Mesophase formation by semirigid polymers: (Poly(n-hexyl isocyanate) in 1-chloronaphthalene

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A study of the persistence length q and of the critical polymer volume fraction v_2' at which the mesophase appears for poly(n-hexyl isocyanate) (PHIC) in 1-chloronaphthalene is presented. The phase diagram was determined over the temperature range 80 to 188°C, corresponding to v_2' from 0.2 to 1.0. The thermal expansion of the system is accounted for in evaluating v_2' and the axial ratio of the Kuhn segment, $2q/d$. As reported for PHIC in toluene, and for several cellulose derivatives, the limiting value of v_2' at large molecular weight can be represented rather well by the Kuhn chain model with a temperature-dependent Kuhn segment length. However, while the thermotropic effect is adequately described by the temperature coefficient of q, the experimental v_2' is somewhat smaller than predicted.

INTRODUCTION

In a previous communication[1] we investigated the effect of temperature on the mesophase equilibrium and on the persistence length of poly(n-hexyl isocyanate) (PHIC) in toluene and tetrahydrofuran. Extrapolation of the axial ratios x_K of the Kuhn segment to the nematic–isotropic transition temperature T_{NI}° of the undiluted polymer gave $x_K=6.8$. This value is in excellent agreement with the critical axial ratio predicted by Flory's theory[2] of mesophase formation by semirigid mesogens which conform to the Kuhn chain model. Indeed, the whole temperature dependence of the critical volume fraction of polymer v_2' could be satisfactorily described by the corresponding temperature dependence of the persistence length q.

In this report, we present a similar study performed for PHIC in 1-chloronaphthalene (1-CN). These results demonstrate that the persistence length in 1-CN is considerably smaller than in toluene or tetrahydrofuran, and that v_2' is somewhat larger in 1-CN. Moreover, the unusually large temperature coefficient of q observed in the two other solvents, $\mathrm{d}\ln q/\mathrm{d}\ln T=-3.6$, is also exhibited in 1-CN. The temperature dependence of v_2' for PHIC in 1-CN can also be satisfactorily described by a temperature-dependent Kuhn segment length.

EXPERIMENTAL

The PHIC samples were synthesized using the method of Shashoua *et al.*[3] Most of these polymer samples are similar to those used in our previous investigations[1,4]. The intrinsic viscosities in toluene (*Table 1*) were used to determine their molecular weights using the relationship of Berger and Tidswell[5]:

$$[\eta]=2.48\times10^{-5}\,M_v^{\,1.05} \tag{1}$$

Sample AI^f is a fraction obtained[4] from an anisotropic solution. The polymer concentration C_p is given as grams PHIC per 100 g solvent. Intrinsic viscosity measurements in 1-CN (Janssen) were performed over the temperature range 25 to 110°C as previously described[4]. Degradation of the polymer in solution was first detected at 120°C. Duplicate measurements of $[\eta]$ at 25°C following the measurements at 110°C gave concordant results. The thermal expansion of the solvent was taken into account in the assessment of the volume fraction of polymer at various temperatures. The critical concentration C_p' at which the anisotropic phase appears was determined as a function of temperature in two ways. One involved observations with a Mettler FP-5 hot stage and an Olympus BH-2 polarizing microscope. These measurements were performed using a heating rate of 3°C min^{-1} within 10°C of the transition. The second method involved data taken with a DuPont 1090 d.s.c. using a scanning rate of 10°C min^{-1} or 20°C min^{-1}. The polymer volume fraction v_2' was calculated from C_p' assuming additivity and using the partial specific volume of the polymer $\bar{v}_2$ and the density of the solvent ρ_1. In a preliminary calculation of v_2', the temperature dependences of $\bar{v}_2$ and ρ_1 were neglected. These v_2' values, referred to as 'uncorrected', utilized the values determined experimentally at 25°C ($\bar{v}_2=0.983\ \mathrm{ml\,g^{-1}}$ and $\rho_1=1.1876\ \mathrm{g\,ml^{-1}}$). The corrected v_2' values at each temperature involved the temperature dependence of $\bar{v}_2$ and ρ_1. Using pycnometric techniques, we found:

$$\mathrm{d}\bar{v}_2/\mathrm{d}T=9.42\times10^{-4}\quad \mathrm{ml\,g^{-1}\,{}^{\circ}C^{-1}}$$

$$\mathrm{d}\rho_1/\mathrm{d}T=-7.7\times10^{-4}\quad \mathrm{g\,ml^{-1}\,{}^{\circ}C^{-1}}$$

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Table 1 Molecular weights and viscosities of PHIC samples

Sample	$[\eta]^a$ (dl g^{-1})	$10^{-5}M_v$	$[\eta]^b$ (dl g^{-1}) 25°C	45°C	90.2°C	110.8°C
DI	4.45	1.009	3.40	3.10	2.02	1.58
TI	4.9	1.105	3.61	3.09	1.99	-
AI^f	6.50	1.447	4.84	4.08	2.64	2.20
DII	9.20	2.015	6.76	5.81	3.40	2.80
KI	12.9	2.780	9.08	7.60	-	3.80

^{a}Solvent: toluene at 25°C
^{b}Solvent: 1-chloronaphthalene
^{f}fraction

RESULTS AND DISCUSSION

Persistence length

Intrinsic viscosities of five PHIC samples in 1-CN at 25, 45, 90.2 and 110.8°C are listed in *Table 1*. In order to deduce the persistence length q, these data were compared with the theoretical $[\eta]$ vs. M dependence predicted by the treatment of Yamakawa and Fujii[6], as shown in *Figure 1*. This procedure has been described in more detail elsewhere[1,4,7–9]. Relevant parameters in this treatment are the chain diameter d and the residue vector l_0, which was taken as 2 Å[4,5]. This corresponds to a mass per unit length of the chain $M_L = 63.5$ dalton Å^{-1}. Evaluation of the chain diameter is complicated by the need to account for strongly bound solvent (i.e. its hydrodynamic diameter[10,11]) and its temperature dependence. Following our previous approach[1,4], we have performed the calculation for two preassigned values of d at 25°C, 16.4 and 10.3 Å. The data for $d = 10.3$ Å are shown in *Figure 1*. This value of d was derived using the equation[12]:

$$d = [M_0/(\rho_2 N_A l_0)]^{1/2} \qquad (2)$$

where N_A is Avogadro's number, $M_0 = 127$ is the molecular weight per repeating unit and $\rho_2 = 1.000$ g ml^{-1} is the polymer density. The larger value of d was derived from molecular models and light scattering data for PHIC in hexane[13].

The q values collected in *Table 2* were obtained by requiring a best fit of the experimental data and the theoretical curves. This table also includes the results obtained for $d = 16.4$ Å. Data for fractionated and unfractionated samples fall on the same curve, suggesting that the correction for polydispersity is unimportant (cf. also ref. 4). Further attempts to derive both q and d by fitting the Yamakawa–Fujii curves, or by allowing the preassigned values of d to change with temperature (using the linear expansion coefficient of PHIC), did not produce a significant alteration of the q values. As can be seen from *Table 2*, the increase of d at 25°C from 10.3 to 16.4 Å causes only a small decrease of q. It is obvious that the small increase of d due to thermal expansion will have a trivial effect upon the persistence length.

The data in *Table 2* reveal that q for PHIC in 1-chloronaphthalene decreases with temperature. Its value at 25°C and $d_{25} = 10.3$ Å ($q = 230$ Å) is closer to that observed for the same polymer in dichloroethane[4], $q = 185 \pm 15$ Å, than to that in toluene, $q = 373 \pm 25$ Å, or tetrahydrofuran[1]. Also included in *Table 2* are values of the axial ratio of the Kuhn segment $x_K = 2q/d$. The diameter was corrected at each temperature using equation (2) and the linear expansion coefficient $\alpha_L = 3.19 \times 10^{-4}$ °C^{-1} calculated from the measured $d\bar{v}_2/dT$. The effect of this correction is small, as can be appreciated by comparison with the uncorrected entries, $2q/d_{25}$, also given in *Table 2*. The least-squares value of $d \ln q/dT$ is -0.011°C^{-1} and $d \ln q/d \ln T = -3.7$.

Thermotropicity

Data for the variation with temperature of the critical concentration of PHIC in 1-chloronaphthalene determined with the polarizing microscope and d.s.c. are collected in *Table 3*. The first column of *Table 3* gives the w/w concentration C'_p, while column 2 gives values of the volume fraction of polymer v'_2, calculated using $\bar{v}_2$ and ρ_1 measured at 25°C. This approach was also used for our evaluation of v'_2 in previous papers[1,4,7–9]. The v'_2 values in the third column include the effect of thermal expansion of the components. It can be seen that the v'_2 values are not significantly altered by the latter

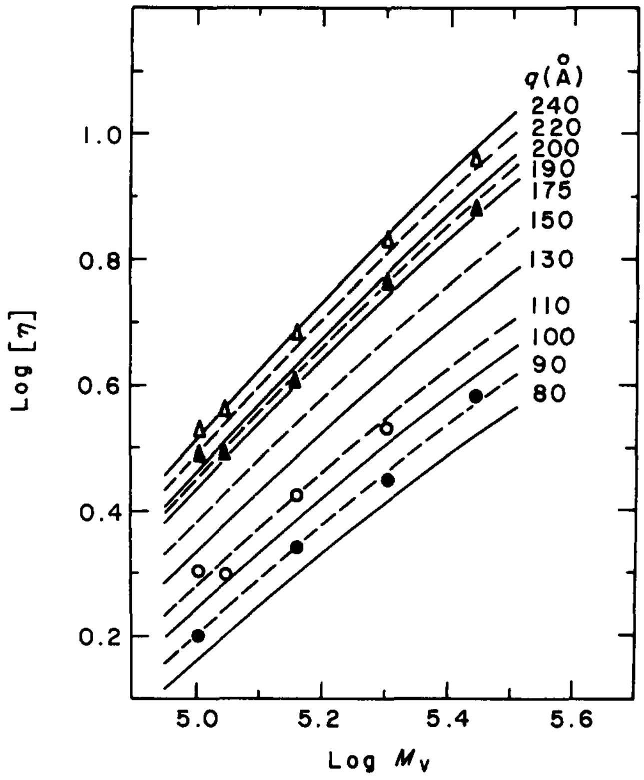

Figure 1 The intrinsic viscosity vs. molecular weight dependence calculated according to Yamakawa and Fujii for several values of the persistence length using $M_L = 63.5$ and $d_{25} = 10.3$ Å. Experimental points for PHIC in 1-CN are taken from *Table 1* at 25°C (△), 45°C (▲), 90.2°C (○) and 110.8°C (●)

Table 2 Persistence length and axial ratio of the Kuhn segment for PHIC in 1-chloronaphthalene

t	$d_{25} = 10.3$ Å			$d_{25} = 16.4$ Å		
(°C)	q	$x = 2q/d_{25}$	$x = 2q/d_t$	q	$x = 2q/d_{25}$	$x = 2q/d_t$
25	230	44.7	44.7	200	24.4	24.4
45	190	36.9	36.5	165	20.1	20.0
90.2	110	21.4	21.0	95	11.6	11.4
110.8	90	17.5	17.0	80	9.8	9.5
184^a	39	7.6	7.3	35	4.3	4.3

^{a}Extrapolation

correction. Thus, the thermotropic effect is not related to the failure to correct v_2' for thermal expansion. The open circles in *Figure 2* represent T_{NI} values obtained for PHIC in 1-CN using the polarizing microscope, while the filled circles indicate values for PHIC in toluene[1]. The value of T_{NI}° for PHIC in 1-CN is about 184°C, as compared to the value 180°C obtained for PHIC in toluene[1]. On the other hand, the T_{NI} values determined by d.s.c. are lower, as can be seen in *Table 3*. These differences may arise from the different heating rates or from the width of the d.s.c. endotherm. The present data furnish a more detailed representation of T_{NI} in the C_{p}' range of 0.3 and 1.0, whereas the data in toluene are more extensive for $v_2' < 0.3$. The temperature dependence of v_2' is similar to that observed for cellulose derivatives[7-9] and for PHIC in toluene[1]. The chain curve in *Figure 2* results from a calculation using the temperature dependence of the Kuhn segment length, $T(\mathrm{d}\ln q/\mathrm{d}T) = -3.7$, in connection with the lattice model in the absence of soft interactions[1]. Agreement with the experimental data is satisfactory, although differences remain, as previously observed for PHIC in toluene and for hydroxypropylcellulose in dimethylacetamide[1]. It appears that the thermotropic effect follows a similar trend for PHIC and cellulose derivatives[7-9], even though $\mathrm{d}\ln q/\mathrm{d}T$ is considerably larger for the former.

Table 3 Nematic–isotropic transitions of PHIC in 1-chloronaphthalene

	v_2'		T_{NI} (°C)	
C_{p} (%)	Uncorr.	Corr.	Microsc.	D.s.c.
0.180	0.203	0.206	80	–
0.202	0.228	0.232	103	103
0.230	0.258	0.263	120	–
0.317	0.351	0.357	132	–
0.370	0.406	0.413	136	117
0.493	0.531	0.539	151	140
0.651	0.685	0.692	168	–
0.710	0.740	0.747	176	152
0.850	0.869	0.874	–	159
0.900	0.913	0.916	175	–
1.00	1.00	1.00	188	177

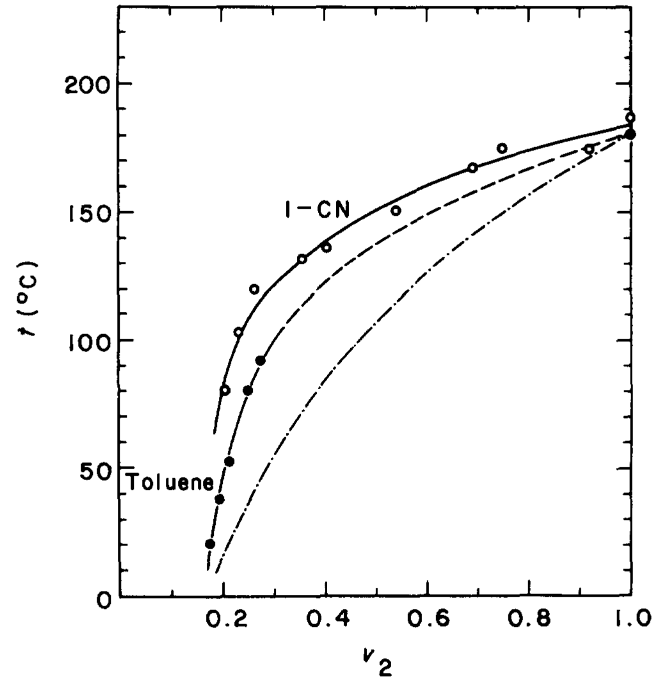

Figure 2 Variation of the nematic–isotropic transition temperature with the critical volume fraction for PHIC sample KI in 1-chloronaphthalene (present data) and in toluene (ref. 1). Data were obtained by optical microscopy using heating rates of 3°C min^{-1} for 1-CN and 1°C min^{-1} for toluene. The chain curve is a theoretical prediction[1] for the Kuhn model with temperature-dependent segment length using $\chi_1 = -0.2$, $x = 2600$ and $\mathrm{d}\ln q/\mathrm{d}T = -0.011$ °C^{-1}. The other curves and points are described in the text

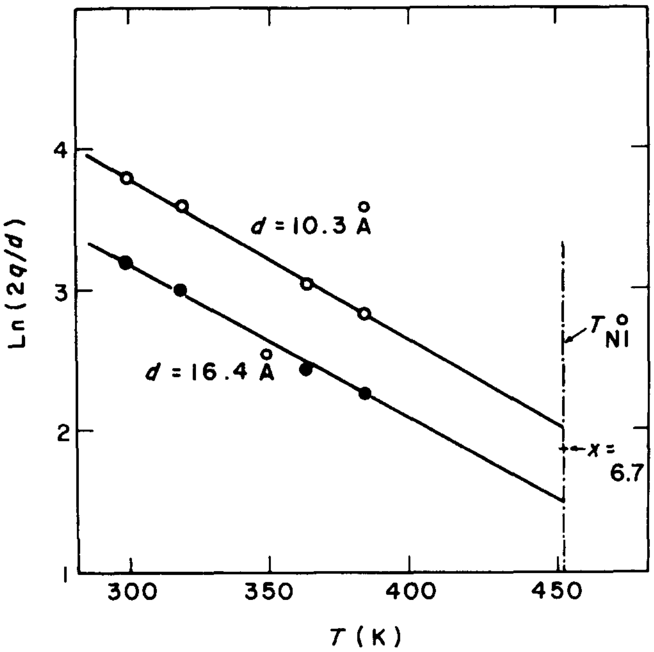

Figure 3 Temperature dependence of the axial ratio of the Kuhn segment length for PHIC in 1-CN corresponding to two values of d_{25} (10.3 and 16.4 Å). Data from *Table 2* corrected for thermal expansion

At a fixed temperature above 80°C, the ratio of v_2' observed in 1-CN and toluene is comparable to the inverse ratio of persistence lengths in these two solvents. This is in agreement with theoretical prediction based on the relation[2]:

$$v_2 \simeq 8/x_{\mathrm{K}} \qquad (3)$$

In terms of this equation, the value $v_2' = 0.23$ at 90°C in 1-CN corresponds to $x_{\mathrm{K}} = 32$. This is significantly larger than the experimental $2q/d$ in *Table 2*, 21.0 for $d = 10.3$ Å and 11.4 for $d = 16.4$ Å. The finding that the predicted v_2' is larger than that observed experimentally by a factor of the order of 2 is entirely concordant with the results obtained for several cellulose derivatives (cf. Table IV of ref. 9). Note that this result pertains to sample KI having a sufficiently large molecular weight to correspond to the limiting behaviour of v_2'.[4]

Values of the axial ratio of the Kuhn segment extrapolated to T_{NI}° (*Figure 3*) depend to some extent upon the chain diameter, but are close to the theoretical value[1] $x_{\mathrm{c}} = 6.7$ calculated for the Kuhn chain with no soft interactions. In terms of the Flory–Ronca treatment of rodlike particles[14], axial ratios smaller than $x_{\mathrm{c}} = 6.4$ require a contribution from soft interactions to stabilize the nematic phase. This contribution is expressed by the parameter T^*, which can easily be evaluated from Figure 1 of ref. 5. If we take d at 25°C equal to 16.5 Å, T^* is about 220 K. This value is rather small, and the need to introduce it arises primarily from the uncertainty in the chain diameter. In fact, we may expect that anisotropic interactions are not of much significance for both PHIC and cellulose derivatives due to the long side chains which prevent close approach of the polarized bonds along the chain.

Other theories of the mesophase behaviour of semirigid mesogens conforming to the wormlike chain model have recently been developed[15–17]. Comparison of the predictions of these treatments with our data for PHIC and the cellulose derivatives will be presented in a forthcoming paper.

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