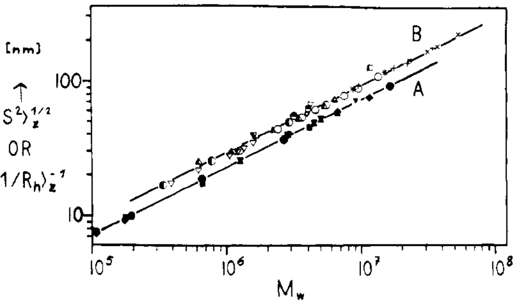

Figure 1. Hydrodynamic radius, $\langle 1/R_h\rangle_z^{-1}$, and radius of gyration, $\langle S^2\rangle_z^{1/2}$, for linear, nearly monodisperse polystyrene in Θ solvents. Data sources: Curve A: (♦) ref 4; (▼) ref 10; (●) ref 11; (▲) ref 3; (■) ref 12. Curve B: (○) ref 15; (⊟) ref 19; (◓) ref 20; (+) ref 13; (×) ref 17; (◐) ref 16; (◧) ref 4; (▽) ref 18; (△) ref 14; (▼) ref 21; (▲) ref 22.

plicitly not taken fully into account in the Kirkwood formulation) and amounting to only 1.7%. The data, as we now show, differ from the above numbers by a considerably larger amount. Figure 1, curve A, exhibits the diffusion data reported by many different investigators.[3,4,10-12] They are well correlated by the expression

$$\langle 1/R_h\rangle^{-1} = 0.0229 M_w^{1/2} \quad (\pm 1.7\%) \quad (\text{nm}) \quad (5)$$

For radii of gyration[4,13-22] we have limited consideration to measurements since 1970, thus taking proper account of improvements in technique, and find (curve B)[4,13-17] the result

$$\langle S^2\rangle_z^{1/2} = 0.0290 M_w^{1/2} \quad (\pm 2.5\%) \quad (\text{nm}) \quad (6)$$

Thus we obtain

$$\rho(\text{exptl}) = 1.27 \pm 0.06 \quad (7)$$

which is seen to be about 15% lower than the theoretical values quoted above. Similar results have been obtained recently with PMMA in a Θ solvent, where a value of $\rho = 1.16$ was found.[23]

No rigorous analytical expression has yet been derived for flexible chains with full unpreaveraged hydrodynamic interactions. A very recent Monte Carlo study by Zimm[24] avoids preaveraging and indeed leads to the result $P = 6.0$, $\rho = 1.28$, in close agreement with the experiments. Unfortunately there is reason[25] to question one aspect of Zimm's procedure; and a different approach, via Brownian dynamical simulation, so far suggests[25] that the Kirkwood formula is within 3% of the right answer for the given model. One may thus be forced to conclude that deficiencies in the model itself (e.g., Oseen perturbation formula treating chain elements as point centers of hydrodynamic resistance, assumed additivity of these interactions, possibility of singularities,[26] etc.) may have to be explored further.

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References and Notes

(1) Kirkwood, J. G. *J. Polym. Sci.* **1954**, *12*, 1.
(2) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(3) Jones, G.; Caroline, D. *Chem. Phys.* **1979**, *40*, 153.
(4) Nose, T.; Chu, B. *Macromolecules* **1979**, *12*, 590.
(5) Schmidt, M. Doctoral Thesis, Freiburg, Feb 1980.
(6) Akcasu, A. Z., private communication.
(7) Vrentas, J. S.; Liu, H. T.; Duda, J. L. *J. Polym. Sci.* **1980**, *18*, 1633.
(8) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: 1971; Chapter 4.
(9) Auer, P. L.; Gardner, C. S. *J. Chem. Phys.* **1955**, *23*, 1546.
(10) Jones, G.; Caroline, D. *Chem. Phys.* **1979**, *37*, 187.
(11) King, T. A.; Knox, A.; McAdam, J. D. G. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 44*, 195.
(12) Han, C. C.; Crackin, F. L. *Polymer* **1979**, *20*, 427.
(13) Hack, H.; Meyerhoff, G. *Makromol. Chem.* **1978**, *179*, 2474.
(14) Miyaki, Y.; Einaga, Y.; Fujita, H.; Fukuda, M. *Macromolecules* **1980**, *13*, 588.
(15) Fukuda, M.; Fukutomi, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Phys. Ed.* **1974**, *12*, 871.
(16) Yamamoto, A.; Fujii, M.; Tanaka, G.; Yamakawa, H. *Polym. J.* **1971**, *2*, 799.
(17) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(18) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(19) McIntyre, D.; Wims, A.; Williams, L. C. *J. Phys. Chem.* **1962**, *66*, 1932.
(20) Krigbaum, W. R.; Carpenter, D. K. *J. Phys. Chem.* **1955**, *59*, 1166.
(21) Outer, P.; Carr, C. I.; Zimm, B. H. *J. Chem. Phys.* **1950**, *18*, 830.
(22) Notley, N. T.; Debye, P. J. W. *J. Polym. Sci.* **1956**, *17*, 99.
(23) ter Meer, H.-U.; Burchard, W. *Colloid Polym. Sci.* **1980**, *258*, 675.
(24) Zimm, B. H. *Macromolecules* **1980**, *13*, 593.
(25) Fixman, M., private communication (Aug 1980).
(26) Zwanzig, R.; Kiefer, J.; Weiss, G. H. *Proc. Natl. Acad. Sci. U.S.A.* **1968**, *60*, 381.

Structure of Noncrystalline Isotactic Poly(methyl methacrylate). Evidence against Double Helices

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The proposal made in 1976[1] that the molecules of crystallized isotactic poly(methyl methacrylate) (i-PMMA) are double helices was the first indication that a nonbiological polymer molecule could exhibit a double-strand structure. To date it still stands as the only example of such behavior. However, examination of the wide-angle X-ray scattering (WAXS) patterns of i-PMMA in its noncrystalline form (as a glass), using both isotropic and oriented specimens, shows that the molecules in this form are neither paired nor regularly intertwined.

Most of the recent conformational energy calculations for i-PMMA have shown that conformations near to all-trans have the lowest energies.[2-6] Such conformations (based on bond rotation sequences ...ϕ_1, ϕ_2, ϕ_1, ϕ_2... with ϕ_1 and ϕ_2 both near zero) will form sinuous helices (except where $\phi_1 = -\phi_2$ where rings are formed). They are thus unlikely to occur in crystal structures unless paired into double helices.

The crystalline conformation of i-PMMA is, however, still the subject of disagreement. Early suggestions were of a 5/2 helix[7] and a 5/1 helix.[2,8-10] More recently, Tadokoro and co-workers[1] have reinterpreted the fiber pattern of crystalline i-PMMA in terms of double helices, each strand of which is a sinuous 10/1 helix ($\phi_1 = 32°$, $\phi_2 = 1°$) but this conclusion has been contested.[11]

Figure 1 shows the WAXS from quenched, and thus noncrystalline, i-PMMA compared with that from syndiotactic and atactic PMMA (s-PMMA and a-PMMA). It can be seen that there is considerable similarity between the three curves, particularly at high s. The scattering from i-PMMA differs from that from s-PMMA in that the first peak (at $s = 0.95$ Å^{-1} for all three polymers) is symmetrical. WAXS from a- and s-PMMAs oriented by

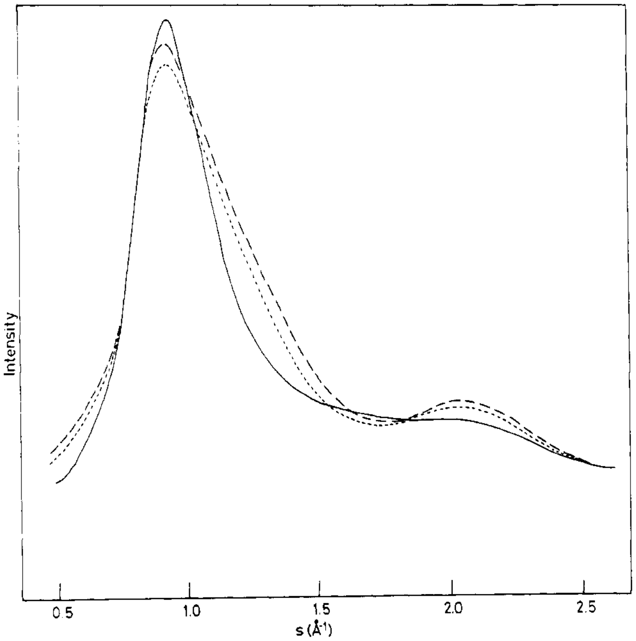

Figure 1. Uncorrected diffracted intensity from (—) quenched i-PMMA, (---) quenched s-PMMA, and (···) a-PMMA. All specimens were unoriented. $s = (4\pi \sin \theta)/\lambda$.

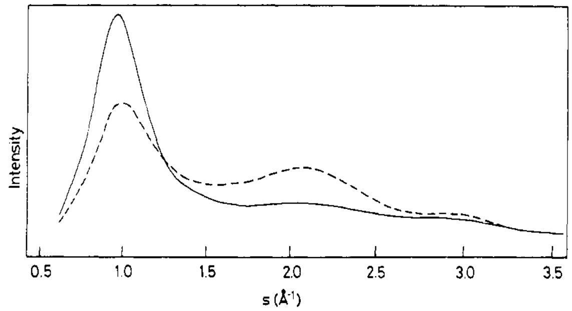

Figure 2. Uncorrected intensity from oriented noncrystalline i-PMMA: (—) equatorial scan; (---) meridional scan.

plastic deformation[12] shows that, although the first peak for a- and s-PMMAs is predominantly equatorial, there is an off-axis component at $s \approx 1.2$ Å^{-1}, which leads to the asymmetry of the peak. For i-PMMA, however, the first peak of the oriented polymer is almost entirely equatorial with no evidence of another component (Figure 2).

The position of the equatorial peak gives a measure of the predominant distance between chains. This distance is most easily determined by transforming suitably corrected scattering data to obtain the radial distribution function (RDF). The sharp equatorial peak in the scattering transforms into a slowly damped oscillation in the RDF.[13] This form of the RDF is generally found for highly disordered structures in which the nearest-neighbor distance is well-defined. Examples of such structures are liquid argon,[14] liquid neopentane,[15] and randomly packed spheres or disks (both real models[16,17] and computer simulations[18,19]).

For a-PMMA, the first broad peak in the RDF has two sharper intrachain peaks superimposed on it.[20] However, a cylindrical distribution function derived from oriented a-PMMA separates these features[21] to show a broad interchain peak centered on 8.2 Å. The similarity in position and peak height of the equatorial scattering from i-PMMA means that the predominant interchain distance is also about 8 Å in the quenched, isotactic polymer. This value is typical for an unpaired PMMA molecule in a near-all-trans conformation, whereas the double helix proposed for the crystalline material has a diameter of at least 12 Å (see Figures 1 and 3 of ref 1). In addition there is no suggestion of a peak in our data near $s = 0.7$ Å^{-1} which would indicate the presence of 12-Å-diameter molecules.

The conclusion is that the molecular diameters for the different isomers of PMMA are similar at around 8 Å. Thus, for quenched or molten i-PMMA, there is no evidence that the molecules are paired as double helices. If double helices are present in the crystal (as has been proposed by Tadokoro and co-workers[1]), then their component molecules would need to pair and regularly intertwine as a part of the crystallization process.

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References and Notes

(1) Kusanagi, H.; Tadokoro, H.; Chatani, Y. *Macromolecules* **1976**, *9*, 531–2.
(2) Tadokoro, H.; Chatani, Y.; Kusanagi, H.; Yokoyama, M. *Macromolecules* **1970**, *3*, 441–7.
(3) Tadokoro, H.; Tai, K.; Yokoyama, M.; Kobayashi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 825–40.
(4) Sundararajan, P. R.; Flory, P. J. *J. Am. Chem. Soc.* **1974**, *96*, 5025–31.
(5) Sundararajan, P. R. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 699–701.
(6) Sundararajan, P. R. *Macromolecules* **1979**, *12*, 575–81.
(7) Stroupe, J. D.; Hughes, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 2341–2.
(8) Liquori, A. M.; Anzuino, G.; Coiro, V. M.; D'Alagni, M.; De Santis, P.; Savino, M. *Nature (London)* **1965**, *206*, 358–62.
(9) Coiro, V. M.; De Santis, P.; Liquori, A. M.; Mazzarella, L. *J. Polym. Sci., Part C* **1969**, *16*, 4591–6.
(10) Tanaka, A.; Ishida, Y. J. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 335–58.
(11) Coiro, V. M.; Liquori, A. M.; De Santis, P.; Mazzarella, L. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 33–4.
(12) Lovell, R.; Windle, A. H. *Polymer*, in press.
(13) Mitchell, G. R.; Lovell, R.; Windle, A. H. *Polymer* **1980**, *21*, 989–91.
(14) Mikolaj, P. G.; Pings, C. J. *J. Chem. Phys.* **1967**, *46*, 1401–11.
(15) Narten, A. H. *J. Chem. Phys.* **1979**, *70*, 299–304.
(16) Scott, G. D. *Nature (London)* **1962**, *194*, 956–7.
(17) Pierański, P.; Malecki, J.; Kuczyński, W.; Wojciechowski, K. *Philos. Mag.*, [*Part*] *A*: **1978**, *37*, 107–15.
(18) Bennett, C. H. *J. Appl. Phys.* **1972**, *43*, 2727–34.
(19) Mason, G. *J. Colloid Interface Sci.* **1976**, *56*, 483–91.
(20) Waring, J. R.; Lovell, R.; Mitchell, G. R.; Windle, A. H., submitted to *J. Mater. Sci.*
(21) Mitchell, G. R.; Lovell, R. *Acta Crystallogr., Sect. A*, in press.

Orientation Studies of Segmented Polyether Poly(urethaneurea) Elastomers by Infrared Dichroism

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Introduction

Recently we compared the composition–structure–properties of two series of polyether poly(urethaneureas) by various physicochemical techniques and careful me-

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