same order of magnitude as the observed value of 0.63 G. Remembering the assumption introduced into this quantitative analysis, one may say that the estimated value of 0.12 G is not completely wrong and the two δ-protons interact nearly equally with the unpaired electron through long-range coupling in the case of the fixed conformation of $\phi = 157°$, $\theta_1 = 51°$, and $\theta_2 = 291°$, as shown in Figure 6d. It may be noted that this conformation is favorable from the viewpoint of steric hinderance, because the main-chain carbons, C_5 and C_2, are situated in the opposite direction. If the local conformation in the vicinity of the unpaired electron of the spin adduct I′ is assumed to be frozen, a favorable conformation is now uniquely determined with some approximation from the quantitative analysis of the component I′ in the observed spectrum, as d in Figure 6.

Scheme I



Values for the angle ϕ and ϕ' calculated from the observed $a_\beta{}^H$ in the other component by using eq 1 are listed in Table I.

Discussion

It is known[1,3] that homolytic cleavage of the NO group from 2,4,6-trichloronitrosobenzene is induced by slight warming in the benzene solution, producing a chlorinated phenyl radical. This phenyl radical abstracts a hydrogen from an adjacent polystyrene molecule to generate a polymer radical. In the case of high molecular weight PSt four spectral components, I, II, III, and IV, were found to be produced by addition of TCNB. Components I and III were assigned to the spin adducts from the secondary carbon radical B. Component II was attributed to the spin adduct of the main-chain scission radical C of the PSt mother molecule. Component IV is assigned to the spin adduct of the tertiary carbon radical A. Remembering the hydrogen abstraction caused by the chlorinated phenyl radical, one may safely assume that radical species A and B were generated by direct hydrogen abstractions from the PSt main chain. The secondary carbon radical responsible for component II is generated by β-scission of radical A. This mechanism is supported by analogous main-chain scissions produced by various means, such as mechanical destruction,[14] ionizing degradation,[10] ultrasonic irradiation,[15] and high-speed stirring.[16] The reaction scheme of PSt which is induced by the addition of TCNB is described in Scheme I. It is well-known that the tertiary carbon radicals are produced from solid polystyrene under γ-irradiation in vacuum.[17,18] Radical A's are thought to couple with each other to form cross-link. Since TCNB traps radical A in benzene solution making the spin adduct IV′ of tertiary carbon radical, TCNB might be called a cross-linking inhibitor. If β-scission through reaction iv really occurs, primary carbon radical D is produced. However, no positive evidence for the presence of radical species D was obtained in our experiments. This result is notably different from those obtained for the PMMA–TCNB system,[1] in which formation of the primary carbon radical $\cdot CH_2\text{-}C(CH)_3(COOCH_3)\sim$ was evidenced by ESR. If main-chain scission of PSt was induced through the processes initiated by the action of TCNB, the decrease of molecular weight of PSt should be caused by the addition of the TCNB into the polymer solution followed by warming, and this was the case.[3]

The local conformation of spin adduct I′ was uniquely determined from quantitative analysis of the ESR spectrum based on both the McConnell and Barfield equations. The ESR spectrum was observed from spin adduct I′ in the liquid phase. It is natural to assume that a polymer molecule undergoes micro-Brownian motion and rotation about any C–C bond in the main chain in the liquid phase at this temperature. The micro-Brownian motion of a polymer seems to be incompatible with the fixed conformations deduced in the preceding section. The C_4–C_5 bond is permitted to oscillate rotationally about the C_3–C_4 bond in Figure 6. If the frequency of this rotational oscillation is less than ca. 10^3 Hz, which corresponds to $a_\delta{}^H = 0.63$ G, the coupling constants of H_{δ_1} and H_{δ_2} appear a little different as 0.63 G and 0.12 G, and the conformation is regarded as a fixed one ($\theta_2 = 291°$), as shown in Figure 6d. If the frequency of the rotation about the axis of C_3–C_4 bond is much higher than 10^3 Hz, the coupling effectively observed is the averaged one of the four coupling constants, 0.63 G, 0.12 G, and 2.0 G corresponding to the three different directions of the two δ-protons, that is, $^1/_4(0.63 + 0.63 + 0.12 + 2.0\ \text{G}) = 0.85$ G. If such rotation occurs, the two δ-protons become equivalent and the coupling constant of the two equivalent δ-protons is 0.85 G, which is not very different from the observed value 0.63 G. Thus, such rapid rotation about the C_3–C_4 bond is compatible with the free rotation of C–C bonds in the main chain as well as equal coupling with the two δ-protons. Although we have no experimental evidence by which one can make a choice between the fixed conformation and the rapid rotation, the rapid rotation about the C_3–C_4 bond may be more reasonable than the fixed conformation because of its compatibility with the micro-Brownian motion as well as the equal couplings with the two δ-protons. Such a rapid rotation may be not permitted for the bond C_2–C_3 because $\phi' = 37°$ is the only value for the direction of the β-proton which agrees with the observed coupling constant $a_B{}^H$. Thus, rotation about the bond N–C_2 is strongly hindered. This rotation is not that on the C–C bonds in the main chain of PSt but the rotation of the dangling bulky group of TCNB. Thus, it is not hard to imagine that such a bulky group may align itself to fit the limited space surrounded by the adjacent phenyl groups of PSt. The consideration described above leads us to believe that the directions of the C_2–C_3 bonds are fixed, except for the rotational oscillation with a small amplitude about this fixed conformation, because of the steric hindrance of the bulky group, i.e., the TCNB moiety, but the rotation about the bond C_3–C_4, which is the rotation of the C–C bond in the main chain, is more rapid than 10^3 Hz. It should also be stressed that the conformation deduced in this study is not for the PSt molecule but for the spin adduct of the PSt radical. Thus, it is reasonable to assume that the conformation of an ordinary PSt molecule is strongly perturbed by the bulky TCNB, and one should not extend this conclusion to the ordinary PSt molecules. However, no experimental technique other than ESR could provide similar information on the local conformation of a polymer molecule in a liquid phase as well as the rotational frequency of the C–C bonds in the main chain. It is worth mentioning that similar long-range coupling due to the δ-protons was detected for the spin adducts of other polymers, such as poly(α-methylstyrene), polyisobutylene, and atactic polypropylene in solution.

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Concentration and Counterion Dependence of Cluster Formation in Sulfonated Polystyrene

Judith A. Lefelar*,[†] and Robert A. Weiss

Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268.
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ABSTRACT: Based on a crystal closest packing approach, models are developed which show that, in carboxylated ionomers, anion packing is determined by the counterion, while in sulfonated ionomers the anion packing is independent of cation. However, in sulfonated ionomers, there is a greater cluster density for divalent than for monovalent cations as a consequence of how the counterion coordinates to the sulfonate ions. SAXS data for the zinc and sodium salts of lightly sulfonated polystyrene (SPS) are analyzed in order to elucidate the cq/a relationship for these materials and to test the proposed model. Results suggest that there is a denser packing in the zinc salts.

Introduction

In the past 10 years several books, reviews, and symposia[1-5] have considered the structure and properties of ionomers. Much of the research on these materials has concentrated on the nature of the ionic cross-link, and evidence for microphase separation of ionic domains has come from a variety of experimental techniques, the most common being small-angle X-ray scattering (SAXS).[6-12] Many studies indicate that there is a certain critical concentration of ionic groups above which properties change, and this concentration is dependent upon the anion and cation used as well as the dielectric constant of the matrix polymer.[13-20]

Lundberg and Makowski[21] and Rigdahl and Eisenberg[22] have concluded from rheological studies that the effect on physical properties is several orders of magnitude stronger for the sulfonate ions than for carboxylate ions. Weiss and Agarwal[23] found that the melt viscosity of a propylene–acrylic acid graft copolymer was higher for the Na^+ than for the Zn^{2+} salts. In related work Navratil and Eisenberg[24] found that for styrene–methacrylic acid ionomers, the rate of stress relaxation was higher for the Ba^{2+} salts than for the Na^+ salts.

Otocka et al.[25] suggested that in mediums of low dielectric constant, such as a hydrocarbon matrix, salts with divalent cations would exist as simple contact ions while monovalent salts would exist as dipole–dipole pairs. It was further suggested that in the case of the monovalent salt the nature of the dipole–dipole attraction would be such that considerable separation could occur while preserving the integrity of the dipole–dipole bond. Otocka, as well as other researchers, predicted that one factor that would influence ionic bonding was the tendency of group 1 cations to six-coordination.

Eisenberg et al.[2] demonstrated that the critical concentration for various counterions could be related if the ratio cq/a, where c is the anion concentration, q is the charge on the cation, and a is the distance separating the centers of charge, is considered. For example, when the glass transition temperature, T_g, was plotted vs. cq/a for various counterions of ethylene–acrylic acid ionomers, the data were collinear. In a similar vein, Gierke, Munn, and Wilson[26] report that the SAXS peak intensity for group 1 cations of Nafion is a linear function of cq/a.

Using the results of past research on model compounds,[27] as well as our own results of SAXS studies of sulfonated polystyrene ionomers, we have developed a conceptual model that accounts for the observed differences in ionomer physical properties for several anions and cations. Schematic representations were developed to model the carboxylate and the sulfonate ions. The cations were considered to be hard spheres of the appropriate ionic radius. The various ways of bonding the anions and cations were considered and plots of SAXS data for the SPS salts were made for each type of bonding as a function of cq/a.

Discussion

The carboxylate anion is planar with only one edge available for bonding to a cation, as shown in Figure 1. Only one bonding length, 0.53 Å from the carbon atom to the midpoint between the oxygen atoms, need be considered. However, there are a number of ways the planar ions can be arranged in layers to coordinate with cations. At worst the ions might be randomly distributed with reference to each other. At best the ions will be equidistant from each other and from the cation.

In Figure 2a a scheme is shown in which the oxygen atoms of the anions are packed in two parallel hexagonally packed layers, with one layer being slightly displaced from the other. The scheme shown in Figure 2b is one in which the hexagonal layers are displaced so that one layer interweaves the other. In Figure 2a a univalent sodium cation fits into the six-coordinated trigonal-bypyramidal hole between the anion layers, as occurs in $NaH(CH_3CO_2)_2$,[27] while in Figure 2b a divalent zinc cation fits into the six-coordinated hole, similar to the structure of $Zn(CH_3CO_2)_2 \cdot 2H_2O$.[27]

Clearly, the array with the small divalent cation is more densely packed as the anions are both closer within a layer and between layers. However, when there is a 1:1 ratio of anions to cations, as in Figure 2a, more anions will have to be shared by cations in order to achieve six-coordination than when the anion to cation ratio is 2:1, as in Figure 2b. Therefore, when the cluster is stressed, more interactions need to be overcome to remove ions from the ionic cluster

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[†] Present address: Monsanto Polymer Products Co., Springfield, MA 01151.