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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 $C_\beta$–$C_\alpha$–$C_\beta$ angle.
(47) The internal self-consistency of the monomer sequence analysis, based on peak areas, showed that there was no significant differential $\eta$ between SMS and SMMS sequences.
(48) Although we have prepared the 1:1 poly(styrene sulfone) by $\gamma$ 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.

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# 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, $\tau_{\mathrm{diel}} = 1/2\pi f_{\max}$, 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:

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

even up to molecular weights exceeding $10^6$. In this expression, which invokes the theoretical $D_{\mathrm{rot}}$ 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 $4 \times 10^4$; 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 $\tau_{\mathrm{or}}$ 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

Table I
$^{13}$C Spin–Lattice Relaxation Times $T_1$ (ms) for Poly(2-methylpentene-1 sulfone) in $CDCl_3$ at 20 MHz

| Carbon atom[a] | $M_v = 1.5 \times 10^5$ at 35 °C | $M_v = 1.4 \times 10^6$ at 35 °C | $M_v = 1.4 \times 10^6$ at 65 °C |
|---|---|---|---|
| b-C | 730 ± 50 | 750 ± 50 | 900 ± 150 |
| b-$CH_2$ | 23 ± 5 | 30 ± 5 | 62 ± 7 |
| $\alpha$-$CH_3$ | 175 ± 15 | 160 ± 10 | 320 ± 20 |
| $\alpha$-$CH_2$ | 33 ± 5 | 60 ± 10 | 75 ± 10 |
| $\beta$-$CH_2$ | 105 ± 10 | 115 ± 25 | 210 ± 50 |
| $\gamma$-$CH_3$ | 385 ± 20 | 430 ± 10 | 840 ± 30 |

[a] b-C denotes quaternary backbone carbon; b-$CH_2$ denotes backbone methylene carbon; greek letters denote side-chain carbons.

spin–lattice relaxation times for backbone carbon atoms imply rates of C–H bond reorientation that are quite normal as compared to the dielectric behavior: Cais and Bovey[15] have studied $SO_2$ copolymers with styrene and butene-1; Fawcett, Heatley, Ivin, Stewart, and Watt[16] have measured $T_1$ and the nuclear Overhauser enhancement for a large number of different poly(olefin sulfone)s, and we have obtained spin–lattice relaxation times for two fractions of poly(2-methylpentene-1 sulfone). In all these cases, the correlation times for C–H bond reorientation are of the order of 1 ns. The conclusion is inevitable that certain local segmental rearrangements can indeed occur in the polysulfones at normal rates, comparable to those found in polystyrene, but that these motions for some special reason are unable to produce relaxation of the electric dipole moment. We offer below a tentative and qualitative rationalization of this behavior, based on the conformational energy analysis of the polysulfones by Fawcett and Ivin.[17]

## Experimental Section

Poly(2-methylpentene-1 sulfone) was synthesized at −60 °C in toluene solution with *tert*-butyl hydroperoxide as initiator. The polymer was subsequently fractionated by precipitation from acetone solution with methanol at 35 °C. Viscosity-average molecular weights of the fractions were obtained from measured intrinsic viscosities in chloroform by means of the relationship given by Bates, Biggins, and Ivin.[18] Two fractions were analyzed by GPC in dimethylformamide containing 0.02 M LiBr. This system is not suitable for accurate characterization, as the solvent causes some degradation of polysulfones,[19] so that the polydispersity indices obtained ($M_w/M_n \simeq 1.5$) are upper limits.

Dielectric permittivity in benzene solution at 30 °C was measured for several fractions in the range $10^2$–$10^5$ Hz with a General Radio 1620-A assembly and a home-built cell. The results were in very good agreement with those of Bates, Ivin, and Williams[2b] and need not be reproduced here.

Solutions of two fractions (ca. 10% of weight) were made up in $CDCl_3$. Their $^{13}$C $T_1$ values were determined at 20 MHz on a Varian CFT-20 spectrometer in the Department of Chemistry at Yale University, thanks to the kind hospitality of Professor Martin Saunders. The standard deviations of $T_1$ are of the order of 10%. A 180–$\tau$–90 pulse sequence was used, about 300 to 500 transients being taken for each spectrum.

## Results and Discussion

The observed $^{13}$C NMR $T_1$ values in 10% deuteriochloroform solution for both fractions are listed in Table I for each of the six carbon atoms in a repeat unit of the polymer. It is seen at once that $T_1$ for each specific carbon atom is independent of molecular weight to within experimental uncertainty, thus showing clearly that truly local motions are being observed. Also, the increase of $T_1$ with increasing temperature indicates that the motions are faster than those corresponding to the minimum in $T_1$. Fawcett, Heatley, Ivin, Stewart, and Watt[16] measured a sample of the same polymer at 25 MHz in deuteriochloroform at ambient temperature. The general disposition of the $T_1$ values is very similar to those obtained by us, and with allowance for differences in detailed conditions the agreement seems satisfactory. For the backbone methylene carbon, the figures are also similar in magnitude to that found by Cais and Bovey[15] for 25% w/v poly(butene-1 sulfone) in chloroform at 40 °C.

Our speculations on the unusual dynamical behavior of the alternating olefin–$SO_2$ copolymers rest on the discovery by Fawcett and Ivin[17] that the polymers with substituents on both backbone carbons (e.g., those based on butene-2, cyclohexene, or cyclopentene) have small and perhaps vanishing permanent electric dipole moments. Since each dipole in a sulfone group can be resolved into two components of equal magnitude directed along the adjacent S–C bonds, this means that in these chains the rotational isomeric states about backbone C–C bonds are essentially 100% trans. Both steric and electrostatic interactions are believed[17] to contribute to the virtual exclusion of gauche states. However, gauche conformations about C–S bonds are plentiful, so that the unperturbed chain dimensions are quite normal. In the 1-olefin sulfone polymers the dipole moment does *not* vanish, so that there must be some allowed gauche conformations about C–C bonds, but the trans state still predominates. With this background we can now consider particular models for the relevant local processes.

Many possible local chain motions may be visualized. A useful classification is due to Helfand,[20] who distinguishes between type 1 motions, which change neither the separation nor the relative orientation of the two portions of polymer chain ("tails") attached to the rearranging sequence of bonds, and those of types 2 and 3, in which the tails alter separation or orientation, respectively. In general, motion of the tails could be expected to slow down the local process, but Helfand concludes that certain type 2 rearrangements can take place at significant rates. Type 1 processes, however, have generally received more attention, and in this preliminary discussion we confine ourselves to them.

The catalog of type 1 motions expands rapidly with the number of bonds involved,[21] but three particularly simple type 1 processes seem to be most commonly adopted as models. One is the classical 5-bond crankshaft discussed by Schatzki[22] and others,[20,21,23] and the other two, which receive prominence in the recent dynamical studies of Valeur, Monnerie, and coworkers,[24] involve 3 and 4 bonds, respectively. The 3-bond rearrangement can be described as moving three bonds from one side to the other of a cyclohexane chair, as depicted in Figure 1, and the 4-bond process is shown in Figure 2. It should be recognized that the *transition states* for these latter motions surely require considerable distortions of bond angles and thus inevitably also produce some relative displacements of the tails; Helfand therefore also refers to them as of type 3* (and possibly 2*), in contrast to the 5-bond crankshaft which requires no displacements of tails and is thus of type 1*. In their studies of local motion in aliphatic polyethers, Gény and Monnerie[25] recognize that more than one segmental rearrangement must occur; for example, neither the 3-bond process nor the 5-bond crankshaft can produce electric dipole reorientation in poly(oxymethylene). For this and other reasons, the 4-bond process is considered by them to be active in polyethers.

The situation in the olefin polysulfones can be qualitatively considered in terms of the above type 1 motions, with the following results:

(1) The 5-bond motion requires the presence of at least one gauche conformation about a C–C bond, both before and after rearrangement.

(2) The 3-bond motion (cf. Figure 1), which would produce dielectric relaxation, inevitably involves a gauche state at the central link. If this should be a C–S bond, then a trans initial

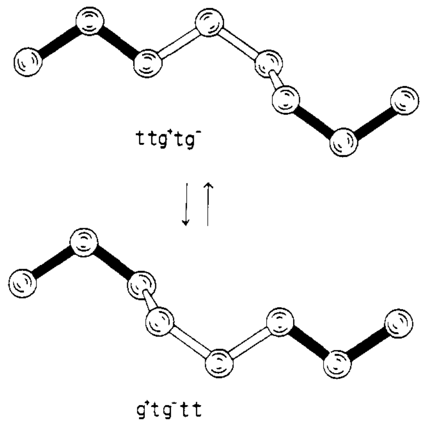

**Figure 1.** Sketch of a 3-bond rearrangement. Two bonds of each "tail" in a particular conformation are shown in black.

conformation is possible for both the neighboring C–C bonds, but then in the final conformation one of these necessarily becomes gauche.

(3) A 4-bond motion with a sulfur atom at the apex (cf. Figure 2), however, need involve only trans conformations at C–C bonds both before and after rearrangement. (It does require a $g^{\pm}g^{\mp}$ sequence, but the great length of the C–S bond renders this sterically innocuous.) Moreover, it produces a reorientation of the C–H bonds attached to the backbone carbon atoms but no change of electric polarization since the dipole moment about the two trans C–C bonds is vanishingly small and the central $SO_2$ group does not change its orientation. If a carbon atom is at the apex, again at least one gauche C—C bond is involved.

We observe that only the above described 4-bond rearrangement with a sulfur atom at the apex can lead to C–H bond reorientation with no attendant electric dipole reorientation, and, by coincidence, it is also the only process involving no gauche C–C bonds. We tentatively propose that this motion plays the dominant role in the observed $^{13}$C relaxation and that all motions involving gauche conformations at C–C bonds are much slower, thus forcing dielectric relaxation in the observable range of chain lengths to proceed by tumbling. For this idea to be correct, the potential energy barriers separating C–C gauche states from the adjacent accessible conformations must in all cases be much higher (by at least 30 kJ mol$^{-1}$) than those controlling the rate of the proposed 4-bond process.

Cais and Bovey[15] have suggested a type 2 motion which, like our 4-bond motion, effects C–H bond reorientation without electric dipole relaxation and which involves only trans conformations about C–C bonds.

At present our observations are not sufficient for unique evaluation of the average correlation time for the proposed process. If we adapt a model recently used for polystyrenes,[13,26] we obtain harmonic mean correlation times for our polysulfone of about 0.65 ns at 35 °C and 0.2 ns at 65 °C. We cannot place much emphasis on these numbers, except to observe that they are similar in magnitude to those calculated by Cais and Bovey[15] on the basis of a single isotropic rotation and that they are indeed enormously shorter than the dielectric correlation times.

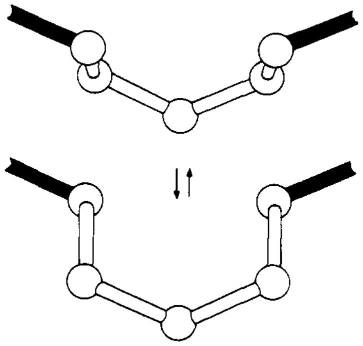

**Figure 2.** Sketch of 5-bond rearrangement. In polysulfones this is proposed to occur with a sulfur atom at the apex, in which case there is no change in the electric moment. The conformational rearrangement is $tg^+g^-t \rightleftarrows tg^-g^+t$.

Much more work is needed on this problem. Experimentally, both $T_1$ and NOE should be observed for as wide as possible ranges of frequency, molecular weight, and temperature. As for polystyrenes,[13] this would allow considerable discrimination among alternative models. Other experimental techniques could also be used. (In this connection, we remark that a preliminary examination of one of our fractions by Ferry and Nemoto[27] indicated only normal viscoelastic behavior, as for dynamically flexible chains.) Theoretically, potential energy surfaces should be studied for both equilibrium and transition-state conformations of these polymers.

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