

of the microphases; a simple thermodynamic feasibility study of this process<sup>8</sup> also involved the variable  $\chi N$ , thus leading to the prediction that the values of  $M_n^*$  at which the phase mixing should stop for two different rubbery segments into styrene microphases should be in the inverse ratio of the corresponding interaction parameters. The ratio of the interaction parameters for polystyrene with polybutadiene to that with poly(dimethylsiloxane) is 0.16, leading to the expectation that the  $M_n^*$  at which phase mixing should stop in styrene-butadiene block copolymers is about  $1.1 \times 10^5$ . This does not happen, even within the large experimental error of these measurements. We would like to suggest that phase mixing is actually a different effect with respect to microphase separation and that its controlling variable may be  $\chi^2 N$ . If so, the expected values of  $M_n^*$  at which phase mixing should stop will be the inverse ratio of the square of the ratio of the corresponding interaction parameters. In that case, the predicted value of  $M_n^*$  at which phase mixing should cease in butadiene-styrene block copolymers is  $7.0 \times 10^5$ , in agreement with our observations.

**Acknowledgment.** We thank C. I. Chung, Department of Materials Engineering, for the use of the Perkin-Elmer DSC-4, and we thank the National Science Foundation, Polymers Program, for support of this work under Grant No. DMR81-06107.

**Registry No.** (Styrene)(butadiene) (block copolymer), 106107-54-4.

## References and Notes

- (1) Krause, S.; Iskandar, M.; Iqbal, M. *Macromolecules* **1982**, *15*, 105-111.
- (2) Lu, Z.-H.; Krause, S. *Macromolecules* **1982**, *15*, 112-114.
- (3) Krause, S.; Lu, Z.-H.; Iskandar, M. *Macromolecules* **1982**, *15*, 1076-1082.
- (4) Granger, A. T.; Wang, B.; Krause, S.; Fetters, L. J. *Adv. Chem. Ser.* **1986**, 127-138.
- (5) Roe, R.-J.; Zin, W.-C. *Macromolecules* **1980**, *13*, 1221-1228.
- (6) Galin, M.; Rupprecht, M. C. *Macromolecules* **1979**, *12*, 506-511.
- (7) Leibler, L. *Macromolecules* **1980**, *13*, 1602-1617.
- (8) Krause, S. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 129-142.

## Depletion Layer of a Lyotropic Polymer Liquid Crystal at the Air-Solution Interface

THEO ODIJK

Department of Physical and Macromolecular Chemistry,  
Gorlaeus Laboratories, University of Leiden,  
2300 RA Leiden, The Netherlands.

Received October 29, 1986

Scaling analyses have proved to be useful in understanding the statistical physics of solutions of nematic or otherwise confined semiflexible polymers.<sup>1-4</sup> Sometimes scaling theories are merely highly simplified versions of theories that are more quantitative and detailed (for a review see ref 3; in addition compare ref 1 with ref 5, 6, and 7, and ref 2 with ref 8 and 9, ref 4 with ref 14). Often scaling ideas are the only ones available because it seems difficult to make headway in some complicated problem. For instance, it is not hard to derive the asymptotic concentration dependence of the elastic constants of polymer nematics,<sup>4,13,14</sup> but a precise theory is still lacking. In a similar vein this note addresses the depletion of nematic polymer chains near an interface by scaling methods only.

First, we look at a nematic solution of slender, hard rods of a bulk density  $\rho_r$ , diameter  $D$ , and length  $L$  in the second

virial approximation.<sup>10</sup> For scaling purposes, it is enough to approximate the orientational distribution function of a test rod by a Gaussian ( $\alpha \gg 1$ )

$$f(\theta) \sim \frac{1}{2}\alpha e^{-(1/2)\alpha\theta^2} \quad (0 \leq \theta \leq \frac{1}{2}\pi)$$

$$f(\theta) \sim \frac{1}{2}\alpha e^{-(1/2)\alpha(\pi-\theta)^2} \quad (\frac{1}{2}\pi \leq \theta < \pi) \quad (1)$$

with  $\int_0^\pi f(\theta) \sin \theta d\theta = 1$  to leading order. The angle  $\theta$  is specified with respect to the director. Then, one can derive the relation<sup>10</sup> between the sharpness of the distribution and the scaled number density  $c_r \equiv b\rho_r$  with the rod-rod excluded volume  $b = (\pi/4)L^2D$

$$\alpha \simeq c_r^2 \simeq L^4 D^2 \rho_r^2 \quad (2)$$

Here and further on we omit numerical coefficients, all of which are of order unity.

Let us assume the director is oriented parallel to the air-solution interface. In solution each rod is allowed orientational freedom only within a cone of approximate angle  $\alpha^{-1/2}$  as can be seen from eq 1, but its freedom becomes yet more severely restricted once its center of mass  $M$  approaches the interface. Auvray has discussed this effect for a variety of problems.<sup>11</sup> When  $M$  is a distance  $d$  from the surface, the cone's angle is reduced to  $dL^{-1}$  provided  $d$  is small enough. Hence, the decrease in confinement entropy per rod is given by<sup>18</sup>

$$\Delta S \simeq -k_B \ln \left( \frac{L}{d\alpha^{1/2}} \right) \quad (3)$$

where  $k_B$  is the Boltzmann constant. Similarly, there is a decrease in the free energy per rod because the excluded volume is diminished<sup>18</sup>

$$\Delta F_b \simeq k_B T \bar{c}_r(d) \left( \frac{d^2 \alpha^{1/2}}{L^2} - \alpha^{-1/2} \right) \quad (4)$$

where  $T$  is the temperature and  $\bar{c}_r(d)$  is a representative scaled number density for layer thickness  $d$ .

Equations 3 and 4 determine the depletion  $\rho_r(d)$  of rods near the surface

$$\rho_r(d) \simeq \rho_r \exp \left( -\frac{\Delta F_b}{k_B T} + \frac{\Delta S}{k_B} \right) \quad (5)$$

Note that  $\rho_r(0) \rightarrow 0$  as it must and  $\rho_r(d) \ll \rho_r$  for  $d = \eta L \alpha^{-1/2}$ , with  $\eta$  a number somewhat smaller than unity.<sup>19</sup> Accordingly, the thickness  $d_r$  of the depletion layer for nematic rods is

$$d_r \simeq L \alpha^{-1/2} \quad (6)$$

Thus, eq 2 and 6 yield the increase in the surface tension

$$\Delta \tau \simeq k_B T d_r \rho_r \simeq \frac{k_B T}{LD} \quad (7)$$

This result, correct to the leading order, does not depend on the concentration, and is in agreement with detailed calculations by Doi and Kuzuu.<sup>12</sup>

The extension of this result to the case of long semiflexible polymers is straightforward. Another length scale, the deflection length  $\lambda$ , enters the description.<sup>1,2</sup> The nematic field exerted by the surrounding macromolecules on a test chain causes it to be deflected toward the director on a scale  $\lambda$  on the average. It is connected to the persistence length  $P$  via<sup>2,3</sup>

$$\lambda = P/\alpha \quad (8)$$

A scaling analysis is fruitful when the chains are long enough—the contour length  $L$  is much longer than  $\lambda$ . As long as the connectedness of the chains is unimportant we

have the following simple tenet: the physical properties of the nematic can be described as if every chain consists of  $L/\lambda$  independent rodlike units. Thus, for semiflexible chains eq 2 becomes

$$\alpha \simeq c_\lambda^2 \simeq \lambda^4 D^2 \rho_\lambda^2 \simeq \alpha^{-2} P^4 D^2 \rho_P^2 \quad (9)$$

Here, the number density of deflection segments  $\rho_\lambda$  is  $\alpha$  times the number density of persistence segments  $\rho_P$ . Equation 9 was previously derived in a different way.<sup>2</sup> Next, the thickness of the depletion layer becomes

$$d_c \simeq \lambda \alpha^{-1/2} \simeq \alpha^{-3/2} P \quad (10)$$

Hence, the increase in surface tension is written as

$$\Delta\tau \simeq k_B T d_c \rho_\lambda \simeq k_B T \left( \frac{\varphi^2}{P D^5} \right)^{1/3} \quad (11)$$

with  $\varphi \equiv (\pi/4) D^2 P \rho_P$  the volume fraction. This result can also be obtained by substituting  $\lambda$  for  $L$  in eq 7.

These equations show that the interfacial behavior of nematic polymers and rods is markedly disparate. The increment in surface tension increases with concentration for long semiflexible polymers but to leading order it is constant for rods. A similar though reversed disparity occurs for the elastic constants.<sup>4,14</sup> Thus, it seems the influence of semiflexibility in nematic solutions becomes apparent especially in the presence of an external field, whatever its nature.

Equations 10 and 11 yield numerical values amenable to measurement, though it remains to be seen whether experimental conditions can conform to the requirements of the calculation. Intermediately long polymers pose a particular problem because of strong end effects.<sup>3,9</sup> An interesting preliminary analysis of these within a "macroscopic" context has been given by Meyer.<sup>13</sup> A

referee has commented on the completely passive role played by the interface: the polymers are hindered by solely steric repulsions. Dispersion forces could well exert a considerable influence on the density profile close to the surface so their effect if any must be assessed when comparing the expressions with experimental results. Little is theoretically understood about the alignment of nematic, anisometric molecules near surfaces,<sup>15</sup> although Meyer has presented convincing arguments why very long semiflexible chains near inert surfaces should align parallel.<sup>13</sup> Anyway, there is some evidence for this in certain cases.<sup>13,16,17</sup>

## References and Notes

- (1) Odijk, T. *Macromolecules* **1983**, *16*, 1340.
- (2) Odijk, T. *Polym. Commun.* **1985**, *26*, 197.
- (3) Odijk, T. *Macromolecules* **1986**, *19*, 2313.
- (4) Odijk, T. *Liq. Cryst.* **1986**, *1*, 553.
- (5) Doi, M. *J. Polym. Sci., Polym. Symp.* **1985**, No. 73, 93.
- (6) Semenov, A. N. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 317.
- (7) Helfrich, W.; Harbich, W. *Chem. Scr.* **1985**, *25*, 32.
- (8) Khokhlov, A. R.; Semenov, A. N. *Physica A (Amsterdam)* **1981**, *108A*, 546.
- (9) Khokhlov, A. R.; Semenov, A. N. *Physica A (Amsterdam)* **1982**, *112A*, 605.
- (10) Onsager, L. *Ann. N. Y. Acad. Sci.*, **1949**, *51*, 627.
- (11) Auvray, L. *J. Phys. (Les Ulis, Fr.)* **1981**, *42*, 79.
- (12) Doi, M.; Kuzuu, M. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1985**, *41*, 65.
- (13) Meyer, R. B. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic: New York, 1982.
- (14) Grosberg, A. Yu.; Zhestkov, A. V. *Vysokomol. Soedin.* **1986**, *28*, 86.
- (15) For a critical review, see: Goossens, W. J. A. *Mol. Cryst. Liq. Cryst.* **1985**, *124*, 305.
- (16) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381.
- (17) Panar, M.; Beste, L. F. *Macromolecules* **1977**, *10*, 1401.
- (18) Equations 3 and 4 are derived by assuming the rods lose their orientational freedom only in the direction perpendicular to the surface.
- (19) When  $\alpha = \mathcal{O}(1)$  and  $\bar{c}_i(d) \simeq 0$ , eq 5 reduces to Auvray's eq 2.<sup>11</sup>

# Communications to the Editor

## Conformational Characteristics of Polyisobutylene: An Error with Consequences

One of us (L.C.D.) has detected a significant error in a paper by Suter, Saiz, and Flory<sup>1</sup> entitled "Conformational Characteristics of Polyisobutylene", in which a simple and detailed rotational isomeric state (RIS) model had been proposed. The matter requires more than a mere Erratum, since later work<sup>2,3</sup> on the X-ray and neutron scattering of polyisobutylene (PIB) was based on the erroneous RIS model; agreement between prediction and experiment had been unusually good and the questions arise why a "wrong" model is able to so convincingly predict detailed and accurate experimental data<sup>2,3</sup> and if a corrected RIS model would still find such strong experimental support in the same data.

The error consisted of inadvertently switching, in the numerical calculations, the values for the two distinct skeletal bond angles in the PIB chain: actually,  $\angle C-CH_2-C = \pi - \theta'$  lies between  $120^\circ$  and  $130^\circ$ , and  $\angle C-C(CH_3)_2-C = \pi - \theta''$  is approximately equal to the tetrahedral value of ca.  $110^\circ$ , but in the calculations  $\pi - \theta'$  was given the smaller numerical value and  $\pi - \theta''$  the larger one.

The limiting value for the characteristic ratio of the end-to-end distance,  $C = \langle r^2 \rangle_0 / nl^2$  ( $n \rightarrow \infty$ ), when calcu-

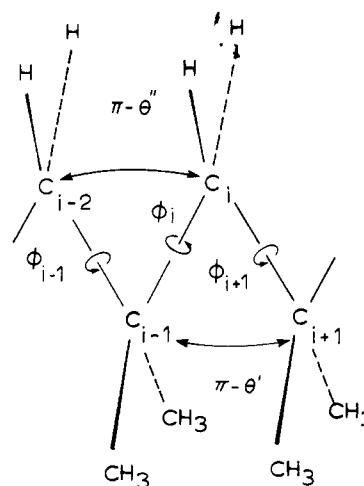


Figure 1. Sequence in a PIB chain.

lated<sup>4</sup> from the erroneous RIS model with a predetermined set of statistical weight matrices and a corresponding set of torsion angles,  $\{\varphi\} = \{+15^\circ, -15^\circ, +130^\circ, -130^\circ\}$ , was 6.7 ( $\pm 0.1$ ), in excellent agreement with several sets of experimental data which indicated that  $6.6 \leq C \leq 6.9$ .<sup>1</sup> If proper bond angles are chosen, however, one obtains, all other