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Isotropic−Cholesteric Phase Equilibrium in Solutions of Cellulose Tris(phenyl carbamate)

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ABSTRACT: The isotropic−cholesteric phase boundary concentrations and interfacial tension were measured for tetrahydrofuran (THF) solutions of fractionated cellulose tris(phenyl carbamate) (CTC) samples. The phase boundary concentrations are compared with the scaled particle theory for the hard wormlike spherocylinder model as favorably as those for other stiffer polymer systems, though the theory does not consider effects of the intramolecular excluded-volume and intermolecular multiple contacts, both of which are appreciable for high molecular weight CTC samples. This may be due to cancellation of the two effects in the isotropic−cholesteric phase equilibrium. The interfacial tension γ between the coexisting isotropic and cholesteric phases for the CTC−THF system slightly decreases with molecular weight, and the asymptotic value is higher than those of other stiffer polymer systems. The dependence of the asymptotic γ on the persistence length is consistent with Cui et al.'s theory based on the second virial approximation, but its magnitude is much larger than the prediction of the theory, indicating that higher virial terms in thermodynamic quantities play a significant role in γ.

1. Introduction

It is known that cellulose and its derivatives exhibit lyotropic liquid crystallinity.[1−9] They are the most flexible among lyotropic liquid-crystalline polymers, and their chain flexibility shifts the isotropic−liquid crystal phase transformation toward a considerably high concentration region.[10]

In the previous study (part 1 of this series of papers),[11] we have determined the wormlike-chain parameters and intermolecular interaction parameters of a cellulose derivative, cellulose tris(phenyl carbamate) (CTC) in tetrahydrofuran (THF). The chain stiffness of this polymer, characterized by a persistence length q of $10._5$ nm, is intermediate between typical stiff and flexible polymers.[12,13] It turned out that due to this low chain stiffness, effects of the intramolecular excluded volume and of the intermolecular multiple contacts become important in dilute solution properties of CTC in THF (a good solvent), when the molecular weight M exceeds ca. 10^5.[11] Therefore, CTC exhibits both rodlike and coillike characters by changing M within an accessible M range.

The two effects of the intramolecular excluded volume and of the intermolecular multiple contacts may also affect the isotropic−liquid crystal phase equilibrium. So far, the phase equilibria in stiff and semiflexible polymer solutions have been compared with theories,[10,14−17] which do not consider the two effects, and good agreements between experiment and theory have been obtained. Thus, it is an interesting problem to examine whether the theories correctly predict the phase boundary for CTC solutions or not.

The isotropic−liquid crystal (cholesteric) phase boundary concentration for cellulose derivatives has been already studied by many workers.[1−9] However, most of polymer samples used so far had heterogeneities in the molecular weight and/or degree of substitution, which made the comparison between theory and experiment obscure. In this study, we have used well-fractionated CTC samples with narrow molecular weight distributions and full substitution to measure the isotropic−cholesteric phase boundary concentrations of their THF solutions. Since the molecular and interaction parameters of CTC in THF have been already determined in part 1, we can compare experimental and theoretical phase boundary concentrations without ambiguity.

In this study, we also measured the interfacial tension between the coexisting isotropic and cholesteric phases of THF solutions of CTC by the sessile drop method. The interfacial tension plays an important role in the kinetics of the isotropic−cholesteric phase separation,[18] but there has been no report on the interfacial tension for cellulose and its derivatives solutions so far.

2. Experimental Section

CTC Samples. Eleven fractionated CTC samples were used for the phase separation experiment and interfacial tension measurements. Among them, seven samples (F9, F11, F13, F16, F18, F20, F22) were the same as used in part 1,[11] and four samples (Q11-4, P2-4, G-4, H-4) were newly prepared in the same procedure as previously. The full substitution of CTC samples was checked in part 1 by elemental analysis. The molecular characteristics of all the samples used in this study are listed in Table 1. For the newly prepared samples, the viscosity-average molecular weights M_v were estimated from

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Table 1. Molecular Characteristics of CTC Samples Used

sample	$M_w/10^4$	$[\eta]/10^2\text{cm}^3\text{g}^{-1}$	k'^{b}	M_w/M_n
F9	55.5	3.35	0.37	
F11	33.9	2.14	0.38	1.10
F13	15.6	1.20	0.37	1.07
F16	10.3	0.834	0.36	1.08
Q11-4	9.9[a]	0.755	0.39	1.05
P2-4	9.6[a]	0.732	0.42	1.06
G-4	7.4[a]	0.568	0.39	1.05
F18	5.87	0.481	0.41	1.07
H-4	4.9[a]	0.373	0.41	1.07
F20	3.94	0.339	0.39	1.06
F22	2.51	0.202	0.45	

[a] Viscosity-average molecular weight estimated from $[\eta]$ data using the $[\eta]$−M_w relation obtained in part 1.[11] [b] Huggins coefficient.

the intrinsic viscosities $[\eta]$ (in the third column of Table 1) using the relation between $[\eta]$ and the weight-average molecular weight M_w obtained in part 1. For all the samples, the ratios of M_w to the number-average molecular weight M_n estimated by GPC were equal to or less than 1.1 (see the fifth column of Table 1), which indicates successful molecular weight fractionation of the samples. In the following, M_v is not differentiated from M_w, and both molecular weights are denoted simply by M.

Phase Separation Experiment. A biphasic solution was prepared by mixing a CTC sample with distilled THF in a test tube and stirring the mixture by a magnetic chip for 1−2 days in a 25 °C air bath. The solution was then centrifuged at 4000 rpm at 25 °C in a Sorval RC centrifuge to achieve a complete phase separation, and the test tube with the biphasic solution was placed into a thermostated water bath at 25 °C gently without disturbance. The volume of each separated phase was determined from its column height measured by a traveling microscope to calculate the volume fraction Φ_{LC} of the cholesteric phase in the biphasic solution. The test tube had been calibrated to estimate the volume of liquid in the tube from its column height. Measurements of Φ_{LC} were performed by changing the initial CTC mass concentration c and the temperature from 10 to 35 °C.

Viscosities of biphasic solutions of CTC solutions with $M > 10^5$ were so high that the complete phase separation could not be achieved by centrifugation without disturbing the phase equilibrium. Thus, such solutions were sequentially diluted with THF to find the concentration where the optical birefringence of the solution disappeared using polarizing microscopy under the crossed polarizers condition, and this concentration was taken as the phase boundary concentration c_I between the isotropic phase and biphasic regions. The same procedure was used also for the lowest molecular weight sample (F22), whose amount available was too small to make the phase separation experiment.

Interfacial Tension Measurements. The isotropic−cholesteric interfacial tension γ was measured for three CTC samples, P2-4, G-4, and H-4, by the sessile drop method.[19] After the centrifugation of a biphasic CTC solution at 25 °C, the coexisting isotropic and cholesteric phases were separately taken out by pipets. The separated isotropic phase was put into a glass rectangular cuvette with a 10 mm width, and a suitable amount of the separated cholesteric phase was placed on the bottom of the isotropic phase in the cuvette, using a microsyringe. Evaporation of the solvent THF was prevented by a Teflon cap on the cuvette along with Teflon seal. Pictures of the sessile drop of the cholesteric phase formed on the bottom of the cuvette were taken sequentially at different times t elapsed after forming the drop, under crossed polar conditions by a CCD camera (Hamamatsu Digital Camera 4742-95) with a Micro-Nikkor (55 mm, *f*/2.8) lens. The magnification of the pictures was determined by a microscope ruler photographed under the same condition (without the cross polares). The sessile drop pictures were analyzed by the established method[19,20] to determine γ between coexisting isotropic and cholesteric phases.

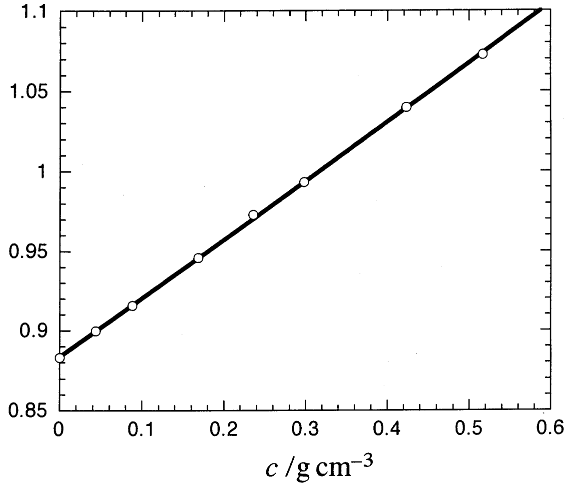

Figure 1. Concentration dependence of the density of THF solutions of CTC at 25 °C.

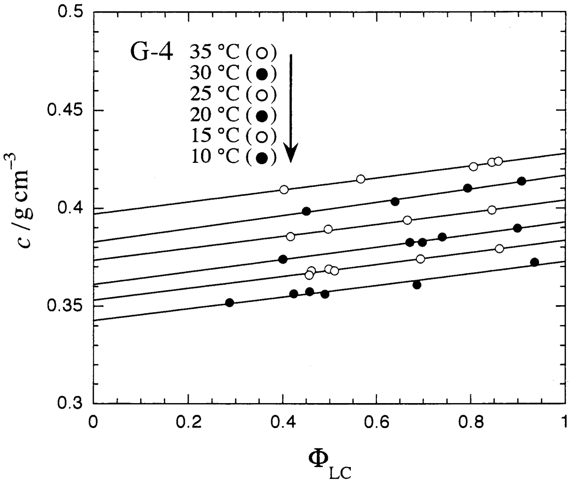

Figure 2. Results of the isotropic−cholesteric phase separation experiments for THF solutions of CTC sample G-4 at different temperatures; c, the initial polymer concentration; Φ_{LC}, the volume fraction of the cholesteric phase in the whole solution.

Density Measurements. The sessile drop method needs the difference in the density ρ between the coexisting two phases to calculate γ, so that ρ of THF solutions of CTC were measured at 25 °C as a function of the polymer concentration using a Lipkin-Davison-type pycnometer with a 5 cm^3 capacity. Figure 1 shows the plot of ρ against the polymer mass concentration c over a concentration wide range, where c was calculated from the polymer weight fraction multiplied by ρ. Although the data points at the two highest c are for cholesteric solutions, all data points follow a single straight line indicated. From the slope of this line, the partial specific volume of CTC in 25 °C THF was estimated to be 0.713 cm^3/g, being in good agreement with the previous result[11] obtained by densitometry at low polymer concentrations (<0.01 g/cm^3).

3. Results and Discussion

Phase Boundary Concentrations. Figure 2 shows the plot of the initial CTC concentration c against the volume fraction Φ_{LC} of the cholesteric phase in biphasic solutions of sample G-4 at different temperatures T. Data points at each T follow a straight line, and the slope of the line slightly increases with T. By extrapolating the data points to $\Phi_{LC} = 0$ and 1, we determined the phase boundary concentrations c_I between the isotropic phase and biphasic regions and c_A between the biphasic and cholesteric phase regions, as functions of

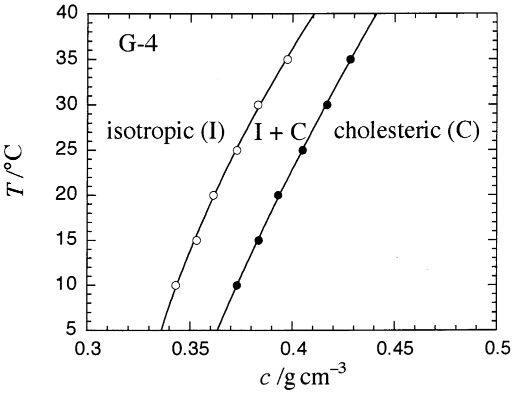

Figure 3. Temperature–concentration phase diagram of the THF solution of CTC sample G-4.

Table 2. Isotropic–Cholesteric Phase Boundary Concentrations and Interfacial Tension of THF Solutions of CTC at 25 °C

sample	L/nm[a]	N[b]	c_I/g cm^{-3}	c_A/g cm^{-3}	γ/10^{-3} N m
F9	534	25.4	0.343[c]		
F11	326	15.5	0.354[c]		
F13	150	7.14	0.361	0.392	
F16	99.0	4.72	0.387	0.417	
Q11-4	95	4.5	0.370	0.402	
P2-4	92	4.4	0.373	0.405	0.0857
G-4	71	3.4	0.373	0.405	0.0939
F18	56.4	2.69	0.384	0.413	
H-4	47	2.2	0.402	0.429	0.107
F20	37.9	1.80	0.398	0.419	
F22	24.1	1.15	0.443[c]		

[a] Calculated from M with the molecular weight per unit contour length $M_L = 1040$ nm^{-1}. [b] Calculated from L with the persistence length $q = 10._5$ nm. [c] Determined by polarizing microscopy.

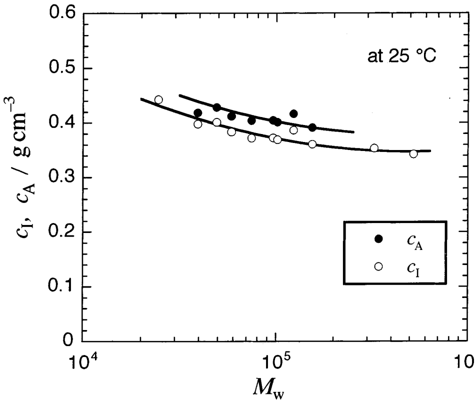

Figure 4. Molecular weight dependence of the phase boundary concentrations c_I between the isotropic and biphasic regions and c_A between the biphasic and cholesteric phase regions at 25 °C.

T. The phase diagram drawn with these phase boundary concentrations is illustrated in Figure 3. Both phase boundary lines are tilted, and the isotropic phase region widens with increasing T. Similar T dependencies of c_I and c_A were observed for other lyotropic liquid-crystalline polymer systems.[4,21–23]

Table 2 summarizes results of c_I and c_A at 25 °C for all CTC samples examined, and Figure 4 shows the molecular weight dependencies of c_I and c_A at 25 °C (unfilled and filled circles). The data for c_I and c_A in the range of $3.9 \times 10^4 < M < 1.6 \times 10^5$ were obtained from the plot of c vs Φ_{LC}, while the data for c_I at $M = 2.5 \times 10^4$, 3.4×10^5, and 5.6×10^5 were determined by polarizing microscopy (cf. Experimental Section). Both c_I and c_A are slightly decreasing functions of M. Asymptotic values of c_I and c_A at high M are much higher than those for toluene solutions of poly(n-hexyl isocyanate) (PHIC) (≈0.2 g/cm^3)[23] and aqueous solutions of schizophyllan (≈0.1 g/cm^3).[22,24] The persistence lengths q of CTC, PHIC, and schizophyllan are $10._5$, 37,[25] and 200 nm,[26] respectively, and their asymptotic values of c_I and c_A are in order of the chain flexibility, whereas ratios c_A/c_I for the CTC–THF system are ca. 1.08 irrespective of M, which are similar to those for the PHIC–toluene system.[23]

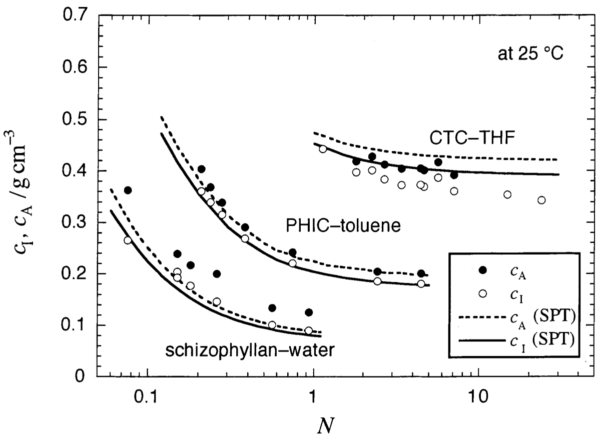

Figure 5. Comparison of experimental phase boundary concentrations for three lyotropic liquid-crystalline polymer systems with the scaled particle theory for the hard wormlike spherocylinder model.

A number of molecular theories were proposed to calculate isotropic–liquid crystal phase boundary concentrations for rodlike or wormlike polymer solutions so far.[10,14–17,27,28] Among them, the scaled particle theory (SPT) based on the hard wormlike spherocylinder model is one of most successful theories, which considers the higher virial terms and the conformational entropy not included in the Onsager theory.[10] The SPT allows to calculate c_I and c_A as functions of the molecular weight M, when the persistence length q, the molar mass per unit contour length M_L, and hard-core diameter d_0 are given. These necessary parameters have already determined for CTC in 25 °C THF in part 1: $M_L = 1040 \pm 70$ nm^{-1}, $d_0 = 1.4 \pm 0.1$ nm, and $q = 10._5 \pm 1$ nm. Figure 5 compares the theoretical prediction by the SPT with the experimental results, where the top solid and dash–dotted curves indicate respectively theoretical values for c_I and c_A calculated by the SPT with $M_L = 1040$ nm^{-1}, $d_0 = 1.4$ nm, and $q = 10._5$ nm, and top series of unfilled and filled circles are the corresponding experimental data for the CTC–THF system. In the figure, N is the number of Kuhn's statistical segments ($=M/2qM_L$), which is calculated from M for each sample. The SPT predicts both experimental phase boundary concentrations quite accurately with no adjustable parameters.

Figure 5 also compares previous results of c_I and c_A for poly(n-hexyl isocyanate) (PHIC)–toluene[23] and schizophyllan (a rigid triple-helical polysaccharide)–water[22,29] systems all at 25 °C with the SPT, where theoretical values were calculated using the molecular parameters determined by the same method as for CTC.[30] For the PHIC–toluene system, both phase boundary concentrations are predicted by the SPT almost perfectly. On the other hand, for aqueous schizophyllan, while experimental data of c_I almost agree with the SPT, experimental c_A are considerably higher and the phase gaps

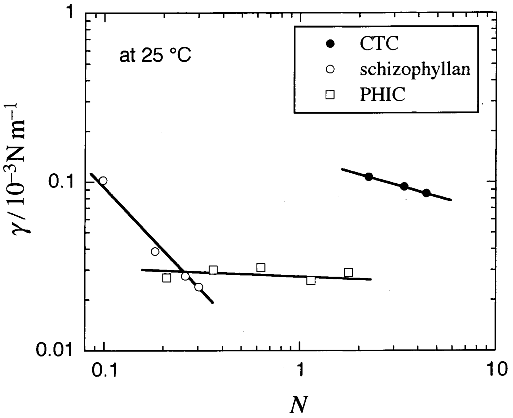

Figure 6. Interfacial tension γ between coexisting isotropic and liquid-crystal phases for three lyotropic liquid-crystalline polymer systems at 25 °C plotted against the number N of Kuhn's statistical segments.

are wider than the theoretical prediction. However, the SPT may not be responsible for these disagreements because molecular weight distributions of schizophyllan samples used were not as sharp as those for PHIC and CTC samples.[31] In comparison with the results for the PHIC−toluene system, the agreement between theory and experiment for the CTC−THF system is less perfect. This discrepancy is however within uncertainties of the molecular parameters previously estimated (see above). For example, if we change d_0 from 1.4 to 1.47 nm, we can obtain almost perfect agreements for the CTC−THF system.

Gupta et al.[32] made dielectric measurements for CTC in dioxane and found that q of CTC in that solvent decreases with increasing T. From their results, we can estimate $\mathrm{d}q/\mathrm{d}T$ at room temperature to be ca. −0.18 nm/°C. Although there is no corresponding result of CTC in THF, the q value in THF is almost identical with that in dioxane at 25 °C (=10.8 nm), and we may expect a similar $\mathrm{d}q/\mathrm{d}T$ in THF. If $\mathrm{d}q/\mathrm{d}T$ in THF is equal to −0.12 nm/°C and M_L and d_0 are invariant with T, we can explain the T dependence of the phase boundary concentrations shown in Figure 3.

Interfacial Tension. Figure 6 shows the N (or the molecular weight) dependence of the isotropic−cholesteric interfacial tension γ for the CTC−THF system at 25 °C (filled circles) as well as those for PHIC−toluene (squares)[33] and schizophyllan−water (unfilled circles)[19] systems at the same temperature. The dependencies for the CTC−THF and PHIC−toluene systems are much weaker than that for the schizophyllan−water system. The magnitude of γ at larger N seems to be in order of the chain flexibility, just like c_I and c_A, although there are no data of γ for aqueous schizophyllan at large N.

Cui et al.[34] calculated the isotropic−nematic interfacial tension for solutions of hard wormlike cylinders in the coil limit. Their final result is simply written as

$$\gamma = 0.11\,\frac{k_\mathrm{B}T}{qd_0} \tag{1}$$

where k_B is the Boltzmann constant. Figure 7 plots $\gamma q d_0/k_\mathrm{B}T$ against N to compare the experimental results with the coil-limit theory of Cui et al. The values of q and d_0 used are the same as those used at calculating the phase boundary concentrations in Figure 5. The weak or no molecular weight dependence of γ for CTC or PHIC solutions is almost consistent with the theory of Cui et al., and the asymptotic values of $\gamma q d_0/k_\mathrm{B}T$ for CTC and PHIC solutions are almost identical, as expected from eq 1. However, magnitudes of the asymptotic $\gamma q d_0/k_\mathrm{B}T$ for those solutions are about 3 times as large as the theoretical prediction. The theory of Cui et al. uses the second virial approximation, which gives c_I and c_A (or the concentrations of the coexisting isotropic and liquid-crystal phases) about twice as high as the experimental for the CTC−THF system. Since the SPT including the higher virial terms in thermodynamic quantities predicts c_I and c_A much more accurately, the higher virial terms may be important also in the calculation of γ and should be incorporated into Cui et al.'s theory to obtain better agreements.

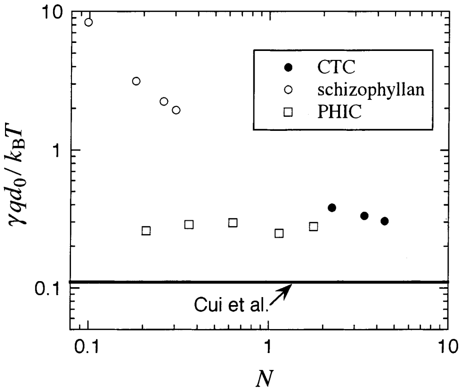

Figure 7. Comparison of experimental γ with Cui et al.'s theory for the wormlike-chain model in the coil limit.

4. Concluding Remarks

As mentioned in Introduction, the CTC chain has a considerable flexibility so that the effects of the intramolecular excluded volume and of the intermolecular multiple contacts become important for CTC at high molecular weights (above few hundred thousand).[11] On the other hand, we have demonstrated above that the scaled particle theory (SPT) for the hard wormlike spherocylinder model predicts the isotropic−liquid crystal phase boundary concentrations for the CTC−THF system as accurately as those for other stiffer polymer systems, though the theory does not consider the above two effects. This indicates that the above two effects do not play significant roles in the isotropic−liquid crystal phase equilibrium or that the two effects cancel each other.

The intramolecular excluded-volume effect on the polymer chain conformation becomes appreciable for CTC in isotropic THF solution at high M, but it may not be important in the cholesteric phase due to the extended conformation of the chain in the phase. Therefore, this effect reduces the conformational entropy of the chain in the isotropic phase and thus the conformational entropy loss at the cholesteric phase formation. Therefore, the effect stabilizes the cholesteric phase, which can shift the phase boundaries to the lower concentration side. However, the chain flexibility provides also the effect of multiple contacts among polymer chains in the isotropic phase, which reduces the intermolecular excluded volume and may stabilize the isotropic phase. We cannot expect such a multiple-contacts effect in the cholesteric phase due to the extended chain conformation in the phase. Therefore, the two effects arising form the chain flexibility are competitive and may cancel each other in the calculation of the phase boundary concentrations. Of course, the above argument is just qualitative, and we have to check quantitatively whether the two effects actually cancel or not, but at present we have no suitable theory for this purpose.

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