Macromolecules **1982,** *15,* 933–935

lecular weight dependence in χ. See Figure 5. These squared deviations should be compared with Figure 2, where ν, A, B, and C are the optimized constants. With χ_0, χ_1, χ_2, and χ_3 used as the constants to fit, δ^2 is more than twice as large as that obtained with a scaling model. More significantly, the analysis in terms of the interaction parameter expanded through the third order still makes predictions for χ that are inconsistent with the reported values in more concentrated solutions.[22] The interaction parameter approach also does not incorporate the observed molecular weight dependence. Rather than considering this concentration range as the edge of the concentrated range, we conclude that the scaling predictions of a separate semidilute phase are verified.

Conclusions

Scaling predictions of a distinct semidilute phase have been confirmed by measuring the amount of light scattered at low angles from polystyrene in toluene. In this phase the chemical potential is proportional to the $d\nu/(d\nu - 1) = 2.38$ power of concentration and independent of molecular weight. The semidilute behavior appears at higher concentrations for polymers of lower molecular weight. The critical exponent $\nu = 0.575$ measured from semidilute measurements is less than the value measured in the dilute limit. This is unexpected.

The approach to the semidilute asymptote is described in terms of the independent variable $(Mc^{1/(d\nu-1)})^{-1}$. Data of different molecular weights fit a universal plot when $(R_0c^{-0.379})^{-1}$ is graphed as a function of $(Mc^{1.379})^{-1}$. This plot should permit generalization to include all good solvent–solute systems.

The scaling approach describes the data in the semidilute region better than the generalization of Flory–Huggins theory to include a concentration-dependent interaction parameter. Calculations of the interaction parameter from the data presented here have concentration dependence with the opposite sign of values reported in more concentrated systems. This observation supports the claim of scaling theory that the semidilute solution is a distinct phase, rather than the extreme portion of the concentrated solution range.

Acknowledgment. This work was supported by National Science Foundation Grant ISP-8011453. Extended discussions with M. V. Ferer, Department of Physics, West Virginia University, and A. M. Jamieson, Department of Macromolecular Science, Case Western Reserve University, have been significant to our understanding of this subject.

References and Notes

(1) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(2) Adam, M.; Delsanti, M. *Macromolecules* **1977,** *10,* 1229.
(3) Chu, B.; Nose, T. *Macromolecules* **1980,** *13,* 122.
(4) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980,** *13,* 1280.
(5) Lin, Y. H.; Chu, B. *Macromolecules* **1981,** *14,* 385.
(6) Yu, T. L.; Reihanian, H.; Jamieson, A. M. *Macromolecules* **1980,** *13,* 1590.
(7) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975,** *8,* 804.
(8) Noda, I.; Kato, N.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981,** *14,* 668.
(9) Stanley, H. E. "Introduction to Phase Transitions and Critical Phenomena"; Oxford University Press: London, 1972.
(10) des Cloizeaux, J. *J. Phys. (Paris)* **1975,** *36,* 281.
(11) For three-component spin (Heisenberg model), $i = 3$; for one-component spin (Ising model), $i = 2$. (Fisher, M. E. *J. Appl. Phys.* **1967,** *38,* 981). The analogous case to polymer solutions is a zero-component spin.
(12) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. Lett.* **1977,** *39,* 95.
(13) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979,** *12,* 276.
(14) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(15) Berry, G. C. *J. Chem. Phys.* **1966,** *44,* 4550.
(16) Klärner, P. E. O.; Ende, H. A. In "Polymer Handbook"; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975.
(17) Kaye, W.; Havlik, A. J. *Appl. Opt.* **1973,** *12,* 541.
(18) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978,** *11,* 1180.
(19) Appelt, B.; Meyerhoff, G. *Macromolecules* **1980,** *13,* 657.
(20) Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* **1978,** *69,* 3647.
(21) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957,** *26,* 1067.
(22) Bawn, C. E. H.; Freeman, R. F. J.; Kamaliddin, A. R. *Trans. Faraday Soc.* **1950,** *46,* 677.

Communications to the Editor

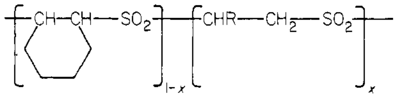
Structural Interpretation of the Origin of the Dipole Moment in Poly(1-olefin sulfones) Which Relaxes at Low Frequencies by Whole-Molecule Motion

We report in a preliminary manner on an experimental investigation by dielectric measurements of the structural origin of the large dielectric dispersion displayed at electric field frequencies below 1 MHz by solutions in benzene of poly(1-hexene sulfone) $[-SO_2CHRCH_2-]_n$ ($R = C_4H_9$). The polymers have been viewed as random coils in which stiffness couples a large component of each sulfone dipole moment perpendicular to the chain contour to a small component that is parallel to the chain contour, in order to account for the magnitude of the dipole moment relaxed at low frequencies and the small dependence of this dipole upon molecular weight.[1,2] Our work was stimulated by the elegant models[3,4] for local chain motions in this polymer which were devised to fit the then known experimental observations of an apparent gross difference between the characteristic time for movement of the sulfone dipoles ($\tau_D \sim 10$ μs if $\bar{M}_n \sim 3 \times 10^5$) and the characteristic time for the movement of the main chain C–H vectors ($\tau_{CH} \sim 1$ ns[3-5]) obtained by ^{13}C NMR measurements. These local motions reallocated C–H bonds in space but left the sulfone dipoles unchanged in orientation: they required that the main-chain C–C bonds be trans in conformation. Our experiments were designed to test the relationships between this requirement, the stiffness of poly(olefin sulfones), and the magnitude of the dipole moment relaxed by the whole-molecule motion. To do this we modified the structure of the polymer chain, a procedure that was found so useful in earlier studies[3,6] but we maintained the feature responsible for the special dynamic behavior of these polymers—the regular alternation of the sulfone group and 2C-atom hydrocarbon unit along the chain backbone. An earlier consideration of poly(olefin sulfone) conformations had suggested a dependence of a C–C bond conformation upon the presence of hydrocarbon substituents on neighboring units.[7]

According to calculations based upon an assumed tet-

0024-9297/82/2215-0933$01.25/0 © 1982 American Chemical Society

rahedral lattice model, variations with C–S bond rotational angle of the electrostatic interactions between neighboring sulfone dipoles would be of the order of a few kT were the intervening C–C bond to adopt the trans conformation,[7,8] but if the C–C bond were fixed in a gauche conformation to bring the sulfone dipoles closer together, much stronger correlations would then be obtained.[7] With the aid of polymers prepared from symmetrical olefins, in which the C–C bonds predominantly adopt trans conformations,[9] we have demonstrated the existence of this feature of the potential energy surface of the chain backbone, a feature that may be the key to understanding the behavior of these polymers in solution. ^{13}C NMR measurements of T_1 in poly(2-butene sulfone) in $CDCl_3$ at different temperatures have indicated[10] that the main chain of this polymer is substantially more flexible than that of poly(1-butene sulfone) under similar conditions.[3,5] It can be deduced that the C–C bonds in poly(1-butene sulfone) have chiefly a conformation other than trans and that the stiffness is a consequence of this. To show with the dielectric apparatus available to us that poly(cyclohexene sulfone) is a flexible polymer, we have prepared for study random terpolymers of cyclohexene, 1-hexene, and SO_2:



In terms of the simple conformational theory,[7] the presence of main-chain methylene groups in the terpolymer permits gauche C–C bonds. The permanent dipole moment thus introduced into a predominantly poly(cyclohexene sulfone) chain was recognized as an increase in the Guggenheim–Smith dipole[11] over the value for poly(cyclohexene sulfone) itself in dielectric constant measurements made upon solutions at frequencies below 1 MHz. The onset of a segmental relaxation of this dipole, permitted by the flexible cyclohexene sulfone sequences, has been detected near 10 MHz.[12] The measurements indicated that the distortion polarization of the sulfone group is less than previously deduced.[2,8] This suggested to us, as indeed is the case,[13] that minor high-frequency dielectric processes might also be present in both poly(cyclohexene sulfone) and in poly(1-hexene sulfone).

Now that both the dielectric and the ^{13}C dynamic NMR evidence is in broad agreement as to the existence in these polymers of motions with relaxation times of the order of 1 ns, there remains the problem of the magnitude of the dipole moment relaxed by whole-molecule motion in the poly(1-olefin sulfones). The transition in the composition of the terpolymers of cyclohexene, 1-hexene, and SO_2 from $x = 0$ to $x = 1$ increases chain stiffness and by modifying the manner in which the dipole vectors are summed, provides one means of understanding the structural origin of $\langle \mu_\parallel^2 \rangle / z$.

The prominence in the dielectric spectrum of $(\langle \mu_\parallel^2 \rangle / z)_x$ at a nearly constant $\bar{M}_n$ is displayed in a reduced form $(\langle \mu_\parallel^2 \rangle / z)_x / (\langle \mu_\parallel^2 \rangle / z)_1$ as a function of x in Figure 1.[12] From the experimental points marked on this figure and the earlier measurements upon poly(1-hexene sulfone)[2] at different degrees of polymerization, it is apparent that the magnitude of the low-frequency dipole is much more sensitive to x ($x \gtrsim 0.5$) than to $\bar{M}_n$. That the structure of poly(1-hexene sulfone) is disrupted considerably by the introduction of a small proportion of the symmetrical olefin indicates that it is highly organized, rather than a random coil, as previously assumed.[2] In the following model we treat the terpolymers and poly(1-hexene sulfone) as sequences of stiff helical sections separated by flexible kinks located at sites where the C–C bonds are trans. Though the conformational energy calculations were very simple in scope, particularly in assuming a tetrahedral lattice, they did find that conformational sequences for the S–C–C–S unit such as g_-g_+t had the lowest coulombic energies.[6] Such sequences, if repeated, would produce a 2/1 helix. For the following treatment of the chain it is, however, not necessary to assume that the helical segments have a particular pitch.

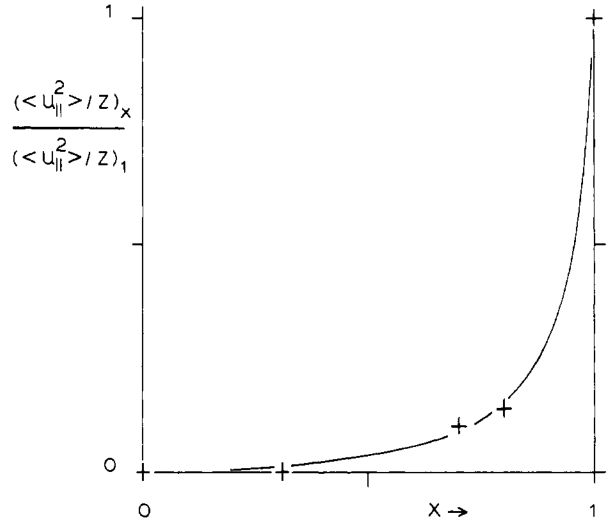


Figure 1. Dependence upon composition, x, of the magnitude of the reduced dipole moment relaxed at low frequencies in the terpolymers. x was obtained from the ^{1}H spectrum of the side chains measured at 90 MHz in $CDCl_3$, where the methyl group and the methylene groups can be distinguished. For these samples $\bar{M}_n \simeq 4 \times 10^5$. For each sample $\langle \mu^2 \rangle / z$ was obtained with the Guggenheim–Smith[11] method near 800 Hz and 1 MHz. As $\mu_\parallel$ relaxes between these frequencies, $\langle \mu_\parallel^2 \rangle / z$ was obtained as the difference between the two values. For x (±2%) = 31%, 70%, and 80%, $\langle \mu_\parallel^2 \rangle / z$ was, respectively, 0.0, 1.2, and 1.4 D.[12] The curve is eq 9, with $p = 0.95$.

Let the terpolymer chain contain z olefin units and have a helical structure, except where cyclohexene units cause a trans C–C bond or where thermal and solvent effects induce a fraction f_t of the C–C bonds in 1-hexene units to adopt the trans state. The fraction of main-chain C–C bonds in the trans state is thus

$$F_t = 1 - x + xf_t = 1 - px \qquad (1)$$

where p is the probability that a 1-hexene unit is part of a helix. If there are N_m segments, each containing m units ($m = 1, 2, 3, ...$), and P_m is the probability of the C–C bonds being in the required sequence of one trans conformation and $m - 1$ gauche conformations, then

$$P_m = \frac{N_m}{\sum N_m} = (1 - px)(px)^{m-1} \qquad (2)$$

assuming that the olefin units are randomly distributed. (In this and subsequent expressions, the summation is performed over all values of the integer m.) When z is so large that end effects can be neglected, the number of helical segments is equal to the number of trans C–C bonds:

$$\sum N_m = z(1 - px) \qquad (3)$$

We suppose that the sulfone group dipole can be represented as two C–S bond dipoles. When a C–C bond is not in the trans state, the two C–S bond dipoles linked to that bond have a nonzero resultant.[7] We assume that the dipole moment of each helix has a component, $\mathbf{M}_{\parallel,m}$, that is directed from one end of the segment to the other and whose magnitude is proportional to $m - 1$, the number of gauche C–C bonds:

$$\mathbf{M}_{\parallel,m} = (m - 1)\mu_p \tag{4}$$

We may assume that the links between the segments are completely free,[14] so that

$$\langle \mu_{\parallel}^2 \rangle_x = \sum N_m M_{\parallel,m}^2 \tag{5}$$

When N_m and $M_{\parallel,m}^2$ are eliminated from eq 5,

$$\langle \mu_{\parallel}^2 \rangle_x = z\mu_p^2(1 - px)^2 \sum (px)^{m-1}(m - 1)^2 \tag{6}$$

or

$$(\langle \mu_{\parallel}^2 \rangle / z)_x = \mu_p^2 px(1 - px)^2 \sum (px)^{m-2}(m - 1)^2 \tag{7}$$

With the aid of the binomial theorem, this simplifies to

$$(\langle \mu_{\parallel}^2 \rangle / z)_x = \mu_p^2 px \frac{1 + px}{1 - px} \tag{8}$$

The reduced parallel component thus depends upon p and x according to

$$\frac{(\langle \mu_{\parallel}^2 \rangle / z)_x}{(\langle \mu_{\parallel}^2 \rangle / z)_1} = x\frac{(1 - p)(1 + px)}{(1 + p)(1 - px)} \tag{9}$$

The curve in Figure 1 has $p = 0.95$ and gives a fairly good fit to the data. Suitable values of p range from 0.94 to 0.96. The average number of olefin units in a segment is given by

$$\langle m \rangle = \frac{\sum m N_m}{\sum N_m} \tag{10}$$

As $z = \sum m N_m$, we obtain from eq 3 and 10

$$\langle m \rangle = 1/(1 - px) \tag{11}$$

In poly(1-hexene sulfone), for which $x = 1$, $\langle m \rangle$ is thus about 20. From eq 8, with $x = 1$ and $(\langle \mu_{\parallel}^2 \rangle / z)_1 = 3.77^2$ D^2, $\mu_p = 0.62$ D. Within this model of the poly(1-hexene sulfone) chain, the variations of $\langle \mu_{\parallel}^2 \rangle / z$ with temperature and with solvent that have been observed[1,2] may be understood as manifestations of variations of f_t and consequent variations in $\langle m \rangle$ ($\langle m \rangle = 1/f_t$, when $x = 1$).

Initially we cited evidence for the existence of a certain amount of kinetic flexibility in poly(olefin sulfones) when C–C bonds are in the trans conformation. The success of the present treatment of the dependence upon x of the magnitude of the dipole relaxed at low frequencies in solutions of the terpolymers of cyclohexene, 1-hexene, and SO_2 in itself demonstrates that the terpolymers and poly(1-olefin sulfones) may be regarded as sequences of stiff helical segments joined by flexible links. It is gratifying that Matsuo, Mansfield, and Stockmayer have independently come to similar conclusions about the configuration of poly(1-olefin sulfone) chains on the basis of quite different methods of studying this problem.[15]

Acknowledgment. We thank Professor W. H. Stockmayer for a most useful discussion and for helpful criticism. S. Fee thanks the department of Education, Northern Ireland, for financial assistance and St. Malachy's High School, Castlewellan, for part-time release from normal duties.

References and Notes

(1) Bates, T. W.; Ivin, K. J.; Williams, G. *Trans. Faraday Soc.* **1967,** *63,* 1964.
(2) Bates, T. W.; Ivin, K. J.; Williams, G. *Trans. Faraday Soc.* **1967,** *63,* 1976.
(3) Cais, R. E.; Bovey, F. A. *Macromolecules* **1977,** *10,* 757.
(4) Stockmayer, W. H.; Jones, A. A.; Treadwell, T. L. *Macromolecules* **1977,** *10,* 762.
(5) Fawcett, A. H.; Heatley, F.; Ivin, K. J.; Stewart, C. D.; Watt, P. *Macromolecules* **1977,** *10,* 765.
(6) Stockmayer, W. H.; Matsuo, K.; Guest, J. A.; Westphal, W. B. *Makromol. Chem.* **1979,** *180,* 281.
(7) Fawcett, A. H.; Ivin, K. J. *Polymer* **1975,** *16,* 569.
(8) Fawcett, A. H.; Ivin, K. J. *Polymer* **1975,** *16,* 573.
(9) Fawcett, A. H.; Ivin, K. J. *Polymer* **1972,** *13,* 439.
(10) Fawcett, A. H.; Fee, S.; Waring, L. C., to be submitted.
(11) When measured in this way, the dipole moment includes a contribution from distortion polarization. Guggenheim, E. A. *Trans. Faraday Soc.* **1949,** *45,* 714. Smith, J. W. *Ibid.* **1950,** *46,* 394.
(12) An account of some measurements performed over a restricted range of frequencies has been given: Fawcett, A. H.; Fee, S.; McKee, S. G.; Quigg, R. K. "Abstracts of Communications", 27th International Symposium on Macromolecules, Strasbourg, July 1981, Vol. II, p 616.
(13) Mashimo, Matsuo, Cole, Winsor, and Stockmayer have extensively characterized these high-frequency processes (personal communication from W. H. Stockmayer).
(14) We thus neglect the slight dependence of $\langle \mu_{\parallel}^2 \rangle / z$ upon z.[2,15] This is not so drastic an assumption as it first appears. If the angle between the axes of successive helices is fixed at θ, a factor $(1 - \cos\theta)/(1 + \cos\theta)$ should be included on the right-hand side of eq 5–8. This factor will, however, not appear in eq 9, with which the experimental data are interpreted. $\langle m \rangle$ (see eq 11) does therefore not depend upon θ.
(15) Matsuo, K.; Mansfield, M. L.; Stockmayer, W. H. *Macromolecules* **1982,** *15,* 935.

Allan H. Fawcett* and Seán Fee
Department of Chemistry
The Queen's University of Belfast
Belfast BT9 5AG, Northern Ireland

Received January 26, 1982

On the Possibility of Helical Structures in Olefin/SO_2 Copolymers

In the accompanying Communication, Fawcett and Fee[1] propose that the unusual conformational and dynamical behavior of 1-olefin/SO_2 alternating copolymers in dilute solution is due to the presence of helical structures. Their conclusion is based on the dielectric response of a series of mixed copolymers containing varying relative quantities of 1-hexene and cyclohexene. We have independently come to the same conclusion, based on experiments with polysulfones bearing longer side chains (up to 18 C atoms) and reinforced by semiempirical conformational energy calculations.

The historical background goes back to 1962, when Ivin, Ende, and Meyerhoff[2] found that the intrinsic viscosities of a 1-hexene/SO_2 copolymer in two dissimilar Θ solvents differed by a factor of 1.5. Moreover, a small departure from random-coil behavior was suggested by a Mark–Houwink exponent of 0.55 under Θ conditions ($A_2 = 0$) in 1-chlorohexane. The former observation was attributed to solvent effects on conformation of such a highly polar chain (the dipole moment of a monomeric dialkyl sulfone being $\mu_1 = 4.5$ D), and the latter was attributed to experimental uncertainty. A few years later Bates, Ivin, and Williams[3] found a strong low-frequency dielectric dispersion for dilute solutions of the same polymer in benzene, toluene, and dioxane. The mean dipole correlation time depended strongly on molecular weight, corresponding quite well to the formula $\tau \cong M[\eta]\eta_0/RT$ even up to $M = 10^6$. This result means that overall rotatory diffusion ("tumbling") of the macromolecules (i.e., the terminal relaxation mode) offers the dominant relaxation path, and it could be explained if the chains had a large longitudinal

0024-9297/82/2215-0935$01.25/0