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there is a shrinking of the backbone at the isotropic–nematic transition since $R_\perp$ (and $R_\parallel$ probably, within the error range) decrease from the isotropic state. This effect has also been noted for this transition, in the case of mesogenic polymethacrylates.[2–4] This phenomenon could be associated with the volume contraction which can occur for this transition[14] as a decrease of the mesogen specific volume. However, the variation of the specific volume observed for this polyacrylate is only of about 2%[15] from 130 to 113 °C, too weak to explain alone such a decrease of R_i.

IV. Discussion and Conclusions. The liquid-crystal side-chain polymers like polymethacrylates and polyacrylates seem to present, in the nematic and smectic A phases, a similar behavior for homologous mesogenic groups. The more the temperature decreases, the more widely the polymer backbone expands perpendicularly to its mesogenic units and approaches an oblate shape. In contrast to the NMR interpretation, we show that the sense of the global anisotropy is not affected by the steric hindrance of the α-methyl group since the polyacrylate and the polymethacrylate, which bear the same side chains, behave alike. These data confirm a general tendancy for all these types of side-chain polymers with one mesogenic unit per chemical unit of backbone. Indeed, the poly(methylsiloxanes), the polymethacrylates, and now this polyacrylate segregate the mesogenic cores from the backbone building zones of backbones and zones of mesogenic cores, which give rise to the lamellar structure. In addition, this polyacrylate has shown the property that one backbone can be highly confined between two smectic layers.

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Registry No. $H_2C{=}CHCO_2(CH_2)_6OPhCO_2PhOCH_3$ (homopolymer), 82200-54-2; $D_2C{=}CHCO_2(CH_2)_6OPhCO_2PhOCH_3$ (homopolymer), 115512-10-2; neutron, 12586-31-1.

References and Notes

(1) Kirste, R. G.; Ohm, H. G. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 179.
(2) Keller, P.; Carvalho, B.; Cotton, J. P.; Lambert, M.; Moussa, F.; Pêpy, G. *J. Phys. Lett.* **1985**, *46*, 1065.
(3) Moussa, F.; Cotton, J. P.; Hardouin, F.; Keller, P.; Lambert, M.; Pêpy, G. *J. Phys. Lett.* **1987**, *48*, 1079.
(4) Hardouin, F.; Noirez, L.; Keller, P.; Lambert, M.; Moussa, F.; Pêpy, G. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 389. Pêpy, G.; Cotton, J. P.; Hardouin, F.; Keller, P.; Lambert, M.; Moussa, F.; Noirez, L. *Makromol. Chem., Makromol. Symp.* **1988**, *15*, 251.
(5) Kalus, J.; Kostromin, S. G.; Shibaev, V. P.; Kunchenko, A. B.; Ostanevich, Yu. M.; Svetogorsky, D. A. (a) *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 347; (b) submitted for publication in *Liq. Cryst.*
(6) Boeffel, C.; Spiess, H. W.; Hisgen, B.; Ringsdorf, H.; Ohm, H.; Kirste, R. G. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 777.
(7) Boeffel, C.; Spiess, H. W., submitted for publication in *Macromolecules.*
(8) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.
(9) Beltzung, L.; Strazielle, C. *Makromol. Chem.* **1984**, *185*, 1145.
(10) Zentel, R.; Strobl, G. R. *Makromol. Chem.* **1984**, *185*, 2669.
(11) Cotton, J. P.; Decker, D.; Benoît, H.; Farnoux, B.; Higgins, J.; Jannink, G.; des Cloizeaux, J.; Ober, R.; Picot, C. *Macromolecules* **1974**, *7*, 863.
(12) Noirez, L.; et al., manuscript in preparation.
(13) Boué, F.; Nierlich, M.; Leibler, L. *Polymer* **1982**, *23*, 319.
(14) Duran, R.; Guillon, D.; Gramain, Ph.; Skoulios, A. *J. Phys. (Les Ulis, Fr.)* **1988**, *49*, 121.
(15) Achard, M. F., private communication.

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On the Screening of Hydrodynamic Interactions in Dilute Polymer Solutions

The concept of screening of hydrodynamic interactions in polymer solutions and the criteria for this effect are well understood.[1–12] The screening length for the hydrodynamic interaction is generally a complicated function of the experimental variables and many different limiting situations of experimental relevance may be identified. By use of the appropriate limits of the hydrodynamic screening length, results of extensive studies of the oscillatory flow birefringence,[13] linear viscoelastic properties,[13] and dielectric relaxation[14] of polymer solutions can be understood. In particular, the concentration dependence of the relaxation times of the internal normal modes of linear chains in dilute solutions have been calculated[7–11] by using the screened hydrodynamic interaction; the results are in reasonable agreement with oscillatory flow birefringence and dielectric dispersion measurements.[13,14]

Recently, a calculation by Shiwa, Oono, and Baldwin[15] has been reported where the authors have derived results which are not only inconsistent with themselves but also in disagreement with the previous theories and a wealth of experimental data. Although Shiwa et al. claim to begin with a new model at a more fundamental level, their formulas for viscosity and mobility are the same[15] as those of the Freed–Edwards theory. Therefore the differences between the work of Shiwa et al. and the previous theories stem from the approximations applied to the various complicated formulas for viscosity, screening length, etc.

We show below that the errors in the work of Shiwa et al. originate from the inconsistent use of formulas for different regimes. For specificity, let us consider the concentration dependence of the relaxation time (τ_p) of the pth normal mode of polymer chains in dilute solutions. The initial concentration dependence of τ_p for linear flexible chains in three dimensions has been derived[7,9,10] to be

$$\frac{\tau_p}{\tau_p^\circ} = 1 + \frac{\pi\rho l l_1^{3/2}(q)}{(12q)^{1/2}} + \dots \qquad (1)$$

where τ_p° is the value of τ_p at infinite dilution, l is the Kuhn step length and $q = 2\pi p/L$. l_1 is a crossover function for the effect of the excluded-volume effect with the limits[6]

$$\begin{aligned} l_1 &\approx q^{-1/5} && \text{good solutions} \\ l_1 &\approx l && \Theta \text{ solutions} \end{aligned} \qquad (2)$$

Therefore, eq 1 can be rewritten as

$$\tau_p/\tau_p^\circ = 1 + a\rho(p/L)^{1-d\nu} + \dots \qquad (3)$$

where the generalization to arbitrary space dimension[10] is included. In eq 3, a is a known factor with appropriate

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units to make $\tau_p/\tau_p{}^\circ$ dimensionless, and ν is the usual exponent relating the molecular weight and the radius of gyration R_g of the chain. It is to be noted that a does not vanish at the Θ temperature and that $\rho L^{d\nu-1}$ is proportional to ρ/ρ^* where ρ^* is the overlap concentration.[1] Furthermore it must be pointed out that eq 3 contains an explicit mode dependence.

In the derivation of eq 1, a screened hydrodynamic interaction has been used. Since the internal modes of the chain are of concern here, the characteristic length scale is shorter than the size of the polymer chain. For lengths shorter than R_g the hydrodynamic screening length ξ_H in dilute solutions has been shown[6-9] to scale as

$$\xi_H{}^{-2} \approx \rho L^{\nu(d-2)-1} \tag{4}$$

so that $(\tau_p/\tau_p{}^\circ) - 1$ is proportional (in this regime) to

$$\rho L^{d\nu-1} \approx \xi_H{}^{-2} l_1/q \tag{5}$$

because $l_1 \sim L^{2\nu-1}$ and $q \sim L^{-1}$. We have suppressed the p-dependence as the present argument does not involve p. The formula of eq 5 has previously been used to successfully predict the concentration dependence of relaxation times.

Shiwa et al. have questioned the correctness of eq 5 (see ref 3 of ref 15). In their discussion[15] of the initial concentration dependence of τ_p, Shiwa et al. have used the relaxation (eq 2.9 of ref 15)

$$\xi_H{}^{-2} \approx \rho \tag{6}$$

Their use of eq 6 for $\xi_H{}^{-2}$ instead of eq 4 in eq 5 leads to a result in disagreement with eq 5. While eq 5 has been derived for the regime of length scales shorter than R_g, eq 6 is not valid in this regime. On the other hand, the calculation of ξ_H in the appropriate region of short length scales ($|\mathbf{k}|R_g \gg 1$, where $\mathbf{k}$ is the wave vector) leads in dilute solutions to (see eq 2.10 of Shiwa et al.)

$$\xi_H{}^2 \approx \frac{L}{\rho} \int_{\mathbf{k}} \frac{S_1(\mathbf{k},q)}{(\mathbf{k}^2 + \xi_H{}^{-2})} \approx \rho^{-1} L^{1-\nu(d-2)} \tag{7}$$

which is in agreement with eq 4 and hence with eq 5. Here S_1 is the double Fourier transform of the static structure factor. Notice that the q dependence of $S_1(\mathbf{k},q)$ must be accounted for in performing the integral of eq 7 since we are interested in length scales shorter than the size of the polymer. Thus the error in the work of Shiwa et al. originates from the inconsistent use of formulas for different regimes.

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References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(2) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, 1986.
(3) Edwards, S. F.; Freed, K. F. *J. Chem. Phys.* **1974**, *61*, 1189.
(4) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(5) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587, 594.
(6) Freed, K. F. In *Progress in Liquid Physics*; Croxton, C. A., Ed.; Wiley: New York, 1978.
(7) Muthukumar, M.; Freed, K. F. *Macromolecules* **1978**, *11*, 843.
(8) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.
(9) Muthukumar, M. *Macromolecules* **1984**, *17*, 971.
(10) Muthukumar, M. *J. Chem. Phys.* **1985**, *82*, 5696; *83*, 3161.
(11) Perico, A.; Freed, K. F. *J. Chem. Phys.* **1987**, *86*, 5830 and references therein.
(12) Richter, D.; Binder, K.; Ewen, B.; Stuhn, B. *J. Phys. Chem.* **1984**, *88*, 6618.
(13) Martel, C. J. T.; Lodge, T. P.; Dibbs, M. G.; Stokich, T. M.; Sammler, R. L.; Carriere, C. J.; Schrag, J. L. *Faraday Symp. Chem. Soc.* **1983**, *18*, 173.
(14) Adachi, K.; Kotaka, T. *Macromolecules* **1988**, *21*, 157.
(15) Shiwa, Y.; Oono, Y.; Baldwin, P. R. *Macromolecules* **1988**, *21*, 208.

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Comments on "On the Screening of Hydrodynamic Interactions in Dilute Polymer Solutions"

In the preceding paper,[1] Muthukumar claims that our paper[2] contains conceptual errors which cause disagreements with previous theories and experimental results. Actually, his criticism is not directed to the main body of our paper, but to one of our footnotes criticizing his work on the nonlinear concentration dependence of relaxation times (i.e., ref 3 in our paper). Furthermore, his comments are confined to a minor part of the footnote, leaving the main points in the note intact. However, we must admit that we have misunderstood his theory in the linear regime. We apologize to Professor Muthukumar for this mistake.

His claim of our results being inconsistent with themselves is based on his misconception of our paper, and we feel that the content of his paper[1] is rather misleading. the essence of our footnote is: the quantity Q introduced by Muthukumar is a complicated nonlinear function of the polymer concentration (or the monomer concentration), so that the identification of Q through matching first-order terms in the concentration is insufficient to fix Q in the higher order expansion formula. Thus, we explicitly wrote, "Since Q is a complicated function of c, the identification (A) [i.e., Muthukumar's identification] is at best legitimate only in the regime with linear c-dependence". Muthukumar directs his criticism to our secondary five-line comment following this main point in the footnote. Our comment says that even in the linear order the identification is not correct, if we accept the relation "$\xi_H{}^{-2} \approx \rho$ as was assumed in *the* theory". The theory in this quotation means Muthukumar's theory. This is due to our misunderstanding of his theory. However, the essential part of our criticism is intact since the main target of his theory is not the linear regime but the nonlinear regime. Besides, it is trivial that the linear order is proportional to the overlap parameter, though Muthukumar explains this at length in his paper. Incidentally, just above eq 6 in his paper, he suggests that our formula (2.9) gives the wrong relation, (6). As is demonstrated by Muthukumar himself in his letter, (2.9) which is equivalent to (2.10) in our paper gives the answer he wants in the dilute limit. Actually, one of our main results is to go beyond this limit to yield, e.g., the scaling relation (3.6), i.e., $(\xi_H/R_g{}^\circ)^2 \sim X^{-2\nu/(d\nu-1)}$. Here $R_g{}^\circ$ is the radius of gyration in the dilute limit and X the overlap parameter.

Judging from the preceding paragraph, we feel we should reemphasize the content of our paper. First of all, we stressed that the starting point of the theory must be internally consistent and that we should try to eliminate ad hoc assumptions as much as possible. Results do not always justify the starting point, especially when the results are robust as the equation for viscosity, etc. Combining a mode-mode coupling theoretical approach and the ac-

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