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Microstructure and Dynamic Behavior of Terpolymers of SO_2, But-1-ene, and But-2-ene

Stephen A. Chambers and Allan H. Fawcett*

Department of Pure and Applied Chemistry, The Queen's University of Belfast, Belfast, Northern Ireland. *Received October 19, 1984*

ABSTRACT: Terpolymers of but-1-ene and but-2-ene with sulfur dioxide have been prepared with a range of compositions and with meso and racemic but-2-ene units so that the microstructure might be characterized by ^{13}C NMR spectroscopy. A model for high-frequency motion of a 1-olefin sulfone and a terpolymer with a high 1-olefin content is proposed; the model views the chain as a series of helices whose rotation is controlled by viscous drag at their surface and by the kinetics of the link articulation. Though a polymer consisting entirely of r_c but-2-ene sulfone units is 50 times as free as the but-1-ene polysulfone, according to T_1 measurements, no extra flexibility results from the inclusion of a small proportion of such but-2-ene units at randomly distributed fixed points in a mainly but-1-ene sulfone chain.

Introduction

In poly(1-olefin sulfone) chains electrostatic interactions between adjacent sulfone groups are sufficiently strong to create order in solution, which in the simplest accounts results in a helical segment model.[1-4] The points of disorder, or kinks, between helical units are randomly created in a poly(1-olefin sulfone) chain when a C–C bond is thermally promoted to the trans conformation so that its flanking sulfone groups are separated and their relative orientations are decoupled. Kinks may also be introduced chemically by the inclusion within the chain of a small proportion of cyclic olefin or 2-olefin structures, according to a simply theory that was supported by some measurements of the equilibrium longitudical dipole moment.[1,5] The dynamic behavior of but-1-ene and of but-2-ene polysulfone has been probed by T_1 and nuclear Overhauser measurements upon the main-chain ^{13}C NMR signals.[6-8] It has been suggested that the consequence of the electrorestrictions present in the former chain is a relatively long correlation time for high-frequency segmental motion (τ_c = 26 ns at 303 K)[6] and that their absence in the latter polymer, where the C–C bonds are trans, permits a much shorter correlation time (τ_c = 0.47 ns at 303 K).[9]

Here we offer a development of some of these ideas. For the poly(1-olefin sulfone) chain a simple hydrodynamic model is proposed for high-frequency rotations of the helical segments about their long axis and is examined by means of T_1 measurements upon the methylene carbon atoms of but-1-ene units in a terpolymer of SO_2, but-1-ene, and but-2-ene. Before that test is performed and assessed, the ^{13}C spectrum of these copolymers is related to the chain microstructure, which has three chief features: olefin sequence effects, the meso/racemic relationship of two chiral centers linked by a sulfone group (m_s/r_s), and the meso/racemic relationship of the two chiral centers within a but-2-ene structure (m_c/r_c). In order to ensure that this latter feature has been properly characterized, a copolymer has been prepared from but-1-ene and *trans*-but-2-ene at such a sufficiently low tempertaure that a large proportion of the 2-olefin units retained the configuration of the active centers to form an m_c unit.[7,10] The substitution parameters, $\gamma_s = -2.7$ ppm and $\delta_s = 1.0$ ppm have been used when making assignments.[7,11]

Model of High-Frequency Motions of the Helices

The terpolymer of SO_2, but-1-ene, and but-2-ene is viewed as a system of linked cylinders, with one residue at a link (or kink) and $m - 1$ but-1-ene sulfone residues within a cylinder. For a cylinder of length l_m and radius a rotating in a medium of viscosity η about its axis defined by the positions of the kinks at each end,[12]

$$\tau_c = \zeta/kT$$

where

$$\zeta = \frac{\text{frictional torque at surface + torque at kinks}}{\text{angular velocity}}$$
$$= 4\pi\eta a^2 l_m + \zeta_k$$

As $l_m = (m - 1)l_o$, we may write

$$\tau_{c,m} = (m - 1)\tau_o + \tau_k$$

where τ_o is the contribution to the relaxation time of a helical section made by a but-1-ene sulfone unit of length l_o and τ_k is the characteristic relaxation time of the link or kink process. If as before,[1] p is the probability that the 1-olefin unit is part of a helix and x is the mole fraction of those units in the chain, the number of helices containing m units is

$$N_m = z(1 - px)^2(px)^{m-1}$$

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and the number of units with a correlation time τ_m is

$$G(\tau_{c,m}) = (m - 1)N_m$$

Thus the mean correlation time measured by a ^{13}C experiment is[13]

$$\bar{\tau}_c = \frac{\sum G(\tau_{c,m})\tau_{c,m}}{\sum G(\tau_{c,m})} = \tau_0 \frac{(1 + px)}{(1 - px)} + \tau_k \tag{1}$$

Whether the correlation time depends upon the kink process or upon the frictional torque exerted by the solvent upon the rotating cylinder can, in principle, be decided by varying x. Increasing p can be achieved by choosing a 1-olefin with a longer hydrocarbon tail,[2,3] but that would also have the effect of increasing the size of the polymer side chains and thus of increasing a and τ_0 simultaneously.

Experimental Section

Preparation of the r_c Terpolymers. To mixtures of but-2-ene, but-1-ene, and sulfur dioxide at −35 to −40 °C was added dropwise a 10% solution of *tert*-butyl hydroperoxide in toluene. Before olefin consumption exceeded 50% the reaction was terminated to reduce the drift in feed composition caused by the small difference in reactivities of the two olefins.[14] These terpolymers were precipitated and purified as had been other polysulfones.[15]

Preparation of Terpolymer with m_c Units. Eight milliliters of *trans*-but-2-ene (B.D.H., 98% pure) was mixed with 8 mL of but-1-ene and about 50 mL of SO_2 (part of which solidified) in a glass tube held at −95 °C in a toluene slush bath. Initiator solution ($5^1/_2$ mL) was cooled to −35 °C and added over 1 h. The mixture was frozen in liquid nitrogen, covered with cold methanol, and allowed to warm to room temperature to leave the polymer suspended as a solid (yield 5.9 g, 25%). Collecting the polymer in this manner caused no further polymer richer in r_c units to be formed during the recovery.[7,10]

A Bruker WM 250 NMR spectrometer was used for the ^{13}C spectra (20% solution in Me_2SO-d_6) and for the ^1H spectra. T_1 measurements were made on a Bruker WH90 instrument.[9]

Results and Discussion

A. Polymer Microstructure. The composition of the but-1-ene–but-2-ene series of sulfone terpolymers in which the latter units were almost entirely r_c in structure was obtained from the 250-MHz spectrum of the protons in chloroform, the shifts of the but-2-ene units being 1.56 ppm (methyl) and 4.04 ppm (methine), and the shifts of the but-1-ene units being 1.17 ppm (methyl), 2.17, 2.03 ppm (methylene of side chain), 3.35 ppm (one main-chain methylene), and 3.79, 3.95 ppm (two remaining main-chain protons). The areas of the peaks at 1.17, 1.56, and 3.35 ppm served as measures of polymer composition, for they were usually well-resolved from the others. The mole fractions of the but-1-ene units, x, so evaluated are entered to the right of each part of Figure 1. The value of x for the polymer containing m_c but-2-ene structures was similarly found from a ^1H spectrum in Me_2SO-d_6.

Figure 1 shows representative ^{13}C spectra of the terpolymers with r_c but-2-ene structures. The chief features of part a are from blocks of but-1-ene sulfone units, the peaks p, q, m, and n being from the side-chain methyl carbon, the side-chain methylene carbon, the main-chain methylene carbon, and the main-chain methine carbon, with fine structure that has been described before.[7] The chief features of the spectrum in part d, the four peaks labeled b and the methyl peak a, came from long r_c but-2-ene sulfone runs. At intermediate compositions the minor peaks in these two spectra became more intense and have been used for two purposes: (i) to understand one part of the fine structure of poly(but-1-ene sulfone) and (ii) to characterize sequences unique to the terpolymers.

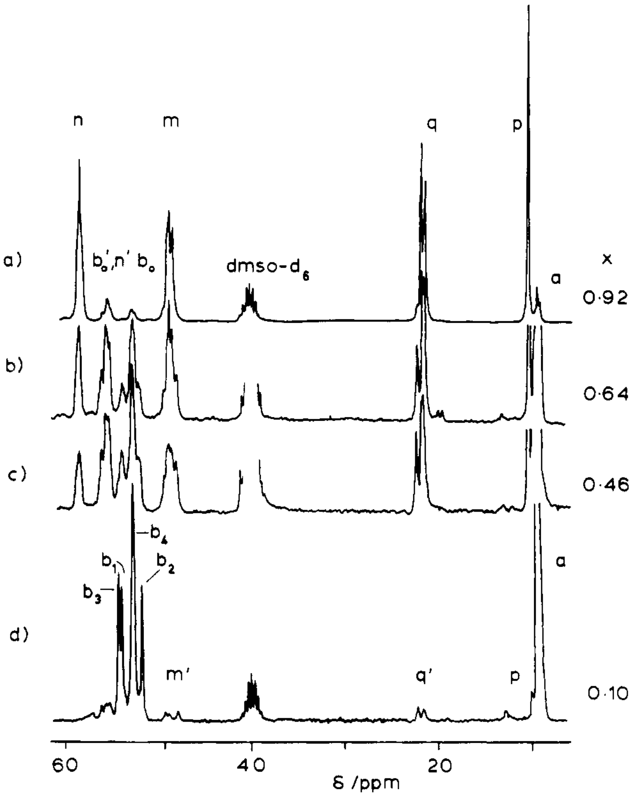
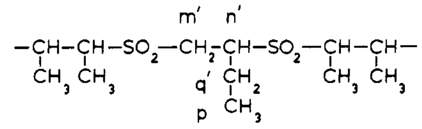


Figure 1. ^{13}C NMR spectra at 63 MHz of four terpolymers of SO_2, but-1-ene, and but-2-ene obtained in Me_2SO-d_6 at 60 °C. Sweep width 12 195 Hz, repetition time 0.67 s, pulse width 12 μs, and at least 3000 scans. The central solvent peak was taken as scale reference, at δ 39.84. The mole fraction of but-1-ene units, x, is given to the right of each part. Limiting viscosity numbers were at least 35 mL g^{-1}.

The direction along the chain from which was produced the m/r diad splitting of peak q may now be elucidated, following an examination of the fine structure from carbon q′ that occurs downfield of the shift of q, of the homopolymer because of a δ_s effect from the methyl group to the right.



$$-\underset{CH_3}{CH}-\underset{CH_3}{CH}-SO_2-\overset{m'}{CH_2}-\overset{n'}{\underset{\underset{CH_3}{CH_2}}{CH}}-SO_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-$$

The diad fine structure of q′ was attributed to the influence of m_s,r_s pairs of methine chiral centers at the two methine carbons flanking the adjacent sulfone group, for in these circumstances carbons β to sulfone groups show splittings of the order of 0.5–1.0 ppm.[7,11] As q′ has no other splitting in Figure 1d, when the unit containing carbon q′ is flanked on its left by another but-2-ene structure, the influence of a chiral methine carbon to the left is negligible. In but-1-ene sulfone homopolymers we therefore attribute the m,r diad microstructure of q, and hence of all similar atoms at the start of the side chain,[4,7] to the influence of the next chiral main-chain atom in the head direction along the chain.

For a but-1-ene unit flanked by two but-2-ene units, as is found in the polymer of Figure 1d, m′ was expected and was observed at about the position of m and had diad fine structure from the m_s,r_s configurations to the right. The shift of the methine carbon n′ was moved upfield by γ_s from its position in the homopolymer to about 55 ppm.

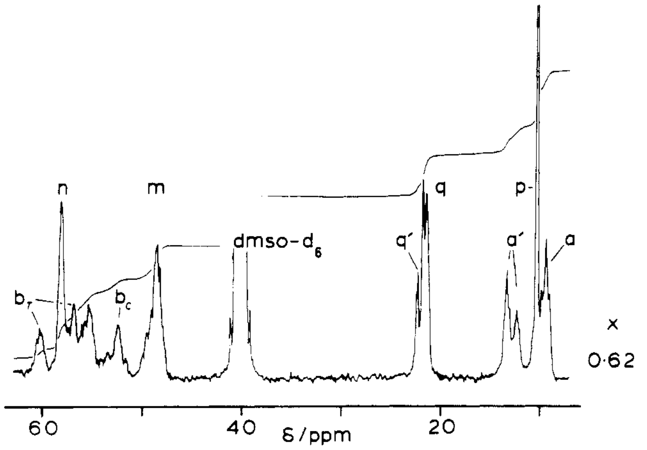
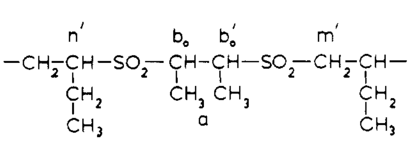


Figure 2. ^{13}C NMR spectrum at 63 MHz of a terpolymer of SO_2, but-1-ene, and but-2-ene that was rich in m_c 2-olefin units. Spectrometer settings as for the spectra of Figure 1, except that 1642 scans were used. The m_c/r_c ratio was estimated from the integral of the upfield shifts, and x from the proton spectrum. The three types of olefin unit were in the ratio of 1-olefin:m_c 2-olefin:r_c 2-olefin = 0.62:0.21:0.17.

We next consider but-2-ene structures flanked by two but-1-ene units as in the case of the copolymer of Figure 1a.



$$-CH_2-\underset{CH_3}{\underset{|}{\underset{CH_2}{\underset{|}{CH}}}}-SO_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-SO_2-CH_2-\underset{CH_3}{\underset{|}{\underset{CH_2}{\underset{|}{CH}}}}-$$

In the absence of the β–C perturbing effects of the adjacent methine carbons of a but-2-ene homopolymer,[7,11] we take the shift of the methine carbons of an r_c unit to be the mean of b_1–b_4, i.e., 52.7 ppm. The peak at 52.5 ppm was assigned to b_0: the absence of diad fine structure is consistent with the nonchirality of carbon m'. In contrast, the shift of b_0' was predicted to be 52.7 ppm less the γ_s upfield shift (m' lacks the substituent present in the but-2-ene homopolymer), i.e., 55.4 ppm. The shift of n' has obscured the splitting that we expected for b_0' from the m_s,r_s pair of chiral centers flanking the sulfone group to the left.

Little new information was detected in the intermediate cases of the spectra of Figure 1, parts b and c, from the main-chain carbons. If the spectra are inspected in ascending order, b_3 appears to fall more rapidly than b_1, and b_1 with b_2 more rapidly than b_4, as the adjacent olefin units progressively lose a chiral center and the signal moves to b_0 and b_0'. In these terpolymers the peaks of the methyl groups a and p were quite distinct and showed no useful fine structure. Near 13 ppm only traces of peaks could be seen from methyl groups in *trans*- or m_c but-2-ene structures that were found at this shift in Figure 2.

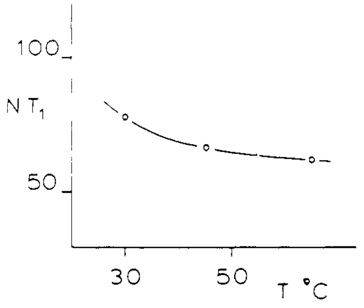


Figure 3. NT_1 at 22.63 MHz for the methylene main chain protons of the x = 0.92 terpolymer plotted against temperature. The solution was approximately 10% w/w in $CDCl_3$.

Table I
Composition, Helix Model Characteristics, and Correlation Times of a But-1-ene Sulfone Homopolymer and a Terpolymer at 30 °C in Chloroform

x	m	$(1 + px)/(1 - px)$	τ_c/ns
1	20	39	26[6]
0.92	8	15	26

The ^{13}C spectrum of the terpolymer prepared with *trans*-2-olefin at −95 °C (Figure 2) should be compared with the spectrum of Figure 1b, whose polymer contained a similar fraction of but-1-ene units. Differences between the two spectra were attributed to the presence of *meso*, m_c, but-2-ene units that had formed by the participation of the charge-transfer complex in the reaction.[10] Besides the a' shift at about 13 ppm, which is characteristic of methyl carbons of m_c units in a poly(but-2-ene sulfone) chain,[7,10] there is a smaller a' peak that we have assigned to such m_c methyl carbons next to a methylene group of a but-1-ene unit. Above the peak p, near 10 ppm, were the shifts of methyl carbons of r_c units, the number of peaks reflecting the perturbing influence of but-1-ene units as well as m_c units, which themselves can cause up to four peaks to be resolved at 63 MHz.[10] The methine carbons of an m_c unit have shifts centered on 57.6 ppm in a poly(but-2-ene sulfone chain);[7,10] in the present case, where the chains are predominantly but-1-ene units, such carbons next to a methylene group are expected $-\gamma_s$ further downfield, in good agreement with the observed shift at 60.3 ppm. The peak at 52.5 ppm is less intense, as there are fewer m_r methine carbons than in the polymer of Figure 1b. Methine carbons on m_c units can be observed at 56.9 ppm; there is nothing at this position in the polymer lacking m_c units.

Apart from the strong preference for r_c but-2-ene units in the terpolymers, unless the low-temperature procedure was followed for producing m_c structures, the microstructure of the chain was almost random in the distribution of chiral centers.

B. Dynamic Behavior of the Terpolymer with x = 0.92. The copolymer of Figure 1b contained but-2-ene units of the r_c type, which if present as the only component in a chain would render it sufficiently flexible that motional narrowing conditions should apply for the T_1 behavior.[9] The limiting viscosity number of this sample, 95 mL g^{-1} in chloroform, was taken to indicate that the molecular weight of the molecules was sufficiently high that T_1 values would be controlled by high-frequency motions. Values of NT_1 were obtained for the main-chain methylene groups of that copolymer containing 0.08 mol fraction of these but-2-ene units randomly distributed, and these are plotted against temperature in Figure 3. Since NT_1 falls as temperature rises, motional narrowing conditions no more apply for this terpolymer than they applied for the but-1-ene sulfone homopolymer.[6,8] From the value of T_1 (39 ± 4 ms) at 30 °C the correlation time for the methylene carbons has been calculated to be 26 ± 3 ns by using the simple isotropic single correlation time model that has been employed before for polysulfones.[6,8,9]

This result, that τ_c for but-1-ene methylene carbons is not reduced by the insertion into the chain of a proportion of ostensibly flexible units, may be first discussed following a reference to Table I, where relevant quantities are entered. The values of $\langle m \rangle$, the mean length of a helical segment,[1] and of $(1 + px)/(1 - px)$ were found with p = 0.95, an assumption that does not appear to be critical. Interrupting the stiff helical sections of the poly(but-1-ene sulfone) chain with enough 2-olefin units to reduce $\langle m \rangle$ by more than 2 has had no significant effect upon τ_c. It may be seen that we have reduced the τ_0 cofactor in eq 1 also by more than 2, yet τ_c has remained unchanged. We conclude that the kink process, rather than viscous drag on the surface of the helices, controls high-frequency motion in these polymers.

That there is a qualitative difference between the behavior of the terpolymers when $x = 0$ (motional narrowing conditions apply) and when $x = 1$ and 0.92 (motional narrowing conditions do not apply) indicates there is a distinct difference in chain dynamics: the simple conclusion obtained above does not thus depend solely upon the use of the anisotropic single τ_c model for interpreting T_1 values. (We note also that the stiff sections in such terpolymers may not be perfectly isotropic helices.[4]) Assuming that the r_c but-2-ene sulfone units, when isolated in the mainly but-1-ene sulfone chain, interrupt the configurational order as do the cyclohexene units in the mainly hex-1-ene sulfone chain,[1,4,5] we can understand the absence of kinetic freedom from the present terpolymer in the following terms: we suppose that in the 1-olefin sulfone homopolymer the kink, created by a trans C–C bond, is capable of moving from one site to the next along the chain so that helix rotation is coupled to kink translation. On the other hand, trans C–C bonds created by the inclusion of isolated but-2-ene sulfone units cannot escape from their site in such a chain and thus cannot introduce further kinetic flexibility. It remains possible that a process not included in our simple model of eq 1, such as high-frequency local librations, is responsible for the magnetic relaxation within the stiffer 1-olefin sulfone sections.

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Dynamical Properties of High Molecular Weight Polystyrene in Tetrahydrofuran in the Dilute–Semidilute Transition Region

Wyn Brown

Institute of Physical Chemistry, University of Uppsala, 751 21 Uppsala, Sweden.
Received November 16, 1984

ABSTRACT: Data are presented for the polystyrene ($M = 8 \times 10^6$ and $M = 15 \times 10^6$)–tetrahydrofuran system, which has been probed by dynamic light scattering in the $1 < qR < 4$ region at $C/C^* \leq 200$. Measurements on the same system were also made by classical gradient diffusion. In dilute solutions the correlation functions were fitted to a bimodal expression to allow evaluation of the first internal mode τ_1 and the translational diffusion coefficient. τ_1 is found to be in approximate agreement with the value given by Zimm's nondraining model. Bimodal autocorrelation functions are also found to typify the semidilute region well above C^* and in a region where unimodal behavior is predicted by de Gennes' theory and are attributed to a composite of fast and slow cooperative modes over the concentration range investigated. It appears unlikely that experimental parameters can be chosen to allow *direct* characterization of a unique pseudogel mode. Such composite character, which appears to be generally valid with samples of very high molecular weight, severely restricts the use of photon correlation spectroscopy for testing models of the semidilute region which are formulated in terms of a specific relaxational mode.

Introduction

Above the critical concentration for overlap of individual polymer coils, C^*, the dynamical structure factor, $S(q,t)$ is predicted[1] to be related to a collective mode which characterizes the transient network formed by intermolecular entanglements. Using photon correlation spectroscopy (PCS) the range of $q\xi$ values where the dynamics of the transient gel should be observable will be wide at high values of (C/C^*) and lie between

$$(C/C^*)^{-1.125} < q\xi < (C/C^*)^{0.75}$$

Here, q is the scattering vector and ξ is a dynamic correlation length of the concentration fluctuations. Between the above bounds the autocorrelation function was predicted to decay exponentially and one can thus define a unique collective diffusion coefficient:

$$D_c = kT/6\pi\eta_0\xi \tag{1}$$

where k is Boltzmann's constant, T is the absolute temperature, and η_0 is the solvent viscosity. The first experimental tests of the above were those of Daoud et al.[2] using neutron scattering and of Adam and Delsanti[3] with PCS measurements on PS/benzene. In the so-called "pseudogel domain" the latter concluded that $S(q,t)$ was a single-exponential function of time. The inverse relaxation time $(\bar{\Gamma})$ was found to be q^2 dependent and $\Gamma \sim C^{0.67}$, in ap-