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Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 2. (Hydroxypropyl)cellulose in Dichloroacetic Acid

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ABSTRACT: The critical volume fraction for mesophase formation, v_2', was determined for fractions of (hydroxypropyl)cellulose (HPC) in dichloroacetic acid (DCA) at 20 °C. The persistence length, q, of HPC in DCA was determined from intrinsic viscosity measurements. v_2' exhibits a pronounced decrease with molecular weight up to $\bar{M}_v \sim 100 \times 10^3$ (corresponding to ~6 Kuhn segments) but tends to an asymptotic value of ~0.15 for larger molecular weights. The persistence length was found to be 100 Å (±10 Å) at 25 °C. q is larger, and v_2' is smaller, than the corresponding values previously measured for HPC in dimethylacetamide. Lattice and virial treatments of hard semirigid mesogens have been compared with experimental results. The treatments of Kuhn chains do not describe the transition from rigid to semirigid behavior below $\bar{M}_v \sim 100 \times 10^3$. The virial treatment of wormlike chains represents the upturn of v_2' below $\bar{M}_v \sim 100 \times 10^3$ but predicts too high values of v_2'. Persistence length vs. temperature data extrapolated to the nematic → isotropic temperature T°_{NI} of undiluted HPC yielded an axial ratio $x \sim 4.8$. This value is in excellent agreement with the Flory–Ronca theory, which predicts $x < 6.4$ at T°_{NI}, and is in line with only a small degree of soft interactions. This finding adds support to the previous conclusion that the large thermotropic effect in DMAc (v_2' changes from 0.35 to 1 between 20 and 210 °C) is essentially controlled by the temperature dependence of q.

In the preceding paper (part 1) we reported the phase diagram and the persistence length, q, of (hydroxypropyl)cellulose (HPC) in dimethylacetamide (DMAc).[1] The formation of the mesophase at a polymer volume fraction, v_2', ~0.35 was satisfactorily described in terms of the lattice theory[2,3] for semirigid mesogens composed of hard rods connected by flexible joints (the Kuhn chain model). This theory predicts that[2]

$$v_2' \cong \frac{8}{x_K}\left(1 - \frac{2}{x_K}\right) \tag{1}$$

where the axial ratio, x_K, of the Kuhn segment is equal $2q/d$, d being the chain diameter.

Some deviations from theoretical predictions were nevertheless observed. In particular, we noticed a small dependence of v_2' upon degree of polymerization and, also, a segregation of low and high molecular weight species in the isotropic and anisotropic phases, respectively.[1] According to the above theory,[2,3] no dependence of v_2' upon molecular weight, and no fractionation effects, should be observed. Moreover, we had to postulate a small degree of soft interactions[4,5] in order to obtain complete agreement between the experimental and calculated values of v_2'.

There are several types of semirigid chains. The Kuhn chain is a simple model easily described by the lattice theory.[2] As Flory pointed out,[6] cellulose derivatives may conform with this model since chain flexibility is essentially due to the occasional occurrence of flexible sugar rings conformers causing sudden alterations of the direction of the molecular axis.[7] When the direction of successive units deviates slightly, and in a more continuous way along the chain axis, the wormlike model[8] may offer a better approximation to the real chain. However, the theory of mesophase formation for wormlike chains[9,10] has not yet been developed to the extent of affording an interpretation of all the above-mentioned deviations. In fact, in a recent report[11] we investigated the mesophase of poly(n-hexyl isocyanate) (PHIC) in the molecular weight range where wormlike behavior prevails. Some of the problems encountered with PHIC were similar to those observed with HPC, in spite of the different type of semirigid chain involved.

Table I
Fractionation and Intrinsic Viscosity Data

sample	W^a	$[\eta]^b$	$[\eta]^c$	DP^d	$\bar{M}_v{}^d$
LF unfractionated		1.42	1.81	355	150 000
A1	0.066	0.23		47	20 600
A2	0.193	0.485		108	46 000
A3	0.333	0.73		169	73 000
A4	0.504	1.11		270	115 000
A5	0.634	1.63		414	175 000
A6	0.860	2.28		600	252 000
A7	1	2.54		677	284 000
B1	0.075	0.22	0.34	45	19 600
B2	0.190	0.485	0.60	108	46 000
B3	0.309	0.64	0.875	146	63 000
B4	0.455	1.11	1.40	270	115 000
B5	0.617	1.68	2.10	428	181 000
B6	0.767	1.80	2.20	462	195 000
B7	1	2.28	2.44	600	252 000

[a] Cumulative weight of the fraction. [b] Viscosity in EtOH at 25 °C. [c] Viscosity in DCA at 25 °C. [d] From eq 2.

In the present work we perform a more detailed analysis of the role of molecular weight and of the persistence length on the mesophase of HPC using dichloroacetic acid (DCA) as a solvent. Preliminary observations by Bedha et al.[12] indicate an extremely low value of v_2' (0.19) in DCA. This suggests that the conformation of HPC in DCA may be significantly more extended than in DMAc, an effect which is substantiated by the determination of the persistence length reported in this paper.

Experimental Section

Materials. The material and the techniques were generally similar to those described in more detail in part 1.[1] The unfractionated LF sample supplied by Hercules Inc. was the starting material. Its intrinsic viscosity, $[\eta]$, in ethanol at 25 °C was 1.42 dL/g, corresponding[13] to a $\bar{M}_v$ = 150 000. Fractionation was performed by stepwise extraction with anhydrous ethanol in n-heptane mixtures as described by Wirick and Waldman.[13] Successive extractions of dried HPC (5 g) using 200-mL mixtures, with ethanol varying between 33% and 40%, yielded six fractions. A seventh fraction comprised the residue, which was completely soluble in pure ethanol. Two independent fractionations were performed in the above manner (cf. Table I). The molecular substitution, MS, was evaluated from ^{1}H NMR spectra using a high-field instrument (CXP-300 Bruker). Spectra were obtained

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for a solution containing 5 mg of HPC in 0.5 mL of Me_2SO-d_6 at 96 °C. D_2O was later added to eliminate the contribution of OH signal. Very well resolved spectra allowed the determination of MS from the ratio of the area of the CH_3 signal of the hydroxypropyl group and the area of the anomeric proton (H-1). The density of the sample was measured pycnometrically at 25 °C, using *n*-heptane.

Intrinsic Viscosities. Degree of polymerization and molecular weights were calculated by using the relationships of Wirick and Waldman[13]

$$[\eta] = 7.2 \times 10^{-3}\mathrm{DP_w}^{0.9}$$

$$[\eta] = 2.6 \times 10^{-5}\bar{M}_{\mathrm{w}}^{0.915} \quad (2)$$

from $[\eta]$ values determined in ethanol at 25 °C (±0.05 °C) using suspended-level Ubbelohde viscometers with flow times for the solvents greater than 100 s. The flow times of solutions in ethanol did not change upon repeating the measurement after 48 h. Intrinsic viscosities in DCA were determined for the evaluation of the persistence length. Also in the case of low molecular weight fractions of HPC in DCA the flow time remained constant. However, a decrease of flow time (up to ≅1%) was detected within 1 h in the case of unfractionated and high molecular weight fractions (no. 5, 6, and 7) of HPC in DCA. To circumvent this problem, the reduced specific viscosities, η_{sp}/c, were measured as a function of time (at 15-min intervals) for samples which were allowed to dissolve for the fixed time of 1 h. The value of η_{sp}/c, extrapolated at zero time, was used for determining $[\eta]$ from the linear η_{sp}/c vs. concentration (c) plots.

Anisotropic Solutions. The concentrated solutions for liquid crystallinity tests were prepared by mixing known weights of polymer and solvent and stirring for 24 h at room temperature (~20 °C). The solutions were then observed with a polarizing microscope at room temperature. Situations observed were either the isotropic monophase or the biphasic mixture (isotropic + anisotropic). We did not extend the measurement into the region of the pure anisotropic phase (cf. seq.). Identification of the anisotropic phase as a liquid crystalline one rests on optical rotatory dispersion performed on the coexisting phases isolated from each other by centrifugation.[1] Separation was obtained after about 60 h at 44000 rpm. ORD was performed as reported elsewhere.[1] The volume fraction of the isotropic phase, ϕ, was determined by measuring the volumes of the two phases separated by centrifugation in a range of C_{p} values.

Results

Persistence Length. The evaluation of the persistence length requires a knowledge of the molecular substitution and of the polymer density necessary for assessing the chain diameter. Our NMR data yielded MS = 4 (±0.5) for the whole sample, supporting the average value used in our previous paper.[1] As previously discussed,[1] we shall not be concerned with the small nonuniformity of substitution. Our results for the density of the whole LF sample yielded ρ = 1.13 (±0.05) g/cm^3. Samuels[14] reports values of ρ = 1.17 g/cm^3 for a HPC film, ρ = 1.09 g/cm^3 for the amorphous sample, and ρ = 2.05 g/cm^3 for the crystal density. The latter value, however, appears unreasonably large.

The persistence length was determined, as previously described,[1,11] by using the Yamakawa–Fujii expression for the intrinsic viscosity–molecular weight dependence for a wormlike chain[15]

$$[\eta] = \phi L'^{3/2}/\lambda^3 M \quad (3)$$

where $L' = \lambda M/M_L$ is the reduced contour length, M_L is the mass per unit length, $\lambda^{-1} = 2q$ is the Kuhn segment (q being the persistence length), and ϕ is a function of L' and of the reduced diameter d' (tabulated by Yamakawa and Fujii). Theoretical $[\eta]$–MW curves have been calculated by using M_L = 76.7 daltons/Å, corresponding to a molecular weight of the repeating unit M_0 = 394 (MS = 4), and to a projection of the repeat unit on the chain axis L_0 = 5.14 Å.[16] The unreduced diameter, d, was allowed to vary between 12.8 Å, as reported by Werbowyj and Gray,[17] and 10.4 Å, as obtained from the equation used by Flory[6]

$$d = (M_0/\rho N_{\mathrm{A}} L_0)^{1/2} \quad (4)$$

where ρ is the polymer density (taken as 1.170 g/cm^3, the largest value reported for semicrystalline samples[14]) and N_{A} is Avogadro's number.

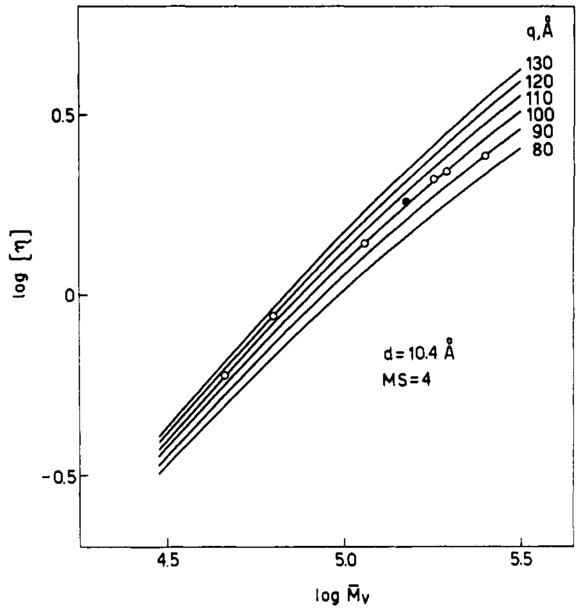

Figure 1. Full lines represent the theoretical intrinsic viscosity–molecular weight dependence for wormlike chain having the indicated value of q and d. M_L = 76.7 daltons/Å. Open points experimental values of $[\eta]$ for HPC fractions (Table I). (●), unfractionated sample. T = 25 °C.

Typical theoretical curves for d = 10.4 Å are reported in Figure 1. The experimental points represent the intrinsic viscosities of HPC fractions in DCA. The molecular weights were determined from the intrinsic viscosities in ethanol according to eq 2. Data are collected in Table I. The series of fractions A and B correspond to two independent fractionations. The data in Figure 1 indicate a persistence length of 100 Å (±10). In the case of d = 12.8 Å (unreported) a lower value of q (~95 Å) is obtained.

Mesophase Formation. The appearance of solutions having concentration C_{p} (given as g of polymer per 100 g of solution) is reported in Table II. The polymer volume fraction v_2, also in Table II, was calculated from C_{p} using the partial specific volume of HPC in DCA, $\bar{v}_2$, the specific volume of the solvent, and assuming additivity. $\bar{v}_2$, measured pycnometrically, was found to be 0.790 mL/g at 25 °C. A plot of v_2 vs. molecular weight is given in Figure 2. Open points correspond to isotropic solutions and black points to biphasic mixtures. The half-blocked points correspond to incipient phase separation. The curve drawn between these points represents the variation of the critical v_2' with molecular weight. Confirming the observation of Bedha et al.,[12] v_2' attains rather low values in DCA. In Figure 2 we also include, for comparison, the smoothed-out v_2'–molecular weight dependence previously determined[1] for HPC in DMAc and in H_2O.

As indicated in the Experimental Section, high molecular weight fractions (no. 5, 6, and 7) and unfractionated HPC exhibited some degradation in DCA. This problem was circumvented in the case of the determination of q by limiting to 1 h the time of preparation of solutions and by

Table II
Appearance of HPC–DCA Mixtures 24 h after Preparation at Room Temperature

sample	$\bar{M}_v$	C_p, g/100	v_2	appearance
LF unfractionated	150000	12.50	0.150	iso
		12.86	0.154	iso
		13.30	0.159	iso + aniso
A1	20600	15.65	0.186	iso
A1	20600	19.89	0.234	iso
B1	19600	24.97	0.291	iso + aniso
B1	19600	29.97	0.345	iso + aniso
A2	46000	18.18	0.215	iso
A2	46000	20.62	0.243	iso + aniso
A3	73000	13.81	0.166	iso
B3	63000	15.20	0.181	iso
B3	63000	16.60	0.197	incipient phase separation
A4	115000	13.27	0.159	incipient phase separation
A5	175000	12.76	0.153	incipient phase separation
B6	195000	12.30	0.148	iso
A6	252000	12.65	0.151	iso
B7	252000	13.10	0.157	iso + aniso
A7	284000	12.87	0.154	iso + aniso

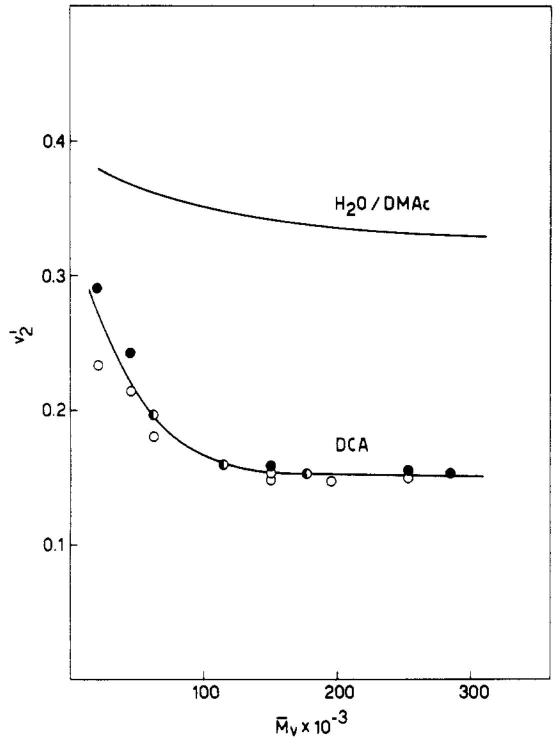

Figure 2. Variation of the critical volume fraction for incipient appearance of the mesophase at 20 °C for HPC in DCA (data points from Table II). The v_2'–MW dependence previously[1] obtained in H_2O and DMAc is also illustrated.

extrapolating the viscosities at zero time. However, this approach could not be applied to concentrated solutions when a minimum equilibration time of 24 h had to be applied (the unreliability of longer equilibration times prevented a more detailed study[1] of concentrated solutions exhibiting the pure anisotropic phase). From the point of view of the v_2' vs. molecular weight dependence illustrated in Figure 2, it is, however, a fortunate circumstance that the data corresponding to fractions no. 5, 6, and 7 and to the unfractionated sample fall in the region where v_2' tends to an asymptotic behavior. To confirm that degradation effects could not have greatly affected the results, we analyzed the molecular weight of aliquots precipitated from a concentrated solution of unfractionated LF in DCA (C_p = 23.5%). Aliquots were precipitated at various times following the mixing of HPC and DCA. After 24 h, we found $\bar{M}_v = 126 \times 10^3$, which can be compared with the value (150×10^3) obtained directly from dilute solution (cf. Experimental Section).

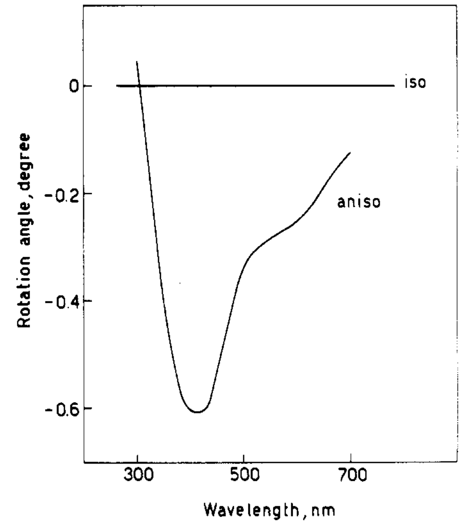

Figure 3. Optical rotation vs. wavelength for sample LF in DCA at 25 °C. Iso and aniso indicate coexisting phases separated by centrifugation from a solution having overall C_p = 15.3%. 0.01-mm-thick quartz cell.

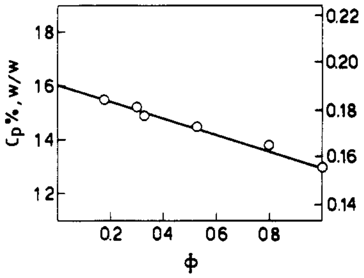

Figure 4. Variation of the volume fraction of isotropic phase with the overall HPC concentration. T = 20 °C.

To confirm that the phase coexisting with the isotropic is indeed a cholesteric one, we present the ORD data in Figure 3. The specific rotation of the isotropic phase is vanishing small. The coexisting phase isolated by centrifugation exhibits instead a considerable negative rotation and a λ_0 (wavelength at which the rotation angle is 0) of ~300 nm. We note that the value of λ_0 is smaller than previously reported.[1,17] However, we observed a considerable scatter of ORD data by repeating the determination even with a fresh solution. Similar effects on the ORD of cholesteric polymers have been observed by others.[18-20]

Finally, an evaluation of the width of the biphasic gap was performed by determining the compositions v_2' and v_2'' of the conjugated phases from the variation of ϕ with C_p illustrated in Figure 4. From the values of C_p at ϕ = 0 and ϕ = 1, the limiting value of the ratio v_2''/v_2' is found to be ≅ 1.2. As in the case of HPC in DMAc, this ratio is considerably smaller than observed for other polydisperse systems.[1]

Discussion

The determination of chain rigidity is a fundamental step for the interpretation of mesophase formation. In the previous paper[1] we compared values of q obtained by using several methods. For HPC in DMAc, we reported q_{YF} = 65 Å, q^0_{BD} = 70 Å, and q^0_{CL} = 65 Å respectively from the Yamakawa and Fujii method, the Benoit–Doty[21] treatment of light scattering data for wormlike chains, and the Gaussian coil limit. The latter two results are corrected

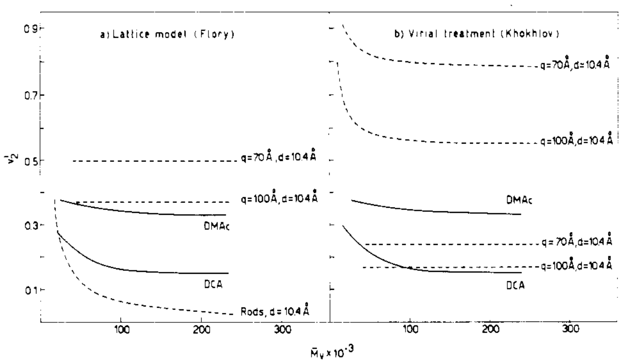

Figure 5. Full lines appearing in (a) and (b) are the experimental variation of v_2' with molecular weight for HPC in DCA and in DMAc (cf. Figure 2). (a) Dashed lines: theoretical variation of v_2' with MW calculated from the lattice theory assuming fully extended chains (lower curve) or Kuhn chains (horizontal lines). (b) Dashed lines: theoretical variation of v_2' with molecular weight calculated from the virial treatment of Kuhn chains (lower horizontal line) or wormlike chains (upper curve). Assumed values of d and q are indicated.

for excluded volume effects since unperturbed dimensions were used. The Yamakawa–Fujii result was lowered to ~50 Å by an approximate correction for excluded volume effects. Saito[22] has recently presented a detailed comparison of persistence lengths for cellulose and its derivatives. In analogy to our results, he finds that in some cases $q^0_{\mathrm{BD}} \cong q^0_{\mathrm{CL}} \cong q_{\mathrm{YF}}$. In other cases, however, q_{YF} is smaller than q^0_{BD}, and q_{YF} is generally smaller than q_{BD} (the Benoit–Doty result uncorrected for excluded volume). However, both Saito[22] and our results[1] indicate that the excluded volume correction is a relatively small one. The observation that $q_{\mathrm{BD}} > q_{\mathrm{YF}}$ is attributed by Saito to the neglect of a free draining effect in the Yamakawa–Fujii theory. Saito appropriately uses the hydrodynamic diameter d_{h} in calculating q_{YF}. According to his results, d_{h} is significantly larger (up to a factor of 2) than the crystallographic diameter. The evaluation of d_{h} is, however, a rather complex one and entails the possibility of considerable error.[22,23] For HPC, also the crystallographic diameter (12.8 Å)[17] appears too large and leads to a too low value of the crystal density.[24] Probably the best estimate of the "unsolvated" diameter of HPC chains is close to 10.4 Å as obtained from eq 4. Our use of such a diameter yields values of q_{YF} which may be somewhat larger than obtained by using a larger d_{h} diameter. However, in view of Saito's[22] observation that inclusion of the free draining effect increases q_{YF} to a value closer to q_{BD}, the error attending the use of the diameter calculated by eq 4 tends to be offset by inaccuracies in the Yamakawa–Fujii theory. In support of these considerations, our previous results for HPC in DMAc indicate $q_{\mathrm{YF}} = 65$ Å when $d = 12.8$, and $q_{\mathrm{YF}} = 68$ Å when $d = 10$ Å. The latter figure is in excellent agreement with our value of q^0_{BD} (70 Å).[1] q^0_{BD} is regarded as the most reliable estimate of the unperturbed persistence length.[22] The effect of other corrections has been discussed elsewhere.[1,11]

The experimental dependence of v_2' upon molecular weight is compared with theoretical predictions in Figure 5. Flory's lattice treatment is considered in Figure 5a. The broken horizontal lines were calculated by using eq 1 and relevant values of persistence length and diameter. Note that the diameter affects not only the values of q but also, and to a larger extent, the axial ratio appearing in eq 1. As discussed above, for HPC in DCA our best estimate is $d = 10.4$ Å and $q = 100$ Å. To represent HPC in DMAc[1,16] we use $d = 10.4$ Å and $q = 70$ Å. Figure 5a reveals that the Kuhn model is defective in two respects. First, it does not predict the pronounced upturn of v_2' when MW $\lesssim$ 100 000 (corresponding to a chain containing less than 6 Kuhn segments; the molecular weight of a Kuhn segment 220 Å long is ~16 000). Second, the asymptotic value of v_2' in the Kuhn limit ($L \gg q$) is *smaller* than predicted from eq 1 for both DCA and DMAc. Equation 1 does, however, illustrate the occurrence of an asymptotic behavior on the v_2' vs. molecular weight dependence. Although it is seen that chain diameter plays a rather important role, it does not appear, for the reasons discussed above, that it could be lowered (and q increased) to the extent of fitting the data with eq 1. As previously discussed, agreement with the lattice theory could be obtained by postulating the occurrence of soft interactions.[1] When[1] the Warner and Flory theory[25] is used, a T^* parameter on the order of 100 K would be required to secure agreement between calculated and experimental v_2' for DMAc.[1] Using Figure 3 of the Warner and Flory paper,[25] it is easy to verify that for DCA agreement between calculated ($q = 100$ Å, $d = 10.4$ Å) and experimental data requires a $T^* \sim 180$ K.

An alternative justification for the failure of eq 1 to represent the asymptotic limit of v_2' is the occurrence of aggregation. This effect has been often mentioned, but seldom explored. In a forthcoming publication[26] we shall analyze the role of aggregation for the system cellulose–DMAc/LiCl.[20] Also included in Figure 5a is the theoretical variation of v_2' with molecular weight for rodlike molecules[6] (obtained from eq 1 using the contour length of the whole molecule to calculate the axial ratio x). HPC in DCA exhibits a crossover from rigid to semirigid behavior at $\bar{M}_v$ ~20 000 (corresponding to ~2.5 persistent units). Note that the less rigid chain in DMAc exhibits an upturn of v_2' at lower molecular weight.

Comparison of experiments with the virial theory is illustrated in Figure 5b. The broken horizontal lines were calculated from the relation

$$v_2' = 3.25/x_{\mathrm{K}} \tag{5}$$

obtained by Grosberg and Khokhlov[27] by applying the Onsager procedure to a Kuhn chain. The limiting value of v_2' in DCA is now close to that predicted from eq 5, in line with the general result that values of v_2' calculated from virial theories are smaller than those from the lattice treatment. Inclusion of soft interactions would lead to poorer agreement between experiment and the virial theory for Kuhn chains. The two dashed curves in Figure 5b were calculated from the equation[9]

$$v_2' = \frac{d}{2q}\left[\frac{3.34 + 11.3L/2q + 4.06(L/2q)^2}{(L/2q)(1 + 0.387L/2q)}\right] \tag{6}$$

derived by Khokhlov and Semenov[9] from the virial treatments of wormlike chains. The trend of v_2' with molecular weight is qualitatively represented by eq 6. However, the actual values of v_2' are much smaller than predicted. Inclusion of soft interactions should improve the performance of eq 6.

None of the above theories quantitatively represents the experimental behavior. If, as suggested below, soft interaction occurs, Flory's treatment offers the best approximation. Nevertheless, the Kuhn chain model fails to predict the upturn of v_2' when MW $\lesssim$ 100 000, and the virial treatment of wormlike chains yields too high values of v_2'. Also in the case of PHIC, which may better conform to the wormlike than to the Kuhn model, we did not obtain quantitative agreement between experiment and theory.[11] However, in the latter case inclusion of soft interactions

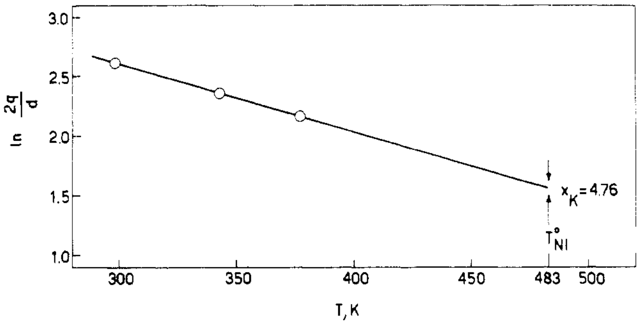

Figure 6. Variation of the axial ratio of the Kuhn segment ($2q/d$) with temperature for HPC in DMAc.

would have improved only the performance of eq 6. The behavior of other types of semirigid polymers (rigid rods connected by flexible sequences) will be presented at a later date.[28]

Due to the problem of degradation, the effect of temperature on the nematic → isotropic transition was not investigated for the HPC–DCA system. For HPC in DMAc it was shown[1] that the large thermotropic effect is essentially controlled by the variation of persistence length with temperature. The effect of soft interactions, which is the prevailing one for low molecular weight liquid crystals,[29,30] played only a minor role. Recently Seurin et al.[31] have shown that for HPC the variation of v_2' with T could be followed up to $v_2 = 1$. The T°_{NI} transition temperature for the pure polymer was ~210 °C. In Figure 6 we present an extrapolation of our previous persistence length–temperature data[1] to 210 °C (the data have been revised taking $L_0 = 5.14$ Å[16] and $d = 10.4$ Å, and a point yielding $q = 45$ Å at 104 °C has recently been determined). The extrapolated axial ratio is $x_K \cong 4.8$. This result is in very good agreement with the Flory and Ronca theory[4] and supports the possible occurrence of a small degree of soft interaction for HPC. According to the latter theory, for a pure substance, x should be ≤ 6.4 at T°_{NI}. A value of $x < 6.4$ indicates occurrence of soft interactions. From Figure 1 of the Flory and Ronca paper, a value of $T^* \cong 150$ is obtained when $x = 4.8$ and $T^\circ_{NI} = 210$ °C. This figure is rather close to the values of T^* postulated above following an alternative approach. It supports the conclusion that the variation of v_2' with temperature is essentially controlled by the temperature dependence of q. A more detailed analysis of the relative role of soft interactions and of the temperature-dependence of persistence length on the thermotropic behavior of polymers will be presented elsewhere.[28] ten Bosh et al.[32] have also considered the inclusion of the latter dependence on the mean-field[30] theory. Application of their theory to HPC in DMAc has been discussed by Seurin et al.[31] A new experimental observation[31,33] concerns the dependence of T_{NI} upon molecular weight which seems to persist to larger DP than observed for thermotropic polyesters.[34]

Some results recently reported for cellulose derivatives should be commented. Meeten and Navard[35] investigated cellulose triacetate in trifluoroacetic acid and suggested that a coil → helix transition takes place at v_2'. They base this suggestion on the supposition that a biphasic region does not occur for cellulose and its derivatives and that the rigidity of these compounds is due to a network of intramolecular hydrogen bonds. None of these suppositions is correct.[1,7] Dayan et al.[36] investigated cellulose acetates in various solvents and concluded that Flory's eq 1 represented the experimental behavior for small L/q, while an earlier Flory's theory[37] for semiflexible chains represents the behavior at large L/q. However, they improperly used eq 1, calculating the axial ratio as q/d (rather than $2q/d$). The unsuitability of the earlier theory for semiflexible chains[37] has been discussed[6] by Flory. Patel and Gilbert[38] investigated cellulose triacetate in mixed solvents. In analogy to our results, they find that the v_2' vs. molecular weight curve crosses the theoretical dependence for rigid rods ($x = L/d$) and tends to an asymptotic limit where v_2' is greater than predicted from the latter theory. However, they concluded that the asymptotic limit of eq 6[9,11]

$$v_2' = 10.48/x_K \qquad (7)$$

represents the experimental behavior at low DP. Clearly eq 7 could only be applied to the asymptotic limit of semirigid chains, and a knowledge of the relevant persistence length is mandatory before comparison between experiment and theory is performed. Finally, Bhadani et al.[33] investigated the benzoic acid ester of HPC in acetone and toluene in which solvents they determined the persistence length. The trend of their v_2' vs. molecular weight dependence, and the lack of correlation between v_2' and q,[11] are similar to our results. They find that the experimental data fall between the curves predicted by eq 5 and 6. Note, however, that these two equations represent the two extreme results obtained from current treatments of semirigid chains. The lattice theory of Kuhn chains yields results intermediate between these two extremes and could therefore afford a relatively better representation than the virial treatment.

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Thermomechanical Behavior of Interacting Tie Molecules in Semicrystalline Polymers

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ABSTRACT: An atomistic model of two interacting tie molecules connecting a pair of parallel crystalline lamellae is studied by computer simulation. The tie molecules are found to be in tension at large interlamellar spacing, to be under compression at small spacing, and to have a zero-force intermediate equilibrium configuration. Interaction between the atoms of the two tie molecules, represented here by a Lennard-Jones potential, is found to have little effect on the force–spacing relation.

I. Introduction

An important structural feature of semicrystalline polymers is the existence of crystalline lamellae that are interconnected by a large number of long-chain molecules as shown schematically in Figure 1. It is believed that these molecules, referred to as tie molecules, along with cilia and loops, form an amorphous zone between the lamellae and, if the temperature is not too low, they are free to execute thermal motion as envisioned in the theory of rubber elasticity. Recent work[1] points to the importance of these amorphous regions and their tie molecules in the understanding of crack propagation in semicrystalline polymers.

In attempting to understand the thermomechanical behavior of these amorphous interlamellar layers, a natural question that arises is the effect of the constraints that the lamellae impose upon the motion of the atoms of the tie molecules. This problem has been treated theoretically by a number of authors.[2–8] Recently, the behavior of a model that can be interpreted as representing a single tie molecule has been studied by computer simulation using the method of Brownian dynamics.[9] In this model, two types of atomic interaction were distinguished: (i) the covalent interactions between neighboring atoms along the tie molecule and (ii) the noncovalent interactions between nonneighboring atoms and between the tie-molecule atoms and the bounding lamellae. It was found that the covalent interactions resulted in a tensile force tending to pull the lamellae together. This is the usual entropic spring effect. On the other hand, the noncovalent interactions between the tie-molecule atoms and the bounding lamellae exerted a pressure upon them, tending to push them apart. The tensile force increases with increasing interlamellar spacing while the pressure decreases; an equilibrium spacing is found at which the two forces just balance.

The work just described[9] treated the behavior of a single tie molecule. The purpose of the present paper is to study the effect of interaction between tie molecules. The model we use is described in section II. Computer simulation results are presented in section III, and section IV contains conclusions and directions for future work.

II. Model System

The model represents two tie molecules that connect the same pair of crystalline lamellae, Figure 2. Each molecule corresponds to a freely jointed chain with N bonds. The positions of the atoms of chain 1 are denoted by $\mathbf{x}_j$, while the positions of those of chain 2 are denoted by $\mathbf{y}_j$, $j = 0, 1, ..., N$. The end atoms of each chain are fixed in the lamellae, which are parallel and at a distance r, and the fixed atoms of the chains are at a distance c from each other. That is, in terms of the coordinate system shown, the (ξ, η, ζ) coordinates of the end atoms are as follows:

$$\mathbf{x}_0\colon\ (0, 0, 0), \qquad \mathbf{y}_0\colon\ (c, 0, 0) \tag{1a}$$

$$\mathbf{x}_N\colon\ (0, r, 0), \qquad \mathbf{y}_N\colon\ (c, r, 0) \tag{1b}$$

The covalent interactions between neighboring atoms along each chain are modeled by the potentials

$$V_c(\mathbf{x}_0, ..., \mathbf{x}_N) = \frac{1}{2}\kappa_c \sum_{j=1}^{N} (|\mathbf{x}_j - \mathbf{x}_{j-1}| - a)^2 \tag{2}$$

for chain 1, and an analogous potential for chain 2, where a is the unstretched bond length and κ_c is a large spring constant that represents the covalent bonds.

In addition to these covalent interactions, noncovalent interactions between all of the noncovalently bonded atoms of the system are modeled by a Lennard-Jones potential

$$V_{\text{L-J}}(\rho) = 4\epsilon\left[\left(\frac{\sigma}{\rho}\right)^{12} - \left(\frac{\sigma}{\rho}\right)^{6}\right] \tag{3}$$

where ρ is the distance between any pair of atoms, and σ and ϵ are parameters characterizing the potential, with σ denoting the effective hard-core radius and ϵ the well depth.

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