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(23) A T_1 value for the quaternary carbon was measured at only one temperature, due to the long relaxation time and the attendantly long experimental time required to obtain reliable data. However, the effect of temperature on this value will follow the same trend as for other carbons.

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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

Table I
Molecular Weights of Poly(styrene sulfone)s (PSS) and Poly(but-1-ene sulfone)s (PBS) Employed in This Work, as Determined by Gel-Permeation Chromatography

Polysulfone	$\overline{M}_w$	$\overline{M}_n$	Polydispersity
PSS-1	104 600	32 400	3.2
PSS-2	627 000	183 000	3.4
PBS-1	48 600	21 200	2.3
PBS-2	182 000	84 400	2.2
PBS-3	272 500	131 200	2.1

chain structures can give rise to variations in segmental flexibility along a given polymer segment, provided that each different structural environment extends over at least as many bonds as are involved in cooperative motion. Thus, T_1 differences have been reported for selected protons or carbons in different stereosequences in homopolymers[15,28,29] and for carbons in different monomer sequences in copolymers[30] and in different chain structures in polybutadienes.[31,32] In view of this, polysulfones having a variable monomer sequence structure might be expected to show shorter correlation times for those sequences in which the supposedly restrictive sulfone groups are separated by several carbon–carbon backbone bonds, as compared to those in which there is only one such bond between adjacent sulfone units.

To test the above premise we report here ^{13}C dynamic results for poly(styrene sulfone)s of variable monomer sequence structure. We have also examined poly(but-1-ene sulfone)s of varying molecular weight, as representative examples of the strictly alternating 1:1 poly(olefin sulfone)s. Our results show that although the sulfone units exert some constraint on segmental mobility in the poly(olefin sulfone), this is not nearly as severe as suggested by the dielectric measurements. When the sulfone units are separated by more than one C–C main-chain bond, as in the poly(styrene sulfone)s examined here, no apparent constraint on backbone motions is observed.

Experimental Section

Materials. The polysulfones were prepared by bulk, liquid-phase, free-radical copolymerizations with sulfur dioxide. Two poly(styrene sulfone)s were examined in this work, designated as PSS-1 and PSS-2, containing 60 and 69 mol % styrene, respectively. PSS-1 was synthesized at 0 °C by ^{60}Co irradiation of the monomer mixture. Styrene (Eastman, stabilized with *tert*-butylpyrocatechol) was degassed on a vacuum line and 20 cm^3 (18 g, 173 mmol) was distilled at 0.13 mPa into a 100-cm^3 reaction flask. Reagent grade acetone (1.0 cm^3) was then distilled into the flask, in order to inhibit the radiation-induced ionic homopolymerization of styrene in liquid SO_2,[33] followed by 171.5 mmol of sulfur dioxide (Matheson Gas Products, anhydrous grade), measured by its pressure in a calibrated bulb. The flask was sealed under vacuum at −196 °C and allowed to warm to 0 °C. The mixture was then irradiated in an ice–water bath for 33 h at an effective dose of 0.424 Mrad/h for a total dose of 14.0 Mrad.

After irradiation, the flask was chilled to approximately −20 °C and opened; 50 cm^3 of chloroform was added to maintain the copolymer in solution while the unreacted sulfur dioxide was allowed to escape at room temperature. The copolymer was precipitated in a large excess of methanol and isolated by filtration. It was redissolved in chloroform and precipitated in cyclohexane, which is a solvent for any adventitious traces of polystyrene. Finally, the copolymer was washed with methanol on a filter flask and dried for 4 h under vacuum at 45 °C. The yield was 15.3 g (53 wt % of total monomer). The monomer feed composition was initially 50 mol % styrene; at the completion of irradiation it was 40 mol % styrene.

PSS-2 was prepared at 40 °C in 10% yield from a 68 mol % styrene monomer feed containing 0.1 mol % azobis(isobutyronitrile) (AIBN) by Mr. L. E. Stillwagon, who generously made a sample available for this work. The poly(but-1-ene sulfone)s were obtained through the kindness of Dr. M. J. Bowden. They were prepared at 40 °C by AIBN initiation from monomer feed mixtures containing about 6 mol % but-1-ene and variable amounts of $CBrCl_3$ as a chain-transfer agent.

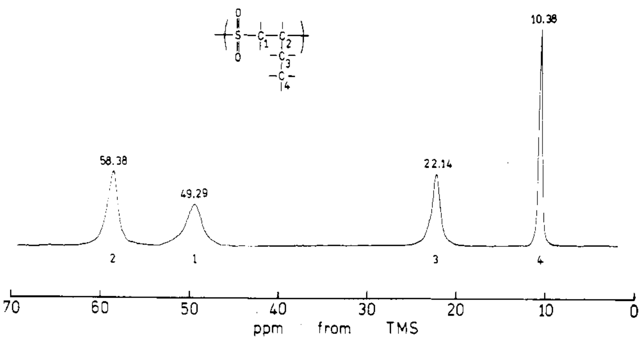

Figure 1. ^{13}C {^{1}H} spectrum (25.16 MHz) of poly(but-1-ene sulfone) sample PBS-2 observed at 40 °C for a 25% w/v solution in chloroform-*d*; 12 800 transients accumulated in 8K data points, 2403 Hz spectral window (208 μs dwell time), pulse interval 3.0 s, 90° pulse, 0.56 Hz digital broadening. Full sweep width not displayed.

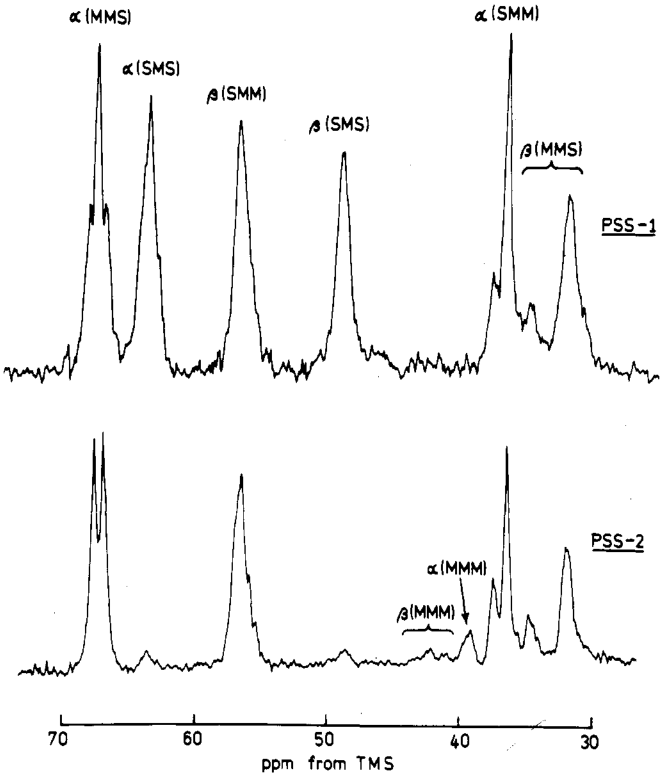

Figure 2. ^{13}C {^{1}H} spectra (25.16 MHz) of poly(styrene sulfone)s PSS-1 and PSS-2, containing 60 and 69 mol % styrene, respectively. Spectra obtained at 40 °C for 25% w/v solutions in chloroform-*d*, each with 8000 transients accumulated in 8K data points, 3521 Hz spectral window (142 μs dwell time), 90° pulses spaced by 3.0 s, 1.64 Hz digital broadening. S = sulfone unit, M = styrene unit in the directional sense $C_\beta \rightarrow C_\alpha$. Observed methine (α) or methylene (β) carbon in central M unit of monomer triad sequence.

Characterization. The molecular weight distributions of the polysulfones were determined by gel-permeation chromatography. Tetrahydrofuran was employed as the solvent, using a Waters Model 501 GPC equipped with a set of μ Styragel columns and calibrated with monodisperse polystyrene standards. The results are shown in Table I.

^{13}C NMR Measurements. The polysulfones were observed by ^{13}C NMR at 25.16 MHz as 25% w/v solutions in chloroform-*d* (Merck and Co.). The solvent and polymer were thoroughly degassed 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.[34] T_1 values were measured by the standard inversion-recovery (π-t-$\pi/2$-T) pulse sequence (accumulating for each

Table II
Results of the Analysis of the Monomer Sequence Distributions in Poly(styrene sulfone)s, According to Ref 36

Poly-sulfone	Unconditional probability of occurrence of monomer triad sequence in copolymer					No. fraction of SM_nS sequence		
	SMS	SMM	MMS	MSM	MMM	$n = 1$	$n = 2$	$n = 3$
PSS-1	0.20	0.20	0.20	0.40	0.00	0.50	0.50	0.00
PSS-2	0.01	0.29	0.29	0.30	0.09	0.04	0.72	0.24

Table III
Effect of Molecular Weight on T_1 and η Values for Poly(but-1-ene sulfone) Samples Observed as 25% w/v Solutions in Chloroform-*d* at 40 °C and 23.5 kG Field

Poly-sulfone	Deg of polymerization[a]	T_1, ms[b] [η (NOE-1)[c]]			
		Backbone		Ethyl branch	
		CH	CH_2	CH_2	CH_3
PBS-3	1091	90	46	75	500
		[0.50]	[0.57]	[0.56]	[1.00]
PBS-2	700	90	47	78	549
		[0.46]	[0.74]	[0.85]	[1.32]
PBS-1	176	85	46	74	541
		[0.49]	[0.53]	[0.64]	[1.16]

[a] Repeat unit = ($-CH_2-CH(CH_2CH_3)-SO_2-$). [b] Reproducible to ±5%. [c] Reproducible to ±20%.

t value 2000 transients for PBS samples, and 8000 transients for PSS samples), with T at least five times the longest T_1 of interest. The peak intensities found with delay time t (I_t) gave good linear plots of $\ln (1 - I_t/I_\infty) = \ln 2 - t/T_1$. The T_1 values for the ortho, meta, and para carbons of the phenyl group in the poly(styrene sulfone)s were not measured, since these carbons could not be individually resolved.

Values of η for poly(but-1-ene sulfone) were obtained with accumulations of 15–20 000 transients. Peak areas were measured first with broad-band proton decoupling and then with the decoupling power turned off. In the latter case, the probe temperature was raised to compensate for the heating effect of the decoupler. The η values for the poly(styrene sulfone)s were not obtained due to the prohibitive time required to obtain a reasonable signal-to-noise ratio for the ^1H-coupled spectrum. T_2 values could not be measured from line widths, as these contained an unknown contribution from unresolved configurational sequences.

Results and Discussion

^{13}C Spectra. The 25.16-MHz ^{13}C spectrum of poly(but-1-ene sulfone) (PBS-2) is shown in Figure 1. This copolymer, like all poly(olefin sulfone)s, has a regularly alternating 1:1 structure.[35] The ^{13}C resonances were assigned from a ^1H-coupled spectrum (not shown), from which the following $J_{^{13}C-^1H}$ coupling constants were obtained: backbone methylene (C_1), 142 Hz; backbone methine (C_2), 142 Hz; ethyl branch methylene (C_3), 134 Hz; and ethyl branch methyl (C_4), 126 Hz.

These resonances are broadened by tacticity effects (the backbone methine carbon being an asymmetric center) and, especially for the backbone carbons, by relatively short T_2 values; e.g., at 25 °C, the line width at half height for C_2 was 86.5 Hz, more than twice the value of 37.5 Hz observed at 55 °C. Only the methyl resonance showed resolved fine structure; it was split into a doublet (this splitting was better resolved at 70 °C, employing 1,1,2,2-tetrachlorethane as solvent), with components of approximately equal intensities at 10.40 and 10.52 ppm. This indicates an atactic structure with equal proportions of meso and racemic configurational dyads. The low-field component of the methyl doublet was partially split further (in the form of a shoulder), suggesting that the methyl carbon in one configurational dyad is sensitive to triad stereosequence effects.

The ^{13}C spectra of poly(styrene sulfone) samples PSS-1 and PSS-2 are shown in Figure 2. The backbone ^{13}C resonances occur from 30 to 70 ppm, and those due to the phenyl ring occur from 127 to 142 ppm (not shown). We have reported previously the assignments of these resonances to particular monomer sequence structures,[36] as shown in Figure 2 for the backbone region. An analysis of these spectra according to our previous procedures[36] gives the values for the unconditional probabilities of occurrence of the five possible monomer triad sequences and the number fractions[37] of SM_nS sequences (S is the sulfone unit and M the styrene unit, in the directional sense $-CH_2-CH(C_6H_5)-$) shown in Table II.

PSS-1 does not contain any MMM sequences and therefore peaks due to methine and methylene backbone carbons in the central M units of SMM and MMS monomer triads can be assigned to these units in SMMS monomer tetrad sequences. As evident from the sequence number fractions in Table II, this copolymer contains equal proportions of single and double styrene units, but none longer, separated by sulfone units. PSS-2 has a more regular monomer sequence structure, consisting predominantly of the repeat sequence (–SMM–), with a negligible proportion of SMS sequences and only a few SMMMS sequences.

Dynamic Results. (i) Poly(but-1-ene sulfone). The effect of molecular weight on the ^{13}C-NMR dynamic parameters is important, in view of the dependence of the critical frequency in the dielectric dispersion measurements on this variable.[1] The results are shown in Table III, for an observing temperature of 40 °C. It is evident that, within experimental error, molecular weights over the range studied have no effect on either T_1 or η for this polysulfone. From this we deduce that the magnitudes of these dynamic parameters are reflecting genuine local segmental reorientations and that the rates of rotatory diffusion are too low to contribute effectively to nuclear relaxation. These results are in accord with literature data for other polymers, the effect of molecular weight on nuclear relaxation being negligible for degrees of polymerization exceeding about 100.[11,15,21]

Table IV shows the effect of temperature on the T_1 and η values of all ^{13}C nuclei in PBS-2. It is significant that an increase in temperature in the range studied leads to a decrease in the backbone carbon T_1 values but an increase in the side-chain carbon T_1 values. Therefore, under our experimental conditions, the correlation times for backbone segmental motions are to the low-temperature (long correlation time) side of the minimum in the T_1 curve, whereas those for the ethyl branch are to the high-temperature (short correlation time) side. We further note that a 2:1 ratio for the backbone methine/methylene carbon T_1 values is found, which shows that for these carbons a dipolar relaxation mechanism with the directly bonded protons strongly predominates[38] and that the backbone motions are effectively isotropic.[39]

In deriving motional correlation times from the ^{13}C dynamic results reported here, we assume the validity of the isotropic, single-τ_c motional model, for which the following equations apply:[40]

$$\frac{1}{NT_1} = \frac{1}{10}\frac{\gamma_H{}^2\gamma_C{}^2\hbar^2}{r_{C-H}}\chi(\tau_c) \tag{1}$$

$$\eta = \frac{\gamma_H}{\gamma_C}\frac{6\tau_c/[1 + (\omega_H + \omega_C)^2\tau_c{}^2] - \tau_c/[1 + (\omega_H - \omega_C)^2\tau_c{}^2]}{\chi(\tau_c)} \tag{2}$$

Table IV
Effect of Temperature on the T_1 and η Values for Poly(but-1-ene sulfone) Sample PBS-2, Observed as a 25% w/v Solution in Chloroform-*d* at 23.5 kG Field Strength

Temp, K	T_1, ms[a] [η (NOE-1)[b]] Backbone CH	Backbone CH_2	Ethyl branch CH_2	Ethyl branch CH_3
328	86 [0.63]	46 [0.83]	88 [0.97]	599 [1.36]
313	90 [0.46]	47 [0.74]	78 [0.85]	549 [1.32]
298	108 [0.54[c]]	51 [0.70]	69 [1.30]	419

[a] Reproducible to ±5%. [b] Reproducible to ±20%. [c] Due to considerable line broadening at this temperature, individual multiplet areas for backbone carbons could not be resolved satisfactorily.

Table V
Correlation Times for Backbone and Side-Chain Motions in Poly(but-1-ene sulfone) (PBS-2) as a 25% w/v Solution in Chloroform-*d*, Deduced from the Simple Isotropic, Single-τ_c Motional Model (see eq 1–3 in text)

Temp, K	τ_c, ns Backbone from NT_1	Backbone from η	Ethyl branch CH_2 from NT_1	Ethyl branch CH_2 from η	Ethyl branch CH_3 from NT_1	Ethyl branch CH_3 from η
328	22	2.6	0.29	1.9	0.027	1.3
313	23	3.1	0.33	2.2	0.030	1.3
298	27	3.4	0.38	2.7	0.039	1.3

where

$$\chi(\tau_c) = \frac{\tau_c}{1 + (\omega_H - \omega_C)^2\tau_c^2} + \frac{3\tau_c}{1 + \omega_C^2\tau_c^2} + \frac{6\tau_c}{1 + (\omega_H + \omega_C)^2\tau_c^2} \qquad (3)$$

The symbols have their usual meanings.[40] Although eq 1 is double valued in τ_c (except at the T_1 minimum), we are able to choose the appropriate τ_c values on the basis of the effect of temperature on the T_1 values (vide supra). The calculated τ_c values are shown in Table V, with r_{C-H} taken as 1.10 Å.

The discrepancy between the τ_c values for motions calculated from NT_1 and from η show that a single-τ_c assumption is not correct. It may be noted that the discrepancy is greatest for the highly mobile methyl group and that whereas NT_1 predicts a longer τ_c than that from the corresponding η for backbone carbons, the reverse is true for side-chain carbons. Although it would be possible to account for both NT_1 and η satisfactorily by a motional model involving a distribution of correlation times,[8] we do not do so here, as the most significant feature of these results for our present purposes is the presence of relatively rapid backbone segmental motions in simple poly(olefin sulfone)s, with correlation times at least four orders of magnitude shorter than those deduced from dielectric relaxation measurements.[1]

We are then left with the question as to why such rapid motions are NMR active but dielectrically inactive. One possible type of motion which would account for this is shown in Figure 3. This is a transition of the "second type" (pair gauche production), as classified by Helfand.[41] Five backbone bonds and six main-chain atoms are involved, i.e., the sequence C–S–C–C–S–C, with concerted segmental transitions about two C–S bonds, allowing interconversion of the three conformational states ttt, g$^+$tg$^-$, and g$^-$tg$^+$. The backbone C–C bond always remains trans, as suggested by other evidence (e.g., ref 4, 42, and literature cited therein), and neighboring pairs of sulfone dipoles cancel in accord with experimental observations of dipole moments in polysulfones.[4,43] Therefore, although the sulfone dipoles are not reorientated by this motion, the C–H bond vectors are.

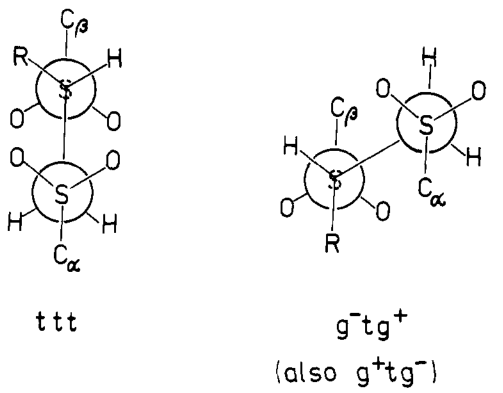

Figure 3. Proposed allowed equilibrium conformational states for poly(α-olefin sulfone)s in solution. Note that the sulfone dipoles cancel and that during the transitions ttt ⇄ g$^-$tg$^+$ ⇄ g$^+$tg$^-$ there is no net reorientation of these dipoles (dielectrically inactive motions), but there is a reorientation of backbone C–H vectors (^{13}C NMR active motions).

It is instructive to compare the correlation times found here for poly(but-1-ene sulfone) with those for but-1-ene homopolymer. Preliminary ^{13}C T_1 and η data obtained in this laboratory for poly(but-1-ene) at 40 °C in pentachloroethane solution[44] reveal backbone segmental motions with correlation times approximating 0.48 ns, i.e., but-1-ene homopolymer is about 50 times more flexible than its copolymer with sulfur dioxide. However, there is little difference in the side-chain T_1 values between these polymers. Evidently, the sulfone units restrict mainly backbone motions, by precluding coupled bond motions which involve rotation about main-chain C–C bonds.

(ii) Poly(styrene sulfones). Table VI shows the T_1 values for backbone carbons in the various monomer sequences in PSS-1 and PSS-2, at three temperatures. These two copolymers have chains sufficiently long (221 styrene, 147 sulfone and 1384 styrene, 610 sulfone units on average, respectively) that the T_1 values must reflect local segmental motions only, as found for the poly(but-1-ene sulfone) samples.

For both poly(styrene sulfone)s we observe an increase in T_1 values with an increase in temperature for all main-chain carbons, irrespective of sequence type, indicating that the correlation times for their motions lie to the high-temperature (short correlation time) side of the T_1 minimum. This is in contrast to the results found above for backbone motions in poly(but-1-ene sulfone)s under identical conditions and shows an order of magnitude greater flexibility for the poly(styrene sulfone)s. The consistent 2:1 ratio for methine (α) to methylene (β) carbon T_1 values in PSS-1 and PSS-2 shows that, as was the case for the poly(but-1-ene sulfone)s, chain motions are essentially isotropic and the ^{13}C nuclei relax exclusively by a dipole mechanism involving only their directly bonded protons. The τ_c values shown in Table VII are derived from the isotropic, single-τ_c motional model (eq 1 to 3)[45] and point to a number of significant conclusions.

As it is likely that a phenyl substituent provides a similar if not slightly greater barrier to conformational transitions as an ethyl substituent,[46] we attribute the difference in backbone τ_c values for PSS-2 and PBS-2 to the different spacing of the sulfone units in the two polymers. The neighboring sulfone dipoles in the 2:1 poly(styrene sulfone) are sufficiently distant to have only a weak correlation, if any, in their orientations,

Table VI
T_1 Values for Backbone Methine (α) and Methylene (β) Carbons in Various Monomer Triad Sequences (see text) in Poly(styrene sulfone)s PSS-1 and PSS-2[a]

Temp, K	T_1, ms ± 5%, for PSS-1 and [PSS-2]					
	α carbons			β carbons		
	SMS	SMM	MMS	SMS	SMM	MMS
328	106	101	101	55	55	53
		[136]	[129]		[71]	[68]
313	96	90	89	52	54	54
		[108]	[108]		[60]	[55]
298	84	78	76	48	43	44
		[89]	[86]		[46]	[44]

[a] Polysulfones observed as 25% w/v solutions in chloroform-d, at 23.5 kG field strength.

Table VII
Correlation Times for Backbone Motions in Poly(styrene sulfone)s PSS-1 and PSS-2 as 25% w/v Solutions in Chloroform-d, Deduced from the Simple, Isotropic Single-τ_c Motional Model

Temp, K	τ_c, ns,[a] for PSS-1 and [PSS-2]	
	Monomer SMS	Sequence SMMS[b]
328	0.49	0.51
		[0.38]
313	0.57	0.62
		[0.48]
298	0.69	0.75
		[0.64]

[a] Calculated from NT_1, by eq 1 and 3 (see text). [b] The monomer triad sequences SMM and MMS must be derived from SMMS sequences in these polysulfones, due to the negligible proportions of MMM sequences.

with no constraint on backbone C–C conformational transitions as deduced above for the 1:1 poly(but-1-ene sulfone). For this reason, it is reasonable to predict that the 2:1 poly(styrene sulfone) would exhibit a high-frequency dielectric loss in solution.

If we compare the backbone methine T_1 values in PSS-2 with those for polystyrene under similar conditions, it appears that the 2:1 poly(styrene sulfone) is slightly more flexible. Thus, for atactic polystyrene observed at 22.6 MHz and 40 °C in chloroform solution (20 wt %), the backbone methine ^{13}C T_1 was 85 ms,[7] somewhat shorter than the α(SMM) and α(MMS) values in PSS-2 (108 ms, Table VI). Assuming that the same motional model applies to both polymers, and allowing for the slight difference in observing frequencies, we deduce that the correlation time for backbone motions in the poly(styrene sulfone) is about 25% shorter than for polystyrene. This difference may be due to the greater bond length of C–S compared to C–C (1.80 vs. 1.54 Å[41]).

Considering now poly(styrene sulfone) (PSS-1), which has equal proportions of SMS and SMMS sequences, it is rather surprising to find no significant differences in the NT_1 (and hence τ_c) values for the backbone carbons in these sequences (Tables VI and VII). Although η values were not obtained, these too must be equal for carbons in both types of sequences, on the basis of our previous statistical analysis[36] of the monomer sequence distributions in these polysulfones.[47] One would expect the 1:1 alternating poly(styrene sulfone) $(\text{-SM-})_n$ to have correlation times for backbone motions comparable to (if not longer than) those found here for poly(but-1-ene sulfone).[46,48] The fact that the rate of reorientation of the ^{13}C–H vectors for SMS sequences in the 1.5:1 poly(styrene sulfone) is several orders of magnitude faster than one might reasonably expect suggests that the motion of SMS sequences is coupled to that of the rapidly reorientating SMMS sequences.[49] The ^{13}C dynamic results thus do not necessarily probe the true internal conformational transition rate in SMS sequences but rather the overall motion in space of this chain segment, which is dominated by the much faster segmental motions of nearby SMMS sequences. Another indication that the motions of SMS and SMMS chain segments are coupled is given by the longer T_1 values (Table VI) for SMMS sequences in the 2:1 polysulfone, compared with the 1.5:1 polysulfone. It appears then that the presence of SMS sequences in the latter copolymer exerts some damping influence on the internal motions of SMMS sequences along the same chain.

Conclusions

Our results demonstrate that segmental motions in poly(but-1-ene sulfone) are not as severely hindered by sulfone units as had been supposed from dielectric observations of similar poly(olefin sulfone)s. However, poly(but-1-ene sulfone) is at least an order of magnitude less flexible than poly(but-1-ene), and we attribute this difference primarily to the constraint of maintaining the backbone C–C bonds fixed in the trans conformation in the polysulfone. When sulfone units are separated by at least five main-chain bonds, as in SMMS sequences of variable-composition poly(styrene sulfone)s, this constraint no longer applies. In a poly(styrene sulfone) containing equal proportions of SMS and SMMS sequences, the SMS backbone segments apparently enjoy a substantially greater degree of motional freedom, although this is likely correlated to the motions of SMMS neighbors.

The large discrepancy between τ_c values computed from T_1 and η results for poly(but-1-ene sulfone) indicates that the single-τ_c motional model is only an approximation and that a treatment of backbone motions in terms of correlated segmental transitions may be necessary. More detailed experimental and theoretical investigations of this interesting class of polymers are warranted.

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(45) Although only approximate, this model does allow useful comparisons of the dynamic behavior of these polymers.
(46) CPK space-filling models of the two polysulfones in question indicate that such an assumption is warranted, provided that the plane of the phenyl ring bisects the backbone C_β–C_α–C_β angle.
(47) The internal self-consistency of the monomer sequence analysis, based on peak areas, showed that there was no significant differential η between SMS and SMMS sequences.
(48) Although we have prepared the 1:1 poly(styrene sulfone) by γ irradiation of a styrene–sulfur dioxide mixture at −78 °C, this material was completely insoluble in all common organic (and inorganic) solvents, precluding its examination by ^{13}C NMR for this work.
(49) Every SMS sequence in PSS-1 has a 75% chance of having at least one neighboring SMMS sequence.

On Chain Dynamics in Poly(alkene sulfone)s[1]

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ABSTRACT: Spin–lattice relaxation times for ^{13}C atoms in poly(2-methylpentene-1 sulfone)s in chloroform solution indicate rapid backbone segmental rearrangements at rates independent of chain length. This is in contrast to the previously known dielectric relaxation, which is slow and strongly dependent on molecular weight, corresponding to over-all tumbling of the macromolecule. A tentative rationalization invokes the known strong steric and electrostatic restrictions on gauche conformations about backbone C–C bonds and identifies as the most likely local process a particular 4-bond rearrangement which reorients C–H bonds but not sulfone group dipoles.

It has been known for many years that dielectric relaxation in solutions of alternating olefin–sulfur dioxide copolymers is an unusually slow process as compared to that in other common polar polymers. Although the electric dipole within each sulfone group essentially bisects the O–S–O bond angle and is thus transverse to the chain backbone,[2a] the apparent dielectric relaxation time corresponding to the frequency of maximum loss, $\tau_{\rm diel} = 1/2\pi f_{\rm max}$, is observed to vary strongly with molecular weight[2b] and to lie quite close to what would be expected for relaxation by rotatory diffusion of a dynamically rigid but randomly kinked (essentially Gaussian) chain:

$$\tau_{\rm or} = 1/2D_{\rm rot} = 2M[\eta]\eta_0/RT \qquad (1)$$

even up to molecular weights exceeding 10^6. In this expression, which invokes the theoretical $D_{\rm rot}$ due to Riseman and Kirkwood[3] and to Isihara,[4] the symbols have their usual meanings. The polysulfones studied by Bates, Ivin, and Williams were those based on hexene-1 and 2-methylpentene-1. Similar dielectric behavior has also been found[5] in benzene solutions of poly(hexadecene-1 sulfone).

A natural deduction from the above observations would be that internal segmental rearrangements within the chain backbone are unusually slow and thus simply unable to compete (over the range of molecular weights studied) with over-all rotatory diffusion ("tumbling") as a path to relaxation of the electric polarization.[2b,6,7] The existence of such competition between local and global motions is well documented, for example, in the dielectric behavior of poly(p-halostyrenes) of sufficiently low molecular weight,[8,9] and has also been observed by ESR in spin-labeled polystyrenes,[10] by ^{13}C NMR relaxation in polystyrene[11,12] and ^{19}F relaxation in poly(fluorostyrene)s.[13] In these styrene polymers the cross-over from tumbling to local relaxation is essentially complete at molecular weights of the order of 4×10^4; in poly(ethylene oxide) and poly(dimethylsiloxane) the local motions are already dominant even at molecular weights of 10^3; but, as stated above, in the poly(1-olefin sulfone)s there is no clear sign of local motions in the dielectric dispersion even at $M = 10^6$, where $\tau_{\rm or}$ is of the order of 10^{-4} s.

The conclusion that segmental motions in the polysulfones are uniquely slow among non-rodlike macromolecules is, however, an uncomfortable one in view of the general properties of these materials[14] (e.g., the enormous permeability to both O_2 and CO_2 of solid hexadecene-1 polysulfone or the relatively low T_g values), and it is therefore natural to use ^{13}C NMR relaxation as an alternative probe. It has now been found by no less than three different groups of workers that