magnitude is proportional to $m-1$, the number of gauche C–C bonds:

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

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

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

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

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

or

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

With the aid of the binomial theorem, this simplifies to

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

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

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

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

$$\langle m \rangle = \frac{\sum m N_m}{\sum N_m} \qquad (10)$$

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

$$\langle m \rangle = 1/(1-px) \qquad (11)$$

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 © 1982 American Chemical Society

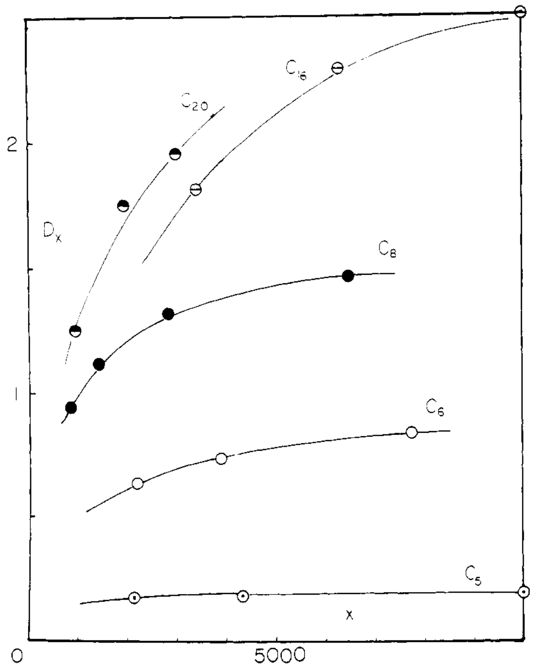

Figure 1. Dipole moment ratios, $D_x \equiv \langle\mu^2\rangle/x\mu_1^2$ of 1-olefin/SO_2 copolymers, $C_nH_{2n}SO_2)_x$, in benzene at 25 °C. The measured mean-square moment per repeat unit is $\langle\mu^2\rangle/x$ and the moment of a single dialkyl sulfone is μ_1 = 4.5 D.

head-to-tail dipole in each repeat unit,[4] as, for example, in poly(ϵ-caprolactone);[5] but it could also occur if the chains were dynamically rigid, whatever their conformations or whatever the orientation of the repeat-unit dipole with respect to the chain backbone. At the time, the former of these alternatives was dismissed as unlikely in view of the primary chain structure[7] and of the very small apparent excluded volume[8] for the equilibrium dipole moments. Thus the latter explanation (which has since proved to be correct for other systems at sufficiently low molecular weights, e.g., for polystyrenes[9] when $M < 10^4$) was perforce adopted, implying the existence of very large barriers to internal rotation within the polysulfone chain. These supposed barriers appeared to be connected to the unusually large electrostatic interactions between neighboring sulfone dipoles, and this notion was strengthened by the observation that in a 2.3/1 styrene/SO_2 copolymer (with more widely separated sulfone groups) the low-frequency dielectric loss peak did not appear.[10]

A startling development came when ^{13}C NMR relaxation measurements[11-13] revealed the C–H orientational correlation times to be typically about 1 ns (4–5 orders of magnitude faster than the dielectric relaxation), independent of molecular weight. To rescue the existing model it then became necessary to postulate[11,13] some rather fanciful crankshaft processes capable of occurring at the high rates demanded by the NMR data but producing no change in the resultant electric dipole vector.

We initiated studies of copolymers involving higher 1-olefins in the hope of observing some departure from the supposed molecular rigidity. Instead, to our surprise, we have found behavior which points to the existence of structures, presumably helical, which can after all possess appreciable head-to-tail longitudinal dipole moments. Some of the measurements of equilibrium dipole moment are shown in Figure 1, where the dipole moment ratio, $D_x \equiv \langle\mu^2\rangle/x\mu_1^2$, in benzene is plotted against degree of polymerization x for different 1-olefin/SO_2 copolymers. It is seen that the ratio tends to a Gaussian limit only at very high x; and the numerical value of the ratio (approaching 3 for large x and long side chains) is not typical of polymers with only transverse dipolar groups, for which figures less than unity are normal.[14] For the same systems, the radii of gyration, as measured by light scattering or inferred from intrinsic viscosities, also suggest modest departures from Gaussian behavior in the observed range of chain lengths. (Recall also ref 2.) These results, and, of course, the low-frequency dielectric relaxation, which is found in all the 1-olefin copolymers,[15] can be explained by the existence of helical sequences interrupted by shorter more random sections. The known head-to-tail primary structure of the polymers[16] ensures a head-to-tail sequence of electric dipoles, in the same direction whether the helix is right- or left-handed.

Conformational energy calculations support the helical postulate. Both electrostatic and steric interactions contribute to helix stability, which increases as the side group is lengthened. The most likely helix has a rather high pitch of 8–9 Å per turn of about 6 repeat units and a longitudinal dipole moment of about 1 D per repeat unit. The latter figure is in satisfactory accord with our observed dipole moments and radii of gyration if the directional correlation between successive helical sequences is low and the average sequence length is of the order of 50. This figure has the same order of magnitude as that estimated by Fawcett and Fee[1] from quite different observations and indicates that the stability of the helix is considerably lower than that found, for example, in poly(alkyl isocyanates).[17]

It should be mentioned that all the olefin/SO_2 copolymers are now known[18] to exhibit dielectric relaxation peaks in the 10–100-MHz region, whether or not they also have the low-frequency relaxation. This is the normal behavior expected of transverse dipoles and is presumably largely due to the nonhelical regions. The corresponding orientational correlation times are quite comparable to those obtained from the NMR data.[11-13]

Some fine points remain to be explored further, such as the possible effects of stereoregularity on helix stability and the known[8] solvent effects on the dipole moments, but we believe that a consistent rational picture is now emerging. Full reports are in preparation.

Acknowledgment. This work supported by the National Science Foundation under Grants DMR76-22987 and DMR79-13227 of the Polymers Program, Division of Materials Research. We thank Dr. Allan Fawcett for enlightening discussions.

References and Notes

(1) Fawcett, A. H.; Fee, S. *Macromolecules* **1982**, *15*, 933.
(2) Ivin, K. J.; Ende, H.; Meyerhoff, G. *Polymer* **1962**, *3*, 129.
(3) Bates, T. W.; Ivin, K. J.; Williams, G. *Trans. Faraday Soc.* **1967**, *63*, 1964.
(4) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.
(5) Jones, A. A.; Stockmayer, W. H.; Molinari, R. J. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 54*, 227.
(6) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(7) With regular head-to-tail addition of 1-olefin units, the longitudinal dipole due to the alkyl side group would not be expected to exceed 0.2 D per repeat unit. Cf.: Baur, M. E.; Stockmayer, W. H. *J. Chem. Phys.* **1965**, *43*, 4319.
(8) Bates, T. W.; Ivin, K. J.; Williams, G. *Trans. Faraday Soc.* **1967**, *63*, 1976.
(9) Stockmayer, W. H.; Matsuo, K. *Macromolecules* **1972**, *5*, 766.
(10) Stockmayer, W. H.; Matsuo, K.; Guest, J. A.; Westphal, W. B. *Makromol. Chem.* **1979**, *180*, 281.
(11) Cais, R. E.; Bovey, F. A. *Macromolecules* **1977**, *10*, 757.
(12) Fawcett, A. H.; Heatley, F.; Ivin, K. J.; Stewart, C. D.; Watt, P. *Macromolecules* **1977**, *10*, 765.
(13) Stockmayer, W. H.; Jones, A. A.; Treadwell, T. L. *Macromolecules* **1977**, *10*, 762.
(14) Mark, J. E. *Acc. Chem. Res.* **1974**, *7*, 218.
(15) Herlihy (Herlihy, E. M.A. Thesis, Dartmouth College, 1977) reported preliminary results for 1-hexadecene/SO_2 copolymers.

(16) Marvel, C. S.; Weil, E. D. *J. Am. Chem. Soc.* **1954**, *76*, 61.
(17) Rubingh, D. N.; Yu, H. *Macromolecules* **1976**, *9*, 681.
(18) Mashimo, S.; Matsuo, K.; Cole, R. H.; Winsor, P., IV; Stockmayer, W. H., in preparation.
(19) Present address: Technisch-Chemisches Laboratorium, ETH-Zentrum, CH-8092 Zürich, Switzerland.
(20) Present address: Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

Keizo Matsuo,[19] Marc L. Mansfield,[20] and Walter H. Stockmayer*

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

Received January 26, 1982

Comment on the Paper of Fahrenholtz and Kwei Concerning the Compatibility of Polymer Mixtures Containing Novolac Resins

In a recent paper published in this journal,[1] Fahrenholtz and Kwei report the results obtained from thermal and infrared spectroscopic studies of a number of polymer blends containing novolac resins. Whereas we believe the results are interesting and pertinent to the overall subject of compatible polymer blend systems, there are nonetheless several factors, primarily concerning the interpretation of the infrared spectra, that deserve comment.

The authors show in Figure 4[1] the infrared spectra of pure polycarbonate (PC), the novolac resin, and a 5% mixture of PC in novolac. In the text the authors state that "the entire carbonyl peak is shifted 20 cm^{-1}, with no portion remaining at the higher value" but upon examination of Figure 4, it is evident this is an overstatement. The band is asymmetric and there is still an obvious contribution at 1770 cm^{-1}. Additionally, Fahrenholtz and Kewi state at a later stage in their paper that "the reason the entire carbonyl peak is shifted in the polycarbonate but not in other cases is that the stringent geometric requirement for hydrogen bonding is more easily met in the relatively unhindered carbonate functional group". While this is a reasonable suggestion it is purely speculative and there is a more obvious reason for the observed frequency shift and the overall shape of the band. PC is a polymer capable of crystallization under favorable conditions where the T_g is depressed by the presence of a plasticizer. We have recently published the results of an FT IR study of the polymer blend system PC–poly(ϵ-caprolactone) (PCL)[2,3] which shows the effect of polymer-induced (PCL) crystallization of PC. The carbonyl stretching frequencies associated with PC in amorphous and preferred ("crystalline") conformations are well separated and occur at 1775 and 1768 cm^{-1}, respectively.[2,3] It is impossible to judge the frequency precision of the spectra shown in Figure 4 of Fahrenholtz and Kwei's paper as they are hand drawn and were obtained on a dispersive instrument but the general shape of the bands is almost identical with those we have observed in the PC–PCL blends. Furthermore, the experimental conditions of sample preparation described by the authors would lead to amorphous PC in the pure state and a semicrystalline PC component in that of the blend.[3] Accordingly, we believe the unique result observed by Fahrenholtz and Kwei for the 5% PC–novolac blend may be explained on the basis of plasticizer-induced crystallization of PC by the relatively low molecular weight novolac resin.

We also believe that the description of the spectra of poly(ethyl methacrylate) (PEMA) and the blend containing 98% novovlac resin, shown in Figure 3 of Fahrenholtz and Kwei's paper, has been overstated. If one were to curve resolve the spectra of the blend, the overall contribution from the lower frequency band would appear quite modest. This suggests that the majority of the carbonyl groups associated with PEMA are not associated with the novolac resin. Fahrenholtz and Kwei suggest that this is due to conformational reasons but this was not substantiated. We are perplexed that in a compatible blend containing a large excess (98%) of the novolac resin only a modest concentration of the carbonyl groups of the PEMA is accessible.

References and Notes

(1) Fahrenholtz, S. R.; Kwei, T. K. *Macromolecules* **1981**, *14*, 1076.
(2) Coleman, M. M.; Varnell, D. F.; Runt, J. P. Paper presented at the Xth Biannual U.S./Japan Polymer Symposium, Palm Springs, CA, Nov 1980 (to be published in *Contemp. Top. Polym. Sci.*).
(3) Varnell, D. F.; Runt, J. P.; Coleman, M. M. *Macromolecules* **1981**, *14*, 1350.

Michael M. Coleman* and Daniel F. Varnell

Polymer Science Section
The Pennsylvania State University
University Park, Pennsylvania 16802

Received September 29, 1981

Reply to Comment on the Paper of Fahrenholtz and Kwei

In our previous paper[1] published in this journal, we reported the results of infrared studies of mixtures of novolac resins with several carbonyl-containing polymers. We observed a 20-cm^{-1} shift in the carbonyl stretching frequency of the blends' spectra relative to the carbonyl frequency in the pure compound. This result was attributed to hydrogen bonding between the carbonyl group and the phenolic OH of the novolac. Coleman and Varnell[2] have questioned the validity of this interpretation on two grounds: (i) the precision of the reported spectra and (ii) the possibility that a more obvious explanation involving crystallinity effects may exist, specifically in the case of the polycarbonate–novolac mixture.

Our original spectra were obtained with a dispersive instrument which admittedly could have contributed to a degree of error in the absolute value of the peak positions and shifts. Subsequent to our publication, Coleman and Varnell[2] found that plasticization of polycarbonate in blends with poly(ϵ-caprolactam) induces crystallinity in the polycarbonate, which results in a lowering of the carbonyl stretching frequency by 7 cm^{-1}. This raises the question of as to whether our reported shifts are indeed substantially larger than 7 cm^{-1}, considering the possible errors in our previous measurements; i.e., Coleman and Varnell suggest that our shifts may be due to crystallinity effects and not hydrogen bonding.

To confirm the validity of our data, we have reexamined several samples using a Digilab Model 15B FT IR spectrometer operating at 2-cm^{-1} resolution (conditions similar to those used by Coleman and Varnell). The carbonyl region of the spectrum of a 2:98 polycarbonate–novolac blend (the novolac is the same as that used in Figure 4, ref 1) is shown in Figure 1. Also shown in Figure 1 is the spectrum of pure polycarbonate showing the carbonyl peak at 1774 cm^{-1}. The absorption band of the blend is asymmetric and obviously includes a contribution from ab-