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Carbon-13 NMR Observations of the Microstructure and Molecular Dynamics of Poly(phenylthiirane)

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ABSTRACT: We have examined the microstructure and molecular dynamics of three poly(phenylthiirane)'s in chloroform solution by ^{13}C NMR at 25.16 MHz. The aromatic quaternary and ortho carbon resonances were sensitive to triad stereosequences, whereas the backbone methine carbon resonance exhibited tetrad splittings. A sample prepared by "autopolymerization" was almost perfectly atactic (Bernoullian, with $P(m) = 0.48$), but heterogeneous catalysis with cadmium compounds produced fairly stereoregular polymers in which the stereosequence distributions conformed to first-order Markov statistics. Defect structures were also observed and assigned to head-to-head monomer placements. Measurements of ^{13}C spin–lattice relaxation times and nuclear Overhauser enhancements indicated that the polymer backbone was highly flexible, with motional correlation times about an order of magnitude shorter than those for polystyrene. Moreover, the results showed that the phenyl ring rotated with frequencies approximating 0.1 GHz, in strong contrast with the restricted motion of this group in polystyrene. Data obtained over the temperature range 10 to 55 °C gave apparent activation energies for segmental motions and phenyl rotation of 18 and 20 kJ/mol, respectively. The results are suggestive of cooperative local motions.

We have shown by ^{13}C NMR that in polymers of the class $[-CH_2CH(C_6H_5)-X-]$ both backbone carbons are sensitive to dyad tacticity and that the chain is substantially more flexible than that of polystyrene when X is a peroxide unit.[1] It was found that the phenyl group in the polyperoxide, unlike that of polystyrene, was able to rotate freely with a rate comparable to that for segmental reorientations along the backbone. In this paper, we extend our ^{13}C NMR studies to the system where X is sulfur, i.e., poly(phenylthiirane).

The structures of several polythiirane's have been examined by NMR. Most attention has been focussed on poly(methylthiirane), and studies by both proton[2,3] and ^{13}C[4,5] NMR have proved valuable in determining the effects of different polymerization catalysts on tacticity. Complete line assignments in the ^{13}C spectrum were made possible by the use of model compounds.[6] Irregular head-to-head structures in poly(methylthiirane) have been detected by ^{13}C NMR,[7–9] which has also been applied to structural studies of butyl, *tert*-butyl, phenyl,[4] and isopropyl[10] polythiirane's, and of 1,1-dimethylthiirane copolymers with thiirane and methylthiirane.[11] In particular, Ivin et al.[4] found for poly(phenylthiirane) that the quaternary and backbone methine carbons revealed dyad and triad stereosequences, respectively. Assignments of the configurational multiplets were made by a comparison of spectra of polymers obtained with different catalysts.

In contrast, there is very scanty NMR relaxation data for polythiiranes. Boileau et al.[7,8] measured ^{13}C T_1 values for poly(methylthiirane) at 25.16 MHz and 60 °C, as a method of confirming assignments in the ^{13}C spectrum. Their reported methine carbon T_1 value of 1.4 s indicates a highly flexible polymer with a motional correlation time approximating 35 ps. The present paper is concerned primarily with the correlation times for local motions in poly(phenylthiirane) in solution, as revealed by the spin–lattice relaxation times (T_1) and nuclear Overhauser enhancement factors (η). Some new structural assignments are also presented.

Experimental Section

Monomer. Phenylthiirane (styrene sulfide or 1,2-epithioethylbenzene) was prepared in 55% yield by the reaction of potassium thiocyanate with phenyloxirane (styrene oxide or 1,2-epoxyethylbenzene) in 50% aqueous dioxane solution, according to the procedure reported by Guss and Chamberlain.[12] The crude phenylthiirane was extracted with ether and isolated by removal of all volatiles boiling at 61 °C under 133 Pa of pressure; ^{13}C NMR showed that the product contained 13% of unreacted phenyloxirane. This mixture was distilled at 0.133 Pa to yield a middle fraction of 95% purity, containing 5%

Table I
Preparative Details and Molecular Weights of Poly(phenylthiirane)'s

Sample	Polym temp, °C	Catalyst	Wt % of catalyst	Conversion, %[a]	$\overline{M}_w$	$\overline{M}_n$
PPT-1	25	[b]		52	36 900	21 400
PPT-2[c]	25	$CdCO_3$	1.6	75	241 000	88 000
PPT-3[d]	−35	$ClCdSC_4H_9$	1.4	72	562 000	178 000

[a] Polymerization time = 79 days. [b] None deliberately added. [c] Gel time = 18 days. [d] Gel time = 15 h.

phenyloxirane. Attempts at further distillation resulted in decomposition of the monomer to styrene and sulfur, as noted by previous workers.[4,12]

Catalysts. Cadmium carbonate (Ultrapure grade) was obtained from Ventron Corp. (Alfa Products). Chlorocadmium butylmercaptide was prepared by the addition of butylmercaptan in ethanol to an aqueous–ethanolic solution of cadmium chloride, as described by Noshay and Price.[13]

Polymerizations. Three polymers were prepared, which differed in molecular weight and tacticity. An atactic polymer with low molecular weight (PPT-1) was prepared without any deliberately added catalyst ("autopolymerization") by sealing in air 25 cm^3 (27.6 g) of monomer in a 50-cm^3 flask, which was allowed to stand at room temperature (~25 °C) for 79 days. Two predominantly isotactic polymers (PPT-2 and PPT-3) were prepared by heterogeneous catalysis with cadmium carbonate (at 25 °C) and chlorocadmium butylmercaptide (at −35 °C), respectively. The catalyst was weighed into a 50-cm^3 flask which was attached to a vacuum manifold. After the catalyst had been evacuated for several hours, 20 cm^3 (22.1 g) of monomer was added under a nitrogen blanket. The monomer was then outgassed by repeated freeze–thaw cycles with pumping and the mixture sealed under vacuum.

After 79 days the flasks were cut open, the swollen polymer mass was dissolved in chloroform, and the solutions were filtered into excess methanol. The recovered polymers were redissolved in chloroform, and the solutions were centrifuged to separate traces of suspended catalyst residue and sulfur.[14] After reprecipitation in methanol, the polymers were dried overnight in a vacuum oven at 40 °C. Polymerization details are given in Table I.

Characterization. Molecular weights were determined in tetrahydrofuran by gel-permeation chromatography, using a Waters Model 501 GPC equipped with a set of μ Styragel columns calibrated with monodisperse polystyrene standards. The results are shown in Table I.

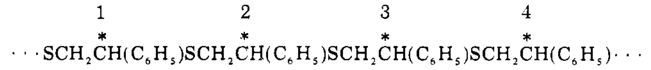
^{13}C NMR Measurements. The polythiiranes were observed by ^{13}C NMR at 25.16 MHz as 20% w/v solutions in chloroform-*d*. The solvent and polymer were thoroughly outgassed on a vacuum line, mixed under vacuum, and sealed in an atmosphere of high-purity nitrogen. Spectra were obtained with a modified Varian XL-100 spectrometer,[15] employing a 12-mm probe. T_1 values were measured by the standard inversion-recovery (π–t–$\pi/2$–T) pulse sequence, with T at least five times the longest T_1 of interest (accumulating for each t value 1200 transients for backbone carbons, 1600 transients for the protonated aromatic carbons, and 400 transients for the quaternary carbon). In all cases good linear plots of $\ln(1 - I_t/I_\infty) = \ln 2 - t/T_1$ were obtained, where I_t is the peak intensity found with delay time t. Values of η were obtained from peak areas measured with an accumulation of 8000 transients, first with broad-band ^{1}H decoupling and then with the decoupling power reduced to zero. In the latter case, the probe temperature was raised to compensate for the heating effect of the decoupler. T_2 values could not be reliably obtained from line widths, as these contained an unknown contribution from unresolved configurational sequences. Other relevant instrumental details are given in the appropriate figure captions.

Spectra Simulation. A computer program was used to simulate resonance patterns arising from configurational sequence multiplicity in the ^{13}C spectra of polymers. This program computes the unconditional probabilities of all "n-ads" (n being an appropriate integer chosen with regard to the level of observed peak multiplicity), according to a specified statistical description of configurational sequence propagation (Bernoullian, Markov of order 1, 2, etc.), with appropriate input parameters. These probabilities are equated to peak areas, from which the resonance pattern is plotted, given as further input individual "n-ad" chemical shifts and line widths, and assuming a Lorentzian line shape. The "best" statistical parameters are chosen on a trial-and-error basis in matching observed and computed spectra. Since the statistical propagation model is built into the program, all conservative laws and relations between configurational sequences[16] are necessarily obeyed.

Results and Discussion

(i) Polymer Microstructure. Figure 1 shows all ^{13}C resonances (other than solvent and reference) observed in solutions of the three poly(phenylthiirane)'s. The assignments to carbon type are in accord with the multiplicity observed in the corresponding ^{1}H-coupled spectra (not shown), from which the following $J_{^{13}C-^1H}$ values were obtained: backbone methine and methylene, 141 Hz; and aromatic, 160 Hz. Although the para aromatic carbon may be unambiguously assigned from its relative intensity, it is not so trivial to assign the ortho and meta resonances. However, we note that one such carbon is a triplet, i.e., it is sensitive to triad stereosequences, and we can reasonably assign this to the ortho carbon, which is closer to the backbone methine chiral center than the meta carbon. These assignments agree with those published by Ivin et al.[4]

Only three carbons show resolved tacticity splittings, these being in order of increasing field strength the aromatic quaternary, aromatic ortho, and backbone methine carbons. Both of the above aromatic carbons are resolved into triplets, indicating triad sensitivity, but the backbone methine carbon is resolved into five peaks (the highest field component of the apparent quartet is actually a doublet) and must therefore reflect partial tetrad splittings.[17] A tetrad configurational sequence may be defined in either of two ways for a backbone methine carbon, e.g., in the sequence



$$\cdots\mathrm{SCH_2}\overset{1}{\overset{*}{\mathrm{C}}}\mathrm{H(C_6H_5)SCH_2}\overset{2}{\overset{*}{\mathrm{C}}}\mathrm{H(C_6H_5)SCH_2}\overset{3}{\overset{*}{\mathrm{C}}}\mathrm{H(C_6H_5)SCH_2}\overset{4}{\overset{*}{\mathrm{C}}}\mathrm{H(C_6H_5)}\cdots$$

the observed carbon is either 2 or 3. This situation arises because the sensitivity of a given asymmetric center to relative configurations with its neighbors is attenuated more rapidly with distance in one chain direction than in the other. The resonance of the aromatic quaternary carbon also exhibits this effect. There is a large dyad splitting (7.5 Hz) induced by the two relative configurations of its directly bonded asymmetric center with one vicinal asymmetric center, upon which the other vicinal center imposes a much smaller dyad splitting (1.5 Hz) for an overall triad sensitivity. Without a study of suitable model compounds, we are unable to identify the chain direction in which configurational sensitivity is more marked.

Figure 2 shows a comparison between the simulated and observed resonances for the aromatic quaternary and backbone methine carbons in the three poly(phenylthiirane)'s. The configurational sequence propagation statistics and related parameters for the simulations are shown in Table II. The line ordering for the quaternary carbon triads and methine carbon tetrads is also indicated on Figure 2, with the appropriate chemical shifts summarized in Table III. In order to make these assignments, we assumed that the cadmium catalysts generated a predominantly isotactic polymer (i.e., one with a preponderance of m dyads[18]), as is known for other polythiirane's.[4] The assignments approximate a trend of increasing shielding as m is replaced by r.

PPT-1 is an almost perfectly atactic polymer, with only a

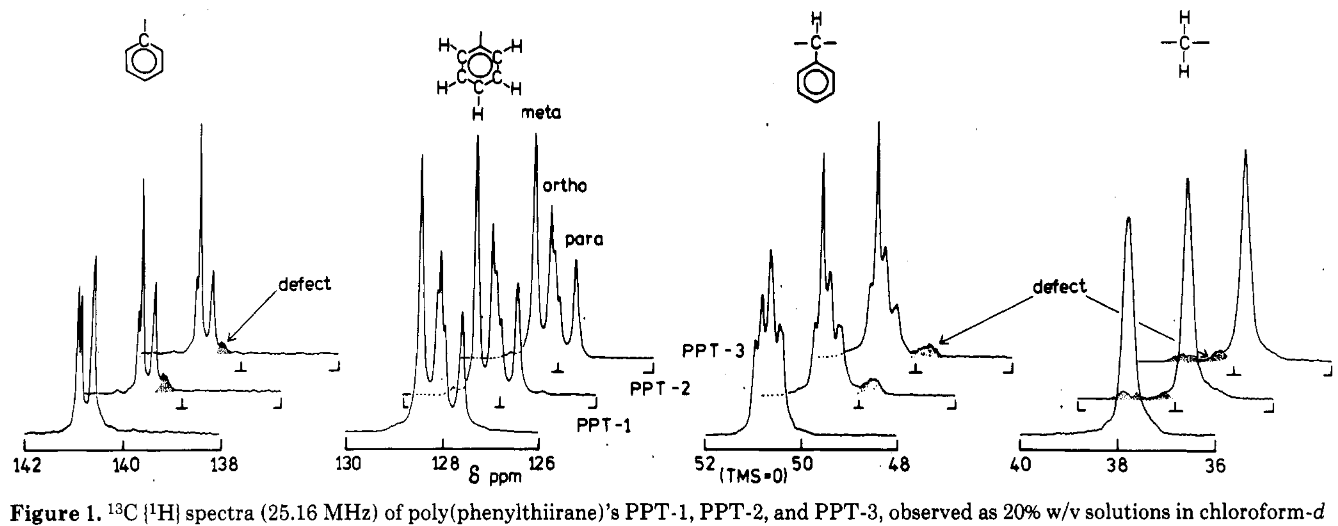


Figure 1. ^{13}C {^{1}H} spectra (25.16 MHz) of poly(phenylthiirane)'s PPT-1, PPT-2, and PPT-3, observed as 20% w/v solutions in chloroform-*d* at 55 °C. Details (all): 8000 transients accumulated in 16 K memory for a spectral window of 4000 Hz (125 μs dwell time); 16.6 μs pulses (90° flip angle) spaced by 3.0 s delay time; digital broadening 0.31 Hz. Lightly shaded peaks are attributed to defect structures (see text).

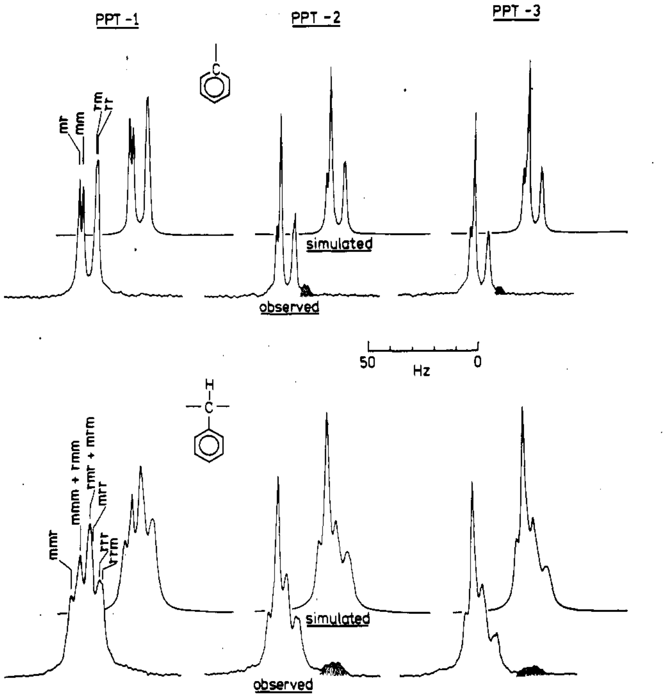


Figure 2. Comparison between simulated and observed aromatic quaternary carbon (top) and backbone methine carbon (bottom) resonances in poly(phenylthiirane)'s PPT-1, PPT-2, and PPT-3. Lightly shaded peaks are attributed to defect structures, which were not included in the simulation. For the parameters employed to generate these simulated spectra, see Tables II and III. Line widths employed for simulation are 1.27 Hz for all quaternary carbon triads and 3.00 Hz for methine carbon tetrads, with the exception of mrr, rrm, and rrr, which were assigned a width of 3.50 Hz.

Table II
Propagation Statistics Used to Simulate the Configurational Multiplet Patterns in the Quaternary and Backbone Methine Carbon Resonances

Polymer	Unconditional probability of m dyad[a]	Propagation statistics
PPT-1	0.48	Bernoullian; $P(m)^b = 0.48$
PPT-2	0.66	Markov 1; $P(m/r)^c = 0.25$, $P(r/m) = 0.50$
PPT-3	0.70	Markov 1; $P(m/r) = 0.25$, $P(r/m) = 0.58$

[a] Measured from quaternary carbon resonance. [b] Unconditional probability of formation of m dyad. [c] Conditional probability of formation of r dyad, given that the preceding configurational dyad in the chain is m.

slight bias toward the formation of r dyads. A similar result was found for poly(styrene peroxide),[1] and the absence of any steric directing influence during propagation may be attributed to the increased spacing (compared to vinyl homopolymerizations) of asymmetric centers by the heteroatom unit. The stereosequence distributions in samples PPT-2 and PPT-3 conform to first-order Markov statistics, with the propagation parameters shown in Table II. However, these values should be interpreted with some caution, as it is probable that the polymers PPT-2 and PPT-3 are a blend of highly stereospecific chains generated on the solid catalyst surface, with atactic chains generated without such contact, especially in view of the facile "autopolymerization" of phenylthiirane.[19] The broader molecular weight distributions of samples PPT-2 and PPT-3, compared with PPT-1 (Table I), also suggest that the first two polymers may be a blend of materials formed by different mechanisms. Noshay and Price found no evidence of a melting point for poly(phenylthiirane)'s, and x-ray analysis confirmed that no crystalline fraction was present.[13] We did not investigate the feasibility of fractionating our samples, as this work is concerned primarily with chain dynamics, which was not influenced by tacticity (vide infra).

The chemical shifts of all polymer ^{13}C resonances are summarized in Table III. In general, these are about 2.7 ppm to higher field than those reported in the literature.[4] We further note the presence of defect structures at a level of 6% in the spectra of PPT-2 and PPT-3 (Figure 1 and Table III). These are assigned to head-to-head structures, indicating that the thiirane ring may open at both the S–CH_2 bond (β cleavage) and the S–$CH(C_6H_5)$ bond (α cleavage). No measureable amounts of these defects were observed in the ^{13}C spectrum of the sample prepared by autopolymerization. It is known that head-to-head structures are present in poly(methylthiirane)'s prepared by various catalysts.[4,8,9]

(ii) Solution Dynamics. The magnitudes of ^{13}C T_1 and η values depend on the frequency at which ^{13}C–^{1}H bonds are reoriented with respect to the laboratory frame, provided ^{13}C nuclear relaxation occurs via a dipolar mechanism involving directly bonded protons.[20] This is usually true for polymers,

Table III
Summary of All Observed ^{13}C Resonance Chemical Shifts and Assignments

Resonance		δ, ppm (TMS = 0.00)		
		PPT-1	PPT-2	PPT-3
Quaternary carbon	mr	140.85	140.88	140.88
	mm	140.79	140.81	140.81
	rm	140.55	140.56	140.56
	rr	140.52	140.54	140.54
	Defect	*a*	140.33	140.37
Meta		128.43	128.45	128.45
Ortho	mm	128.08	128.12	128.12
	mr + rm	128.02	128.04	128.06
	rr	127.92	127.94	127.94
Para		127.55	127.59	127.61
Backbone methine	mmr	50.85	50.88	50.90
	mmm + rmm	50.72	50.72	50.74
	rmr + mrm	50.57	50.57	50.58
	mrr	50.51	50.51	50.53
	rrr	50.37	50.37	50.39
	rrm	50.31	50.31	50.33
	Defect	*a*	49.73	49.71
Backbone methylene	Defect	*a*	39.05, 38.77	39.07, 38.83
	Regular	37.72	37.74	37.76

[a] Not observed.

Table IV
Effect of Molecular Weight on the ^{13}C Dynamic Parameters at 23.5 kG for Poly(phenylthiirane)'s Observed at 55 °C for 20% w/v Solutions in Chloroform-*d*

			T_1 (ms) ± 5% η (NOE-1) ± 20%					
			Backbone		Phenyl ring			
Sample	$\overline{DP}_n$[a]	$\overline{M}_w/\overline{M}_n$	CH[b]	CH_2	C_1[b]	C_2[b]	C_3	C_4
PPT-1	157	1.72	385 1.9	190 2.0	4100 1.6	465	464 1.8[c]	370
PPT-2	646	2.74	371 2.0	191 2.1	3900 1.4	412	410 1.7[c]	370
PPT-3	1321	3.13	380 1.8	192 2.0	4000 1.2	424	436 1.8[c]	375

[a] Repeat unit = $(-CH_2-CH(C_6H_5)-S-)$. [b] No effect of tacticity. [c] Individual peak areas could not be resolved in the ^{1}H-coupled spectrum of the protonated aromatic carbons.

and even quaternary carbons relax principally by dipolar interactions with protons on neighboring carbons.[21] With the available magnetic field strengths, both T_1 and η for ^{13}C are most sensitive to frequencies in the range 10^7 to 10^{10} Hz and are therefore ideally suited to the examination of local segmental motions in polymers.[22]

The T_1 and η data for all carbons in the three poly(phenylthiirane)'s at 55 °C are listed in Table IV. The values are equal within experimental error for given carbons. There is no discernable influence of molecular weight over the range studied. Consequently, the magnitudes of T_1 and η depend solely on the frequencies of the rapid internal local motions, with no contribution from the comparatively slow overall tumbling motions of the chains. We did not observe any effect of tacticity on these results, so that different stereoisomeric environments play no role here in modulating the local dynamic behavior.

The effect of temperature on T_1 and η for sample PPT-3 is shown in Table V. We find that T_1 increases with temperature for all carbons.[23] The correlation times (τ_c) for local motions in poly(phenylthiirane) must therefore be on the high-temperature side of the minimum in the T_1 vs. τ_c curve at our observing temperatures. This is also borne out by the large values of η, which approach the theoretical maximum of 1.989, obtained only when τ_c is sufficiently short for the "extreme narrowing" condition to apply.[20] Our data also show that the ratio of the backbone methine to methylene carbon T_1 values is 2:1, attesting to a purely dipolar relaxation mechanism involving directly bonded protons, and with an effectively isotropic backbone motion.[21]

A significant feature of these results is the considerably longer T_1 for both the ortho (C_2) and meta (C_3) aromatic carbons compared to the para (C_4) carbon. This was also found for poly(styrene peroxide)[1] and results from rapid rotation of the phenyl ring, which contributes to the relaxation of the off-axis carbons. The methine and C_4 carbons, which are on the phenyl group rotational axis, have equal T_1 values. From this we can rule out any significant contribution from wagging or "window-wiper" motions[24] of the phenyl ring with respect to the chain backbone. The quaternary (C_1) carbon has a very long T_1 value at 55 °C (4.0 s), as it is relaxed primarily by neighboring nonbonded protons (but see below).

We have shown that η values approach the theoretical maximum and are insensitive to the motional τ_c values. However, there may be a real reduction in η for the quaternary carbon, which may point to a contribution from some relaxation mechanism other than dipolar. We can exclude the effect of dissolved oxygen[25] because of the thorough deoxygenation of the polymer solutions, but it is possible that chemical shift anisotropy may have a finite contribution even at the rela-

Table V
Effect of Temperature on the ^{13}C Dynamic Parameters of Sample PPT-3 at 23.5 kG, Observed as a 20% w/v Solution in Chloroform-*d*

	T_1 (ms) ● 5% η (NOE-1) ± 20%					
	Backbone		Phenyl ring			
Temp, K	CH	CH$_2$	C$_1$	C$_2$	C$_3$	C$_4$
328	380	192	4000	424	436	375
	1.8	2.0	1.2		1.8^a	
313	277	155		310	307	270
	1.7	1.9	1.7		1.7^a	
298	194	99		223	224	199
	1.9	2.0	1.2		1.6^a	
283	140	75		153	156	143
	1.6	1.9	1.0		1.5^a	

[a] Individual peak areas could not be resolved for the protonated *aromatic carbons in the ^{1}H-coupled spectrum.*

tively low field strength employed,[26] because of the inefficiency of dipolar relaxation of the quaternary carbon in such a flexible polymer.

Motional correlation times are derived here only from T_1, in view of the insensitivity of η to both the motional model and τ_c values in the "extreme narrowing" region. The scope of our data does not justify or allow a detailed treatment of polymer motion in terms of a nonexponential autocorrelation function for backbone in reorientation,[27,28] with the inclusion of an anisotropic part for the internal rotation of the phenyl group. However, Heatley and Cox have recently shown that when the "extreme narrowing" condition is attained, then the single correlation time motional model gives an adequate description of the chain dynamics.[28] Accordingly, we appeal to the isotropic, single-τ_c, motional model,[21] with consideration of two types of local motions: backbone segmental reorientations and rotation of the phenyl ring. Segmental motions (seg) determine the value of the backbone methine carbon T_1, whereas both (seg + rotn) determine the ortho and meta carbon T_1 value. The correlation time for phenyl rotation alone may be estimated from the approximate relation in eq 1.[29]

$$\frac{1}{\tau_c(\text{seg} + \text{rotn})} = \frac{1}{\tau_c(\text{seg})} + \frac{1}{\tau_c(\text{rotn})} \qquad (1)$$

The derived τ_c values are shown in Table VI.

From the temperature dependence of τ_c, we deduce an apparent activation energy of 18 kJ/mol for segmental motions and 20 kJ/mol for phenyl group rotation. Rather surprisingly, the former value lies in the range of those reported for segmental motions in polystyrene's (14 to 27 kJ/mol; see ref 30 for a summary of the data), yet in the polythiirane these motions have correlation times about an order of magnitude shorter than those measured by ^{13}C relaxation data on polystyrene under comparable conditions.[27] We postulate therefore that the C–S bonds in poly(phenylthiirane) do not act independently as swivel joints with low torsional barriers and that segmental motions may extend cooperatively along a section of the chain so as to require on average a simultaneous rotation about a C–C bond for every rotation about a C–S bond. The C–C rotation provides the major barrier, which is comparable to that in polystyrene. These cooperative motions will minimize the viscous drag on polymer segments which are translated through the solvent medium by conformational transitions. However, compared with polystyrene, the poly(phenylthiirane) appears to have a larger number of energetically feasible pathways for interconverting conformational states, resulting in more rapid motions because of a more favorable entropy of activation.

Table VI
Motional Correlation Times Derived from T_1 Values for Sample PPT-3

Temp, K	Motional correlation times, ns^a Seg,^{b}	Seg + rotn^c	Rotn^d
328	0.13	0.11	0.94
313	0.18	0.16	1.2
298	0.26	0.22	1.7
283	0.37	0.33	2.9

[a] Derived from the familiar equation relating T_1 and τ_c (e.g., see ref 21). [b] From backbone methine T_1 values. [c] From phenyl ring ortho T_1 values. [d] Calculated according to eq 1 in the text.

As expected, the barrier to phenyl group rotation is significantly lower in the polythiirane than in polystyrene (calculations have placed a minimum barrier in polystrene at 43 kJ/mol[31]). In polystyrene, ^{13}C relaxation data discern only a low-frequency libration of the phenyl ring[32] (although some recent data from Raman line shape analysis appear to contradict this[33]). The interesting feature of our results is that phenyl rotation is approximately ten times slower than backbone motions, although with a comparable energy barrier. This suggests that phenyl rotation does not take place independently of backbone motions but must couple with them by occurring only when favorable conformational environments are accessed.

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(18) Although usage of m and r for "meso" and "racemic" dyad placements in polymers is strictly defined only for vinyl homopolymers where every second backbone carbon is a pseudoasymmetric center, we adopt these terms here for convenience to designate structures in which adjacent pairs of asymmetric centers have like (RR and SS) and unlike (RS and SR) chiralities, respectively.
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The Molecular Dynamics of Poly(but-1-ene sulfone) and Poly(styrene sulfone)s in Solution as Observed by ^{13}C NMR Relaxation Measurements

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ABSTRACT: We report here our observations by ^{13}C NMR at 25.16 MHz of the molecular dynamics of poly(but-1-ene sulfone)s and poly(styrene sulfone)s in chloroform solution at 25, 40, and 55 °C. Three poly(but-1-ene sulfone)s were examined, with number-average molecular weights of 48 600, 182 000, and 272 500. There was no effect of molecular weight over this range on the ^{13}C dynamic parameters (spin–lattice relaxation times and nuclear Overhauser enhancement factors), showing that their magnitudes reflected internal segmental motions only. These motions were at least an order of magnitude slower for the backbone than those in poly(but-1-ene) under comparable conditions. A motional model which accounts for the reported absence of a high-frequency dielectric loss in poly(olefin sulfone)s is proposed. Unlike the poly(but-1-ene sulfone)s, which always have a 1:1 olefin/sulfone ratio, the poly(styrene sulfone)s examined here had a 1.5:1 and a 2:1 styrene/sulfone ratio. It was found from ^{13}C T_1 values that the poly(styrene sulfone)s were at least an order of magnitude more flexible than poly(but-1-ene sulfone). We attribute this difference to the larger separation of motionally restrictive sulfone units in the poly(styrene sulfone)s.

Measurements of the dielectric dispersion in solutions of alternating 1:1 copolymers of sulfur dioxide with hex-1-ene and 2-methylpent-1-ene have revealed that there is no high-frequency loss region (>MHz),[1] normally observed for segmental motions in flexible polymers which have dipole components orthogonal to the direction of the chain backbone.[2,3] Instead, the critical frequency at which the maximum loss occurred in these polysulfones was found to be inversely proportional to the degree of polymerization raised to the power ~1.5–2.0, being for example at about 24 kHz for poly(hex-1-ene sulfone) ($\overline{M}_n$ = 210 000) in benzene solution at 25 °C. From this it was concluded that overall tumbling of the polymer chain was the only effective motional process for relaxation of the molecule under the influence of an oscillating electric field.[1] This motion will produce a dielectric dispersion for polymers having dipole components along their backbone,[2] as is the case for polysulfones with unsymmetrical olefin units. By contrast, polysulfones prepared from symmetrical olefins like cyclopentene, cyclohexene, and but-2-ene do not show any dielectric dispersion over the frequency range 2×10^2 to 1.2×10^7 Hz.[4]

The absence of a high-frequency dielectric dispersion (>MHz) was attributed[1] to a severe restraint on segmental mobility by the sulfone units, resulting in segmental correlation times exceeding 10^{-4} s.[1] This conclusion is indeed surprising, since relatively "stiff" vinyl polymers such as polystyrene and poly(methyl methacrylate), with glass-transition temperatures (100 and 105 °C, respectively[5]) comparable to those for poly(olefin sulfone)s (e.g., 97 °C for poly(but-1-ene sulfone)[6]), have correlation times for segmental motions in solution of the order of nanoseconds, as determined by ^{13}C relaxation measurements.[7,8] Clearly, an examination of the dynamic behavior of polysulfones in solution by ^{13}C NMR is called for. This is done here and in the accompanying papers by Stockmayer, Jones, and Treadwell[9] and Fawcett, Heatley, Ivin, Stewart, and Watt.[10]

Although the ^{13}C spin–lattice relaxation times, T_1, of polymers in solution have often been interpreted by a motional model of isotropic rotational diffusion characterized by a single effective correlation time τ_c,[7,11–18] it is becoming increasingly apparent from concurrent measurements of the nuclear Overhauser enhancement (NOE) factors η, and in suitable cases the spin–spin relaxation times T_2, that this model is only approximate.[19] A more realistic motional model must take into account the cooperative nature of segmental reorientations in polymers, which is better described by a combination or a distribution of correlation times.[8,19–22] However, the exact form of the distribution function (derived from the motional auto-correlation function) remains an area of active research.[23–26] To date, ^{13}C relaxation data alone do not appear sufficient to discriminate among possible distribution functions.[8] Recently, Heatley and Cox[27] have examined ^{1}H T_1 and η values in poly(vinyl acetate) under various conditions and concluded that the conformational-jump model of Valeur et al.[25] provides a good description of the chain motions.

Since co-operative effects occur during conformational transitions in polymers, an important question with regard to the motional model concerns the number of backbone bonds over which these motions must correlate. Different local