The conformational origin of flexibility and stiffness in poly(olefin sulphones) demonstrated by means of dynamic C^{13} n.m.r. measurements

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From previous calculations of electrostatic energies which cause third order Markov correlations of orientation of the dipoles in poly(olefin sulphones) $-(SO_2-C-C-)_nSO_2-$, the lack of a strong interaction of one dipole with its immediate neighbour is predicted in the alternating copolymers prepared with symmetrical olefins. Using an approach developed by Bovey to detect stiffness in polysulphones in solution by means of C^{13} spin-lattice relaxation time measurements upon carbons in the main chain it is shown that poly(but-2-ene sulphone) and poly(cyclohexene sulphone) do have significantly shorter correlation times for motion of their backbones, and are thus more flexible than poly(but-1-ene sulphone). In the flexible polymers the C–C bonds are predominantly *trans* in conformation so that neighbouring sulphone groups are sufficiently well separated in space that each has thermal motions independently of the other. Stiffness in poly(1-olefin sulphones) is thus a consequence of their C–C bonds being predominantly in a *gauche* conformation, which permits the close approach of each pair of adjacent dipoles and the development of strong mutual ordering through the dipoles' electric fields.

Keywords Poly(olefin sulphones); backbone mobility; dynamic C^{13} nuclear magnetic resonance (T_1); electrostatic ordering of dipoles; conformational-dependent correlations

INTRODUCTION

The dynamics of poly(olefin sulphones) in solution and the intimately related conformational properties are not yet fully understood. In principle the three bonds of the repeat unit $-SO_2-CHR_1-CHR_2-$ provide three axes of rotation to allow a variety of relative orientations of adjacent sulphone groups to facilitate segmental motions. It was soon realized that the electrostatic forces between dipoles are important: the size of the poly(hex-1-ene sulphone) chain is influenced by solvent polarity[1]. Subsequently a prominent dielectric dispersion was discovered in solutions of two poly(1-olefin sulphones) at frequencies low enough to correspond to rotational diffusion of the whole molecule[2]. It was concluded from the small dependence of $\langle\mu^2\rangle/z$ upon molecular weight that the polymers should be classified as stiff random coils[3], though the structural cause of the stiffness was then obscure. Since solutions of symmetrical olefin polysulphones, such as those prepared from but-2-ene and cyclohexene, lack the low frequency process[4], the appearance of a dipole moment in the polymers was rationalised in terms of the conformation of the C–C bond (if this were trans adjacent C–S bond dipoles would cancel)[4]. It is rare to find third-order Markov correlations the *dominant* factor controlling chain conformations and segmental movements[5], yet this is what emerged as possible when simple calculations found electrostatic energies between pairs of sulphone dipoles ($\mu = 4.4$D) to be larger than bond rotation potentials and the likely conformational energies of alkyl sulphones[6].

The present study was undertaken to verify by ^{13}C dynamic n.m.r. measurements a feature shown by crude calculations of the electrostatic energies: that the correlation of the orientation of one sulphone dipole with its neighbour, in a medium of low dielectric constant would be weak provided that the C–C bond between the dipoles was in the *trans* conformation. This idea, which was expressed earlier[6], is illustrated in a novel way in *Figure 1b*, where a three dimensional grid represents the three internal degrees of freedom of the segment of *Figure 1a*. At the vertices of the grid are the electrostatic energies for the 27 positions corresponding to the three equally-spaced values (0, $2\pi/3$, $4\pi/3$) of the rotational angles of each covalent bond[6]. Movements along a line in the grid and within one plane correspond respectively to the rotation of a single bond and to the simultaneous rotation of two bonds. In any one plane the range of electrostatic energies is a measure of electrostatic control upon movement within that plane. The numbers have the same range of 30 kJ mol^{-1}, which is large relative to thermal energies in all but the central horizontal plane. This exception corresponds to rotation about the two C–S bonds, with the C–C bond fixed in the *trans* conformation. It would be valuable to show by experiment that the two dipoles are free of each other under these circumstances, when the two sulphone groups are as far apart as is possible within the constraints of the covalent bonding system. We assume that it is sufficient for segmental motion that there is one covalent bond about which a rotation of some magnitude

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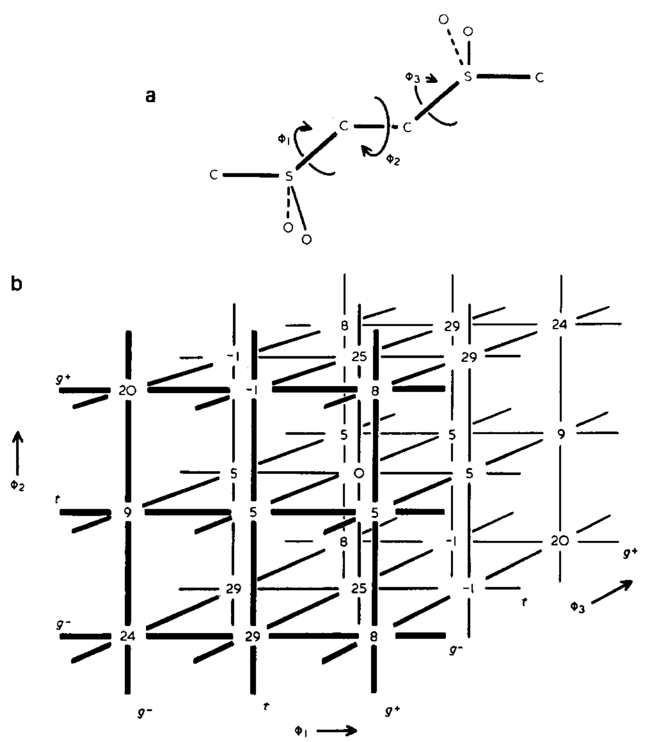

Figure 1 (a) Three axes of rotation in the repeat unit. (b) A three-dimensional display of the electrostatic energies in kJ mol^{-1} which arise from dipole–dipole interactions[6]. Third order correlations are important

might occur. Motion at the other end of the segment consists of smaller amplitude distortions of several bonds. This view of polymer dynamics is supported by computer simulations[7] and experimental investigations of polymers containing units whose internal rotational characteristics are known[8]. We are thus seeking an explanation of polysulphone dynamics which is different in character from the lattice jump models that were proposed by others[9,10], but which is more consistent with our earlier work[6,11].

Despite the limitations which will become apparent, we will use the simple single correlational time model for interpreting spin lattice relaxation time (T_1) and Nuclear Overhauser factor (η) values. In the equations of this model the symbols have their usual meaning[12].

$$\frac{1}{NT_1} = \frac{\mu_0}{4\pi}\,\frac{\gamma_H^2\gamma_C^2\tau^2}{10\,r_{CH}^6}\,\{J_0(\omega_H-\omega_C)+3J_1(\omega_C)\}$$

$$+6J_2(\omega_H+\omega_C) \tag{1}$$

$$1+\eta = 1+\frac{\gamma_H}{\gamma_C}[6J_2(\omega_H+\omega_C)-J_0(\omega_C-\omega_H)]$$

$$[J_0(\omega_H-\omega_C)+3J_1(\omega_C)+6J_2(\omega_H+\omega_C)] \tag{2}$$

$$\text{with } J_n(\omega) = \frac{\tau_c}{1+\omega^2\tau_c^2} \tag{3}$$

According to T_1 measurements the hydrocarbon units in the backbone of poly(but-1-ene sulphone) move about 50 times as slowly as in polybut-1-ene, so that motional narrowing conditions do not apply[10,14]. That τ_c is longer than the reciprocal of the Larmor frequency frequency was demonstrated by the fall in T_1 when the temperature was raised[9,13], and was attributed to the presence of the sulphone groups[9,13,15,16]. The opposite behaviour was shown by the more flexible polybut-1-ene[14], and also by a poly(styrene sulphone)[9]. In this the dipoles were irregularly spaced along the main chain (...–SO_2–CHϕ–CH_2–SO_2–CHϕ–CH_2–CHϕ–CH_2–SO_2–....), being more dilute in the one dimension of the chain contour than in the poly(but-1-ene sulphone). This provided extra degrees of freedom and decoupled the sulphone groups. The subsequent observation of a large dielectric dispersion at the high frequencies expected of a segmental process[17] confirmed the correspondence between the prevalence of motional narrowing conditions and unhindered motion of sulphone dipoles.

We chose to study poly(but-2-ene sulphone) in chloroform for a comparison with the well known behaviour of poly(but-1-ene sulphone) in that medium[9,13], and to study poly(cyclohexene sulphone in benzene, the solvent which has been used for dielectric measurements[4,18], to discover whether the conformation of the C–C bond does influence chain dynamics in alternating poly(olefin sulphones).

EXPERIMENTAL

The samples of the two copolymers were prepared and purified by reprecipitation in the usual way[4]. From the limiting viscosity numbers the molecular weights of these unfractionated samples were at least 800000 and 25000 for the poly(but-2-ene sulphone) and poly(cyclohexene sulphone) respectively[4]. Thus the T_1 and η values, particularly in view of the results themselves, were thought to be controlled by high frequency segmental motions. The polymer and solvent were subject to three freeze–pump–thaw cycles before being sealed under nitrogen. The standard inversion recovery pulse sequence ($\pi-\tau-\pi/2-T$), with T longer than five times the largest T_1, was used to measure T_1 on a Bruker WH90. To reduce the effect of any small but progressive drifts in field homogeneity, the transients for each τ were obtained at different periods during the measurements. In all 1200 transients were obtained at each τ for the T_1 determination (sweep width 6024 Hz) and 400 transients for each η measurement (sweep width 5000 Hz). For the latter the transients were obtained with the decoupler alternately on and off.

RESULTS AND DISCUSSION

The spectrum of the poly(but-2-ene sulphone), (*Figure 2*, showed less fine structure than may be seen under optimal conditions[13] because a large line broadening factor (10 Hz) was used to smooth the data. The stereochemistry of the hydrocarbon unit corresponds to *trans* addition to *cis* olefin[13]. Probably only $m_sr_cr_s$ sequences contributed to the CH(i) peak, the other three structures being grouped under the CH(i) peak[13]. There is only a small though consistently present difference between the T_1 values of the two methine peaks, but for both the trend with temperature is very different from that found by Cais and Bovey for poly(but-1-ene sulphone) in the same solvent[9], as may be seen in *Figure 3*. The two polymers lie on different branches of the log T_1 vs. log τ_c plot, the but-2-

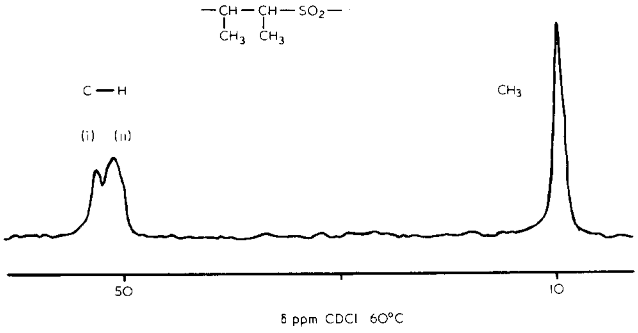

Figure 2 ^{13}C {-H} spectrum of poly(but-2-ene sulphone) at 22.63 MHz, showing two methine peaks and one methyl peak. $CDCl_3$ solvent at 60°C. The chemical shift is measured in ppm from TMS

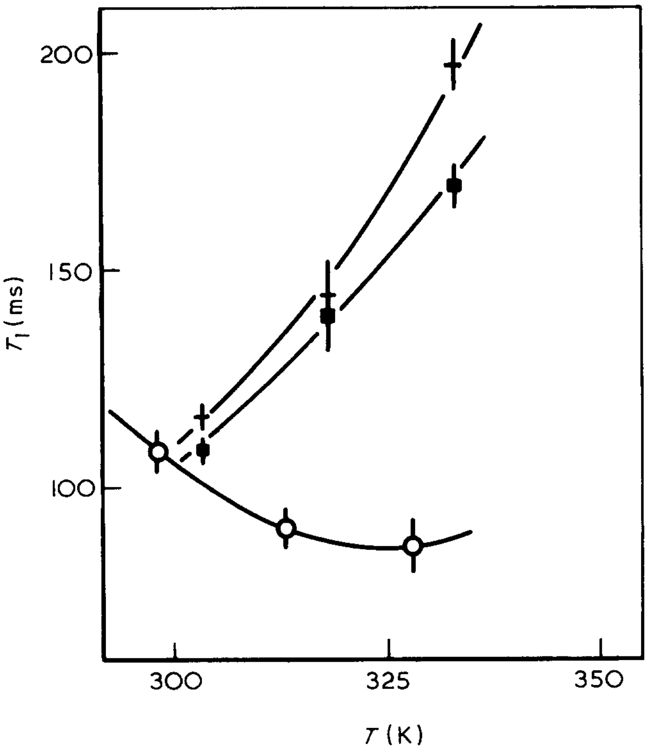

Figure 3 T_1 values for poly(butene sulphones). ┼ and ▮ are the values for CH(i) and CH(ii) respectively, which were distinguished in the spectrum of poly(but-2-ene sulphone), as is shown in *Figure 2*. The values marked by ⦽ are for poly(but-1-ene sulphone), and were measured in the same solvent, but at a slightly different frequency (25.16 MHz) by Cais and Bovey[9]. The two polymers differ in their dynamics

ene polymer being significantly the more flexible and much closer to the motional narrowing conditions.

Though for poly(cyclohexene sulphone) temperature has a smaller effect upon T_1 of the main chain carbons, yet it is clear from the entries in *Table 2* that the rising trend with rising temperature is established, and that this second symmetrical olefin polysulphone is also more flexible than the poly(1-olefin sulphone).

That the methyl groups of poly(but-2-ene sulphone) have T_1 values nearly three times as large as those of the main chain carbons is to be expected for such freely rotating groups attached to a fairly rigid backbone[19]. In contrast the side group carbons of the poly(cyclohexene sulphone) have correlation times only a little shorter than the main chain, so that all the atoms of the six-membered ring have essentially the same dynamics.

When the correlation times of backbone motion of poly(but-2-ene sulphone) at 303K obtained from the T_1 measurements (*Table 1*) are compared with the value of 26 ns obtained in a similar manner for poly(but-1-ene sulphone)[9], it appears odd that the first polymer, with two

Table 2 Poly(cyclohexene sulphone) in benzene[a]: T_1 and η values for the methine and methyl carbons, and correlation times for their motions deduced from the simple, single τ_c motional model at 22.63 MHz

Temperature (K)	T_1 (ms)[b] η			τ_c (ns)[d]	
	CH	CH_2(i)	CH_2(ii)	CH	CH_2
343	79(±4)	49(±2)	52(±1)	0.72	0.53
338	81(±2)	50(±1)	51(±1)	0.70	0.53
	0.20(±0.05)	*0.07(±0.03)*		*12*	–
308	66(±2)	39(±2)	39(±1)	0.96	0.75
303	65(±2)	38(±1)	39(±1)	0.97	0.72
	0.06(±0.03)	*0.02(±0.03)*		–	–

[a] Weight fraction 25%. [η] = 10 ml g^{-1} in benzene at 25°C. The chain was assumed to be atactic, as in previous samples, since the fine structure in the spectrum was not resolved[13]

[b] The data from the inversion recovery experiments were least-squares fitted with a three parameter exponential expression to better establish the trend with temperature

[c] The two CH_2 signals were resolved in the T_1 experiment but not in the η measurement. CH_2(i) is downfield of the other, and is bonded to the backbone. η values are in italics

[d] Calculated from equations (1) to (3). For the methylene groups the mean of the T_1 values was used. Only one η value lay within the range predicted by the motional model

Table 1 Poly(but-2-ene sulphone) in $CDCl_3$[a]: T_1 and η values for the methine and methyl carbons, and correlation times for their motions deduced from the simple, isotropic single τ_c motional model at 22.63 MHz

Temperature (K)	T_1, (ms)[b] η[c]			τ_c (ns)[d]		
	CH(i)	CH(ii)	CH_3	CH(i)	CH(ii)	CH_3
333	197(±6)	169(±5)	475(±7)	0.26	0.30	0.035
	0.7_0		*1.3*	*3.0*		*1.5*
318	142(±5)	139(±4)	387(±7)	0.36	0.37	0.043
	0.5_0		*1.2*	*4.0*		*1.7*
303	116(±3)	108(±4)	298(±7)	0.45	0.49	0.055
	0.3_6		*0.9*	*5.4*		*2.4*

[a] Weight fraction 11%. [η] 108 ml g^{-1} in dioxane at 25°C

[b] Errors are one standard deviation as calculated by the Nicolet software

[c] The η of the two CH peaks could not be measured separately. η values ±*0.05* are given in italics

[d] Calculated from equations (1) to (3)

side chains per repeat unit, should be substantially less stiff than the second, which has only one side chain per repeat unit. The extra alkyl group of PMMA *vis à vis* PMA introduces a steric hindrance[20] which reduces the rate of dipolar motions by a factor of 20, and polyisoprene is much stiffer than polybutadiene[21]. Furthermore, causing the two atoms of the main chain to be part of a ring, as in poly(cyclohexene sulphone), might be expected to restrict segmental motions relative to poly(but-1-ene sulphone) by reducing the number of axes of rotation. Paradoxically the polysulphone chains which are subject to these constraints are substantially the more flexible, when T_1 values are properly interpreted. The ring does have some stiffening effect (τ_c of the backbone of poly(cyclohexene sulphone) is longer by a factor of two than that of the but-2-ene polysulphone) but another cause must be found for the stiffness of the poly(1-olefin sulphone). In agreement with the introduction, we identify electrostatic attractions between adjacent sulphone dipoles as the source of the stiffness. The presence of methylene groups in the main chain of poly(but-1-ene sulphone) permits *gauche* C–C bonds which is a requirement for the close packing of a sulphone dipole behind its neighbour. These stable arrangements are not accessible to polymers prepared from olefins in which both alkene carbons have substituents[6], so that the C–C bonds are *trans*, the sulphone groups are well separated from each other, and backbone motions are not electrostatically constrained.

These conclusions depend entirely upon the correlation times provided by the T_1 measurements upon the polymers: the Nuclear Overhauser Effect is very similar for the two butene polysulphones. The anisotropic model is more appropriate for the present random coil polymers than for the poly-1-olefin sulphones, which contain isotropic helical sections[22,23]. The disparity between the values of τ_c obtained from T_1 and η for the but-2-ene polymer might be attributed to our neglect of a possible wide distribution of correlation times,[21] though the similarity of the τ_c values for the CH peaks of different microstructures does not support this. Poly(cyclohexene sulphone), with fewer degrees of freedom, may have a large range of rates of motion, for the dipole correlation time ($\sim$20 ns)[24] is longer than τ_c from the T_1 measurements at 25°C in the same solvent (0.97 ns). Moreover at that temperature η lies outside the range allowed by the equations (2) and (3). While a better theory for interpreting n.m.r. experiments upon polysulphones is required, and is being developed, the simple model has an empirical ability to distinguish between polysulphones prepared from symmetrical olefins and 1-olefins on the basis of their T_1 behaviour. Main chain dynamics in these polymers depends upon the strength of dipole–dipole correlations, which are important if the C–C bonds are predominantly *gauche* and less significant if the C–C bonds are predominantly *trans* in conformation.

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24 The existence of this minor process in solutions of poly(cyclohexene sulphone) in benzene[18,23] and in solutions of poly(but-2-ene sulphone) in dioxane[25] indicates that a small proportion of the C–C bonds do have a conformation other than *trans*. This is not significant in the present context
25 Fawcett, A. H., unpublished results