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Isotropic–Liquid Crystal Phase Equilibrium in Solutions of Semiflexible Polymers: Poly(hexyl isocyanate)

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ABSTRACT: The isotropic–liquid crystal phase equilibrium was investigated for solutions of poly(hexyl isocyanate) (PHIC) in toluene and dichloromethane. Substantially monodisperse samples were used to determine the dependence of the phase diagram on molecular weight, temperature, and solvent. The determined molecular weight dependence greatly differed from the prediction of the theories of Onsager and of Flory for rigid rods. This was attributed to the flexibility of PHIC characterized by the persistence length q of 21–41 nm in these solvents. The data for the solutions of PHIC in toluene, together with those for aqueous schizophyllan (a triple helical polysaccharide, q = 200 nm), were compared almost quantitatively with the prediction of the theory of Khokhlov and Semenov for wormlike cylinders with hard-core repulsive potential. However, this theory failed to explain the data for the dichloromethane solutions, where q was as small as 21 nm and the phase boundary concentrations were relatively large. This failure was taken to suggest that the second virial approximation basic to this theory would be inaccurate at higher concentrations.

It has been shown theoretically[1-4] that an asymmetric shape of a molecule such as a rod or disk is mainly responsible for the formation of a liquid crystal phase. Indeed, many rodlike polymers have been found to form lyotropic liquid crystals above a certain critical concentration, which decreases with increasing molecular weight of the polymer.[5-19] This finding seems to support the above theoretical prediction, but agreement between experiment and theory remains only qualitative.[8,10,14-16,18] This is most probably due to the fact that there is no such completely rodlike polymer as assumed in the theoretical treatments, but any real polymer may appear more or less flexible at large molecular weights.

Khokhlov and Semenov[20,21] have taken this finite stiffness into their theoretical formulation of semiflexible polymers, where they have extended the theory of Onsager[1] for rods to wormlike chains; the persistence length q of the chain plays a central role. In a recent review article, Odijk[22] has shown that the Khokhlov–Semenov theory agrees well with data on such slender polymer chains as schizophyllan,[13-16] poly(γ-benzyl L-glutamate) (PBLG),[11] and DNA.[19] However, his analysis is limited to relatively stiff polymers, namely, those with large q. The validity of the theory may not be fully appreciated unless it is proved in a wide range of q.

In their phase equilibrium study, Conio et al.[25] chose poly(hexyl isocyanate) (PHIC), which is known to be a typical semiflexible polymer having different stiffness in different solvents[23,25-29] and exhibiting liquid crystallinity.[24,25,30,31] Analyzing data for critical concentrations in toluene and in dichloromethane (DCM) as functions of molecular weight, they arrived at a conclusion against the Khokhlov–Semenov theory.[25] However, their conclusion is based on the phase-equilibrium data for polydisperse samples whose molecular weights and wormlike chain parameters seem to be of insufficient accuracy.[29] Therefore, we have undertaken another experimental study of this phase behavior using essentially monodisperse samples with a wide range of molecular weight and toluene and DCM as the solvents; the wormlike chain parameters of PHIC in these solvents have been determined recently from intrinsic viscosity–molecular weight relationships.[29] In this paper, we present data from these phase-equilibrium experiments and combine them with similar data published for aqueous schizophyllan[13-17] to test the Khokhlov–Semenov theory using the known values for the wormlike chain parameters for the respective polymers. In contrast to Conio et al.,[25] the result shows that the theory is almost quantitative provided the polymer chain is reasonably stiff.

Table I
Molecular Weights of the PHIC Samples Studied

sample	$M_w/10^4$	M_z/M_w
W-5	1.14	1.15
W-4	1.29[a]	1.05[b]
W-3	1.52[a]	1.05[b]
Z-2	2.09	1.06
L-2	4.07	1.06
NRX-12	13.3	1.06
Z-20	24.4	1.06

[a] M_v determined by using the $[\eta]$–M_w relationship in toluene at 25 °C. [b] Determined by GPC.

Table II
Wormlike Chain Parameters of PHIC[29] and Schizophyllan[32]

polymer	solvent	temp/°C	M_L/nm^{-1}	q/nm
PHIC	toluene	10	730	41
		25	740	37
		40	750	34
	DCM[a]	20	740	21
schizophyllan	water	25	2150	200

[a] Dichloromethane.

Experimental Section

Polymer Samples. Seven fractionated samples of poly(hexyl isocyanate) (PHIC) were selected from our stock. They were characterized by light scattering, sedimentation equilibrium, viscosity, and gel permeation chromatography and were very narrow in molecular weight distribution as shown in Table I.[29] Therefore, these samples will be treated as "monodisperse" in the discussion to follow.

Solution Preparation. A biphasic solution was prepared in a calibrated stoppered tube (7 mm in i.d., 60 mm in length) by mixing appropriate amounts of a PHIC sample dried in vacuo overnight and a purified solvent. All the manipulations were carried out in a nitrogen atmosphere. The mixture became transparent within 1 day. Dissolution was ensured by stirring the mixture by a magnetic bar.

The polymer weight fraction w was determined gravimetrically. The polymer volume fraction ϕ was calculated from w and the partial specific volume v_p of the polymer by

$$\phi = v_p w/[w v_p + (1 - w) v_0]$$

where v_0 is the specific volume of the solvent. Density measurements were made on dilute solutions of PHIC in toluene and DCM, by using a Lipkin–Devison type pycnometer of about

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Table III
Phase Boundary Weight Fractions for Solutions of PHIC in Toluene and DCM

	toluene								20 °C DCM	
	10 °C		25 °C		30 °C		40 °C			
sample	w'	w''	w'	w''	w'	w''	w'	w''	w'	w''
W-5			0.394	0.438					0.361	0.396
W-4	0.358	0.394	0.373	0.403	0.378[a]	0.406[a]				
W-3			0.347	0.372						
Z-2	0.283	0.311	0.298	0.322	0.306	0.330			0.261	0.296
L-2	0.232	0.253	0.247	0.270			0.270	0.292	0.221	0.262
NRX-12	0.194	0.210	0.209	0.230			0.231	0.252	0.190	0.236
Z-20			0.204	0.225						

[a] Determined from one data point by assuming the same slope for the w versus ϕ plot as that for toluene at 25 °C.

30-cm^3 capacity. The resulting data were analyzed to obtain v_p of PHIC, with the results $v_p = 0.987$ and 1.002 cm^3 g^{-1} in toluene at 25 and 40 °C, respectively, and 0.992 cm^3 g^{-1} in DCM at 20 °C. The value of v_p in toluene at 10 °C was estimated to be 0.972 cm^3 g^{-1} by assuming a linear dependence of v_p on temperature.

Table II gives reported values for the wormlike chain parameters for PHIC in toluene and DCM[29] and schizophyllan in water,[32] which will be used in the subsequent discussion; M_L is the molar mass per unit contour length of the polymer. To be consistent with these M_L values and the known values of v_p, we take the diameter d of the polymer to be 1.25 and 1.67 nm for PHIC and schizophyllan, respectively.

Phase Separation. A given biphasic mixture thoroughly stirred by a magnetic bar in a calibrated tube at room temperature was stirred again for 1 to several days in an air bath thermostated at a specified temperature. Then the mixture was kept standing for 1 day in the air bath at the same temperature without stirring. To effect complete phase separation, we finally centrifuged the mixture at a rotor speed of about 4000 rpm at the same temperature in a Hitachi 65P-7 automatic preparative centrifuge with a RSP27-2 rotor. The centrifugation was continued until each layer became almost clear, usually within 2 h. Highly viscous mixtures containing a high molecular weight polymer were centrifuged for less than 7 h/day and then allowed to stand in the air bath. This procedure was repeated until the two layers became almost clear, with the expectation that the centrifugation would help the already phase-separated mixture separate macroscopically without disturbing the phase equilibrium. It was confirmed that the equilibrium was not disturbed discernibly by the centrifugal field unless the field was too strong or applied for too long a period of time.

Next the volume of each separated phase was determined from its column height within 1% error, with appropriate corrections made for the volume of the magnetic bar and the shapes of the liquid–liquid and liquid–air interfaces; the volume of the isotropic phase relative to the total solution volume is denoted by Φ. In some cases, the mixture was diluted further with an appropriate amount of the solvent, and the above operation was repeated. For toluene solutions at 25 °C, each separated phase was finally taken out and diluted with benzene. The polymer in the benzene solution was recovered by freeze-drying, weighed to evaluate the weight fraction w in the separated phase, and subjected to $[\eta]$ determination in toluene at 25 °C. It was also analyzed by gel permeation chromatography (GPC) according to the procedure established before.[29]

Results

Phase Boundary Concentrations. Figure 1 shows plots of w versus Φ for all the seven PHIC samples in toluene at 25 °C, where w is the polymer weight fraction and Φ the relative volume of the isotropic phase in the biphasic mixture. It can be seen that for each sample, w decreases linearly with Φ and can be extrapolated to the liquid crystal phase $\Phi = 0$ and the isotropic phase $\Phi = 1$, yielding with reasonable accuracy the phase boundary weight fractions w'' and w', respectively. Figure 2 presents plots of w versus Φ for PHIC in DCM of 20 °C. Similar experiments were performed also on solutions of PHIC in toluene at 10, 30, and 40 °C and analyzed in the same way. All the values for w' and w'' thus determined are summarized in Table III.

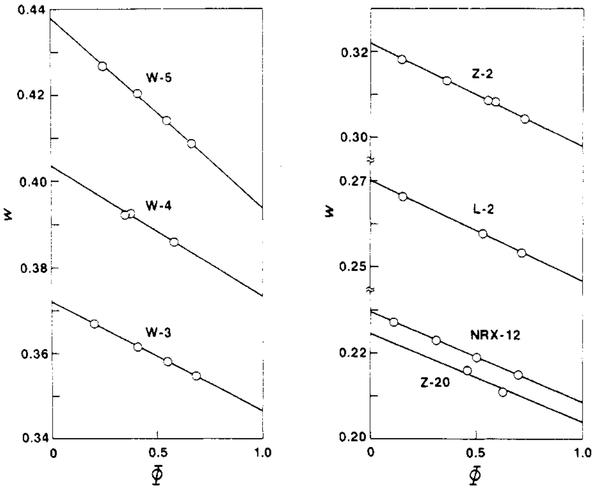

Figure 1. Plots of w versus Φ for the indicated PHIC samples in toluene at 25 °C: w, the weight fraction of PHIC in the whole solution; Φ, the relative volume of the isotropic phase.

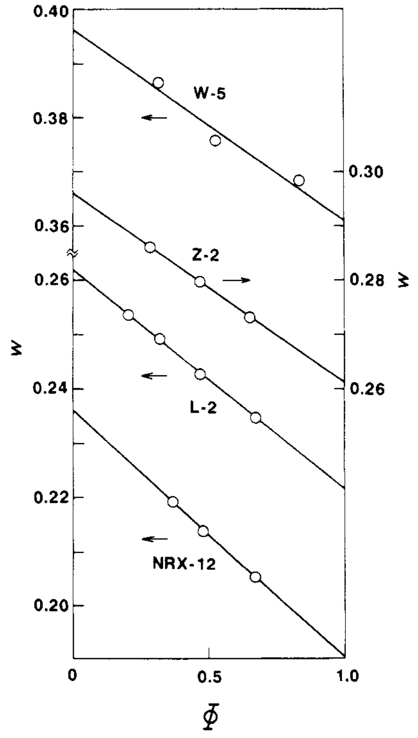

Figure 2. Plots of w versus Φ for PHIC in DCM at 20 °C.

Table IV presents the results from analyses of the phases separated from PHIC plus toluene solutions at 25 °C. Here, w_{sp} denotes the polymer weight fraction for a given

Table IV
Polymer Weight Fractions and Intrinsic Viscosities of PHIC in the Conjugates Phases in Toluene at 25 °C

sample	w	w_{sp}'	$[\eta]'$	w_{sp}''	$[\eta]''$
W-5	0.4089	0.406	0.171	0.428	0.174
W-4	0.3860	0.379	0.201[a]	0.401	0.210[a]
W-3	0.3547	0.347	0.254	0.371	0.261
Z-2	0.3083	0.297	0.39[a]	0.318	0.40[a]
L-2	0.2534	0.246	1.10	0.270	1.12
NRX-12	0.2150	0.211	4.76	0.236	5.0
Z-20	0.2111	0.214	8.8	0.235	9.6

[a] In 1-chlorobutane at 25 °C.

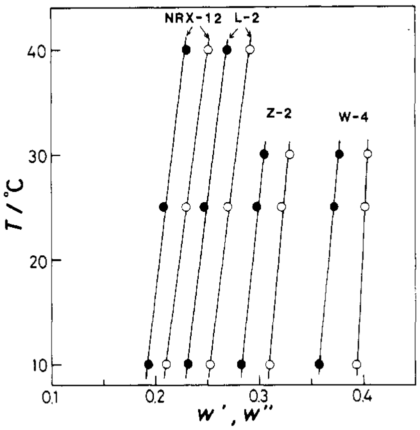

Figure 3. Temperature–concentration phase diagrams for PHIC in toluene: (●) w', the critical polymer weight fraction above which the nematic phase appears; (○) w'', the critical polymer weight fraction above which the isotropic phase disappears.

separated phase, and the quantities with a prime and a double prime refer to the isotropic and liquid crystal phases, respectively, and those without a prime to the whole mixture. It can be seen that each w_{sp}' or w_{sp}'' is close to the corresponding phase boundary weight fraction (w' or w'') given in Table III. The values of w_{sp}' and w_{sp}'' for Z-20 are somewhat larger than those for w' and w'' determined above. This is probably because of the loss of the solvent during the sampling procedure of these viscous solutions. The intrinsic viscosity of the polymer recovered from each phase ($[\eta]'$, $[\eta]''$) is very close to that of the original one. It was also found that the GPC curves for the polymers recovered from the coexisting phases were almost indistinguishable from that of the original polymer; the peak position did not differ more than 0.1 count between the original and recovered samples; the average breadth of the GPC curves was about 8 counts.

All these findings together with the linear relationship between w and Φ shown in Figures 1 and 2 indicate that the lever rule holds accurately, as is naturally expected for the narrow distribution samples used. However, close examination of Table IV reveals that $[\eta]''$ is about 3% larger than $[\eta]'$ on average, which corresponds to the difference in M_v of 4%. This manifests itself with molecular weight fractionation taking place on the phase separation, where higher molecular weight components tend to exist slightly in excess of lower molecular weight ones in the liquid crystal phase.

Figure 3 shows temperature–weight fraction phase diagrams of PHIC in toluene, where filled circles and unfilled circles refer to the boundary between the isotropic and biphasic regions (w') and to that between the biphasic and liquid crystal regions (w''), respectively. It can be seen that both w' and w'' for a given sample increase linearly with raising temperature and the four pairs of lines are almost parallel. The increases in w' and w'' with raising temperature from 10 to 40 °C are about 15% for this system and larger than those reported for aqueous schizophyllan (6% or less).[13,14]

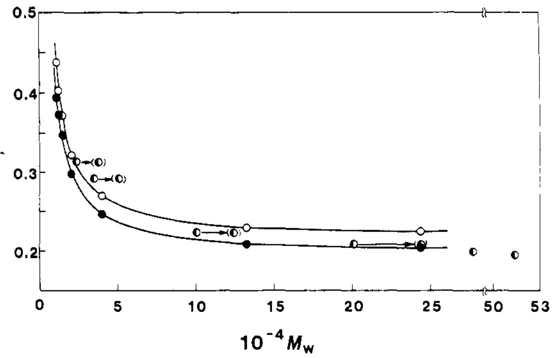

Figure 4. Plots of w' and w'' versus M_w for PHIC in toluene: ● (w') and ○ (w''), present data at 25 °C; ◐ (w'), Conio et al.[25] data at 20 °C. Points in parentheses are based on recalculated M_w (see text).

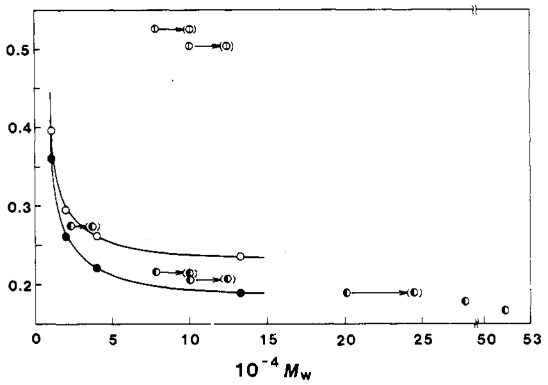

Figure 5. Plots of w' and w'' versus M_w for PHIC in DCM at 20 °C: ● (w') and ○ (w''), present work; ◐ (w') and ⦶ (w''), Conio et al.[25] Points in parentheses are based on recalculated M_w.

Molecular Weight Dependence of the Phase Boundary Concentrations. In Figure 4, our values of w' (filled circles) and w'' (unfilled circles) for PHIC in toluene at 25 °C are plotted against M_w; those of Conio et al.[25] in toluene at 20 °C (half-filled circles) are also shown for comparison. Both w' and w'' decrease steeply with increasing M_w at lower M_w and tend to approach asymptotic values at higher M_w.

The data of Conio et al. were determined mostly by direct observation of appearance of birefrigence with a polarizing microscope. Their data points for three intermediate molecular weight samples are close to our points, but their w' values become a little larger when corrected for the temperature effect on phase boundary concentrations shown in Figure 3. On the other hand, their data points for two lower molecular weight samples appear deviated significantly above ours, and the deviation becomes larger if the temperature correction is made. Conio et al. determined the molecular weights of their samples using the $[\eta]$ versus M_w relationship for PHIC in toluene at 25 °C of Berger and Tidswell,[26] which differs from ours as mentioned elsewhere.[29] If the molecular weights of their samples are recalculated by using our relationship, they become larger than the reported values especially for the two samples of lower molecular weight; the data points in parentheses in Figure 4 are based on the recalculated molecular weights.

Figure 5 shows plots of w' and w'' versus M_w for PHIC in DCM at 20 °C together with those of Conio et al.[25] for the same system. The M_w dependences of w' and w'' for this system are similar to those in toluene at 25 °C. Two

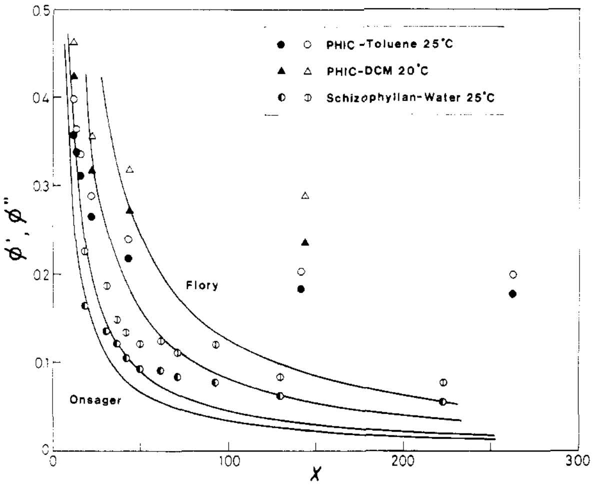

Figure 6. Plots of ϕ' and ϕ'' versus x for PHIC and aqueous schizophyllan;[13-17] axial ratio $x = M_w/(M_L d)$. Solid curves show the predicted values by the Onsager theory for straight rods[1] and by the Flory theory for athermal solutions of rods.[3]

data points for w'' of Conio et al. appear far above our points. Thus, we see that there exists a substantial difference between their data and ours. One of the reasons for this disparity may be the polydispersity of their samples, though roughly fractionated, whose effect on the phase behavior is difficult to estimate. For this reason, we will use only our data in the analysis to follow.

Discussion

Comparison of the Experimental Data with the Theories for Rigid Rods. Let us first compare the isotropic–liquid crystal phase boundary concentrations for PHIC in toluene and DCM with the predictions of the Onsager theory[1] and of the Flory theory.[3] The experimental weight fractions w' and w'' were converted to the volume fractions ϕ' and ϕ'', respectively. The axial ratio x was calculated from M_w by $x = M_w/dM_L$, where the M_L values given in Table II were used and d was taken to be 1.25 nm, the average of the values calculated from v_p under the solvent conditions investigated.

Figure 6 shows the plots of ϕ' and ϕ'' against axial ratio x for PHIC in toluene and DCM, together with those for schizophyllan in water at 25 °C; the two pairs of solid curves represent the theoretical predictions of Onsager for hard-core cylinders and of Flory for athermal solutions of rigid rods. At any value of x, the values of ϕ' and ϕ'' for the DCM solutions are larger than those for the toluene solutions, although the corresponding values of w' and w'' do not differ very much. The ϕ' and ϕ'' values for the aqueous schizophyllan are much smaller than those for PHIC in toluene, though they show similar x dependences.

It is important to note that neither the Onsager theory nor the Flory theory can describe the molecular weight dependence of w' and w'' for these systems. We have noted a similar discrepancy for PBLG.[18] In agreement with the previous notion, this is due to the semiflexible nature of the polymers investigated. Indeed, as shown in Table II, q for PHIC in DCM at 20 °C is only 21 nm, and that in toluene at 25 °C is 37 nm. On the other hand, q is as large as 200 nm for schizophyllan in water at 25 °C. In addition, as shown in Figure 3, w' and w'' for PHIC in toluene become higher with raising temperature, that is, with decreasing q. Thus, we see that the phase boundary concentrations are strikingly affected by the flexibility and are higher for smaller q. Therefore, we will next attempt to compare all these experimental results with the theory of Khokhlov and Semenov[21] for semiflexible polymers.

Theory of Khokhlov and Semenov for Semiflexible Polymers. Khokhlov and Semenov[21] extended the Onsager theory[1] for rigid rods to semiflexible polymers. Their model is a wormlike cylinder characterized by q, d, and the contour length L of the cylinder. Similarly to the Onsager theory, the Helmholtz free energy F of the system containing N_p polymers in a volume V is expressed as

$$F/(N_p kT) = \text{constant} + \ln c' + \sigma_N + N b_N c_N' \rho \qquad (1)$$

where $N = L/2q$ is the number of Kuhn statistical segments per molecule, c' the number concentration of polymer, c_N' the number concentration of Kuhn statistical segment ($c_N' = Nc' = N_p N/V$), and $b_N \equiv (\pi/4)(2q)^2 d$. The term $\ln c'$ corresponds to the ideal solution translational entropy of the system and σ_N to the entropy loss due to orientation and conformation change. The last term representing the free energy of polymer–polymer interactions in the second virial approximation is obtained by analogy with the corresponding term for rigid rods ($bc'\rho$, $b\rho$ = the excluded volume per rod in the liquid crystal phase). They have actually equated the second virial term for semiflexible polymers to that for rigid rods, that is, $N b_N c_N' \rho = bc'\rho$.

Khokhlov and Semenov have derived an expression allowing evaluation of σ_N for arbitrary N. The derived expression was very complicated, but it was expanded with respect to N. At the rod limit of $N \ll 1$

$$\sigma_N = \ln \alpha - 1 + N(\alpha - 1)/3 \qquad (2)$$

and at the coil limit of $N \gg 1$

$$\sigma_N = N(\alpha - 1)/2 + \ln (\pi/4) \qquad (3)$$

where α is the parameter characterizing the trial function of Onsager for the equilibrium orientation distribution function. σ_N is much larger at $N \gg 1$ than at $N \ll 1$.

The phase boundary volume fractions ϕ' and ϕ'' are calculated at these two limits. For cylinders only with hard-core repulsive potential, they are expressed at $N \ll 1$

$$\phi'/(d/2q) = 3.340/N + 9.98 \qquad (4a)$$

$$\phi''/(d/2q) = 4.486/N - 2.916 \qquad (4b)$$

whereas at $N \gg 1$

$$\phi'/(d/2q) = 10.82 + 1.910/N \qquad (5a)$$

$$\phi''/(d/2q) = 12.39 + 1.781/N \qquad (5b)$$

These asymptotic relations are interpolated in the intermediate region $N \sim 1$ by using the simplest ratio of the two polynomials, yielding[21]

$$\phi'/(d/2q) = \frac{3.34 + 11.94N + 6.34N^2}{(1 + 0.586N)N} \qquad (6a)$$

$$\phi''/(d/2q) = \frac{4.486 + 22.48N + 70.16N^2}{(1 + 5.66N)N} \qquad (6b)$$

These equations indicate that $\phi'/(d/2q)$ and $\phi''/(d/2q)$ depend only on the reduced variable $N = L/2q$.

Figure 7 shows the theoretical dependence of ϕ' and ϕ'' on $x = L/d$ according to eq 6 for d of 1.25 nm and two q values, 20 and 40 nm, together with the Onsager prediction, which is represented by the leading terms in eq 4. For a given value of x, the ϕ' and ϕ'' due to the Khokhlov and Semenov theory are much larger than those due to the Onsager theory for smaller q. These tendencies are qualitatively consistent with the experimental data for

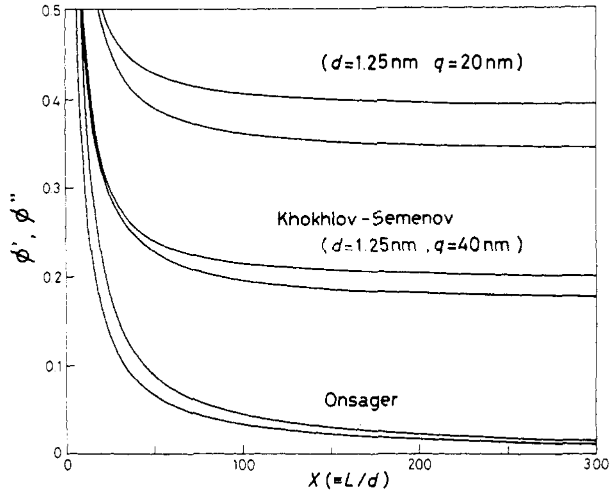

Figure 7. Dependence of ϕ' and ϕ'' on $x = L/d$ according to eq 6: ϕ', the lower curves; ϕ'', the upper curves. The Onsager values of ϕ' and ϕ'' for the same d are also shown for comparison.

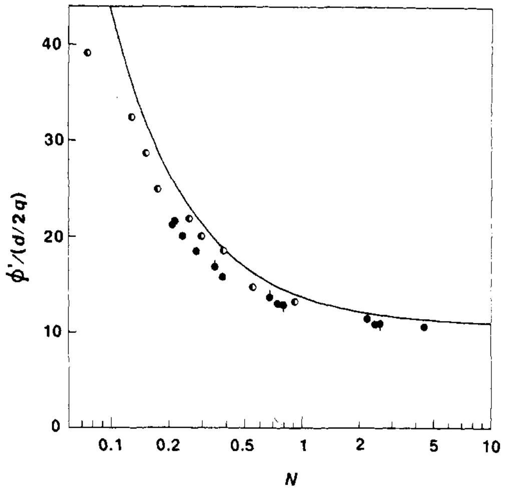

Figure 8. Comparison of the measured and theoretical values for $\phi'/(d/2q)$ as functions of $N = L/2q$: PHIC in toluene ● (10 °C), ● (25 °C), ● (40 °C); ◐, schizophyllan in water at 25 °C;[13-17] solid curve, theoretical values calculated by eq 6a.

PHIC shown in Figure 6. The essential difference of the Khokhlov–Semenov theory from the Onsager theory lies in σ_N, where it considers the conformational as well as orientational entropy losses in the liquid crystal phase. In the isotropic phase, each molecule takes its equilibrium conformation and is randomly oriented. However, in the liquid crystal phase, it has to be elongated to some extent and oriented to a given direction to avoid mutual repulsion. For a large N, the entropy loss due to elongation proportional to N is larger than that due to orientation, thus giving larger σ_N and hence larger ϕ' and ϕ'' than does the Onsager theory, where no such entropy contribution exists.

Ronca and Yoon[33] developed a theory of nematic systems of semiflexible polymers on the basis of the wormlike chain with limiting curvature (WCLC), achieving a reasonably good representation of the data of Conio et al. for PHIC. However, we have not discussed it here because no simple procedure is available for evaluating the necessary WCLC parameters and computing theoretical ϕ–L relationships.

Test of the Khokhlov–Semenov Theory. Let us test the theory of Khokhlov and Semenov of semiflexible polymers with the experimental phase diagrams. Here we use our data for PHIC in the two solvents mentioned above and also those for aqueous schizophyllan.[13-17] Figure 8 shows plots of $\phi'/(d/2q)$ versus $N = L/(2q) = M/(2qM_L)$ for aqueous schizophyllan at 25 °C and for PHIC in toluene at three different temperatures; d is taken to be 1.67 nm for schizophyllan and 1.25 nm for PHIC, and the M_L and q values given in Table II are used. These M_L and d values are consistent with the experimental values of the second virial coefficient for the respective solutions. It can be seen that all the data points, irrespective of polymer and solvent condition, form a single composite curve, which appears rather close to the theoretical values indicated by a solid curve. The agreement between experiment and theory is rather quantitative.

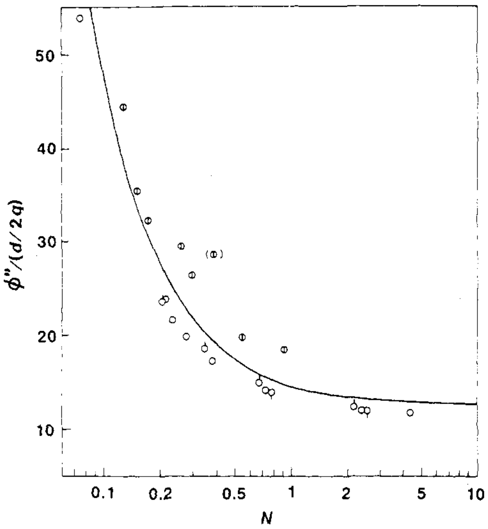

Figure 9. Comparison of the measured and theoretical values for $\phi''/(d/2q)$ as functions of N. PHIC in toluene ȯ (10 °C), ○ (25 °C), ♀ (40 °C); ⦶, schizophyllan in water at 25 °C;[13-17] point in parentheses, polydisperse sample; solid curve, theoretical values calculated by eq 6b.

Figure 9 shows a similar test of the Khokhlov–Semenov theory with the data for ϕ'' of the same polymer–solvent systems, where the same parameter values as those in Figure 8 are used. The data points appear to scatter above and below the theoretical curve indicated, but they are not much removed from it. A remarkable improvement in the Onsager theory is recognized when these figures are compared with Figure 6. It must be emphasized that this agreement between experiment and theory has been achieved by using the molecular parameters determined from dilute solution data but with no adjustable parameters being involved. Thus, we conclude that the validity of the Khokhlov–Semenov theory is now well substantiated experimentally with respect to its two important parameters, namely, chain length and persistence length. For PHIC in toluene, the phase diagram appears to change with temperature only through q, suggesting that there is no substantial temperature dependence in thermodynamic interactions between polymer chains.

Figure 10 summarizes the data of ϕ' and ϕ'' for PHIC, where those in DCM at 20 °C are also included. As noted above, the data points for toluene at the three temperatures appear rather close to the theoretical curves indicated, but those in DCM are seen plotted somewhat below them. Although agreement between experiment and theory is much better when compared with Figure 6, a systematic downward deviation from the theoretical curves is clearly seen for the DCM data, where q is as small as 21 nm. It can be shown that the deviation is much larger for solutions of cellulose derivatives,[34-37] for which q is at most 10 nm or less. This manifests itself as some approximate nature of the Khokhlov–Semenov theory, which is probably related to the second virial approximation to

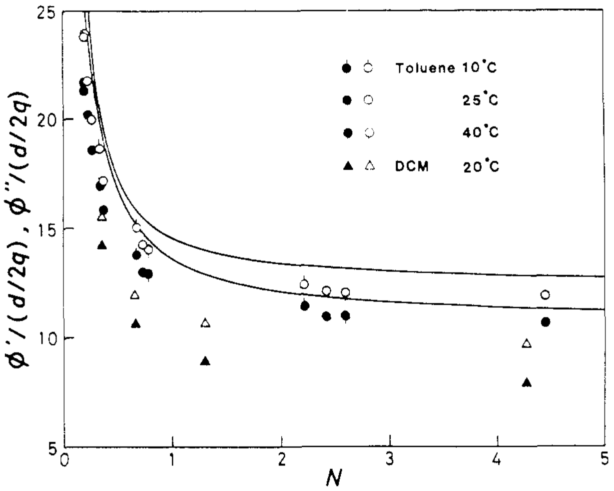

Figure 10. Plots of $\phi'/(d/2q)$ and $\phi''/(d/2q)$ versus N for PHIC in toluene and DCM: DCM at 20 °C, ▲ (ϕ'), △ (ϕ''). The other symbols are the same as those in Figures 8 and 9; solid curves, theoretical values calculated according to eq 6.

free energy inherent in the Onsager theory,[1] where all the terms in concentration higher than the third virial term in free energy are neglected. This approximation may not be accurate for such small q as that in DCM, where the critical concentrations ϕ' and ϕ'' are quite high. This problem will be discussed in a future publication in connection with solvent chemical potential data for the two PHIC solutions considered.

Registry No. PHIC, 26746-07-6.

References and Notes

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Effect of Lattice Coordination Number on the Dynamics of Models of Dense Polymer Systems

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ABSTRACT: Dynamic Monte Carlo simulations of both simple cubic and face-centered cubic lattice models of dense polymer systems have been performed and analyzed by studying the autocorrelation functions of the first three Rouse coordinates. A significant difference between the two lattices is found in the concentration dependence of the scaling exponent that describes the chain length dependence of the relaxation times. This difference is due to the necessity of using bead movement rules with two different length scales in the simple cubic lattice model, while in the face-centered cubic model elementary motions with a single length scale are sufficient. Implications of this result are discussed. The normal mode analysis also provides some insight into the nature of the entanglement constraint in dense polymer systems.

Introduction

The dynamics of polymer chains in entangled systems is a topic of intense recent interest. Much of the discussion centers around the validity of the reptation model introduced long ago by de Gennes.[1] The reptation model, which proposes that the constraints on the motion of a single polymer chain provided by all the surrounding chains can be modeled by a confining tube, is simple and physically

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