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Configurational Order and Kinetic Flexibility in Polysulfones Studied at Low and High Frequencies by Dielectric Means Using Solutions of Terpolymers of Sulfur Dioxide, Hex-1-ene, and Cyclohexene

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ABSTRACT: A conformational analysis of poly(olefin sulfone) chains emphasizing the role of third-order Markov correlations of bond conformation resulting from electrostatic interactions between adjacent sulfone dipoles on the main chain led us to prepare terpolymers of SO_2, hex-1-ene, and cyclohexene and to study their dielectric behavior at low and high frequencies in dilute solution in order to measure the equilibrium dipole moments that characterize the ordered structures. Chain stiffness, as measured by the magnitude of the low-frequency relaxing dipole moment, develops strongly in the terpolymers as the mole fraction of hex-1-ene sulfone residues nears unity and is interpreted by a model that falls between the random flight model and the wormlike chain model. Stiff polar segments are created by a sequence of gauche main-chain C–C bonds where the dipoles nest together in favorable electrostatic situations. The size and shape of these stiff segments cannot both be determined, but their configuration is probably close to that of a helix, and their mean content in poly(hex-1-ene sulfone) is about 20–25 atactic hex-1-ene residues. At high frequencies a new form of the time-domain system has found the relaxation time of the segmental relaxation discovered in these terpolymers not to be significantly reduced by the inclusion of a small proportion of cyclohexene sulfone residues, yet the poly(cyclohexene sulfone) chain itself is kinetically more flexible.

Introduction

Since the report in 1967 that dielectric measurements had revealed a prominent dispersion at low frequencies in solutions of alternating copolymers of sulfur dioxide and certain 1-olefins,[1] there has been an inadequate understanding of the nature of the stiffness in these polymers. It was first thought that the chains should be classed as stiff random coils, in which a high barrier to segmental motion caused for each sulfone group the large component of the dipole moment perpendicular to the chain contour to be coupled to a smaller component parallel to the chain contour created (as apparently in poly(propylene oxide)[2]) by the slight dissimilarity of the two hydrocarbon structures flanking each sulfone group. Upon the discovery that the low-frequency dielectric process, which involves rotation of the whole molecule, was not present in solutions of polysulfones prepared from symmetrical olefins such as cyclohexene[3] and that these solutions had a dielectric increment attributable entirely to distortion polarization (because its magnitude was similar to that of poly(hex-1-ene sulfone) at frequencies above its low-frequency loss process), the appearance of a dipole moment in these polymers was associated primarily with the conformation of the C–C bonds.[4] Upon resolution of a sulfone dipole into equal C–S bond dipoles, it was recognized that the two such dipoles of an S–C–C–S segment would cancel when the central bond had the trans conformation. Following an appreciation of the role of electrostatic forces between adjacent dipoles, a simple conformational theory was proposed to account for the difference between the two types of polymer.[4] It allowed gauche conformations of the C–C bond only if one of the two C atoms flanking the segment was no larger than a methylene group, for only then could unfavorable electrostatic and steric repulsions be avoided. In the apparent absence of a dipole moment in the symmetrical olefin polysulfones, it was not possible to show whether these polymers were stiff, but following theoretical indications that this might not be so, a rotational isomeric state treatment of the poly(cyclohexene sulfone) chain was made.[5]

A second phase of work on these polymers was stimulated by the availability of pulsed Fourier transform NMR spectrometers, with which T_1 and nuclear Overhauser effect values were obtained for poly(but-1-ene sulfone)[6,7] and poly(2-methylpent-1-ene sulfone).[8] The information on the hydrocarbon sections, being complementary to the earlier indications concerning the sulfone dipoles, seemed to suggest that the C–H vectors, but not the electric dipole vectors, were rapidly reorienting, and local jump models satisfying these conditions were devised.[6,8,9] However, each model required trans C–C conformations, which would have eliminated the dipole moment, and begged the questions of the exclusiveness of the relaxation mode and the origin of the stiffness in the chain.

The present phase of work was prompted by the recognition that an incomplete and even inconsistent view was provided by the earlier studies. Our approach to the issue of the dielectric behavior of poly(hex-1-ene sulfone) was conceived in terms of and was designed to test the earlier conformational analysis[3] and led us to prepare for study terpolymers of hex-1-ene, cyclohexene, and sulfur dioxide in a series so that the structure of the chain is progressively modified.[10] Stockmayer et al. chose to study the effect of varying the length of the side chain in poly(1-olefin sulfones), which has been shown to have an influence upon the chain backbone, as has been recorded in their recent paper.[11] Independently in New England[11,12] and in Northern Ireland[10] a high-frequency loss process was discovered in olefin–sulfur dioxide alternating copolymers, which has allowed the recognition of the correct nature of the dielectric behavior.[13,14]

We first seek to show that the strong mutual ordering of the electric dipoles may be the cause of stiffness in polysulfone chains and that the effect between adjacent dipoles may be critically sensitive to the conformation of the intervening C–C bond. Elsewhere it has been reported that ^{13}C NMR measurements of the spin–lattice relaxation of main-chain carbons have detected a greater freedom for segmental motion in two polysulfones prepared from symmetrical olefins, in which the C–C bonds have pre-

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dominantly the trans conformation, than in poly(but-1-ene sulfone).[15] This is consistent with the association of hindrance to segmental relaxation with gauche conformations of the C–C bonds. Viewing the chain as a sequence of stiff sections linked flexibly in configurational terms at sites where the residues have trans C–C bonds, we show how the low-frequency and high-frequency relaxing components of the experimental dipole moment reflect the order within the stiff sections of poly(hex-1-ene sulfone) and in terpolymers of hex-1-ene, cyclohexene, and SO_2.[13] Finally, we discuss the frequency of the faster relaxation in the terpolymers in relation to the kinetic flexibility of the kinks.

This was the first application of an improved form of the time-domain system, which is here described.

Factors Governing Main-Chain Conformation

Information from experiments on the carbon–sulfur bond is limited but adequate for the conclusion that rotation about a single C–SO_2 bond is comparatively free: the threefold barrier to methyl rotation in dimethyl sulfone[16] is 3.35 kcal mol^{-1}, and the difference between the conformational energies of trans and gauche methyl ethyl sulfone[17] is only 22 (±90) cal mol^{-1}. In a number of simple sulfones and disulfones that contain the isopropyl or *sec*-butyl group linked to the sulfone group and where because of steric congestion the conformations of the two C–S bonds are interdependent and correlate with each other in a manner similar to that which may be encountered in the poly(cyclohexene sulfone) chain,[5,18] conformational energy differences of 200 cal mol^{-1} or less have been deduced from studies of β-C ^{13}C shift differences as a function of temperature.[18,19] In the di-*n*-alkyl sulfones the ^{13}C shifts of the β-carbons indicated[18] that the C–S bonds have trans conformational weights of about $^1/_2$. Moreover, it has been observed that the proportion of one sulfone group to about two styrene units in a poly(styrene sulfone) renders the polymer slightly more flexible than polystyrene itself.[6,20] Since the presence of one flexible C–S bond per repeat unit in an alternating copolymer would be sufficient to destroy a strong correlation of orientation of adjacent sulfone dipoles deriving from first- or second-order Markov correlations of bond conformations, we may neglect from further consideration any possible hindrance to segmental rotation from the rotation potential of the C–C bond, though this should be small, and must seek elsewhere a cause for strong third-order correlations. Previous calculations of the magnitude of electrostatic energies between adjacent dipoles showed that these might be significant,[3] and they have been revised somewhat, as is now described.

We represent the dipole moment (4.4 D)[1] as a quadrupole with charges of magnitude 0.245 e on the oxygen and carbon atoms of the group. For the calculations of the Coulombic energies of Figure 1a in its 27 conformations produced by equally spaced conformational angles of each of the three bonds ($\varphi = 0, 2\pi/3$, and $4\pi/3$), interatomic distances were measured on a molecular model and ϵ, the dielectric permittivity, was chosen to be 2.00.[3] To show the structure of the correlations the three axes of the segment require a three-dimensional display of the results, as is given in Figure 1b. The energies are not negligible when compared with $3RT$, ranges of −2.6 to +6.3 kcal mol^{-1} being present in every plane except the central horizontal one. Within this plane movement corresponds to rotations of one or two C–S bonds, while the central C–C bond remains trans. It appears that if the C–C bond could be held in the trans conformation, the two sulfone groups would be quite free of each other, but if the central C–C bond were in a gauche conformation electrostatic energies would tend to couple the two sulfone dipoles together. The quadrupole representation has produced a lower energy (−2.6 kcal mol^{-1}) for the most stable states such as g_+g_-t than that obtained with the tripole representation,[3] so these states, where the dipoles nest one behind the other, are now favored by the electrostatic factor. The view suggested by this study of the electrostatics of a pair of dipoles resembles that provided by Bjerrum's treatment of the formation of ion pairs.[21] In this case bond rotation angles vary to separate the interacting species and so perform a similar role to interion distance in that case. We note that there is some spectroscopic evidence for a simple alkyl sulfone being an associating liquid.[22]

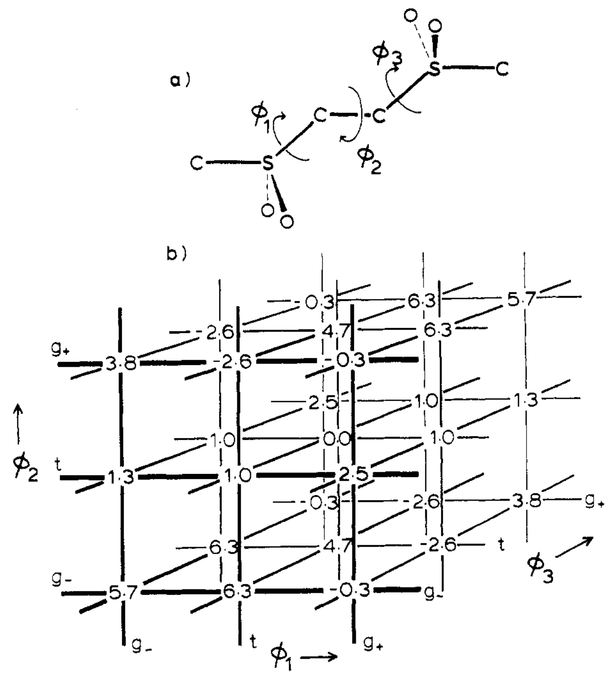

Figure 1. (a) A polysulfone chain segment, showing the three axes of rotation between a pair of sulfone dipoles. (b) A three-dimensional display of the structure of the electrostatic energies (kcal mol^{-1}) at equally spaced values of the three rotational angles.

The full potential energy surface which determines the conformational populations and the rates of transfer between them is also a function of relatively small conformational energy differences and bond rotation potentials, such as those given above, and steric effects, which may be very severe, depending on the structure of the olefins used.[3] Mansfield has investigated the potential energy surface,[23] but unfortunately used our earlier somewhat elementary tripole representation of the dipole moment[3] as a feature in the set of empirical force field parameters and may therefore have underestimated the electrostatic effects. According to our earlier suggestion, which was confirmed by Mansfield's calculations, gauche states for the C–C bond are accessible only if methylene groups are present in the main chain, for otherwise a severe steric strain would arise. Thus, for example, only if the right-hand carbon of Figure 1 were part of a methylene group could the conformational sequences tg_-g_+ and tg_+g_- be adopted. Even more stable configurations might be obtained at combinations of the three rotation angles that correspond to points somewhat off the sparse tetrahedral lattice, as is suggested by the asymmetry of the pattern of energies in Figure 1b and as was found by Mansfield[23] when intrachain packing effects are best accommodated. While deviations from the simple lattice are to be expected when the electrostatic third-order correlations are as large

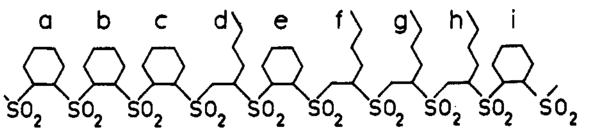

Figure 2. Segment of the terpolymer chain, showing the various residue sequences discussed in the text.

as the first-order rotation potentials, they are not found when the C–C bond is trans and the dipoles are as far apart as is possible within the constraints of the covalent bonds: in the crystal structures of α-meso-(2,3-diisopropylsulfonyl)butane[24] and 1-(methylsulfonyl)-2-(phenylsulfonyl)ethane,[25] where the central C–C bonds are trans, C–S bonds do have normal trans and gauche orientations.

This analysis led us to the preparation of terpolymers of sulfur dioxide with cyclohexene and hex-1-ene, with the following expectations. In the sequence of units shown in Figure 2, the absence of methylene groups from the main-chain residues of a and c would prevent ring b from having a gauche C–C bond, but the methylene group in unit d would permit c to have a gauche C–C bond. As the equilibrium in cyclohexyl benzyl sulfone strongly favors the equatorial isomer[26] and as c has two substituents, the diequatorial or gauche conformation will be strongly favored. In contrast, units d and h can adopt only the trans conformation. The C–C bond of g, which is typical of a residue in a poly(hex-1-ene sulfone) chain, adopts a gauche conformation predominantly, but not exclusively, according to the Coulombic energy results. Contributions to a dipole moment for the chain are made by residues c, e, f, and g, but not by residues d and h. Thus as hex-1-ene residues are introduced into a poly(cyclohexene sulfone) chain, an equivalent number of dipoles are created, which may relax by a segmental process because of the flexibility characteristic permitted by the trans C–C bonds of the chiefly cyclohexene sulfone polymer chain. As the chain becomes richer in hex-1-ene units, stiffness develops and might be investigated by measurements on the magnitude of the dipole moment component that relaxes at low frequencies. Other methods of investigating the origin of stiffness in poly(olefin sulfones) have been proposed—spacing the sulfone dipoles by four main-chain bonds[27] or by varying the proportion of 3- and 5-bond units[6]—but each was frustrated by polymer insolubility and neither identified a bond conformation as a critical factor.

Time-Domain Reflectometry Measurements: 1–147 MHz

This method of measuring the dielectric permittivity of dilute solutions of polymers has been described in detail by Cole, Mashimo, and Winsor,[28,29] so only the improvements implemented for the present measurements are covered here. The arrangement of the 50-Ω 7-mm precision coaxial line system is shown in Figure 3. The incident voltage, $V_0(t)$, traveled to the sample and was reflected from it as $R(t)$: these were both monitored by the sampler in the line system. The basic equation was

$$\frac{y}{G_c} = \frac{v_0 - r}{v_0 + r} \tag{1}$$

where y is the termination admittance, G_c is the characteristic conductance of the line, and v_0 and r are the Laplace transforms of $V_0(t)$ and $R(t)$, respectively.

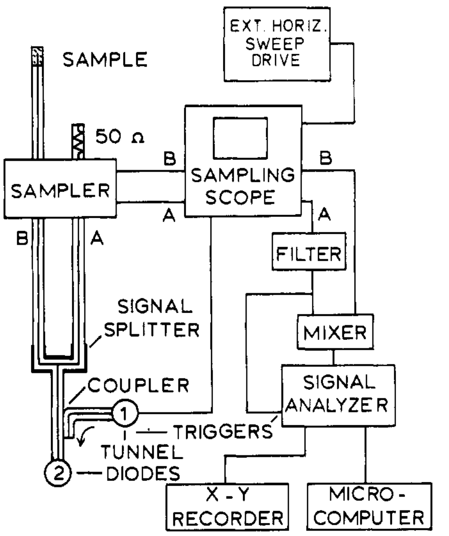

Figure 3. Block diagram of the time-domain reflection system.

Since the relaxation effect to be characterized was small relative to the solvent permittivity, we measured the difference between the admittance of the polymer solution and that of the pure solvent. The TDR configuration of Figure 3 allows two ways of doing this. In the first, two identical cells would terminate channels A and B, one for solution and one for solvent. $R_s - R_x$ and $R_s + R_x$ might then be observed directly (R_s and R_x are respectively the reflections of the cell filled with solvent and with solution). As we had only one cell of suitable length for these measurements, we used the second method. For this, channel A was terminated by a 50-Ω resistance, channel B was terminated by the cell, and R_s and R_x were obtained in succession. For either method the working equations are the same, provided that in the first case both channels and cells have identical response characteristics and the time scale is less than the round trip travel time from termination to signal splitter and that for the second case the apparent time drift is insignificant between the recording of R_s and R_x. Solution of eq 1 for the ratios r_s/v_0 and r_x/v_0 provided

$$\frac{r_s - r_x}{r_s + r_x} = \frac{(y_x - y_s)/G_c}{1 - (y_s/G_c)(y_x/G_c)} \tag{2}$$

where r_s and r_x are the Laplace transforms of the experimental observables R_s and R_x. This was rearranged to provide the basic working equation for difference measurements:

$$\frac{y_x - y_s}{G_c} = \frac{\left[1 - \left(\frac{y_s}{G_c}\right)^2\right]\left(\frac{r_s - r_x}{r_s + r_x}\right)}{1 + \frac{y_s}{G_c}\left(\frac{r_s - r_x}{r_s + r_x}\right)} \tag{3}$$

y_x/G_c and y_s/G_c depend upon the permittivity of the sample and reference as well as the characteristics of the cell, as will be discussed below.

Since the description of the TDR arrangement in ref 28 and 29, the major change made for the present study was the substitution of a modified General Radio TDP power divider for the previously used directional coupler. The signal analyzer was triggered from the incident pulse on channel A, to virtually eliminate systematic timing errors that might have developed in the time it took to replace the reference solvent with the solution in the cell. R_s and R_x were recorded on the signal analyzer and smoothed, and their sum and difference were obtained before being transferred to a Hewlett-Packard HP-85 microcomputer for numerical analysis.

The sample cell used is shown in Figure 4. The centering washer placed between the two outer shell extensions had serrations to permit the injection and complete

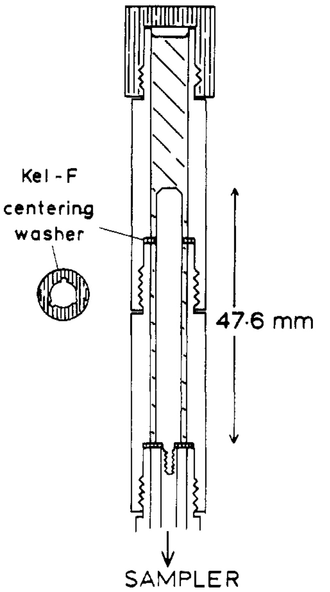

Figure 4. Drawing of liquid sample cell that terminated channel B.

removal of liquid with a syringe without a complete disassembly of the cell. The cell constant, γd, was expressed in terms of the equivalent length d of center conductor. The correction factor, γ, allowed for the larger 5-mm inner conductor diameter, as compared to 3 mm for 50-Ω coaxial line.

The relative admittance of the liquid-filled cell, according to transmission line theory,[30] is given by

$$\frac{y}{G_c} = \frac{i\omega d}{c}\left(\frac{\tan Z}{Z}\right)\epsilon^* \tag{4}$$

where ω is frequency in radians/second, c is the speed of light, and $Z = (\omega d/c)\epsilon^{*1/2}$. By substitution into eq 3 we have

$$\frac{\tan Z_x}{Z_x}\epsilon^*_x - \frac{\tan Z_s}{Z_s}\epsilon^*_s = \left[1 + \left(\frac{\omega\gamma d}{c}\right)^2 \epsilon^{*\,2}_s \left(\frac{\tan Z_s}{Z_s}\right)^2\right]\left[\frac{c}{i\omega\gamma d}\,\frac{r_s - r_x}{r_s + r_x}\right] \Bigg/ \left\{1 - \left(\frac{\omega\gamma d}{c}\right)^2 \epsilon^*_s \left(\frac{\tan Z_s}{Z_s}\right)\left[\frac{c}{i\omega\gamma d}\,\frac{r_s - r_x}{r_s + r_x}\right]\right\} \tag{5}$$

To calibrate the cell we used a liquid of known dielectric constant ϵ_x as sample and air as reference. Taking $\omega = 0$, we obtained the cell constant as

$$\gamma d = \frac{c}{\epsilon_x - 1}\,\frac{\int_0^\infty [R_s(t) - R_x(t)]\,dt}{[R_s(t) + R_x(t)]_{t=\infty}} \tag{6}$$

Using the approximations $(\tan Z)/Z = 1 + {}^1/_3Z^2$ and $Z \cot Z = 1 - {}^1/_3Z^2$ from eq 5, we obtained after some rearrangement

$$\epsilon^*_x - \epsilon^*_s = \left[1 - \tfrac{1}{3}(\epsilon^*_s + \epsilon^*_x)\left(\frac{\omega d}{c}\right)^2\right] \times \left[\frac{1 + \left(\frac{\omega\gamma d}{c}\right)^2 \epsilon^{*\,2}_s \frac{c}{i\omega\gamma d}\,\frac{r_s - r_x}{r_s + r_x}}{1 - \left(\frac{\omega\gamma d}{c}\right)^2 \epsilon^*_s \frac{c}{i\omega\gamma d}\,\frac{r_s - r_x}{r_s + r_x}}\right] \tag{7}$$

This equation was used for the calculation of sample permittivities from the TDR reflection sum and difference records. The maximum available time window with the line system used was 35 ns, which was just adequate for the polymer solutions. $R_s(t) - R_x(t)$ was approximated outside that window by an exponential decay function with a time constant of 10–20 ns, whose value was obtained by fitting to the latter part of the measured function. For the numerical Laplace transforms six frequencies per decade were used, spaced at equal intervals in log f.

When benzene (x) was compared with cyclohexane (s) at 25 °C in five measurements, $\epsilon'_x - \epsilon'_s$ at 1, 10, and 147 MHz was 0.258 (±0.013), 0.258 (±0.012), and 0.259 (±0.015), which compare well with the literature value[31] of 0.251. Negligible loss values were obtained within that range, but at higher frequencies this was not so; moreover, the ϵ' values there showed systematic errors and deteriorating precision.

Experimental Section

Preparation of Polymers. The olefins were refluxed over sodium–potassium alloy, and a central fraction was obtained during distillation with a 1-m column of Fenske helices. Sulfur dioxide was condensed from a cylinder in the reaction vessel, a conical flask fitted with a plug of cotton wool, before the cooled olefins were added. Copolymers of hex-1-ene and cyclohexene were prepared as before,[1,3] but during the preparation of the terpolymers attention was given to reducing the change of terpolymer composition with extent of reaction, as the following descriptions show, because of the nonlinear dependence of $\langle\mu_\parallel^2\rangle/z$ upon x.

Terpolymer X31X. The designation indicates that 31% of the olefin residues were derived from hex-1-ene. During one preparation of this from a feed of 45 mL of cyclohexene, 15 mL of hex-1-ene (molar ratio 3.91:1), and 150 mL of SO_2 at −29 °C, small samples were removed after 7, 33, and 50 min, when 1.9, 6.0, and 8.0 mL, respectively, of 0.0035 M *tert*-butyl hydroperoxide in toluene had been added. From the ^1H NMR spectra (see below) the 1-olefin compositions of these samples were respectively 32%, 31%, and 30%, which showed a negligible drift with polymer production up to the final 22% yield: $[\eta]$ = 22 mL g^{-1} in benzene at 25 °C.

Terpolymer X93X. After initial exploratory experiments, the polymer was prepared in three batches from mixtures of 100 mL of hex-1-ene, 10 mL of cyclohexene (molar ratio 1:0.120), and 157–197 mL of SO_2 by the addition of 2.6–5.3 mL of 0.035 M initiator dropwise over a period of 95 min. The yields of 10–14 g, produced by precipitation into acidified methanol, were 7.5–10.6% of the total possible polymer weight—small enough to prevent a significant drift in feed composition. $[\eta]$ = 123 mL g^{-1}.

Polymer Fractionation. This was achieved in the conventional way[3] by incremental temperature decreases with 1% solutions in benzene or toluene and the nonsolvent methanol. After reprecipitation each fraction was dried in vacuo at about 50 °C for several hours.

Polymer Characterization and Dielectric Measurements. Benzene and other liquids were dried over and fractionally distilled from a sodium–potassium alloy. Viscometric measurements and osmotic pressure measurements were made and interpreted as before.[3] Bruker WH90 and WM250 instruments were used for NMR spectra.

Dielectric constants were measured at frequencies between 800 Hz and 20 kHz on a system based on a Wayne Kerr B221A universal bridge and between 0.1 and 12 MHz with a WTW multidecameter, in each case calibrating liquid or polymer solutions being contained in a thermostated DFL-2 cell. On the TDR line the cell was fitted within a polyethylene sleeve inside a stirred water bath. Its cell constant, obtained by using eq 6, was obtained from six measurements with benzene or cyclohexane as γd = 120.0 (±0.8) mm, making γ = 2.52.

Polymer Characterization

For analysis of the chemical composition of the terpolymers, elemental analysis being unsuitable, two NMR methods were used. The 90-MHz ^1H spectrum of solutions

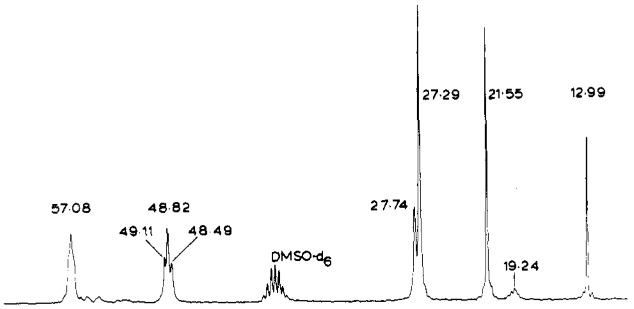

Figure 5. ^{13}C NMR spectrum at 62.89 MHz of terpolymer X93X measured in Me_2SO-d_6 at 70 °C. Shifts are given in ppm relative to the Me_2SO shift of 39.67 ppm. Pulse width 12 μs, acquisition time 0.67 s, line broadening 2 Hz, 3572 scans, 20% (w/v) solution. The prominent peaks are from the hex-1-ene residues: triad fine structure is evident at 49 ppm in the main-chain CH_2 signal, and diad fine structure causes the first methylene carbon of the side chain to give the small peak at 27.74 ppm (the other part of the diad lies under the peak of the second methylene carbon, at 27.29 ppm[18]).

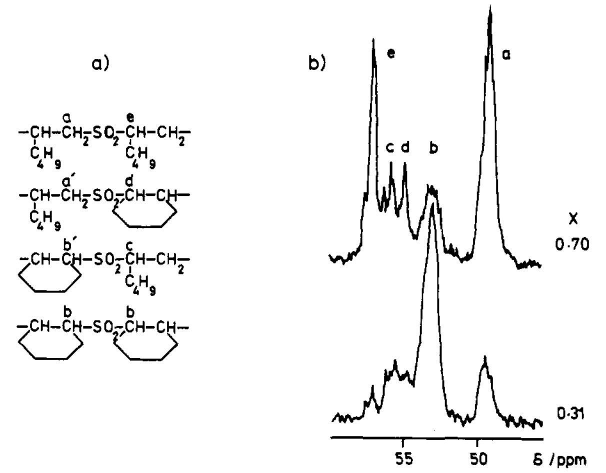

Figure 6. ^{13}C NMR spectra at 62.89 MHz of the main-chain carbons of terpolymers X70X and X31X and the residue sequence diads.

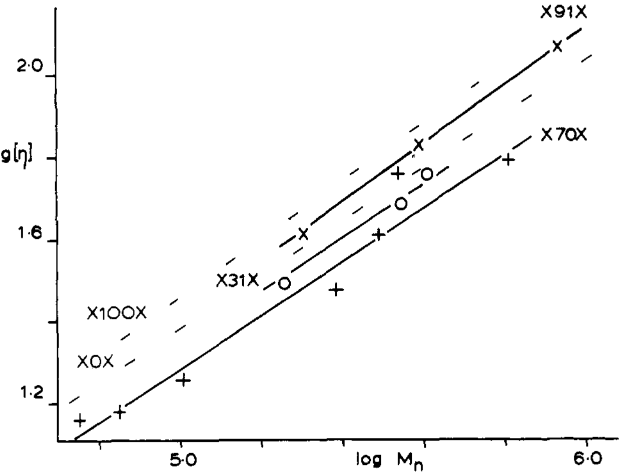

Figure 7. Mark–Houwink plots for the terpolymers in benzene at 25 °C: (×) X91X; (O) X31X, (+) X70X. The dashed lines are literature lines for XOX[3] and X100X[33], as the labels imply.

in chloroform showed peaks from the main-chain protons between 4.5 and 3.0 ppm, distinct from the side-chain resonances. The methyl group of the hex-1-ene residues was well resolved from the side-chain methylene signals as a distorted triplet with $\delta = 0.94$. From the areas of the methylene and methyl groups the mole fraction, x, of the hex-1-ene sulfone residues was found to within about 1% from

$$(1 - x)/x = {}^3\!/_8(A_{CH_2} - 2A_{CH_3})/A_{CH_3} \qquad (8)$$

when $x \lesssim 0.8$. For larger values of x, the numerator was less precise, so the ^{13}C spectrum was used. In the typical spectrum of Figure 5 it may be seen that the two methylene carbons most remote from the main chain in the cyclohexene residue can be distinguished at 19 ppm. The four carbons of the linear side chain cause the sharp peaks between 10 and 30 ppm. Part of the diad fine structure of the first methylene carbon coincided with the single peak of the second carbon at $\delta = 27.29$, while the peak of the next methylene carbon obscured the signal from the two methylene carbons adjacent to the main chain in the ring structures.[7] From a spectrum obtained in the absence of the nuclear Overhauser effect, x was found from

$$I_{19}/(\text{integral of all other side-chain C}) = (1 - x)/(1 + x) \qquad (9)$$

For polymer X80X this method gave $x = 0.78$, which was in satisfactory agreement with the value obtained from the proton spectrum (0.80).

Two aspects of the chain microstructure were found by ^{13}C NMR spectroscopy. As in Figure 5 the first atom of the side chain displayed diad fine structure, and the main-chain methylene carbon showed triad fine structure at 49 ppm. Incipient triad splitting was suggested by the appearance of shoulders on the methine carbon peak at 57 ppm. Apparently, in the hex-1-ene copolymer and terpolymers X93X and X91X, whose spectra all showed these features, the runs of hex-1-ene sulfone units are essentially atactic, in agreement with conclusions reached earlier for other 1-olefin polysulfones prepared by a free radical reaction.[7]

In principle, the shifts of the main-chain carbons in the terpolymer characterize the sequence diads shown in Figure 6a. We predict that the shifts of carbons a′ and b′ will be similar to those of a and b, respectively,[7,18] and that the shifts of carbons c and d will be 55.4 and 54.7 ppm, respectively, by combining the shifts of the carbons in the homopolymers with the values of the shift parameters γ_s (−2.7 ppm) and δ_s (1.0 ppm) (which are associated with shift effects that operate across an S atom). Though there are prominent peaks in the spectrum of X91X (Figure 5) and in other terpolymers (Figure 6) close to these positions, the evident extra fine structure, presumably from chirality effects, makes the assignments a little uncertain and also prevents a quantitative analysis of the sequence diads. As with the poly(but-1-ene sulfone-*co*-but-2-ene sulfone) case,[32] however, these spectra have the appearance expected of a series of terpolymers with a random, rather than blocky, placement of the two olefin units. The greater reactivity of the 1-olefin, measured by the factor f = (olefin ratio in polymer)/(olefin ratio in feed), which had values of 1.7_5 and 1.6_2 for the terpolymers X31X and X93X, respectively, depended only slightly upon the feed composition, so that the copolymerization of the two olefins may be close to Bernoullian.

Molecular weights were measured for some fractions of three of the terpolymers to supplement the measurements of limiting viscosity numbers. Only for X70X were sufficient measurements made to determine both Mark–Houwink parameters, but for this and for the other two terpolymers examined it was found that the points on the plot of log [η] vs. log $\bar{M}_n$ lay close to the literature lines for poly(cyclohexene sulfone)[3] and poly(hex-1-ene sulfone)[33] in the same solvent, benzene (Figure 7). The Mark–Houwink parameters of these polysulfones are given in Table I.

Table I
Mark-Houwink Parameters for Copolymers and Terpolymers in Benzene at 25 °C

x^a	$K \times 10^2$, mL/g	a	ref
0	1.3_3	0.65	3
0.31	1.2_2	0.65^b	
0.70	1.0_7	0.65	
0.91	0.8_4	0.70^b	
1.00	0.8_9	0.70	33

[a] Fraction of hex-1-ene residues. [b] Assumed value; see text.

Dielectric Behavior Observed at Low Frequencies with the Bridge Systems

Certain dielectric permittivity measurements made with the bridge systems on terpolymers with similar $\bar{M}_n$ and $[\eta]$ values are displayed in Figure 8. For sample X70X two relaxation processes have been detected. Between 1 and 100 kHz a low-frequency process was evident, and a high-frequency process appeared to start above 1 MHz. The low-frequency process was not observed in the 5% (w/v) solutions of X31X (on both bridge systems the dielectric increments were identical at 100 kHz and between 1 and 10 kHz within experimental error) nor was it seen in the solution of XOX.[3] As the proportion of hex-1-ene residues in the terpolymer rose above 30%, the low-frequency response appeared and became prominent. This feature seems to require runs of hex-1-ene units. The critical frequency of the process was similar to the frequency for whole-molecule tumbling, which may be obtained[1] from $f_c = RT/2\pi\eta_0[\eta]\bar{M}_n$.

The values of the dipole moments at the low-frequency limits, $(\langle\mu^2\rangle/z)^{1/2}$, were calculated for the terpolymers by the Guggenheim–Smith method[34] from the dielectric increment, $d\epsilon'/dw_2$ at the low-frequency limit and the refractive index increment, $dn_D{}^2/dw_2$.

Above 1 MHz the terpolymers displayed a high-frequency relaxation, which is undoubtedly the segmental relaxation of a transverse dipole moment. A chain composed predominantly of cyclohexene sulfone units but containing a proportion of the polar gauche C–C bonds that are permitted by the presence of main-chain methylene units within a hex-1-ene residue, is evidently not dynamically stiff. The high-frequency feature became more prominent as the proportion of hex-1-ene units rose toward $x = 0.9$, which is also consistent with the introduction of methylene groups into the chain backbone increasing the proportion of gauche C–C bonds (which do not permit the adjacent C–S dipoles to cancel). The magnitude of the segmental dipole moment $(\langle\mu_\perp{}^2\rangle/z)^{1/2}$ was also obtained from the dielectric increment at an intermediate frequency near 1 MHz by the Guggenheim–Smith method. Using the equation

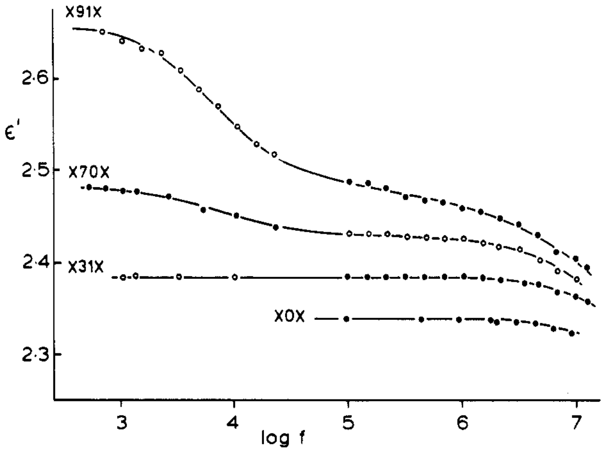

Figure 8. Permittivity, ϵ', of solution of the terpolymers in benzene at 25 °C measured at different frequencies on the bridge systems. The sample characteristics are entered in Table II. Open circles correspond to 5.00% (w/w) solutions; filled circles correspond to measurements made at slightly different concentrations, which were adjusted to 5.00% (w/w) assuming the dielectric increment proportional to solute concentration.

$$\langle\mu^2\rangle/z = \langle\mu_\parallel{}^2\rangle/z + \langle\mu_\perp{}^2\rangle/z \qquad (10)$$

we then obtained the magnitude of the low-frequency relaxing dipole. Table II contains the experimental quantities and the derived dipole moments.

The measured dipole moments are plotted as a function of hex-1-ene sulfone content in Figure 9. Between $x = 0.7$ and $x = 1.0$ there are two significant features to this figure: the great sensitivity of $\langle\mu_\parallel{}^2\rangle/z$ to x, and the dominance of the low-frequency relaxing feature over the high-frequency relaxing component. It appears that a small proportion of symmetrical olefin residues disrupts considerably the organization of electric dipoles normally present within 1-olefin polysulfone chains. The predominance of the longitudinal component in a chain where the C–C bonds are prevalently of a gauche conformation is attributed to the nesting of one sulfone dipole moment behind its neighbor in the chain, which is permitted by sequences of tg$^+$g$^-$ or of tg$^-$g$^+$ conformations for the three bonds between a pair of dipoles. The asymmetry of the

Table II
Characterization of the Polymer Samples Studied by Dielectric Means with Bridge Systems at 25 °C in Benzene

	polymer						
	XOX[a]	X31X	X70X	X80X[a]	X91X	X93X	X100X
$\bar{M}_n \times 10^{-5}$	8.7	4.1	3.5	1.7			3.9_5
$[\eta]$, mL g^{-1}	97	56	61	23	59	59	
$d\epsilon'/dw_2$ (lf)[b] (±0.10)		2.2_2	4.1_4	4.7_6	7.6_4	8.2_8	c
$d\epsilon'/dw_2$ (mf)[d] (±0.10)	1.47	2.2_2	3.0_0	3.3_5	3.8_2	3.7_7	3.5_2 (±1.0)
$dn_D{}^2/dw_2$	0.17	0.07	0.06	0.08	0.09_7	0.11	0.12
$(\langle\mu^2\rangle/x)^{1/2}$ (lf),[e] D		1.70	2.36	2.53	3.20	3.44	4.36[f]
$(\langle\mu_\perp{}^2\rangle/z)^{1/2}$ (mf)[e] (±0.03), D	1.44	1.70	2.02	2.11	2.28	2.23	2.15 (±0.30)
$(\langle\mu_\parallel{}^2\rangle/z)^{1/2}$,[g] D			1.21 (±0.04)	1.38 (±0.06)	2.25 (±0.03)	2.62 (±0.03)	3.79 (±0.17)
$(\langle\mu_\perp{}^2\rangle/z)^{1/2}$,[h] D	1.09	1.41	1.79	1.89	2.08	2.02	1.93
$D_{\perp,x}$[i]					1.16 (±0.16)	1.10 (±0.15)	1.0
$D_{\parallel,x}$	0	0.00	0.10_1 ($\pm 0.01_1$)	0.13_3 ($\pm 0.01_7$)	0.38_8 ($\pm 0.02_4$)	0.47_8 ($\pm 0.02_8$)	1.00

[a] Unfractionated samples. [b] Low-frequency value. [c] Low-frequency limit not obtained with this sample. [d] Medium frequency, near 1 MHz. [e] Calculated by the Guggenheim–Smith method.[34] [f] Obtained by extrapolation of $\langle\mu^2\rangle/z$ values[1] to infinite $\bar{M}_n$ by plotting against $\bar{M}_n{}^{-1}$. [g] Calculated with eq 10. [h] After the subtraction from the Guggenheim–Smith value of a distortion polarization contribution of 0.89 D^2. [i] Orientation dipole only.

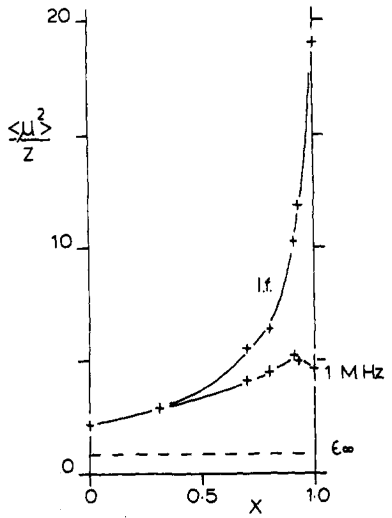

Figure 9. Guggenheim–Smith values of the two dipole moments of the terpolymers plotted as a function of the fraction of hex-1-ene residues, x. The dashed line corresponds to the distortion polarization, equivalent to 0.9 D, obtained from the time-domain values of ϵ'_∞.

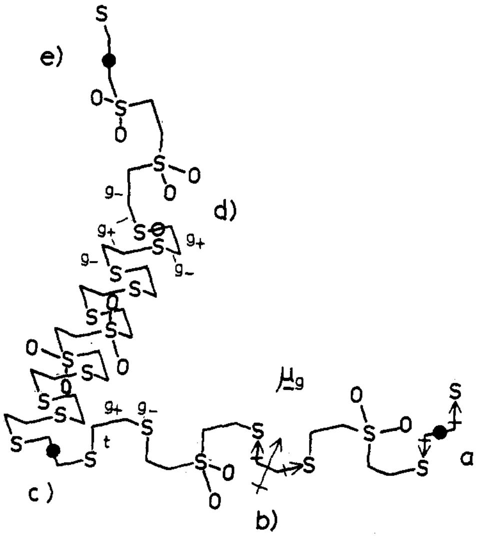

Figure 10. Conformational model of the polysulfone main chain, assuming a tetrahedral lattice. Filled circles mark trans C–C bonds, where adjacent C–S bond dipoles are antiparallel and thus cancel; open circles mark a change of helix sense at a C–S bond; the two C–S bonds flanking a gauche C–C bond have a resultant, μ_g, as at b, which contributes to the two components of the helix dipole moment that are directed along and perpendicular to the helix axis.

$-CHR-SO_2-CH_2-$ sequence affects the conformational potential energy surface through the difference in the steric size of the CH_2 and CHR groups and thus the mean angle the dipole vector makes with the chain contour. In the next section we develop a model to interpret the trend of dipole moment with x that neglects the implications of the presence of the minor high-frequency relaxing dipole in poly(cyclohexene sulfone).

A Simple Model To Interpret the Dependence of $\langle\mu_\parallel^2\rangle/z$ and $\langle\mu_\perp^2\rangle/z$ upon x

We view the chain as a series of stiff sections, created by the strong electrostatic coupling that accompanies gauche C–C bonds, each separated by a more flexible unit where a trans C–C bond prevents the development of these strong Markov correlations (see sites a, c, and e of Figure 10). In the simplest view,[13] which is adopted here as the starting point for a fuller study, the stiff sections are 2/1 helices, being generated by repetitions of g^+g^-t (or g^-g^+t) conformational sequences of S–C–C–S bonds.

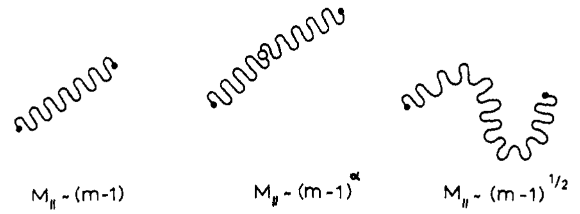

Figure 11. Scaling characteristics of the stiff segments, showing how the exponent, α, may be used to describe the shape of a segment.

We assume that the sum of the $m - 1$ dipoles, μ_g as at b of Figure 10, can be resolved into two components: one, $\mathbf{M}_{\parallel,m}$, pointing along the chain contour from one point of flexibility to the next, and the second, $\mathbf{M}_{\perp,m}$, being directed perpendicular to this. As before[13]

$$\mathbf{M}_{\parallel,m} = (m-1)\mu_\parallel \tag{11}$$

but $\mathbf{M}_{\perp,m}$ is either $\mu_\perp$ or zero and for an even number of perpendicular dipoles (m odd) will have a zero resultant:

$$\mathbf{M}_{\perp,m} = \cos(m\pi/2)\mu_\perp \tag{12}$$

We show such a segment between a and c in Figure 10. At d within another stiff segment there is shown a reversal in helix sense or handedness. This reversal might be the consequence of a particular sequence of chiral centers. The elementary view of the poly(1-olefin sulfone) chain has gauche C–C bonds with a probability p whenever a methylene group is present and does not take into account methine carbon chirality, but Mansfield's treatment[23] obtained a helix only by requiring that within each helical section the methine carbons should all have the same chirality. The absence of this condition is clear from the ^{13}C spectrum, as we noted above when discussing Figure 5. A possible consequence of a helix sense reversal is that $\mathbf{M}_{\parallel,m}$ may be no longer proportional to $m - 1$. Were the stiff section to have a random configuration, then $\mathbf{M}_{\parallel,m} \sim (m-1)^{1/2}$. For the general case we write

$$\mathbf{M}_{\parallel,m} = (m-1)^\alpha\mu_\parallel \tag{13}$$

with $\alpha = 1$ for a helix, $^1/_2$ for the random coil, and of intermediate value for the intermediate case (see Figure 11).

For the transverse component a more elaborate treatment is required. If the configuration is the random coil, we have

$$\mathbf{M}_{\perp,m} = (m-1)^{1/2}\mu_\perp \tag{14}$$

The special condition of the 2/1 helix—the mutual cancellation of alternate $\mu_\perp$ dipoles—does not arise. The intermediate case may be given by

$$\mathbf{M}_{\perp,m} = (m-1)^{1-\alpha}(\cos(m\pi/2))^{2\alpha-1}\,\mu_\perp \tag{15}$$

The following treatment of $\langle\mu_\parallel^2\rangle_x/z$ assumes that the chains have Gaussian configurational statistics at high molecular weight when the number of kinks becomes large. Excluded volume effects, deriving from the polymer–solvent interaction, are therefore ignored, though benzene is a good solvent for the terpolymer series, as the Mark–Houwink exponents probably lie between 0.70 and 0.65 (see Table I). Whether a kink arises by the thermal promotion of a C–C bond in a run of 1-olefin units to the trans conformation or from the influence of an adjacent cyclic olefin unit, in each case it is a 1-olefin unit that is the

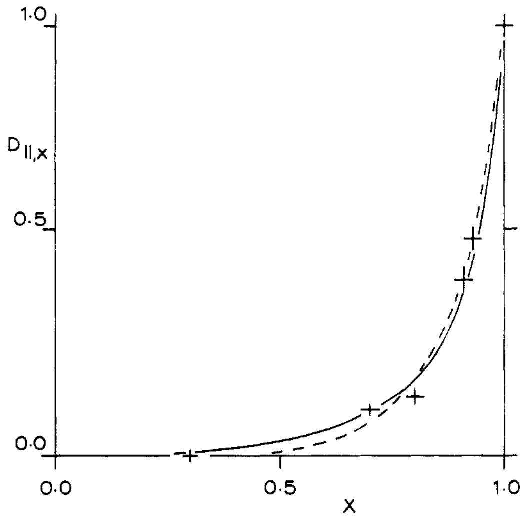

Figure 12. Experimental values of $D_{\parallel,x}$ and two fitted curves. The full curve was obtained from eq 21 with $p = 0.94$, $\alpha = 1.0$, and $q = 2$ and the dashed curve was obtained with $p = 0.92$, $\alpha = 1.0$, and $q = 5$. Table III has other suitable sets of parameters.

Table III
Model Parameters of Eq 21 That Provide Fits to the $D_{\parallel,x}$ Data

set	p	α	q	$\langle m\rangle$[a]
1[b]	0.94	1	1	18
2	0.94	1	2	18
3	0.92	1	5	13
4	0.96	0.9	1	25
5	0.96	0.9	2	25
6	0.95	0.9	5	20
7	0.96_5	0.8	5	29

[a] Mean length of stiff section: $1/(1 - p)$. [b] For this set $\mu_\parallel$ of eq 18 is 0.69 D, assuming that $K_{\parallel,\theta,\varphi} = 1$.[13]

immediate site of the kink, so we may assume that the mean geometry is independent of its cause. If that geometry is characterized by $K_{\parallel,\theta,\varphi}$ and by $K_{\perp,\theta,\varphi}$, where θ and φ are respectively the angle between the axes of successive helices and a mean rotational angle,[13,23] then

$$\langle \mu_\parallel{}^2\rangle_x = K_{\parallel,\theta,\varphi}\Sigma N_m M_{\parallel,m}{}^2 \tag{16}$$

and

$$\langle \mu_\perp{}^2\rangle_x = K_{\perp,\theta,\varphi}\Sigma N_m M_{\perp,m}{}^2 \tag{17}$$

Upon substituting the expression for N_m obtained earlier for a chain with a Bernouillian distribution of the two olefin residues,[13] we find that

$$\langle \mu_\parallel{}^2\rangle_x = z\mu_\parallel{}^2 K_{\parallel,\theta,\varphi}(1 - px)^2\Sigma(px)^{m-1}\,(m - 1)^{2\alpha} \tag{18}$$

and

$$\langle \mu_\perp{}^2\rangle_x = z\mu_\perp{}^2 K_{\perp,\theta,\varphi}(1 - px)^2\Sigma(px)^{m-1}(\cos\,(m\pi/2))^{4\alpha-2}(m - 1)^{2(1-\alpha)} \tag{19}$$

The factor p is the probability that in a 1-olefin polysulfone chain the C–C bond has the gauche conformation.[13] When $\alpha = {}^1/_2$, eq 18 may be simplified to give

$$\langle \mu_\parallel{}^2\rangle_x = z\mu_\parallel{}^2 K_{\parallel,\theta,\varphi}px$$

For a random coil we therefore have the reduced low-frequency dipole depending upon x as

$$D_{\parallel,x} = (\langle \mu_\parallel{}^2\rangle_x/z)/(\langle \mu_\parallel{}^2\rangle_1/z) = x \tag{20}$$

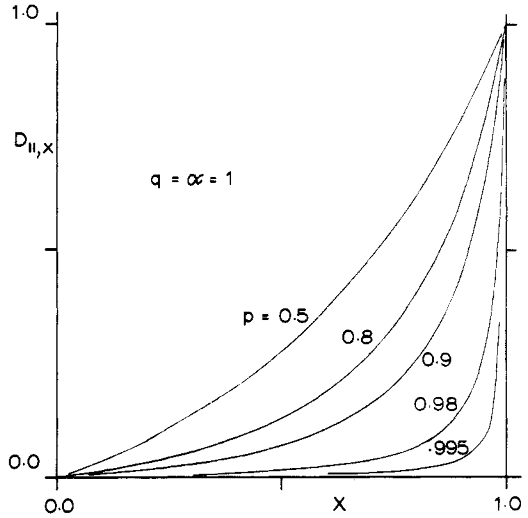

Figure 13. $D_{\parallel,x}$ computed from eq 21, showing the dependence upon x for selected values of p, the probability that in a 1-olefin sulfone chain the C–C bond has a gauche conformation.

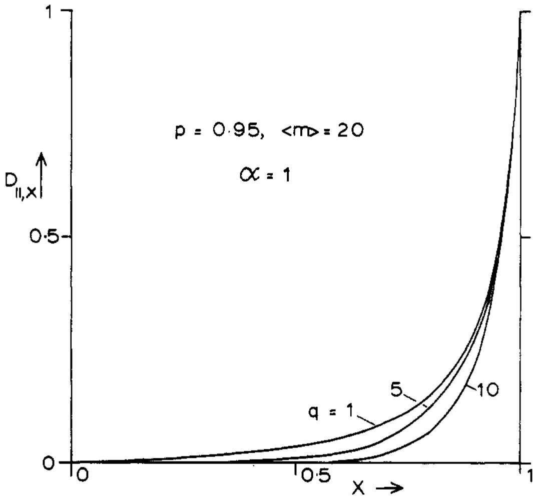

Figure 14. $D_{\parallel,x}$ computed from eq 21, showing the dependence upon x for selected values of q, the threshold parameter.

This simple result is not followed by the terpolymers (see Figure 12): in them therefore the dipoles are ordered in some way.

To explore this order we have computed numerically the expression

$$D_{\parallel,x} = \frac{(1 - px)^2 x \sum\limits_{m=q}^{\infty} (px)^{m-2}(m - 1)^{2\alpha}}{(1 - p)^2 \sum\limits_{m=q}^{\infty} p^{m-2}(m - 1)^{2\alpha}} \tag{21}$$

for different values of x, q, p, and α. We have introduced q to express a threshold effect—that the formation of a stiff segment requires a run of at least q 1-olefin residues. All the curves obtained when these parameters are varied lie below the $D_{\parallel,x} = x$ curve, as may be seen in Figures 13–15. Increasing each of the factors, p, q, and α causes the curve to sink further down. Increasing p and α have the effect through emphasizing the order in the homopolymer chain ($x = 1$) while increasing q adds to the disorder produced in the terpolymers that accompanies the links associated with the cyclic olefin, particularly when the cyclohexene residues are closely spaced.

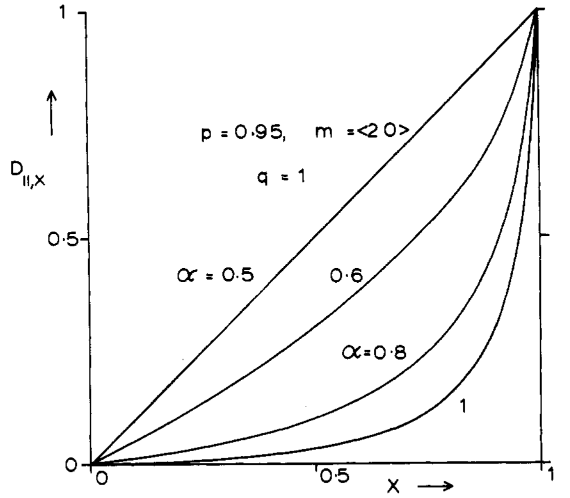

Figure 15. $D_{\|,x}$ computed from eq 21, showing the dependence upon x for selected values of α, which characterizes the shape of the stiff segments (see Figure 11).

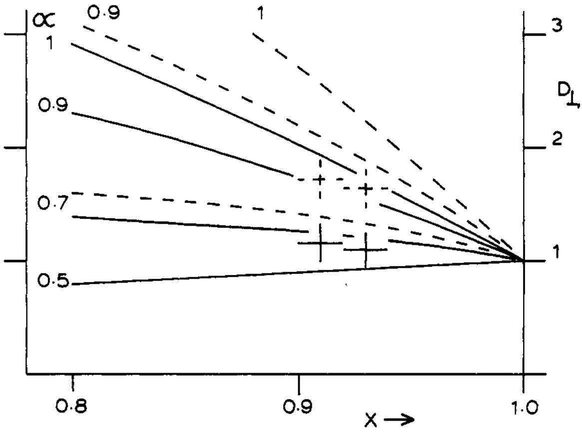

Figure 16. $D_{\perp,x}$ computed from eq 22 as a function of x. The full curves are for $p = 0.92$ ($\langle m \rangle = 13$) for $\alpha = 1.0, 0.9, 0.7$, and 0.5, as indicated. The dashed curves were for $p = 0.95$ ($\langle m \rangle = 20$) and the same values of α. The full crosses are the experimental values of this study, and the other points were obtained with the $\langle \mu_\perp^2 \rangle_1/z$ value of ref 11.

The high-frequency dipole has been examined similarly in terms of the reduced expression

$$D_{\perp,x} = (\langle \mu_\perp^2 \rangle_x/z)/(\langle \mu_\perp^2 \rangle_1/z) = \frac{\{(1 - px)^2 \sum (px)^{m-1} (\cos (m\pi/2))^{4\alpha-2} (m-1)^{2(1-\alpha)}\}}{\{(1-p)^2 \sum p^{m-1} (\cos (m\pi/2))^{4\alpha-2} (m-1)^{2(1-\alpha)}\}} \qquad (22)$$

For the simple helix this becomes, since $\alpha = 1$,

$$D_{\perp,x} = \frac{(1 - px)(1 + p)x}{(1 + px)(1 - p)} \qquad (23)$$

a function descending to unity as x tends to 1, for all suitable values of p, while for the random chain ($\alpha = 1/2$) the simple result is obtained that

$$D_{\perp,x} = x \qquad (24)$$

The general case of eq 22 has been computed numerically for x values between 0.8 and 1.0. As is shown in Figure 16, $D_{\perp,x}$ is sensitive to p, x, and α, tending to unity from above as $x \to 1$, with a slope that is steeper the greater the order in the chain (i.e., when α and p are both high). As α decreases towards $1/2$, $D_{\perp,x}$ is less sensitive to x and becomes independent of p. The threshold parameter q was not introduced into this calculation, but if there is a threshold for the formation of a helix or a stiff section, short runs of 1-olefin units would not be in that form and would contribute directly to $\langle \mu_\perp^2 \rangle_x/z$, and consequently $D_{\perp,x}$ might then decrease more with x.

The treatment of $D_{\|,x}$ does not depend upon the assumption of a 2/1 helix when $\alpha = 1$, but for $D_{\perp,x}$ eq 12, 19, and 22 would require a more elaborate treatment had another pitch been adopted. We postpone interpreting the experimental dipole moment measurements until the high-frequency measurements have been described.

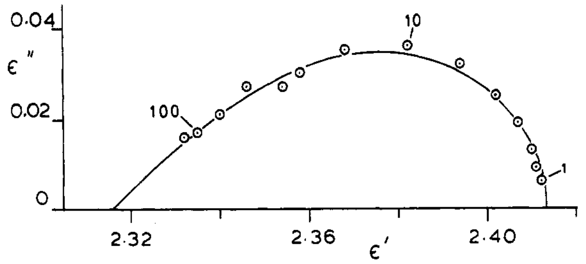

Figure 17. Complex plane plot for a 5.00% (w/w) solution of X70X in benzene at 25 °C. The points are the mean of three separate measurements; the curve was obtained by least-squares fitting the data with eq 25, which found $\epsilon'_0 = 2.413$, $\epsilon'_\infty = 2.316$, $\tau = 22.7$ ns, and $\beta = 0.495$. The numbers labeling the points are the frequencies in megahertz.

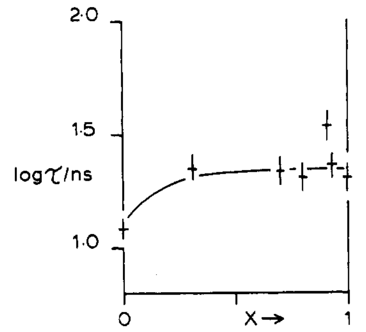

Figure 18. Cole–Davidson correlation times for the terpolymers as a function of x. The polymers were 5.00% (w/w) solutions in benzene at 25 °C.

Results from the Time-Domain System

In the complex plane diagram of Figure 17 are plotted the averages of three sets of measurements of ϵ' and ϵ'' for the sample X70X in benzene. Trials were made of fitting the semicircular arc relationship of Debye, which involves a single correlation time,[35] and of fitting the Cole–Cole relationship,[36] the Cole–Davidson relationship,[37] and the Havriliac–Negami relationship,[38] which encompases them all. In the latter case the factor α of the $(i\omega\tau)^{1-\alpha}$ term was found to have values close to or equal to 0.00, so the Cole–Davidson relationship was adopted to analyze the data.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + i\omega\tau)^\beta} \qquad (25)$$

The parameters ϵ_0, ϵ_∞, τ, and β were systematically adjusted by using a computer program to reduce to a minimum the sum of the squares of the residuals between the calculated and experimental values of ϵ' and ϵ'', each residual being given equal weight in the fitting.[39] The curve so fitted to the data is shown in Figure 17. Correlation times obtained as a function of x from the polymer samples studied are plotted in Figure 18.

For the samples studied the analysis found the parameter β to have a mean value of 0.55 (±0.06), which is characteristic of a highly skewed arc. For the simple 2/1 helix, Glarum's defect diffusion model[40] is attractive but does not apply in detail. It would interpret the low value of β as the consequence of the rate of diffusion of defects along a one-dimensional system of coupled dipoles being similar to the rate of rotation of a single dipole. According to Anderson's analysis of an Ising lattice model of a one-dimensional chain of dipoles,[41] in which strong coupling causes adjacent dipoles to be aligned antiparallel to each other, the high-frequency relaxation would have a value of $\beta = 0.50$.

The high-frequency process may have two distinct origins in our simple model. In the first, kinks articulating helix rotation about the long axis, it may be required that the two bonds on each side of a trans C–C bond simultaneously jump from one set of conformations to another. Alternatively, the magnitude and orientation of the transverse components, $\mathbf{M}_{\perp}$, of two adjacent stiff segments will be altered if a polar residue moves from one segment to another. This is equivalent to the diffusion along the chain of the point of disruption or kink, which featured in the model explored by Anderson. Kink diffusion would involve the cooperative change in the conformation of a number of adjacent bonds and might well require that the adjacent helices both rotate at the same time, one releasing a length of chain and the other taking it up.

We develop the helix rotation model before considering further the experimental results. Assuming that each helix has the same transverse dipole moment, high-frequency dielectric measurements measure the number-average correlation time, in contrast to ^{13}C NMR measurements of T_1 on main-chain carbons of the 1-olefin residues, which measure indirectly the weight-average correlation time for helix rotation.[32] If τ_k is the relaxation time of a pair of kinks and τ_0 is the contribution to the relaxation time made by viscous drag on the surface of each 1-olefin sulfone residue, we have for a helix of m residues[32] $\tau_m = \tau_k + (m-1)\tau_0$. The mean dielectric correlation time is readily shown to be

$$\bar{\tau}_{\mathrm{d}} = \sum N_m \tau_m / \sum N_m = \tau_k + \tau_0/(1-px) \qquad (26)$$

If viscous drag were the controlling feature, so that $\tau_k \ll \tau_0$, $\bar{\tau}_{\mathrm{d}}$ would increase with x, particularly as x nears 1. Moreover, the distribution function for τ_m would be biased toward low values of τ_m, as N_m diminishes progressively with m ($N_m \sim (px)^{m-1}$).[13] The experiments found neither feature. The Cole–Davidson mean correlation times did rise as x ranged from 0 to 1, but only from about 12 ns to about 22 ns, and most of the variation probably occurs below $x = 0.5$ (see Figure 18). That the Cole–Davidson function fitted the complex plane data implies a bias in the distribution function toward long rather than short correlation times. We conclude that $\bar{\tau}_{\mathrm{d}} = \tau_k$.

The slightly greater kinetic flexibility of the poly(cyclohexene sulfone) chain when compared to the poly(hex-1-ene sulfone chain) found here has been noted by others.[11] Inserting a small proportion of cyclohexene residues into the poly(hex-1-ene sulfone) chain disrupts considerably the equilibrium configurational order normally present in the poly(1-olefin sulfone chain) but has caused no significant increase in the kinetic flexibility in the terpolymers. If the extra kinks next to cyclohexene residues are kinetically ineffective in reducing $\bar{\tau}_{\mathrm{d}}$, this may be because these kinks cannot diffuse along the chain. Measurements of T_1 on terpolymers of SO$_2$, but-1-ene, and but-2-ene upheld this view for that polysulfone.[15]

The average value of ϵ'_{∞} from the Cole–Davidson fits for the 5.00% (w/w) solutions in benzene of the terpolymers was 2.314 (±0.006), giving a value of $\mathrm{d}\epsilon'/\mathrm{d}w_2$ of 0.80 (±0.12). Upon substitution of this into the Guggenheim–Smith equation we obtained the result that for the terpolymers the mean distortion polarization is equivalent to about 0.94 D. A dashed line on Figure 9 has been inserted to indicate this lower limit to the orientation polarization.

Chain Configuration

In Figure 12 the experimental $D_{\parallel,x}$ values are shown fitted with two curves we obtained by numerically evaluating eq 21. Other sets of parameters gave satisfactory visual fits and are also entered in Table III. With $\alpha = 0.8$, it was not possible to fit a curve to all the points by varying p, if q was 1 or 2, so smaller values of α were not employed. With this set of data there is no unique solution. The values of $D_{\perp,x}$ are less useful as a means of obtaining model parameters, as it is less sensitive, and our assumption of a 2/1 helix when $\alpha = 1$ may be critical. (As our value of $\langle \mu_{\perp}^2 \rangle_1 / z$ was subject to the difficulty of resolving the two dielectric relaxations near 1 MHz, we have included points based on the value from ref 11 in Figure 16.) $D_{\perp,x}$ does fall as $x \rightarrow 1$, which is consistent with relatively high values of α and p.

It is clear from the dipole moments of the terpolymers and the 1-olefin polysulfone that the chains do consist of a series of ordered segments that are created by the electrostatic interactions that accompany gauche main-chain C–C bonds. It is not possible to decide both on the mean extent of the ordered segment, as measured by p or $\langle m \rangle$, and on the shape of the ordered unit, as characterized by α. If the atactic structure makes the value of $\alpha = 1$ unsuitable, parameter set 4 or 5 of Table III probably gives a good description of the ordered segments. There is limited configurational flexibility at the junctions between segments: $\langle \mu^2 \rangle / z$ only reaches a limiting value at high molecular weights with the hex-1-ene polysulfone[14] and even in a Θ-solvent at quite high molecular weights $[\eta]/\bar{M}_{\mathrm{n}}^{1/2}$ does show some variation.[42] In this study using polymers of similar molecular weights the $K_{\parallel,\theta,\varphi}$ factor has not been explored.

Discussion

This study of olefin sulfone terpolymers was based upon a simple conformational analysis of the main chain, whose value can now be judged in terms of the experimental support found by the measurements. Certain predictions of the theory have been supported by the experimental findings. By progressively replacing cyclohexene residues with 1-olefin residues and thus introducing methylene groups into the main chain, the dipole moment was observed to increase (x = 0–0.3), in keeping with the corresponding creation of gauche C–C bonds, which has the consequence that adjacent C–S bonds of the residue do have a resultant. The recognition of a segmental relaxation in such terpolymers confirmed the view that chains with a predominance of trans C–C bonds would lack strong electrostatic hindrances to motion. The discovery that there is a small dipole moment in the poly(cyclohexene sulfone) chain itself means that the C–C bonds in this polymer's main chain do not all have exactly trans conformations: either the diaxial placements of C–S bond vectors are distorted from the antiparallel arrangement or a certain proportion of the residues have an axial–equatorial placement. (This is contrary to what we have assumed for the treatments of $D_{\parallel,x}$ and $D_{\perp,x}$, with the consequence that derived values for p may be slightly overestimated.)

Increasing the mole fraction of hex-1-ene residues in the terpolymers has been shown to be effective in increasing the stiffness of the chain, as measured by the magnitude of the component of the equilibrium dipole moment that is coupled to the chain contour. Near $x = 1$ the response at low frequencies is particularly strong, and its magnitude is very sensitive to the presence of even a small proportion of cyclohexene residues. Not only do the chains there have a large proportion of gauche C–C bonds, so that the two flanking C–S dipoles do have a resultant, but the sulfone groups can then nest close to each other in a stable electrostatic situation where their dipoles are significantly correlated in orientation. The atactic chain may, according to a tetrahedral lattice model, form kinks with a probability p where trans C–C bonds interrupt the mutual ordering of dipoles. As the electrostatic interactions have little directional character and the packing of the chain into its most stable configuration would involve a foresaking of the simple lattice and place more emphasis on the shape of the residues, and thus on tacticity, we have introduced the scaling parameter, α, and allowed it to have values somewhat less than the value of unity appropriate to a true helix. Good fits to the $D_{\parallel,x}$ vs. x data have been found with a number of sets of model parameters, and the trend in $D_{\perp,x}$ with x interpreted.

The time-domain apparatus in its new form has been used to discover how kinetic flexibility varies with chain composition. While the poly(cyclohexene sulfone) chain has a high-frequency segmental relaxation that is faster ($\tau \sim 12$ ns) than the high-frequency relaxation in poly(hex-1-ene sulfone) ($\tau \sim 22$ ns), the insertion of a small proportion of cyclohexene units into a predominantly hex-1-ene sulfone chain does not improve its flexibility. The kink process rather than viscous drag on the surface of the variable length cylinders controls the rate of the high-frequency process. Perhaps the cyclohexene residues are incapable of providing kinetic flexibility, though they do disrupt the configurational order, because they cannot diffuse along the chain backbone.

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Registry No. (1-Hexene)(cyclohexene)(sulfur dioxide) (copolymer), 81647-54-3.

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