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Registry No. Cellulose, 9004-34-6; LiCl, 7447-41-8; DMAc, 127-19-5.

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Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 4. Cellulose in *N,N*-Dimethylacetamide–Lithium Chloride

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ABSTRACT: A study of the solubility and mesophase formation of cellulose in *N,N*-dimethylacetamide (DMAc) containing from 2% to 10% LiCl is reported. The cellulose samples and the method of preparation of the solutions are those described in the preceding paper where a study of dilute solution parameters and of aggregation was reported. The solubility of all samples increases with LiCl concentration. However, for several samples the solubility is too low to allow the attainment of the critical concentration for mesophase formation. Aggregated samples prepared by acid hydrolysis never attain the mesophase. The possibility of observing the latter at high LiCl content is confined to samples which show molecular dispersion in dilute solution and DP below ~600. Even in these cases the cholesteric phase is often metastable with respect to the crystal. The critical concentration increases with LiCl content. From the preceding paper we know that irregular patterns of association occur at these concentrations. The interpretation of this complex situation in terms of independent or associated particles is discussed.

In the first two papers of this series we investigated the liquid crystallinity of (hydroxypropyl)cellulose (HPC) in *N,N*-dimethylacetamide (DMAc)[1] and in dichloroacetic acid (DCA).[2] The results could be interpreted in terms of existing theories for semiflexible chains composed of rigid segments connected by flexible joints.[3] Basically, the HPC/DMAc system approached the behavior expected for independent and monodisperse rods[3] having an axial ratio corresponding to the Kuhn statistical link. The occurrence of a small degree of soft interaction[4] had to be postulated in order to obtain complete agreement between the theoretical and experimental values of the critical volume fraction.

In the accompanying paper[5] (part 3) we reported a light scattering and viscosity study of unsubstituted cellulose dissolved in DMAc + LiCl. Cellulose does not present the problems associated with the nonuniform substitution of HPC and also appears to be a somewhat more rigid polymer than the latter. However, the above results show that considerable aggregation occurs depending, in a nonanticipated manner, upon sample preparation, molecular weight, LiCl concentration, and polymer concentration.

Studies with cellulose, particularly with its concentrated solutions, have been hampered by its poor solubility. Exotic solvents such as *N*-methylmorpholine *N*-oxide,[6,7] trifluoroacetic acid + chlorinated alkanes,[8] liquid ammonia + NH_4SCN,[9] and DMAc + LiCl[10] have been reported to dissolve cellulose at concentrations at which the mesophase may be formed. For some of the above solvents, however, degradation is appreciable, while for others the occurrence of a true mesophase was not fully investigated. In no case was an attempt made to correlate the critical volume fraction with dilute solution data obtained in the same solvent. In this paper we report a study of mesophase formation of cellulose in DMAc + LiCl and discuss the problems associated with the occurrence of aggregation.

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Table I
Characteristics of Samples Investigated

sample	supplier	$[\eta]$,[a] dL/g	DP	M_v	$[\eta]$,[b] dL/g
G	Snia Fibre[c]	0.63	102	16 500	
D	Avicel	0.92	155	25 100	
A	Snia Fibre[d]	1.61	288	46 700	3.0
L	Snia Fibre[d]	1.62	290	47 000	3.0
C	Buckeye Corp[e]	2.40	449	72 800	4.9
I	SSCC, Milan[d]	3.45	460	74 500	5.0
E	Snia Fibre[f]	3.85	760	123 000	7.5

[a] In 0.5 M cupriethylenediamine at 25 °C. [b] In DMAc–5% LiCl at 25 °C. [c] Sample E, hydrolyzed with HCl. [d] Cellulose II regenerated. [e] V68 prehydrolyzed Kraft. [f] Mischia latifoglia Kraft.

Preliminary data concerning the phase diagram have already been reported.[11] The cellulose/DMAc + LiCl system was described in a patent by Turbak et al.,[10] who showed that no appreciable degradation occurs. Although they did not prove the occurrence of a mesophase, spinning from concentrated solutions produced ultrahigh-modulus fibers. Our own study of fiber spinning from the present system will be presented at a later date.

Experimental Section

Materials. Seven cellulose samples similar to the corresponding ones described in the preceding paper[5] were used. Their characteristics are collected in Table I. Molecular weights were evaluated from the intrinsic viscosities[5] measured in 0.5 M cupriethylenediamine (CED) using the relationship[12]

$$[\eta] = 1.01 \times 10^{-4} M_w^{0.9} \tag{1}$$

Solutions in CED, obtaining by stirring for 24 h small pieces of dried cellulose, exhibit molecular dispersion and virtual absence of degradation.[5]

Phase Diagram. Solutions in DMAc/LiCl were prepared following the method described by Turbak et al.,[10] as described in more detail in the preceding paper.[5] Polymer concentration, C_p, is given as grams of cellulose per 100 g of ternary solution. C_p varied between ~0.3% and 17%. Salt concentration, C_s, is given as grams of LiCl per 100 g of binary (LiCl + DMAc) solution. C_s varied between ~2% and 10%. Virtual absence[10] of degradation of cellulose in DMAc/LiCl solutions was confirmed[5] by measurement of $[\eta]$ in CED on samples which had been reprecipitated from the former solvent.

Solutions were observed under the polarizing microscope at room temperature (~20 °C) at various times (up to 3 months) following the preparation of the solutions. Situations observed were (i) isotropic solutions, (ii) isotropic solutions containing a solid in the form of small fibers, (iii) solutions containing an isotropic and a birefringent phase, and (iv) solutions of the latter type containing also undissolved fibers. In no case was a single anisotropic phase observed. The birefringent phase observed in case iii was separated from the isotropic one for a solution with C_p = 11.5% and C_s = 7% in the following way: 14 mL of the latter solution was centrifugated at 44 000 rpm at 20 °C as previously described.[1] After about 350 h, the birefringent phase sedimented at the bottom of the polyallomer tube and occupied about 10% of the total volume. However, even after this extensive centrifugation, a little birefringent phase remained above the boundary, its amount increasing as the boundary was approached. The clear part of the isotropic phase and the bottom part of the anisotropic one were separated. From aliquots of these phases, the polymer was precipitated and the corresponding C_p'' (anisotropic) and C_p' (isotropic) were determined along with the respective intrinsic viscosities.

Optical rotatory dispersion was performed on the phases separated by centrifugation (the large amount of LiCl prevented circular dichroism measurements). The rotation angle was measured by using a Jasco ORD UV/5 spectropolarimeter between 500 and 700 nm at room temperature.[1]

The polymer partial specific volume, $\bar{v}_2$, was determined pycnometrically at 25 °C using sample A. In DMAc + 3.5 LiCl, $\bar{v}_2$ = 0.615 mL/g. In DMAc + 5% LiCl, $\bar{v}_2$ = 0.621 mL/g. The molar volume V_1 of DMAc + 5% LiCl was found to be equal to 1.0187 mL/g. The latter data were used to convert C_p into polymer volume fraction.

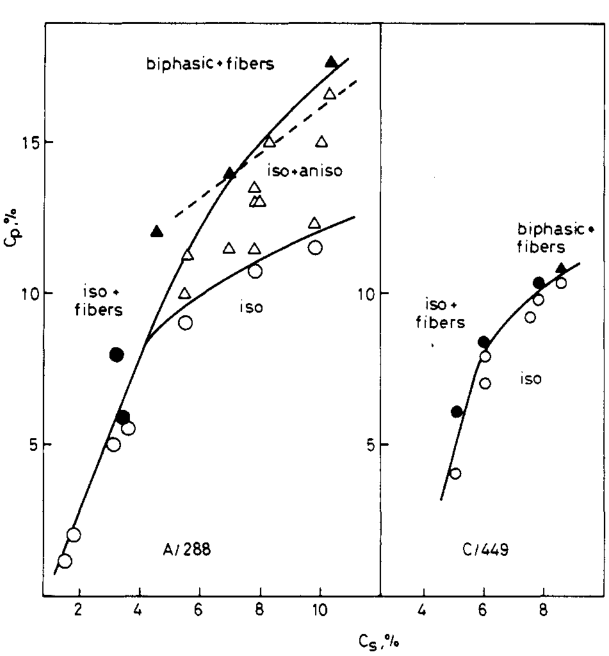

Figure 1. Phase diagrams for cellulose, samples A and C, in DMAc with varying LiCl concentration at 20 °C: (○) isotropic solution; (●) isotropic solution + solid; (△) biphasic solution; (▲) biphasic solution + solid. Broken line indicates the upper limit of the biphasic gap if $C_p''/C_p' \sim 1.3$.

Results and Discussion

The phase diagram for samples A and C are plotted in Figure 1 as polymer concentration vs. LiCl concentration. The curves represent the boundaries between the various phases and the experimental points indicate the appearance of the solutions a long time after preparation. The dotted line, describing the composition of the pure anisotropic phase for sample A, was drawn by taking the ratio C_p''/C_p' of the composition of the pure anisotropic phase and isotropic phase equal to 1.33. This ratio is obtained from the results of the determination of C_p' (=11.0) and C_p'' (=14.7%) in the case of a solution having overall C_p = 11.5% and C_s = 7% (cf. Experimental Section). This ratio, describing the width of the biphasic gap,[3] is larger than that determined for HPC in DMAc and DCA[1,2] and that expected for a rather narrow molecular weight distribution.[1,13,14,15] (A more extensive discussion of these relationships and of theories relating the critical volume fraction to the axial ratio may be found in ref 15.) It is evident from Figure 1 that for sample A the solubility line is rather close to the line describing the composition of the anisotropic solution. Therefore, formation of the anisotropic phase is associated with crystallization.[15] Situations in which the solubility line crosses the narrow region have been described by Balbi et al.,[16] Papkov,[17] and Ciferri and Krigbaum.[18] Since the rate of nucleation of the liquid crystal is generally larger than that of the crystalline material, the former may be observed even under metastable conditions. In the case of sample C, the anisotropic phase is not observed unless extremely high C_s (>8%) are used. It is seen that the solubility of sample C is considerably smaller than for sample A, preventing the former from attaining the critical concentration for mesophase formation. We note that for both samples the solubility is increased by increasing C_s.

A closer inspection of Figure 1 reveals that the solubility difference between samples A and C decreases with C_s (the difference is ~100% at C_s = 5% and ~50% at C_s = 8%).

Table II
Axial Ratios

		$v_2'^{b}$		$x_{\text{exptl}}{}^{c}$				
sample (DP)	L,[a] Å	$C_s = 5\%$	$C_s = 7.8\%$	$C_s = 5\%$	$C_s = 7.8\%$	$x = L/5.8$[d]	$x = 2q/5.8$[e]	$x = L/17$[f]
A (288)	1480	0.058	0.079	137	99	255	43	87
L (290)	1490		0.082		96	257	43	88
I (460)	2364		0.066		120	408	43	139

[a] Contour length = DP × 5.14 Å. [b] Data from Figure 3. [c] Derived by using eq 2. [d] Axial ratio corresponding to rod of length L. [e] Axial ratio corresponding to q = 125 Å. [f] Axial ratio corresponding to aggregate of length L and d = 17 Å.

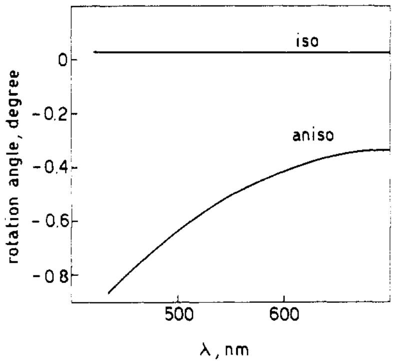

Figure 2. Optical rotation vs. wavelength for coexisting isotropic and anisotropic layers of cellulose in DMAc + 7% LiCl separated by centrifugation. Overall C_p is 11.5%. 0.01-mm-thick quartz cell.

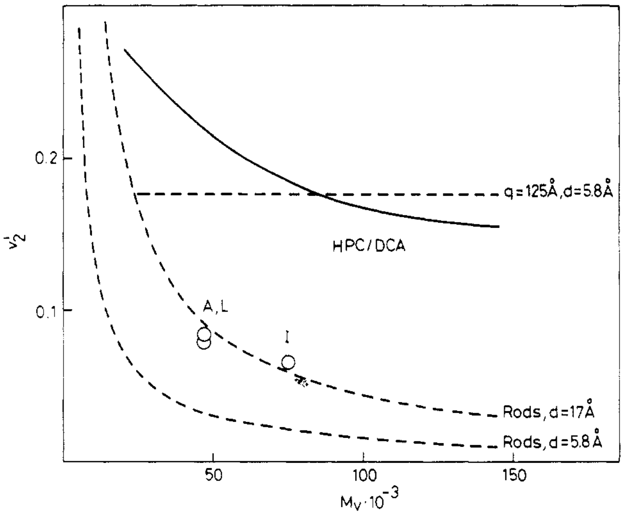

Figure 3. Variation of the critical volume fraction for mesophase formation at 20 °C for cellulose in DMAc + 7.8% LiCl (data points refer to samples A, L, and I). The dashed lines represent theoretical variations of v_2' with M_v calculated by using eq 2 with $x = L/d$ (rods) and $x = 2q/d$. The v_2'-M_v dependence previously observed for HPC in DCA is included.

Thus, the lower solubility of sample C with respect to sample A cannot be entirely ascribed to its higher DP. In fact, we found (unreported) that samples such as D and G having a DP smaller than sample A (Table I) had very low solubility and could not attain the critical concentration. From the results in the accompanying paper[5] we know that hydrolyzed samples such as C, D, and G may exhibit stable aggregation even at $c \to 0$. In contrast, samples such as A, L, I, and E (not subject to acid hydrolysis) exhibited molecular dispersion at $c \to 0$. Sample C was peculiar because, when prepared at $C_p > 3\%$, it exhibited aggregation at $C_s = 5\%$ and molecular dispersion at $C_s = 7.8\%$. It thus appears that the solubility of cellulose in DMAc/LiCl is conditioned by both aggregation and DP, making it unlikely for both aggregated samples and samples exhibiting molecular dispersion, but too large DP (e.g., sample E), to attain the critical concentration.

In the case of sample A, the proof that the phase separated by centrifugation is indeed a cholesteric one is given by the ORD data reported in Figure 2. Here, while the rotation of the pure isotropic phase is extremely small, the pure anisotropic phase exhibits a large negative rotation typical of cholesteric mesophases. The effect observed is of the same order of magnitude as that observed with HPC.[1,2] We note that often the shape of the ORD curve exhibited considerable irreproducibility, probably due to incomplete equilibrium or too thick samples.

Other features of the phase equilibria include the determination of $[\eta]$ for the coexisting isotropic and anisotropic phases (overall $C_p = 11.5\%$; $C_s = 7\%$). The results, $[\eta]_{\text{aniso}} \simeq [\eta]_{\text{iso}} \simeq 1.30 \pm 0.05$ g/dL, fail to reveal the selective enrichment of high molecular weight species in the anisotropic phase which was observed with other systems.[1,2,16]

The dependence of the critical volume fraction v_2' upon the DP of cellulose in DMAc + 7.8% LiCl is exhibited in Figure 3. The only samples which could be included are regenerated cellulose II (samples A, L, and I) having a relatively low DP (sample C exhibited some evidence of mesophase only at $C_s > 7.8\%$). In Figure 3 we have included the previously reported[2] behavior of semirigid HPC in DCA to show the considerable difference between the critical volume fraction of HPC and cellulose. The behavior of cellulose is closer in several respects (including poor solubility and LiCl effect) to that observed with rigid poly(p-benzamide).[16]

To describe the various theoretical curves represented in Figure 3, we explore the correlation between the critical concentration and axial ratio. The critical concentration C_p' increases with salt content in analogy with the case of poly(p-benzamide).[16] Sample A, for instance (cf. Figure 1), at $C_s = 5\%$ has $C_p' = 9.2 \pm 0.3\%$, which corresponds to a polymer volume fraction $v_2' = 0.058 \pm 0.002$. At $C_s = 8\%$, C_p' is between 10.8% and 11.3% or $v_2' = 0.079 \pm 0.002$. Using the relationship[3,19]

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

we can evaluate the apparent axial ratio of cellulose which conforms with the hard rod theory.[19] At $C_s = 5\%$, we obtain $x = 137$ and at $C_s = 8\%$, $x = 99$. These data, and similar evaluation of x for the samples in Figure 3, are included in Table II.

In previous work, values of x have been determined a priori from either the contour length (for rods) or the persistence length (for semirigid chains) in the assumption that molecular dispersion prevailed.[1,2,15] In view of the association and aggregation phenomena occurring in the present system,[5] it is appropriate to consider x as a parameter to be determined using eq 2, as indicated above, and then compared with various models of molecularly dispersed and aggregated species. Assuming a rodlike model and nonaggregated chains, the axial ratio is simply the contour length L divided by the chain diameter d. On

Table III
Persistence Length Data

sample (DP)	L,[a] Å	$\langle R_G^2\rangle^{1/2}$,[b] Å	q_{CL},[c] Å	q_{BD},[d] Å	q_{YF},[e] Å
C (449)	2308	375 ± 20%	117–(263)	140–(420)	110 ± 10
I (460)	2364	400 ± 20%	130–(292)	160–(500)	110 ± 10
E (760)	3906	490 ± 20%	118–(265)	130–(330)	110 ± 10

[a] Contour length = DP × 5.14 Å. [b] From ref 5. [c] Using eq 4. [d] Using eq 5. [e] From Figure 4.

the basis of the density of rayon[20a] (ρ = 1.52 g/cm^3), the diameter, calculated according to[13]

$$d = (M_0/\rho N_A L_0)^{1/2} \qquad (3)$$

where L_0 is the projection of the residue unit on the chain axis, turns out to be 5.8 Å. (The density of cellulose II[20b] from X-ray analysis is 1.6 g/cm^3, corresponding to d = 5.7 Å.) Results, included in the fifth column of Table II and represented by the lower line in Figure 3, show that this model is untenable.

The persistence length can be evaluated by using the light scattering and viscosity data determined in the accompanying paper[5] under conditions in which molecular dispersion occurs. The intrinsic viscosities in DMAc + 5% LiCl listed in Table I for the samples investigated here correspond to molecularly dispersed cellulose (data were obtained when $c \rightarrow 0$ and C_p was smaller than the value at which stable aggregation occurs[5]). These data are compared in Figure 4 with theoretical $[\eta]$–M_w curves calculated according to the theory of Yamakawa and Fujii[21] for wormlike cylinders

$$[\eta] = \Phi L'^{3/2}/\lambda^3 M \qquad (4)$$

where $L' = \lambda M/M_L$ is a reduced contour length (M_L being the mass per unit length), $\lambda = 1/2q$, and Φ is a function of L' and the reduced cylinder diameter d' tabulated by Yamakawa and Fujii. M_L was taken to be equal to 31.5 daltons/Å (corresponding to a residue vector of 5.14 Å[22,23]). The unreduced diameter d was allowed to vary[20] between 4.5 and 6.0 Å. The experimental points in Figure 4 suggest q_{YF} = 110 ± 10 Å. Evaluation of the possible errors on q from the diameter and other sources, as described elsewhere,[1] gave indeterminations which do not exceed the indetermination caused by the scatter of the data point in Figure 4.

Alternative determinations of q are possible using the light scattering data.[5] For samples C, I, and E the radii of gyration determined in the preceding paper[5] are reported in Table III (third column). They are affected by a large indetermination, on the order of 20%. From $\langle R_G^2\rangle$, the persistence length in the Gaussian coil limit is given by

$$q_{CL} = 3\langle R_G^2\rangle/L \qquad (5)$$

Values of q_{CL} are reported in the fourth column of Table III. Using the Benoit–Doty treatment of wormlike chains[24] it also possible to obtain the persistence length, q_{BD}, according to

$$\langle R_G^2\rangle = q^2\{\tfrac{1}{3}(L/q) - 1 + (2q/L) - (2q^2/L^2)[1 - \exp(-L/q)]\} \qquad (6)$$

The results of this calculation are reported in the fifth column of Table III. The comparison of the various estimates of q collected in Table III reveals that $q_{YF} < q_{CL} < q_{BD}$. This result is at variance with out data for HPC.[1,2] However, Saito[25] found that in several cases $q_{YF} < q_{BD}$, by a factor up to ~2. He suggested that the neglect of a free-draining effect in the Yamakawa–Fujii theory is responsible for the lower value of q_{YF}. Yamakawa[26] has recently commented on the problems associated with the proper value of the chain diameter required for the wormlike cylinder. We observe, however, that the large error affecting $\langle R_G^2\rangle$ is primarily responsible for the large scatter of q_{CL} and q_{BD}. The lower limits of these quantities are rather close to the q_{YF} values.

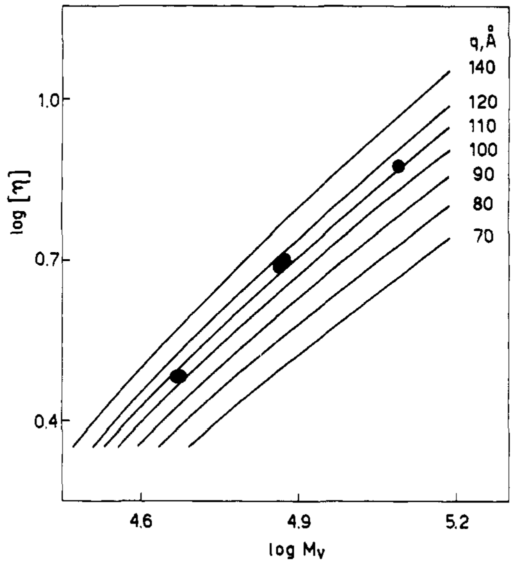

Figure 4. Full lines represent the theoretical intrinsic viscosity–molecular weight dependence for wormlike cylinders having the indicated values of q and diameter 5.8 Å. M_L = 162/5.14 daltons/Å. Black points are the experimental values of $[\eta]$ for cellulose in DMAc + 5% LiCl for molecularly dispersed samples.

By averaging the lowest figures obtained by light scattering with the viscosity result, we obtain q ~ 125 Å, which represents a lower limit for q in DMAc + 5% LiCl. Using q = 125 Å we have calculated the axial ratio of the Kuhn segment given by $x = 2q/d$. According to Flory's treatment of semirigid chains[3] (cf. introduction), the latter axial ratio should be related to v_2' using eq 2. The results, shown in Table II (sixth column) and by the horizontal line in Figure 3, indicate that the Kuhn model does not represent the experimental variation of v_2' with DP and overestimate the absolute values of v_2'. The deviation between the Kuhn model and the experimental data for cellulose in DMAc/LiCl is in the same direction as that previously observed for HPC in DMAc and in DCA.[1,2] In the latter cases—when molecular dispersion likely prevailed—we postulated the occurrence of soft interactions[4] to secure agreement between experiment and theory. In the present case, a T^* ~ 130 K (already within the wide region) would be required[4] to fit the Kuhn model to the v_2' measured for the sample with largest DP. The large indetermination affecting q (which for the present system is even larger than the indetermination affecting $d^{1,2}$) prevents, however, a too strict assessment of the deviation between experiment and the Kuhn model. Although, with proper adjustment of q, and possibly T^*, the Kuhn model might represent the limiting value of v_2' at a given C_s, it is unlikely that the variation of v_2' with C_s could be explained by the effect of LiCl on q. Both the viscosity and light scattering data in the accompanying paper[5] rule out a significant decrease of q when C_s is increased from 5% to

7.8%. A decrease of T^* with C_s would be required to justify the observed trend, making rather unsatisfactory the interpretation based on molecularly dispersed species.

We therefore consider the axial ratio to be expected without the assumption of molecular dispersion. The results in the accompanying paper[5] reveal the existence, under given conditions, of stable aggregate particles composed of about 7 extended molecules with a side-by-side organization. The axial ratio for such particles should be given by the contour length divided by a diameter on the order of 17 Å. Data thus obtained for samples A, L, and I are included in the last column of Table II. They show better agreement with the values of x deduced from eq 2 than the values calculated by assuming molecular dispersion (compare the last four columns in Table II and Figure 3). There are, however, at least two considerations which cast doubts on the validity of this simple model. The first consideration is that, as indicated earlier, the instances in which such an aggregate was observed correspond to situation of low solubility, in fact preventing the attainment of the critical concentration. The second consideration is that the model of the aggregated particle does not readily explain the smooth increase of v_2' with C_s. It was shown[5] that increasing C_s results in the disruption of the aggregates. However, molecularly dispersed species were observed at high C_s, but only at low polymer concentration. At large C_p and C_s, *association* equilibria set in, with a more irregular pattern of interchain contacts than observed with the stable aggregates, making the evaluation of x a rather problematic task.

The occurrence of an association equilibria could be handled in the following manner. With proper choice of a model, the size distribution of associated species could be evaluated (the pattern of association could include side-by-side organization with *partial* overlap along the chain axis). The corresponding axial ratio distribution could be related to the critical volume fraction using an approach similar to that used by Flory and Frost[14] for the most probable distribution of molecularly dispersed rods (neglecting a shift in the association equilibrium upon crossing the narrow region). Although we do not propose a quantitative analysis along the above lines, we observe that some of the present results would be qualitatively in line with the model. In particular, the observation of a biphasic gap wider than exhibited by HPC, coupled with a negligible disproportion of high and low molecular weight species between the conjugated phases, would not be surprising. The pronounced increase of v_2' with C_s would be compatible with a reduction of asymmetry resulting from the experimentally observed[5] increase of association with C_s.

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