between the oligomers (see Table II)

$$\left(\frac{\Delta r}{\Delta T}\right)_{\mathrm{n,i}} < \left(\frac{\Delta r}{\Delta T}\right)_{\mathrm{s,n}} \lesssim \left(\frac{\Delta r}{\Delta T}\right)_{\mathrm{s,i}}$$

which shows the same effect on r on the phase transformation temperature as P has for low molar mass l.c.'s. This interpretation makes the $T_{\mathrm{tr}}(r)$ behavior of the oligomer system B4 in Figure 7 easier to understand.

While a nematic phase can be induced by pressure on low molar mass l.c.'s (Figure 12), a cholesteric phase is induced by increasing r of the B4 oligomers. So far the experiments show that the phase transformation temperatures of oligomers are changed by r in a way similar to the change in phase transformation temperatures of low molar mass l.c.'s with pressure. The specific volume decreases with increasing r of the oligomers and increasing pressure on the low molar mass l.c.'s, indicating a denser packing of the molecules. This denser packing of the mesogenic molecules due to their linkage to the polymer backbone might be a major factor for increasing the phase transformation temperature with r.

We think that detailed P–V–T measurements on l.c. monomers and the corresponding oligomers and polymers are necessary to gain a better understanding of the change of the l.c. phase behavior with polymerization.

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Mesophase Formation by Semirigid Polymers: Poly(*n*-hexyl isocyanate) in Dichloromethane and Toluene

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ABSTRACT: The liquid crystal phase behavior of solutions of poly(*n*-hexyl isocyanate) (PHIC) in dichloromethane and toluene was investigated by using unfractionated and fractionated samples of PHIC covering the molecular weight range from 24 000 to 524 000. The volume fractions of polymer in the coexisting isotropic and anisotropic phases, v_2' and v_2'', were determined by microscopic and analytical techniques, and the molecular weight and molecular weight distribution of the polymer in the coexisting phases were determined by solution viscosity and gel permeation chromatography. The persistence lengths, q, of PHIC in dichloromethane and toluene, 185 ± 15 and 375 ± 25 Å, were evaluated by using the hydrodynamic theory of wormlike chains. Since the contour length for the lowest molecular weight is approximately equal to the persistence length for PHIC in toluene, the dependence of v_2' could be investigated in the region where PHIC changes from rigid to semirigid chain behavior. None of the existing theories for freely jointed or wormlike chains offers a quantitative description of this dependence or of the fractionation effect, and only the qualitative trend of the molecular weight dependence is in line with the approximate virial treatment of wormlike chains.

Introduction

Rigid and semirigid polymers can be differentiated on the basis of the relative magnitudes of the contour length L and the persistence length q. We will arbitrarily define as rigid those polymers having $L \leq q$, and as semirigid those for which $L > q$. It is clear from this definition that a rigid polymer must have a large persistence length (e.g., $q > 100$ Å), while semirigid polymers may either have more flexible chains ($q < 100$ Å) or have a large persistence length coupled with very high molecular weight. The phase behavior of rigid-chain liquid crystalline polymers has been extensively investigated, both theoretically[1] and experimentally.[2] In this case the formation of the mesophase is controlled by the axial ratio, $x = L/d$, where d is the diameter of the chain. By contrast, our understanding of the phase behavior of semirigid mesogenic polymers is more rudimentary.[1,2] Although the wormlike chain model has received preliminary consideration,[3] most theoretical treatments of the mesophase behavior have involved the Kuhn model chain.[1,4] The latter is predicted[4] to be equivalent to a collection of rigid rods having axial ratio $x = 2q/d$, so that the critical concentration for the appearance of the mesophase should be independent of both the contour length and molecular weight distribution of the polymer.

(Hydroxypropyl)cellulose (HPC) is the most extensively studied[5,6] example of a semirigid polymer. HPC obeys the definition of semirigid chains given above, even at low molecular weight, because $q = 65$ Å.[5] This polymer may

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Table I
Characteristics of Whole Samples Investigated

sample	$[\eta]$,[a] dL/g	$\bar{M}_v$[b]	$[\eta]$,[c] dL/g
AI	3.44	79 000	2.28
AII	5.90	131 900	
DI	4.45	100 900	3.04
DII	9.20	201 500	6.17
KI	12.9	278 000	7.30
KII	24.6	514 000	12.6

[a] Toluene, 25 °C. [b] From eq 1. [c] DCM, 20 °C.

also conform reasonably well to the Kuhn chain model, since flexibility arises primarily from an occasional flexible glucose ring conformer.[7] The experimental observations for HPC agree with theoretical predictions in most respects, although some problems remain.[5] For example, it was necessary to invoke a small degree of soft interactions to achieve complete agreement with the predicted critical volume fractions. Also, some molecular weight partitioning was observed[5] between the two phases, which would not be expected for mixtures of independent and monodisperse rods.

It is of interest to investigate the behavior of polymers that can better be represented as wormlike chains, i.e., those having persistence length in the range 100–400 Å. The behavior of such polymers changes with increasing molecular weight from rigid through semirigid to random coil. In the present paper we investigate the liquid crystal phase behavior of poly(n-hexyl isocyanate) over a molecular weight range that spans the rigid and semirigid chain behaviors. The chain extension of PHIC appears to be strongly affected by the solvent.[8–10] A rather large extension has been observed[8] in tetrahydrofuran, where the persistence length is 425 Å, but a less extended conformation is indicated in $CHCl_3$ by comparison of the intrinsic viscosities in the two solvents.[9] We compare the behavior of PHIC in two solvents, dichloromethane (DCM) and toluene, and demonstrate that there is a large difference of the persistence length in these two solvents. Systematic variation of the persistence length and molecular weight permits a characterization of the behavior of wormlike chains. The liquid crystalline nature of PHIC in various solvents was investigated in pioneering work of Aharoni and co-workers.[11,12] Our emphasis, however, is on the dependence upon persistence length and molecular weight, as related to the change in behavior from a rigid to a semirigid chain.

Experimental Section

The six PHIC samples were synthesized by the method of Shashoua et al.,[13] and their characterization appears in Table I. The molecular weight was determined from the intrinsic viscosity measured in toluene at 25 °C by using the relation reported by Berger and Tidswell:[8]

$$[\eta] = 2.48 \times 10^{-5} M_v^{1.05} \tag{1}$$

The polymerization should yield products having a rather narrow molecular weight distribution (e.g., $\bar{M}_w/\bar{M}_n$ about 1.4).[12] Sample AI, however, is expected to have a broader distribution since it is a mixture of several polymerization batches (a larger amount of this polymer was required for the more extensive studies performed). Moreover, we noticed that the polymer obtained by evaporating dichloromethane solutions was lower in molecular weight than the original. Successive solution and evaporation cycles did not further affect the molecular weight. The solvents used were reagent grade toluene and Chromasolv dichloromethane stabilized with amylene, all produced by Riedel-de Haën AG. These were used without further purification.

Viscosity measurements in toluene and DCM were performed as previously described[14] with an Ubbelohde suspended-level viscometer with three bulbs to detect any shear-rate dependence. This was only significant for the sample of highest molecular weight, for which the reported intrinsic viscosity has been extrapolated to zero shear rate.

Solutions used for phase equilibrium studies were prepared by adding a weighted amount of solvent to a known weight of PHIC that had been previously dried under vacuum at room temperature for 24 h. Special precautions were taken with the DCM solutions to prevent losses due to the evaporation of this volatile solvent. Hermetically sealed centrifuge tubes containing the polymer and solvent were agitated at 20 °C for at least 10 days. The polymer concentration, C_p, is given as g of PHIC per 100 g of solvent. The volume fraction of polymer, v_2, was calculated from C_p assuming additivity and making use of the partial specific volume of the polymer, $\bar{v}_2$, and the molar volume of the solvent. The values of $\bar{v}_2$ determined pycnometrically at 20 °C for PHIC were 1.050 mL/g in DCM and 1.000 mL/g in toluene. The critical concentration, C_p', of the isotropic phase at which birefringence first appears was determined at 20 °C in two ways. A Reichert-Zetopan polarizing microscope was used for direct observation of the appearance of birefringence. In some cases, C_p' was determined by extrapolation of plots of C_p vs. the volume fraction, ϕ, of the isotropic phase. This extrapolation also furnished the composition, C_p'', of the conjugated anisotropic phase. Biphasic mixtures were centrifuged at 3000–6000 rpm for times ranging from 4 to 24 h to effect a clean separation of the two phases. Samples of higher molecular weight required longer times and higher rotation speeds due to their higher solution viscosities. As observed for PHIC in tetrachloroethane by Aharoni and Walsh,[12] the isotropic phase sedimented to the bottom of the centrifuge tube. In fact, the density of DCM, 1.327 g/mL, is larger than that of PHIC, 1.000 g/mL.[12] The volume fraction, ϕ, of the isotropic phase was determined by calibration of the centrifuge tubes.

In the case of sample AI, aliquots of the two phases were dried at 40 °C under vacuum for 12 h to determine the variation of the compositions C_p' and C_p'' with ϕ. The molecular weight of the polymer partitioned in the two phases was evaluated from its intrinsic viscosity in toluene, and the molecular weight distributions were determined by using a Waters HP GPC instrument with four μ-Styragel columns (porosities 10^3, 10^4, 10^5, and 10^6 Å) at room temperature. For the latter measurements 0.2 g/100 mL solutions in DCM were used with a pumping rate of 1 mL/min and the detector was operated at 254 nm. Calibration was performed with anionic polystyrene standards dissolved in DCM. For polystyrene the elution volume, V_E^p (corresending to the peak in the chromatogram), is related to the molecular weight and intrinsic viscosity as follows:

$$\log (M[\eta]) = 14.532 - 0.316 V_E^p \tag{2}$$

Results

The critical compositions C_p' and v_2' determined microscopically for solutions in DCM and toluene are given in Table II, and v_2' values for these two solvents appear plotted against polymer molecular weight in Figure 1. The data include low molecular weight fractions obtained by isolation of the isotropic phase from solutions of sample AI. The values of v_2' decrease with increasing molecular weight, rapidly at first and then more gradually. Also solutions in toluene, in which PHIC has a larger persistence length, give systematically smaller values of v_2'. Figure 2 illustrates the determination of v_2' and v_2'' by extrapolation of a plot of the overall volume fraction of polymer, v_2, vs. the volume fraction, ϕ, of the isotropic phase. Values of v_2' (v_2 extrapolated to $\phi = 1$) and v_2'' (v_2 extrapolated to $\phi = 0$) are given in Table II. The former are in excellent agreement with the corresponding values determined by microscope observations. The width of the biphasic region, characterized by $v_2''/v_2' = 1.9$, is larger than the values reported (1.4–1.6) for other systems.[1,12,15]

The volume fractions v_2' and v_2'' given above are limiting values for the conjugate phases. However, the compositions of the conjugate phases and the volume fraction ϕ are affected by the overall composition v_2 within the bi-

Table II
Limiting Compositions at 20 °C

		toluene microscopically		DCM				
				microscopically		C_p vs. ϕ		
sample	$\overline{M}_v$	C_p', %	v_2'	C_p', %	v_2'	v_2'	v_2''	v_2''/v_2'
AI (fraction)	24 000	31.5	0.284	25.5	0.323			
AI (fraction)	35 300	29.3	0.263					
AI	79 000			20.0	0.258	0.264	0.490	1.85
AII	131 900							
DI	100 900	22.5	0.200	19.0	0.246	0.246	0.468	1.89
DII	201 500	21.0	0.186	17.5	0.228			
KI	278 000	20.0	0.177	16.5	0.216			
KII	514 000	19.5	0.173	15.5	0.203			

Table III
Composition and Viscosity of Conjugated Phases (Sample AI)

				$[\eta]^{\text{iso}}$, dL/g		$[\eta]^{\text{aniso}}$,	dL/g
overall C_p,[a] %	C_p',[a] %	C_p'',[a] %	ϕ[a]	toluene	DCM	toluene	DCM
25.1			0.76	2.02	1.37	8.40	4.70
27.0	24.5	31.8	0.66	1.48	1.04	7.65	4.60
29.0	25.7	33.3	0.56	0.98	0.78	6.50	4.05
30.2	26.2		0.50				
32.9	29.0	35.0	0.40	1.22	0.85	5.55	3.31
35.0			0.28				

[a] DCM.

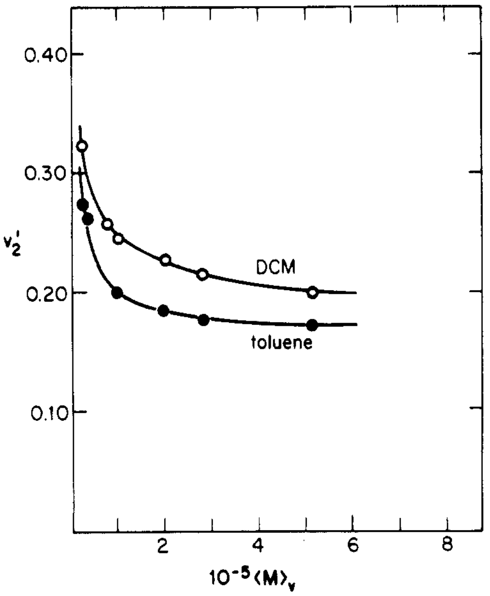

Figure 1. Molecular weight dependence of the critical volume fraction for incipient appearance of the anisotropic phase at 20 °C in dichloromethane (DCM) (○) and toluene (●).

phasic gap.[1,15] The effect is related to the molecular weight distribution, and hence a fractionation is expected.[1,16] In Table III are collected values for sample AI of the polymer compositions and of the intrinsic viscosity (measured in toluene and DCM) for the polymer in each phase. The same data appear in Figure 3, where the volume fractions and molecular weights of the polymer in the isotropic and anisotropic phases are plotted against ϕ. The trend of the data is similar to that observed[15] for other systems; however, the efficiency of fractionation is much larger in the present case. The ratio of the intrinsic viscosities in the two phases, $[\eta]''/[\eta]'$, is as high as 6 in the present instance, whereas ratios between 1.8 and 3.3 have been reported for other systems.[12,17,18] The latter value is close to the theoretical limit predicted[1,16] for a most probable distribution. We attribute this exceptional efficiency to the rather broad molecular weight distribution of sample AI. The intrinsic viscosity of the polymer separated into the conjugate phases was also determined for sample DII. At $\phi = 0.5$ we obtained $[\eta]' = 7.75$ dL/g ($\overline{M}_v = 171\,000$) and $[\eta]'' = 10.48$ dL/g ($\overline{M}_v = 227\,400$). The ratio $[\eta]''/[\eta]' = 1.34$ is considerably smaller for this polymer than that observed for sample AI. For sample KI at still higher molecular weight (278 000), the $[\eta]''/[\eta]'$ ratio is approximately unity.

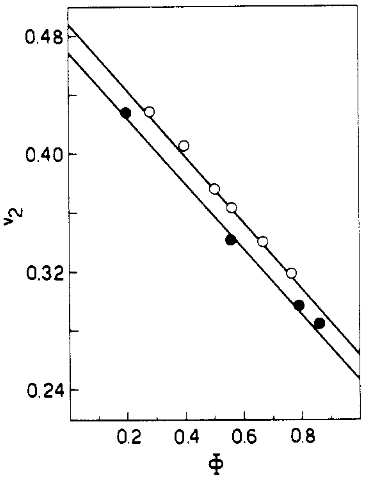

Figure 2. Overall composition, v_2, vs. the volume fraction of the isotropic phase in DCM at 20 °C for sample AI (○) and sample DI (●).

Gel permeation chromatography (GPC) was used to analyze the molecular weight distributions of the polymers that separated in the conjugate phases. It was first ascertained that the calibration curve for polystyrene also applies to PHIC. It was found that the elution volumes V_E^p were nicely represented by eq 2 when plotted against the product $[\eta]M$. The molecular weight dependence of the intrinsic viscosity of PHIC in DCM (data in Table I) can be described by

$$[\eta] = 6.6 \times 10^{-5} M^{0.923} \qquad (3)$$

By combining eq 2 and 3 we obtain

$$\log M = 9.7306 - 0.1643 V_E^p \qquad (4)$$

which was used to convert the abscissa of the chromatogram to a molecular weight scale. Chromatograms con-

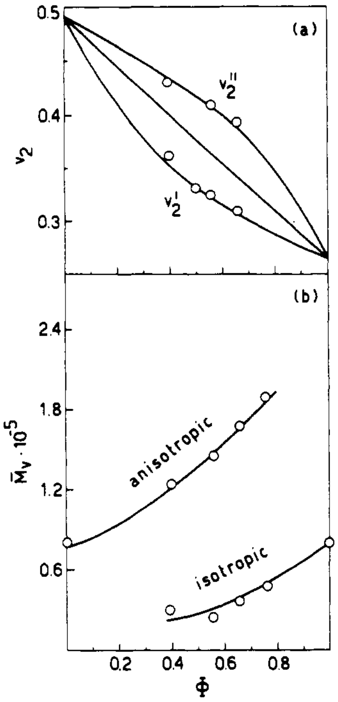

Figure 3. (a) Dependence upon the volume fraction, ϕ, of the isotropic phase of the volume fractions of polymer in the isotropic phase (v_2') and anisotropic phase (v_2''). (b) Corresponding variation of the molecular weights partitioned into the two phases for sample AI in DCM at 20 °C.

Table IV
GPC Fractionation Data (Sample AI)

	whole	$\phi = 0.66$	
		isotropic	anisotropic
$\bar{M}_v{}^a$	79 000	35 300	167 000
$\bar{M}_w$	112 000	38 600	250 000
$\bar{M}_n$	13 600	11 200	41 000
$\bar{M}_w/\bar{M}_n$	8.2	3.4	6.1
$\bar{M}_w''/\bar{M}_w'$		6.4	
$\bar{M}_v''/\bar{M}_v'{}^a$		4.7	

[a] From intrinsic viscosity in toluene.

verted in this way for the polymers in the conjugate isotropic and anisotropic phases are compared in Figure 4 with that for the whole AI sample (broken line). The ordinate represents the weight fraction, w_i, of species in each phase having molecular weight M_i. The average molecular weights calculated from these distribution curves are given in Table IV. Clearly, the polymers that separated into the two phases have narrower distributions than the whole polymer. The magnitudes of $\bar{M}_w$ obtained from GPC are somewhat larger than those determined from $[\eta]$. This discrepancy probably results from column dispersion and inadequacy of the calibration at high molecular weight.

The persistence length of PHIC in DCM and toluene was determined from the $[\eta]$ and $\bar{M}_w$ data collected in Tables I and III using the Yamakawa–Fujii treatment[19] of wormlike chains. The relations are

$$[\eta] = \frac{\phi_\infty L^{3/2}}{M}[1 - \sum_{i=1}^{4} C_i L'^{-i/2}]^{-1} \qquad (L' \geq \sigma) \qquad (5)$$

and

$$[\eta] = \frac{\pi N_A L^3}{24M \ln (L'/d')} f(L') \times [1 + \sum_{i=1}^{4} A_i \{\ln (d'/L')\}^{-i}]^{-1} \qquad (L' > \sigma) \quad (6)$$

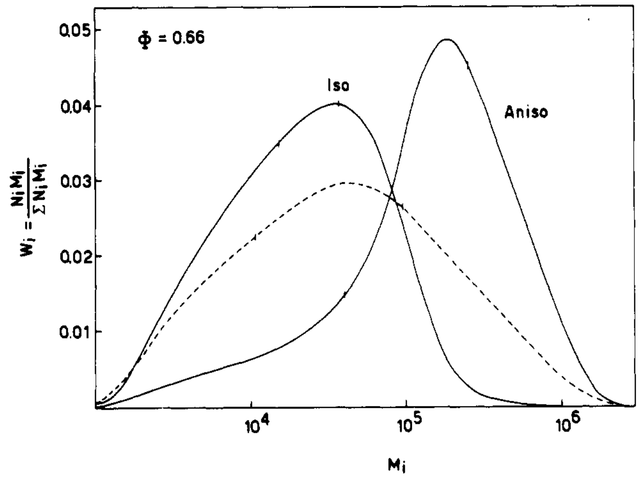

Figure 4. GPC chromatograms for PHIC sample AI in DCM at 20 °C. Full curves represent the molecular weight distributions of the polymer in the isotropic and anisotropic phases when ϕ = 0.66. The distribution of the whole sample is indicated by the broken curve.

Here, the reduced contour length is $L' = \lambda M/M_L$, where M_L is the mass per unit length of the chain and λ, the reciprocal of the Kuhn chain length, is given by $\lambda = 1/2q$. Also, the reduced chain diameter, d', is given by $d' = \lambda d$, N_A is Avogadro's number, $\phi_\infty = 2.870 \times 10^{23}$, $\sigma = 2.278$, and relations for $f(L')$ and the constants A_i and C_i are given by Yamakawa and Fujii. The coefficient of the third term in the expression for C_3 is 43898.88.[14] Theoretical $[\eta]$–M curves have been calculated according to eq 5 and 6 for various values of q. M_L was taken as 63.5 daltons/Å (a value of 2 Å was taken for the residue vector,[8] l_0), and the diameter (not reduced) was varied between 10.3 and 16.4 Å. The former value was obtained from the equation[1] $d = (M_0/\rho N_A l_0)^{1/2}$, where $M_0 = 127$ and the polymer density is $\rho = 1.000$ g/mL. The latter value of d was deduced from molecular models.

Points representing the intrinsic viscosities measured in DCM and toluene, along with the theoretical curves, are given in Figure 5. The data are compatible with a persistence length $q = 185 \pm 15$ Å in DCM and 375 ± 25 Å in toluene. An increase in the diameter from 10.3 to 16.4 decreases q by about 14%. The effect of other corrections has been discussed elsewhere.[5] The fact that the experimental points for fractions and whole polymers fall nicely on the same curves suggests that the correction for polydispersity is unimportant. It is clear that the solvent may have a rather large effect on q for this polymer, so it is mandatory that a comparison of the critical polymer concentration and chain rigidity be made with values for the same solvent. Factors affecting the conformation of PHIC in various solvents have been discussed by others.[8-10,20]

Discussion

We begin our comparison of the experimental results with the theoretical predictions for rodlike molecules. Flory's lattice model treatment of rodlike polymers gives for the critical volume fraction at the point of incipient separation of the anisotropic phase

$$v_2' \cong (8/x)(1 - 2/x) \qquad (7)$$

where $x = L/d$. Two curves in Figure 6a were calculated from eq 7 with d = 10 Å (dashed) and d = 16 Å (dotted). Since this treatment concerns rodlike molecules, v_2' is dependent upon the contour length but not upon persistence length. In view of the wormlike behavior of PHIC, it would be expected to obey this behavior only at low

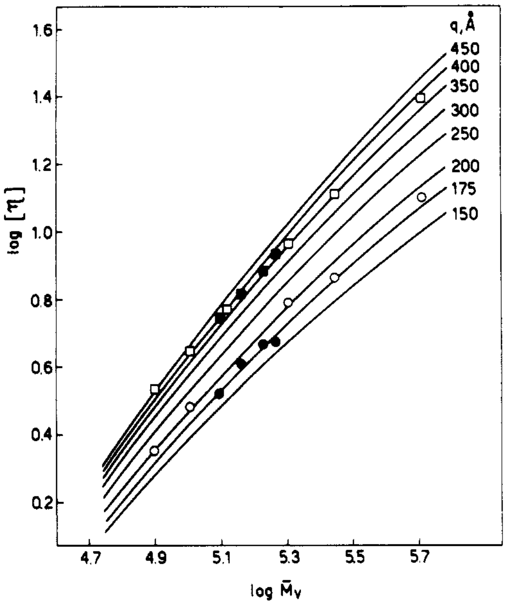

Figure 5. Full curves represent the predicted[19] molecular weight dependence of the intrinsic viscosity for wormlike chains for the indicated values of the persistence length, q. Open and filled circles represent intrinsic viscosities of whole samples and fractions, respectively, of PHIC in DCM at 20 °C and open and filled squares indicate values for whole samples and fractions, respectively, of PHIC in toluene at 25 °C.

molecular weights. At high molecular weights PHIC should obey Kuhn statistics. If the Kuhn chain is represented[4] as a sequence of rods connected by flexible joints, then $x = 1/\lambda d$, where $\lambda^{-1} = 2q$. Hence, in this limit the critical volume fraction is predicted to be dependent upon the persistence length but independent of the contour length. We have taken q = 200 and 400 Å to represent approximately the values for PHIC in DCM and toluene, respectively. The limiting behaviors predicted according to eq 7 for d = 10 Å are represented by the two horizontal dashed lines in Figure 6a and by the two horizontal dotted lines for d = 16 Å. The predicted dependence upon the persistence length of the limiting value of v_2' in the Kuhn limit ($L \gg q$) appears to be stronger than that found experimentally. One could, of course, achieve agreement by assuming a different chain diameter in the two solvents, such as q = 200 Å and d = 10 Å in DCM and q = 400 Å and d = 16 Å in toluene; however, this would require independent justification.

Grosberg and Khokhlov[21] applied the Onsager virial procedure to the Kuhn chain, obtaining

$$v_2' = 3.25/x \qquad (8)$$

where $x = 2q/d$. This predicts a lower critical volume fraction than eq 7, in accordance with the general result that virial treatments[23,24] lead to lower values of the critical volume fraction than the lattice treatment of Flory.[1] However, Khokhlov and Semenov[3] then extended the Onsager approach to wormlike chains with a rather surprising result. They conclude that the configurational entropy of the wormlike chain in the limit $L \gg 2q$ is much larger than that of the equivalent Kuhn flexibly linked chain, leading to a lower value of the order parameter and a larger value of v_2' for the asymptotic behavior of the wormlike chain:

$$v_2' = 10.48/x \qquad (9)$$

They also obtained an approximate expression for the wormlike chain in the semirigid chain region:

$$v_2' = d\lambda\left[\frac{3.34 + 11.3L\lambda + 4.06(L\lambda)^2}{L\lambda\{1 + 0.387L\lambda\}}\right] \qquad (10)$$

These relations are displayed in Figure 6b. The horizontal dashed lines represent values calculated for q = 200 Å according to eq 8 and 9. The former (appearing below) represents the behavior of a flexibly linked Kuhn chain, while the latter (above) is the result predicted by these authors for the wormlike chain in the limit $L \gg q$. The two dashed curves display the results calculated according to eq 10 for q = 200 Å (above) and q = 400 Å (below). Although this is the only theoretical relation that correctly predicts the general trend of the experimental data in the

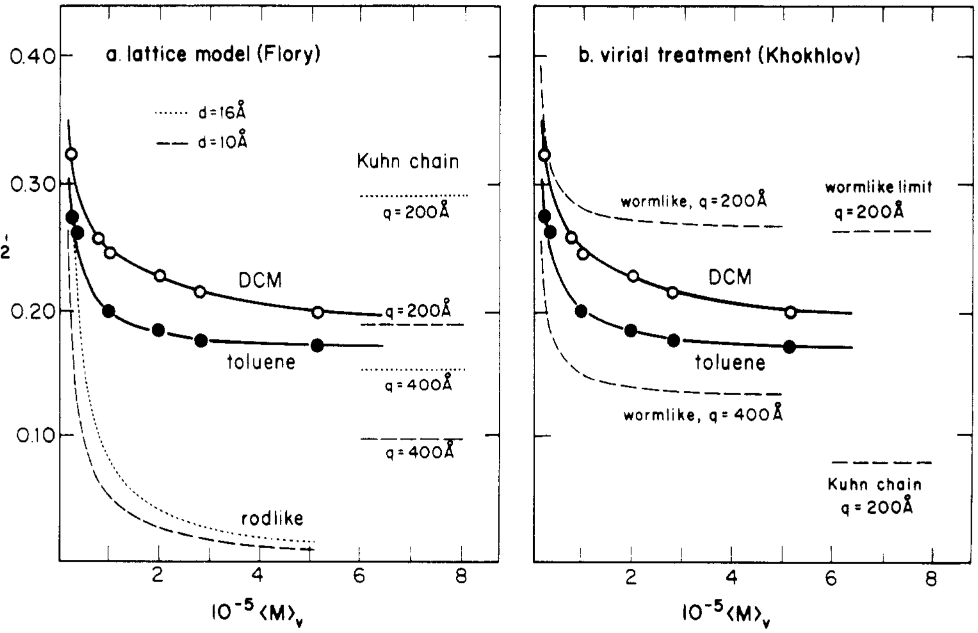

Figure 6. (a) Molecular weight dependence of the experimental v_2' values for PHIC in DCM and toluene compared with the predictions of the lattice model treatment of rodlike molecules having d = 10 Å (dashed curve) and d = 16 Å (dotted curve) and for flexibly linked Kuhn chains (horizontal lines) having the indicated persistence lengths, q. (b) Comparison of the same data with the predictions for virial treatment of Kuhn chains (lower dashed line), the wormlike chain in the limit $L \gg q$ (upper dashed line), and the wormlike chain having the indicated persistence length (dashed curves).

semirigid region, the quantitative agreement is somewhat poorer than with the lattice model because the predicted dependence upon the persistence length is even stronger than that observed experimentally. Inclusion of soft interactions[5,22] would lower the predicted values of v_2' somewhat.

We next turn to a consideration of the fractionation that occurs within the biphasic region. The predictions concerning fractionation indicated in the preceding section were based upon the rigid rod theory.[1,16] Flexibly linked rods would not be expected to exhibit fractionation since a variation of the contour length has no effect upon the Kuhn segment length.[1] No theoretical treatment of fractionation effects for wormlike chains has appeared. The extensive data for sample AI, for which $L = 1250$ Å, reveal that considerable separation occurs for wormlike chains having an average of about 3.5 Kuhn segments per chain. The results obtained for sample DII ($L = 3170$ Å) indicate that fractionation still occurs when there is an average of about 9 segments per chain. The fact that the density of the anisotropic phase is lower than that of the isotropic phase weighs against the explanation that nonequilibrium effects following sedimentation could have simulated true fractionation.[5] The observation that fractionation was detected in dilute solution mitigates against the possibility that aggregation (and a distribution of aggregated species) is responsible for the separation of the anisotropic phase. Moreover, fractionation appears to have become vanishingly small for sample KI, as expected for the asymptotic Kuhn chain behavior. Thus, any theory of wormlike chains should account for the continuation of fractionation effects to a molecular weight of 200 000. A newer theory of semirigid chains has been presented by Ronca and Yoon,[25] but it has not yet been extended to polymer solutions.

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Registry No. Poly(hexyl isocyanate) (homopolymer), 26746-07-6; poly[(hexylimino)carbonyl] (SRU), 37727-37-0.

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