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Nuclear Magnetic and Dielectric Relaxation of Poly(styrene oxide) in Dilute Solution

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ABSTRACT: Carbon-13 spin-lattice relaxation times of poly(styrene oxide) in chloroform-*d* and benzene-d_6 solution have been measured at 15 MHz as functions of molecular weight, concentration, and temperature. As previously observed for poly(styrene sulfide) by Cais and Bovey, both segmental backbone and phenyl-group twisting motions are more rapid than in polystyrene. Observations of the backbone motions were also made by dielectric time-domain reflectometry in benzene solution, reinforcing the NMR results. Phenyl and backbone motions of several styrene-related polymers are compared on the basis of a single uniform model.

Introduction

Many investigations have been conducted on the dynamics of polystyrene and several of its derivatives in dilute solution by means of dielectric relaxation,[1-8] magnetic relaxation,[9-17] and fluorescence depolarization[18] methods. Most of these studies lead to essentially similar conclusions regarding the rates of segmental reorientation in the chain backbone, although a detailed picture of the motions themselves remains elusive.

The situation is less clear with respect to a possible twisting motion ("internal rotation") of the phenyl substituent about its C_1–C_4 axis. Qualitative evidence for such a motion is seen in dielectric[5] and ^{19}F NMR relaxation[16] behavior of poly(fluorostyrenes) and in ^{13}C relaxation[9,12-14] and ^{2}D relaxation[15] data for the parent polymer as well as for poly(4-vinylpyridine).[17] In all cases the twisting motion is as slow as, or slower than, the backbone segmental rearrangement. Some investigators have considered this motion to be a limited torsional oscillation, while others have favored a two-minimum hindered rotation model. Existing semiempirical calculations with either stiff[19] or flexible[20] valence angles indicate strong steric interactions between neighboring phenyl groups and therefore predict that the amplitude of the twisting motion in polystyrene must remain low and impeded by high barriers, except in relatively rare conformations.

Relief of steric crowding by interjection of foreign chain atoms could be expected to facilitate the phenyl twisting motion, and this is indeed found in the ^{13}C NMR studies of Gronski et al.[21] on styrene/butadiene copolymers and of Cais and Bovey on poly(styrene peroxide)[22] and poly(styrene sulfide).[23] In the present paper another example is offered, that of poly(styrene oxide), hereafter PSO, also called poly(phenyloxirane). From ^{13}C spin-lattice relaxation times correlation times are evaluated for both backbone and phenyl twisting motion, and the former motion is also investigated by means of the TDR method of dielectric measurement. The various data on the phenyl-group motion are then intercompared by application of a single uniform dynamical model.

Experimental Section

The polymer was made by the procedure of Allen, Booth, and Hurst.[24] Freshly distilled styrene oxide (Aldrich) was polymerized in dioxane at 60 °C under vacuum with the following reagent concentrations: styrene oxide, 4.3 M; diethylzinc, 0.143 M; water, 0.114 M. The diethylzinc had been prepared[25] from zinc, ethyl bromide, and ethyl iodide. Subsequent fractionation was performed in toluene/hexane at 30 °C and nine fractions were collected. The polymer is presumed[24] to have a predominantly isotactic structure. Intrinsic viscosities in chloroform and toluene for five fractions are given in Table I, together with molecular weights based on the published correlation of Allen and coworkers[26] for the latter solvent.

Table I
Intrinsic Viscosities and Molecular Weights of Poly(styrene oxide) Fractions

fraction no.	[η] in dL/g at 25 °C in $CHCl_3$	[η] in dL/g at 25 °C in toluene	$M_v \times 10^{-3}$
F2	0.497	0.436	93
F5	0.271	0.212	36
F7	0.117	0.099	13
F8	0.078	0.065	7.8
F9	0.049	0.042	4.4

Table II
T_1 for PSO F2 in $CDCl_3$

temp/ °C	concn/ % (w/w)	T_1/ms para	meta	ortho	methine	methylene
10	3.9	139	173	174	125	
	6.5	128	174	178	120	81
	10.2	121	148	148	110	
	20.0	92	119	117	93	52
36	3.9	233	325	323	252	113
	6.5	231	327	319	235	120
	10.2	230	289	285	216	
	20.0	172	226	227	145	

For the NMR measurements, chloroform-*d* or benzene-d_6 solutions of PSO were prepared by weight in 10-mm NMR tubes, which were sealed with a minimum of vapor space (to minimize "bumping" at higher temperatures) after five cycles of freezing, pumping, flushing with dry N_2, and thawing to remove oxygen. Spin-lattice relaxation times T_1 for ^{13}C nuclei were obtained by the standard inversion-recovery pulse sequence method at a frequency of 15.04 MHz in a JEOL 60Q spectrometer, with complete noise decoupling of the protons. The magnetic field was locked on the deuterium resonance, and reproducibility of T_1 was better than 10%. Overhauser enhancements were evaluated from the ratio of peak areas under conditions of complete proton decoupling and under gated decoupling only during data acquisition following each pulse. In all cases the NOE values were equal within experimental error to the extreme-narrowing limit of 2.99. Temperatures were varied over the range −2 to +76 °C and were controlled to within 1 °C.

Complex dielectric permittivities at 20 °C in 5.0% (w/v) benzene solutions were obtained for fractions F3 and F4 by a recently developed time-domain reflectometry difference me-

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Table III
Observed ^{13}C Spin-Lattice Relaxation Times for Poly(styrene oxide) in $CDCl_3$ [a]

temp/ °C	fraction	T_1/ms (±10%) para	meta	ortho	methine	methylene
76	F2	517	655	680	497	
	F5	519	709	701	480	
	F7	480	641	641	468	230
	F8	524	714	734	480	249
	F9	553	678	699	481	
64	F2	441	583	573	440	225
	F5	404	580	577	420	222
	F7	413	554	551	415	222
	F8	422	574	571	418	227
	F9	486	591	580	434	
50	F2	367	460	442	348	165
	F5	395	480	498	376	
	F7	396	472	464	376	164
	F8	385	472	483	327	200
	F9	415	553	564	375	176
36	F2	231	327	319	235	120
	F5	239	318	325	230	142
	F7	253	329	320	211	161
	F8	237	330	322	238	
	F9	317	375	389	260	118
24	F2	196	232	246	174	102
	F5	199	253	249	186	104
	F7	199	256	265	170	108
	F8	209	274	272	166	
	F9	216	304	312	197	
10	F2	128	174	178	120	81
	F5	134	168	171	136	66
	F7	140	171	176	142	67
	F9	175	214	213	143	
−2	F2	100	135	131	113	45
	F5	105	127	125	105	
	F7	103	135	131	95	66
	F8	114	143	143	105	
	F9	126	158	161	110	50

[a] Concentration: 6.5% (w/w).

thod.[27,28] The results for the two fractions coincide to within experimental precision.

Results and Discussion

Spin-lattice relaxation times for fraction F2 in chloroform were evaluated over a considerable range of concentration at two temperatures, as shown in Table II. The assignment of peaks in the NMR spectrum to the five types of carbon atoms (para, meta, and ortho ring carbons; methine and methylene backbone carbons) is unambiguous and follows that for poly(styrene sulfide).[23] It is seen that the data at the two lowest concentrations agree to within the reproducibility (~10%) of T_1; therefore the other samples were measured at 6.5% (w/w) concentration and the results taken to be dilute-solution values. These are shown for five fractions and seven different temperatures in Table III. Fraction F3 was also measured in benzene at 12.5% (w/w) and 36 °C.

A glance at the figures in Table III reveals certain general features of interest: (a) The values of T_1 for ortho and meta carbons are perceptibly longer than those for the para carbon, giving unequivocal evidence for phenyl-group rotation. (b) The relaxation times for ortho and meta carbons are the same to within experimental precision, as expected from dipole–dipole relaxation involving only immediately bonded protons and a reorientation about the C_1–C_4 axis. (c) The values for para and methine carbons are substantially the same, although those for para are more often the larger. The small difference is ignored in subsequent calculations. (d) The methylene carbon data are less precise than the others, but the value of T_1 is roughly half as great as for the methine carbon, as would be expected if both groups move rigidly together in the basic segmental reorientation processes. These features are similar to those of poly(styrene sulfide).[23]

The effect of polymer molecular weight on the spin-lattice relaxation time is seen to be minor, although there is a slight increase of T_1 with decreasing chain length, presumably due to the intrusion of overall molecular tumbling. The correlation time τ_0 for such overall rotatory diffusion can be estimated as heretofore[15,29] from the formula

$$\tau_0 = 2M[\eta]\eta_0/3RT \tag{1}$$

in which η_0 is solvent viscosity. For the lowest fraction F9 at 300 K in chloroform, this gives $\tau_0 \cong 30$ ns, which is about an order of magnitude greater than the internal correlation times to be estimated below and thus accounts nicely for the small trend observed.

To estimate correlation times for the internal motions we use only the data for the two highest molecular weight fractions F2 and F5. Of the several models available for this purpose we choose the one most familiar to us[29] (hereafter the JS model) which leads to a small finite number s of correlation times. It has been demonstrated[30] that this and alternative existing models are equally successful in fitting data and that they also give similar magnitudes for mean correlation times. For details of the JS model the original references[29,31] should be consulted. Since the NOE for PSO is at the extreme-narrowing limit and the molecular-weight effect on T_1 is small, there is no experimental guide as to the best value of the index s, which reflects the extent of correlation of the segmental rearrangement along the chain backbone. We have made calculations for the two choices $s = 1$ (single-exponential decay of the correlation function: classical BPP dynamics) and $s = 3$, the latter being typical for some polymers studied previously.

For the meta and ortho carbon atoms, the internal "rotation" of the phenyl group about the C_1–C_4 axis is depicted by a two-site jump model, and when the corresponding Woessner[32] treatment is combined with that for a three-bond segmental rearrangement according to the JS model, the spectral density function becomes[31]

$$J_i(\omega_i) = 2\sum_{k=1}^{s} G_k \left[\frac{(A + C)\tau_k}{1 + \omega_i^2\tau_k^2} + \frac{B\tau_{bk}}{1 + \omega_i^2\tau_{bk}^2} \right] \tag{2}$$

$$\tau_{bk}^{-1} = \tau_k^{-1} + \tau_{ir}^{-1}$$

$$i = 0, 1, 2$$

Here A, B, and C are Woessner's[32] geometrical constants depending on the angle Δ between the relevant C–H axis and the axis of the internal rotation. The correlation time τ_k refers to the kth mode in the backbone segmental rearrangement dynamics[29] and τ_{ir} is the correlation time for the phenyl-group twisting in the two-site model. The sum of the s weight factors G_k is unity. For the methine and para carbon atoms the angle Δ is zero, $A = 1$, and $B = C = 0$, while for the meta and ortho carbons we have $\Delta = \pi/3$, $B = {}^9/_{16}$, and $A + C = {}^7/_{16}$.

Setting $\omega\tau_k \ll 1$ and $\omega\tau_{bk} \ll 1$ in eq 2 (extreme-narrowing condition), we then fit the observed T_1 values with the standard expressions

$$1/T_1 = W_0 + 2W_1 + W_2 \tag{3a}$$

$$W_0 = \gamma_H^2\gamma_C^2\hbar^2 J_0(\omega_0)/20r^6; \qquad \omega_0 = \omega_H - \omega_C \tag{3b}$$

$$W_1 = 3\gamma_H^2\gamma_C^2\hbar^2 J_1(\omega_1)/40r^6; \qquad \omega_1 = \omega_C \tag{3c}$$

$$W_2 = 3\gamma_H^2\gamma_C^2\hbar^2 J_2(\omega_2)/10r^6; \qquad \omega_2 = \omega_H + \omega_C \tag{3d}$$

Table IV
Harmonic Mean Correlation Times τ_h of Segmental Rearrangement

temp/°C	τ_h/s × 10^{10} (±20%)	
	$s = 1$	$s = 3$
76	0.93	0.27
64	1.10	0.32
50	1.26	0.37
36	2.0	0.58
24	2.5	0.73
10	3.5	1.01
−2	4.5	1.30

Table V
Correlation Times τ_{ir} of Phenyl-Group Rotation

temp/°C	τ_{ir}/s × 10^{10} (±50%)	
	$s = 1$	$s = 3$
76	1.4	2.5
64	1.3	2.1
50	2.7	4.3
36	2.3	4.0
24	4.1	7.3
10	5.2	8.9
−2	7.5	13.3

using the C–H distance $r = 0.109$ nm. First, the data for the methine and para carbons were averaged and used at each temperature to evaluate the harmonic mean segmental correlation time τ_h, defined by

$$\tau_h^{-1} = s^{-1} \sum_{k=1}^{s} G_k \tau_k^{-1} \qquad (4)$$

With this value in hand, the data for meta and ortho carbons were then used to obtain τ_{ir}. The results for the two selected values of s are shown in Tables IV and V. Since τ_h decreases with increasing s, the corresponding value of τ_{ir} must increase to preserve numerical agreement.

Our results in hexadeuteriobenzene are meager but reinforce those obtained in deuteriochloroform. At 36 °C and 12.5% (w/w) the observed T_1 values are 210 ms for the methine carbon and 260 ms for ortho and meta carbons. A glance at Table II reveals that there is little difference in behavior between the two solvents when compared at the same temperature and concentration. This is to be expected, as the solvent viscosities differ by less than 20%.

The temperature dependence of the correlation times is smooth and gives, for both values of s, activation energies 17 ± 3 kJ mol^{-1} for backbone rearrangement and 20 ± 3 kJ mol^{-1} for phenyl-group rotation. These figures are comparable to those for poly(styrene sulfide) and poly(styrene peroxide). Presuming a diffusion-controlled process of the Kramers type,[6,7] we can subtract the viscous-flow activation energy of 6 kJ mol^{-1} for chloroform and arrive at apparent barrier heights of 11 and 14 kJ mol^{-1} for backbone and phenyl-group motions, respectively.

The dielectric measurements in benzene at 20 °C reveal a single loss peak, fairly narrow and not highly asymmetric, with a maximum in the loss factor ϵ'' at a frequency of 450 MHz, which corresponds to a mean dielectric correlation time of 0.35 ns. This is seen to be about 1.5–4 times as great as the corresponding NMR-based value of τ_h at 20 °C, depending on which s value is chosen. If the backbone motion concertedly involves both oxygen and methine carbon atoms and if the small difference in solvent viscosity is ignored, it would be expected[33] that the dielectric correlation time would be 2–3 times longer than that from the NMR data. The agreement between NMR and dielectric measurements is therefore more than adequate and indeed is better than for the poly(halostyrenes).[7,16]

Table VI
Correlation Times for Backbone and Phenyl Twisting Motions in Styrene-Related Polymers, $[\text{-X-CH}_2\text{CH(C}_6\text{H}_5\text{)-}]_n$[a]

X	freq/ MHz	concn/%	τ_h/ns[b]	τ_{ir}/ns[b]	ref
none	25	13 w/v	0.52	1.0	12[c]
O	15	20 w/w	0.39	0.4	*d*
S	25	20 w/v	0.25	0.6	23
OO	25	22 w/v	0.19	0.1	22[e]
SO_2	25	25 w/v	0.64		36

[a] In $CDCl_3$ at 25 °C except as noted. [b] Calculated with $s = 1$ (see text). [c] In cyclohexane-d_{12} at 35 °C. [d] Present work. [e] At 33 °C.

The decrease in dielectric constant ϵ' through the observed dispersion region is 0.032 ± 0.001, which corresponds to a mean-square dipole moment per repeat unit, $\langle\mu^2\rangle/x$, of 0.60 D^2. This figure is somewhat smaller than that for poly(ethylene oxide).[34] Conformational properties, including dipole moments, have been discussed for polyethers by Abe and co-workers,[35] but in the absence of accurate knowledge of the tacticity of our PSO we do not attempt to apply their results here.

To compare our dynamic measurements on PSO meaningfully to those previously published for polystyrene and related polymers, it is important to treat all the data in the same way. For this purpose we employ the JS model with $s = 1$ and represent the phenyl twisting motion by the two-site jump model, just as for Tables IV and V. Some results of such recalculations are shown in Table VI, where we have selected as far as possible similar solvents, concentrations, and temperatures. Though the conditions are only roughly the same and the errors are large (cf. Tables IV and V), certain conclusions can be drawn. They are not altered if another value of s (e.g., 3) is used.

First, intercalation of oxygen or sulfur atoms or peroxide links between styrene units facilitates backbone segmental motions as compared to those in polystyrene. However, introduction of a bulkier and highly polar substituent, in the case of the styrene/SO_2 copolymer, is seen to have no such "plasticizing" effect.

Second, the phenyl twisting motion is also facilitated by introduction of spacers between styrene units, as already seen earlier by Gronski and co-workers[21] for styrene/butadiene copolymers. In this connection it should be pointed out that our figures in Table VI are not the same as those extracted from the same data with alternative models. Thus, for example, Cais and Bovey[22] give $\tau_h = 0.20$ ns and $\tau_{ir} = 0.34$ ns for their styrene peroxide polymer, and they report[23] $\tau_h = 0.26$ ns and $\tau_{ir} = 1.7$ ns for poly(styrene sulfide); but their calculations treat the phenyl motion as spatially isotropic. It is seen that our model gives (for $s = 1$) essentially the same values of τ_h as theirs but leads to appreciably lower figures for τ_{ir}.

A remark should be added about the statement made by Grandjean, Sillescu, and Willenberg,[15] on the basis of their deuteron NMR relaxation experiments, that "the motion of the phenyl ring is faster than that of the backbone". By this they mean only that the *total* mobility, due to both backbone rearrangements and twisting, is greater for ring deuterons than for backbone deuterons. In terms of our model, this means simply that τ_{bk} is shorter than τ_k. In fact, their results correspond to the inequality $\tau_{ir} > \tau_h$, which is consistent with the results of others[12] (cf. Table VI).

Finally, we remark that the difference in observed T_1 values between para and methine carbons is definitely greater in polystyrene than in PSO (cf. Table III) or poly(styrene sulfide)[23], where it is negligible. Although this difference can be attributed in some part to the effects of the protons in vicinal methylene groups, it must also reflect the importance of bond-angle flexing in the backbone motions of polystyrene. The importance of the bond-angle coordinates in conformational entropy calculations has recently been demonstrated by Karplus and Kushick.[37]

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^1H NMR Study of Low Molecular Weight Analogues of Poly(diethylene glycol terephthalate) and Poly(thiodiethylene glycol terephthalate)

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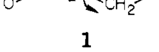
ABSTRACT: The rotameric probability about CH_2–CH_2 bonds in poly(diethylene glycol terephthalate) (PDET) and poly(thiodiethylene glycol terephthalate) (PSDET) was obtained from ^1H NMR studies of the respective low molecular weight analogues diethylene glycol dibenzoate (ODB) and thiodiethylene glycol dibenzoate (SDB). The fractions of gauche states X_g about the moiety 1, where X is O for ODB and S for SDB, were 0.89 ± 0.05 and 0.60 ± 0.05, respectively, in deuterated benzene. The fractions X_g in ODB and SDB increase with the polarity of the medium, their values being, respectively, 0.94 ± 0.05 and 0.66 ± 0.05 in deuterated acetone. These results, interpreted in terms of the rotational isomeric state model, suggest that gauche states about CH_2–CH_2 bonds in both PDET and PSDET have an energy ca. 0.5 kcal mol^{-1} lower than similar states about these bonds in poly(oxyethylene) (POE) and poly(thiodiethylene glycol) (PTDG), respectively.



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Introduction

The configuration-dependent properties of polymers can be analyzed within the framework of the rotational isomeric state (RIS) approximation provided that the neighbor-dependent character of the conformational energies is taken into account.[1,2] Experimental values of these energies can be obtained either from spectroscopic studies of model compounds or by comparison between theoretical and experimental values of some configuration-dependent properties.[1,3] In addition, semiempirical potential functions are also used to calculate conformational energy maps which can provide very important information regarding

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