There is a linear relation, within the accuracy of our measurements, between the intensity of the D-LAM band and the level of crystallinity over the range of crystallinities 0–90%. The liquidlike content as measured by the D-LAM approaches zero concentration in the crystallinity region of about 90%. This result indicates that the disorder in such very high crystalline regions is significantly different either in the trans–gauche ratio or in the lengths of the sequences or in both.[25]

Acknowledgment. The support of this work by the National Science Foundation Polymer Program, Grant DMR 84-037-11 to the University of California, Berkeley, and Grant DMR 83-14679 to Florida State University, is gratefully acknowledged.

Registry No. Polyethylene, 9002-88-4.

References and Notes

(1) Maroncelli, M.; Strauss, H. L.; Snyder, R. G. *J. Chem. Phys.* **1985**, *82*, 2811.
(2) Snyder, R. G.; Poore, M. W. *Macromolecules* **1973**, *6*, 708.
(3) Levin, D. W.; Bush, S. F. *Biochim. Biophys. Acta* **1981**, *640*, 760.
(4) Mizushima, S.; Shimanouchi, T. *J. Am. Chem. Soc.* **1949**, *71*, 1320.
(5) Strobl, G. R.; Eckel, R. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 913.
(6) Goltin, M.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 29.
(7) Glotin, M.; Mandelkern, L. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 807.
(8) Rabolt, J. F. *CRC Crit. Rev. Solid State Mater. Sci.* **1985**, *12*, 165.
(9) Snyder, R. G. *J. Chem. Phys.* **1982**, *76*, 3921.
(10) Snyder, R. G.; Wunder, S. L. *Macromolecules*, **1986**, *19*, 496.
(11) Mandelkern, L. *Polym. J. (Tokyo)* **1985**, *17*, 337.
(12) Geil, P. "Polymer Single Crystals"; Wiley-Interscience: New York, 1963.
(13) Stuart, H. A. *Ann. N. Y. Acad. Sci.* **1959**, *83*, 3.
(14) Lindenmeyer, P. H. *Science (Washington, D.C.)* **1956**, *147*, 1256.
(15) Flory, P. J.; Yoon, D. Y.; Dill, K. A. *Macromolecules* **1984**, *17*, 862.
(16) Yoon, D. Y.; Flory, P. J. *Macromolecules* **1984**, *17*, 868.
(17) Mandelkern, L. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 310.
(18) Mandelkern, L. *J. Phys. Chem.* **1971**, *75*, 3290.
(19) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(20) Snyder, R. G.; Scherer, J. R. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 421.
(21) Maxfield, J.; Mandelkern, L. *Macromolecules* **1977**, *10*, 1141.
(22) Takeuchi, H.; Tasumi, M. *J. Chem. Phys.* **1980**, *47*, 395.
(23) Scherer, J. R.; Snyder, R. G. *J. Chem. Phys.* **1980**, *72*, 5798.
(24) In our definitions, $I_i = 45\bar{\alpha}'^2$ and $I_a = 7\beta'^2$ where $\bar{\alpha}'$ and β' are the invariants of the derived polarizability tensor. See: Wilson, E. B.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955; Chapter 3.
(25) It has been established that the degree of crystallinity that is obtained calorimetrically is always less than that found by density, the difference being attributed to the interfacial structure.[11] Hence the crystallinity value of 90% should be considered to be a lower limit for the loss of the D-LAM band since it arises from the liquidlike structure.

Mesophase Formation and Polymer Compatibility. 4. Cellulose/Cellulose Acetate/Diluent Systems

E. Marsano, E. Bianchi, A. Ciferri,* G. Ramis,[†] and A. Tealdi[‡]

Istituto di Chimica Industriale, Università di Genova, Genoa, Italy. *Received June 5, 1985*

ABSTRACT: The phase diagram of a system composed of a rigid polymer (cellulose), a flexible polymer (cellulose acetate, CA), and a diluent (*N,N*-dimethylacetamide (DMAc) + 7.8% LiCl) was investigated. A series of samples covering a range of degree of polymerization (cellulose) and degree of substitution (CA) were analyzed. The binary cellulose/diluent system exhibits a mesophase above a critical volume fraction $v_2' = 0.065$ (DP = 460). The CA/diluent system is always isotropic, in line with a small value of the persistence length (~40 Å) attributed to the presence of the salt. The ternary systems show incompatibility of the two polymers even in rather diluted solution, when two isotropic phases are observed. Above a combined polymer volume fraction of ~0.1, one anisotropic and one isotropic phase coexist. The anisotropic "phase" may actually be an intimate mixture of two phases. Analysis of the composition of each phase reveals a complete exclusion of CA from the mesophase and of cellulose from the conjugated phase. These findings cannot be represented by Flory's theory of phase equilibria between a rigid and flexible polymer due to the assumption of athermal behavior. The role of mutual interaction parameters for a quantitative interpretation of the results is pointed out.

In the first paper of this series[1] we reported the behavior of two ternary systems composed of a solvent, a rigid mesogen, and a more flexible polymer. The systems were poly(*p*-benzamide) (PBA)/polyterephthalamide of *p*-aminobenzhydrazide (X-500)/*N,N*-dimethylacetamide (DMAc) + 3% LiCl and PBA/poly(acrylonitrile) (PAN)/DMAc + 3% LiCl. We found that the flexible polymer was invariably excluded from the mesophase formed above a critical concentration of the two solutes. The rigid polymer was, however, mixed with the flexible one in the conjugated isotropic phase, and a fractionation of the former polymer in the latter phase was also observed. These observations were in satisfactory agreement with a theory[2] which predicts that the incompatibility is due to the interference of the random coil with the mutual orientation of the rigid polymer in the mesophase.

The above theory does not include the role of the interaction based on enthalpy parameters χ_{23} for the polymer pair. The latter is the basis for the compatibility, or incompatibility, between conventional polymers in the isotropic state.[3] In fact, we evaluated the χ_{23} parameter for the PBA/X-500 and PBA/PAN pairs and showed that

Table I
Characteristics of Samples Investigated

sample	origin	$[\eta]^{25\,°C}$, dL/g	$\bar{M}_v$	DP
A, CA, DS = 2.84	Fluka Buchs SG	3.63[a]	214 000	781
B, CA, DS = 2.30	Eastman Kodak 4655	1.90[a]	115 000	447
C, CA, DS = 0.9	Courtanz DS = 2.5 deacetylated[7]	1.74[a]	86 000	421
I, cellulose	SSCC, Milan (regenerated cellulose II)	2.45[b]	74 500	460
L, cellulose	SNIA Fibre (regenerated cellulose II)	1.62[b]	47 000	290

[a] In DMAc; cf. ref 7. [b] In 0.5 cupric ethylenediamine.

[†] Thesis submitted to the University of Genoa for the Doctoral degree in Chemistry.

[‡] Centro Studi Macromolecole, CNR.

both systems should have been compatible in the composition range we had investigated. Thus, the incompatibility exhibited by the two polymer pairs in the mesophase could unambiguously be attributed to the entropy effect considered in the above-mentioned theory.[2] Some differences between the behavior of the PBA/X-500 and PBA/PAN pairs led, however, to speculations about a possible role of chemical constitution. In fact, the latter pair, which had the larger χ_{23} parameter, also exhibited the larger deviation of the slope of the tie lines from theoretical prediction.[1]

In this paper we consider a case in which the rigid and the more flexible polymer show such a large χ_{23} parameter as to be incompatible, for chemical reasons, in the concentration range in which the mesophase occurs. The phase diagram for such a system (cellulose/cellulose acetate (CA)/DMAc + 7.8% LiCl) is very different from that theoretically predicted[2] on the basis of ideal mixing.

The contribution of the role of chemical compatibility to the theoretical phase diagram for ideal mixtures of two polymers with similar rigidity has already been investigated (parts 2[4] and 3[5]). The expected compatibility[6] between rigid mesogens in the mesophase was not observed,[4,5] reflecting the important role of the χ_{23} parameters on the equilibria involving polymer liquid crystals.

Experimental Section

Materials and Solutions. The three cellulose acetate samples (A, B, C) used were similar to those characterized in previous work.[7] The diacetate (B, DS = 2.30) is the sample most extensively used for the ternary diagrams. The triacetate (A, DS = 2.84) and the monoacetate (C, DS = 0.9) were used for an exploration of the effect of DS on selected features of the phase diagram. Origin and characteristics of the CA samples are included in Table I. As previously described, the molecular weights were obtained from the intrinsic viscosity in DMAc by using the relationships $[\eta] = 2.64 \times 10^{-4} \bar{M}_v^{0.75}$, $[\eta] = 1.34 \times 10^{-4} \bar{M}_v^{0.82}$, and $[\eta] = 19 \times 10^{-4} \bar{M}_v^{0.6}$ reported by Kamide and co-workers respectively for DS = 2.92,[8] DS = 2.46,[9] and DS = 0.49.[10] The degree of substitution was determined by proton NMR and by standard chemical analysis as described in ref 7. The two cellulose samples (I,L) used are also similar to those already characterized.[11] Molecular weights (Table I) were determined from the intrinsic viscosity in 0.5 M cupric ethylenediamine, as previously described,[11] by using the relationship[12] $[\eta] = 1.0 \times 10^{-4} \bar{M}_v^{0.9}$. Intrinsic viscosities were determined at 25 °C as previously described.[1,7] The DMAc solvent was an analytical-grade Carlo Erba product treated with molecular sieves to remove traces of water. LiCl was added to DMAc in a relatively large amount (C_s = 7.8% w/w) to ensure solubilization of cellulose.[11]

The samples were separately dissolved in the solvent. Solubilization of CA in DMAc + 7.8% LiCl was achieved by stirring at room temperature for up to 1 month. Stock solutions had concentrations up to 33%. Solubilization of cellulose was achieved by using the method of Turbak et al.[13] As described in more detail elsewhere,[11] the latter requires heating to the reflux temperature followed by cooling at 100 °C, when LiCl is added. Concentration, C_p, is given as grams of polymer per 100 g of solution. Alternatively, the polymer volume fraction, v_2, was calculated from C_p by using the partial specific volume of the polymer ($\bar{v}_{CA}$ or $\bar{v}_{cell}$), the specific volume, V_1, of the diluent (DMAc + 7.8% LiCl), and assuming additivity. Pycnometric determination at 25 °C gave $\bar{v}_{CA}$ = 0.71 mL/g (sample B) and V_1 = 0.9998. $\bar{v}_{cell}$ = 0.638 mL/g was obtained by extrapolation of data in the C_s range between 3.5% and 8%.

Phase Diagrams. Ternary mixtures were prepared by mixing known amounts of binary stock solutions and stirring by slow rotation at ~20 °C for up to 1 month (needed for the very viscous solutions obtained at high C_p). More dilute ternary mixtures were obtained either by adding diluent or by using a CA (sample B) solution with low C_p. To confirm the attainment of equilibrium values, longer stirring times and various thermal treatments were performed. The C_p of the overall mixture is given for CA as $[g_{CA}/(g_{CA} + g_{cell})]100$ and for cellulose as $[g_{cell}/(g_{cell} + g_{CA})]100$.

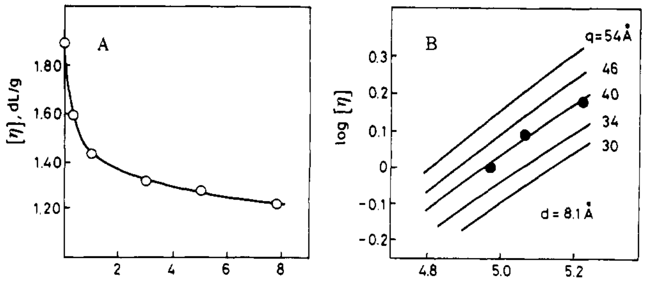

Figure 1. (a) Intrinsic viscosity at 25 °C of CA sample B vs. LiCl concentration in DMAc. (b) Intrinsic viscosity–molecular weight plot for CA samples A, B, C in DMAc + 7.8% LiCl at 25 °C. The full lines represent the theoretical[15] $[\eta]$–MW dependence for the indicated values of q and d (M_L = 50.5 Da/Å).

The mixtures were examined with the polarizing microscope to determine the occurrence of one or more phases and their anisotropy. ORD measurements[14] on the binary cellulose–DMAc + LiCl system confirmed the occurrence of a cholesteric mesophase. Separation of coexisting phases was obtained by centrifugation at 44 000 rpm at 20 °C for up to 150 h, as previously described.[4] (Under these conditions no sedimentation of the individual polymers was observed, and ample time for reequilibration was allowed before analysis of composition.[4]) The volume fraction of each phase was determined by calibration of the centrifuge tube. The composition of each polymer in the individual phases was determined, as previously described,[4] by using two weighted aliquots of each phase. The first aliquot was used for assessing the overall C_p by precipitating the two polymers with 96% EtOH. The second aliquot was used for assessing the C_p of cellulose, which was precipitated with acetone, a solvent for CA (sample B). Total indetermination on C_p did not exceed 2%.

Results

Determination of the critical volume fraction for binary cellulose–DMAc + 7.8% LiCl systems yielded $v_2' \cong 0.065$ and 0.08 respectively for samples I and L, in line with previously obtained results (cf. Figure 3 of ref 14). The binary CA–DMAc + 7.8% LiCl system yielded no mesophase in the accessible concentration range. This may seem at variance with the results reported in ref 7, where it was shown that sample B in pure DMAc had a critical volume fraction of 0.33. However, the presence of LiCl in the presently used system has the effect of greatly reducing the rigidity of CA. Data in Figure 1a illustrate the effect of LiCl on the intrinsic viscosity of sample B. In Figure 1b we show the log $[\eta]$–log $\bar{M}_v$ plot for DMAc + 7.8% LiCl. The experimental points define the equation

$$[\eta] = (3.88 \times 10^{-4})\bar{M}_v^{0.7}$$

The full lines in Figure 1b represent the Yamakawa–Fujii[15] theory

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

where $L' = \lambda M/M_L$ is a reduced contour length, M_L being the ratio of the molecular weight of the repeating unit M_0 = 259 (DS = 2.30) to the residue vector L_0 = 5.14 Å,[16] $\lambda = 1/2q$ where q is the persistence length, and ϕ is a function of L' and of the reduced diameter d' tabulated by Yamakawa–Fujii. The molecular diameter d was taken equal to 8.1 Å, as discussed elsewhere.[7] The experimental points suggest $q \sim 40$ Å. The latter theory yielded q = 70 Å for CA in pure DMAc[7] and q = 110 Å for cellulose in DMAc/LiCl, essentially unaffected by salt content between 5% and 7.8%.[14] The value $q \sim 40$ Å observed here corresponds to an axial ratio of the Kuhn segment $2q/d \sim 10$, which is too small to allow the formation of a mesophase containing an appreciable quantity of diluent.[7,17]

Seven ternary mixtures composed of CA (sample B) and cellulose I and seven ternary mixtures of B and L were

Table II
Overall Composition of Ternary Mixtures

mixture	cellulose I C_p, %	cellulose I v_2	CA sample B C_p, %	CA sample B v_3	$C_{cell} + C_{CA}$, %	appearance after equilibration
1	1.0	0.0064	1.0	0.0071	2.0	homogeneous, isotropic
2	2.6	0.0169	2.5	0.0180	5.1	biphasic, isotropic
3	4.0	0.0262	4.0	0.0292	8.0	biphasic, isotropic
4	5.0	0.0330	5.0	0.0367	10.0	biphasic, isotropic
5	5.0	0.0333	7.9	0.0585	12.9	biphasic, isotropic
6	5.0	0.0335	10.1	0.0753	15.1	biphasic, isotropic, anisotropic
7	5.0	0.0337	12.0	0.0899	17.0	biphasic, isotropic, anisotropic
	cellulose L		**CA sample B**			
mixture	C_p, %	v_2	C_p, %	v_3	$C_{cell} + C_{CA}$, %	appearance after equilibration
11	2.0	0.0129	2.0	0.0144	4.0	homogeneous, isotropic
12	3.0	0.0195	3.0	0.0217	6.0	biphasic, isotropic
13	4.0	0.0262	4.0	0.0292	8.0	biphasic, isotropic
14	5.0	0.0335	10.0	0.0745	15.0	biphasic, isotropic
15	5.0	0.0337	12.0	0.0899	17.0	biphasic, isotropic, anisotropic
15′	5.0	0.0337	12.0	0.0899	17.0	biphasic, isotropic, anisotropic
16	5.0	0.0340	15.2	0.1151	20.2	biphasic, isotropic, anisotropic

Table III
Compositions of Conjugated Phases[a]

	phase I				phase II				
	cellulose I		CA sample B		cellulose I		CA sample B		
mixture	C_p, %	v_2	C_p, %	v_2	C_p, %	v_2	C_p, %	v_2	ϕ[b]
2	3.0	0.0194	1.2	0.0086	1.5	0.0098	5.1	0.0369	0.66
3	5.5	0.0358			1.4	0.0093	10.6	0.0780	0.62
4	7.3	0.0478			1.0	0.0067	13.8	0.1024	0.65
5	9.2	0.0607					17.2	0.1285	0.54
6	10.0[a]	0.0662[a]					18.9	0.1419	0.46
7	12.3[a]	0.0821[a]					20.7	0.1563	0.43
	phase I				phase II				
	cellulose L		CA sample B		cellulose L		CA sample B		
mixture	C_p, %	v_2	C_p, %	v_2	C_p, %	v_2	C_p, %	v_2	ϕ[b]
12	3.4	0.0220	1.0	0.0072	2.2	0.0144	6.6	0.0482	0.62
13	5.0	0.0325	0.2	0.0014	2.8	0.0185	7.8	0.0572	0.48
14	9.7	0.0641			1.8	0.0122	16.8	0.1262	0.41
15	12.0[a]	0.0800[a]					20.5	0.1547	0.41
15′	11.7[a]	0.0780[a]					21.7	0.1638	0.42
16	16.2[a]	0.1098[a]					21.6	0.1636	0.30

[a] All phases are isotropic, except cholesteric phase I of mixtures 6, 7, 15, 15′, and 16. [b] Volume phase I/total volume.

prepared. The overall composition of these mixtures (expressed as C_p or volume fraction of the binary solutions before mixing) is given in Table II and Figures 2–4 (Figures 2 and 3 refer to CA + cellulose I, and Figure 4 refers to CA + cellulose L). The phase diagrams have been constructed by using the approach previously described.[1,4,5] The indexes 1, 2, and 3 refer to diluent, cellulose, and CA, respectively. Inside the diagram $v_2 + v_3 = 1 - v_1$, but along the binary axes $v_2 = 1 - v_1$, $v_3 = 1 - v_1$, and $v_3^d = 1 - v_2^d$ (the superscript d indicates that no diluent is present along the binary cellulose–CA axis). Upon equilibration all mixtures are composed of two phases, except for mixture no. 1 and 11 which show a single phase. Moreover, all single- and two-phase mixtures are isotropic, except for mixture no. 6, 7, 15, 15′, and 16 which exhibit an isotropic phase coexisting with an anisotropic one.

The analysis of the composition of each phase in the two-phase range yields the results collected in Table III and in Figures 2–4. It is evident that one phase (I) is rich in cellulose and the other (II) is rich in CA. The dotted lines in Figures 2–4 are tie lines linking the compositions of conjugated phases on the binodal curves. Their strong inclination reflects the disproportion of the mixtures having the overall composition indicated by the half-filled circles. When the overall C_p increases, the partitioning of the two polymers in the two phases increases. The binodal for phase I coincides with the binary cellulose–diluent axis already when $v_2 < v_2'$. Therefore, the mesophase does not contain any CA.

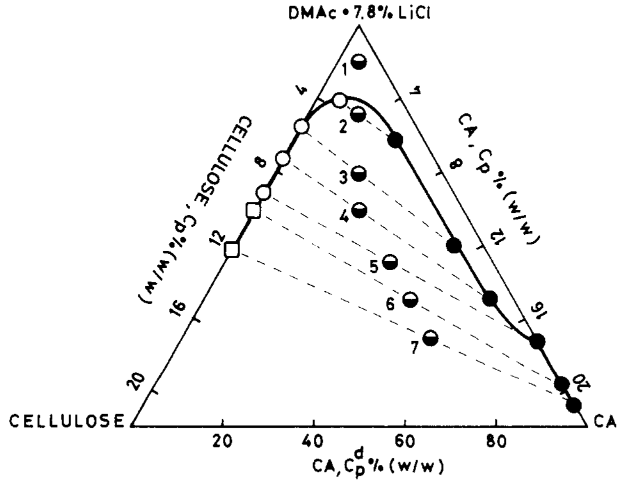

Figure 2. Phase diagram for the system cellulose (sample I)/CA (sample B)/DMAc + 7.8% LiCl at 20 °C: (◒) overall composition of mixtures; (○) composition of conjugated phase I (isotropic); (●) composition of conjugated phase II (isotropic); (□) composition of anisotropic phase I.

Comparison of Figures 3 and 4 reveals that an increase of the molecular weight of cellulose enhances the exclusion of CA from phase I and of cellulose from phase II.

The effect of the degree of substitution of the cellulose acetate on the maximum of the binodal C_p* (plait point[3]

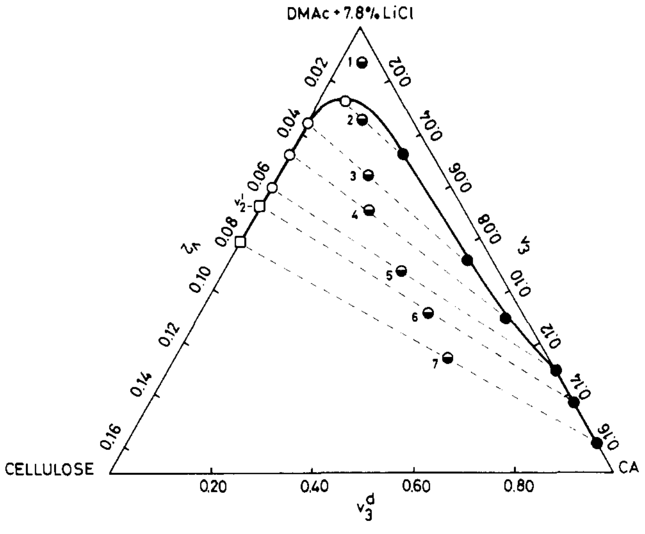

Figure 3. Same data as Figure 2 with compositions given as volume fraction.

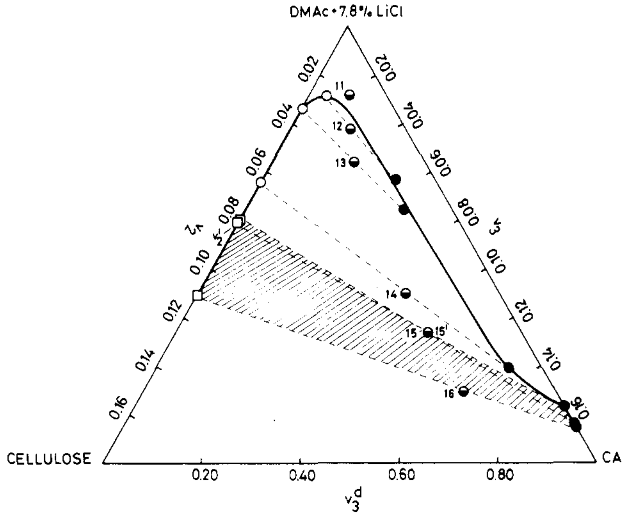

Figure 4. Phase diagram for the system cellulose (sample L)/CA (sample B)/DMAc + 7.8% LiCl at 20 °C. Same symbols as in Figure 2.

Table IV
Effect of the DS on the Concentration at the Plait Point

system	DS of CA	$\bar{M}_v$ of CA	C_p*, %
cellulose L + CA sample A	2.84	214 000	3.5 ± 0.5
cellulose L + CA sample B	2.30	115 000	4.5 + 0.5
cellulose L + CA sample C	0.9	86 000	8.5 ± 0.5

or critical concentration) was investigated by using cellulose sample L and CA samples A, B, and C. The results are collected in Table IV. Decreasing DS causes an enlargement of the field of stability of the single isotropic region, in line with the expected increase of compatibility of the two polymers (note, however, that the observed effect also includes a reduction of the molecular weight of the CA samples).

Discussion

The experimental diagrams in Figures 3 and 4 can be compared with the phase diagram predicted by Flory[2] for an ideal mixture of a rigid and flexible polymer. The latter, Figure 5, was obtained by assigning axial ratios x_2 and x_3 (respectively to the rigid and the flexible polymer) which simulate those of cellulose and CA. x_2 was taken equal to 125, as obtained from the experimental v_2' value for sample I by using the equation[17]

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

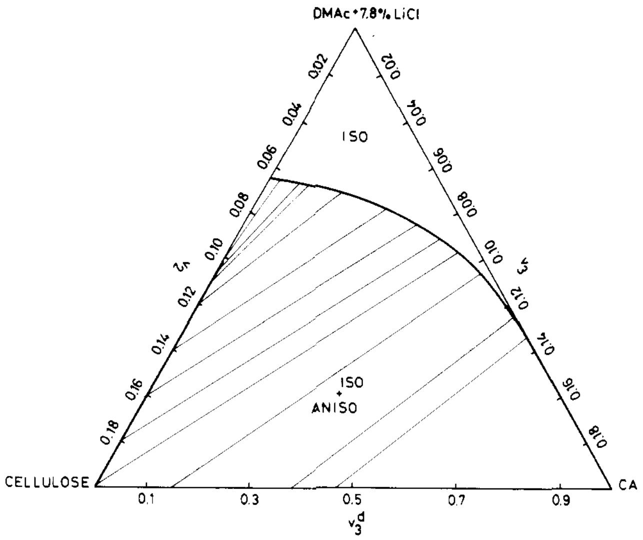

Figure 5. Phase diagram calculated from Flory's theory[2] for x_2 = 125 and x_3 = 275.

x_3 for CA was taken equal to 275, as obtained from the equation[17] $x = \bar{M}_v L_0 / M_0 d$. Note that x_3 for CA refers to the contour length and not to the persistence length as requested by theory.[2] Similar results were obtained by using the Matheson–Flory theory[2] for rigid and semirigid polymers. Obviously, there is a large difference between the theoretical and experimental shape of the binodal, the inclination of tie lines, and the region of stability of the phases. This situation does not arise from inadequacy of theory (which is in fact able to represent the behavior of the PBA/X-500 and PBA/PAN systems), but is due to the incompatibility of cellulose and CA already in the isotropic state.

To put the foregoing conclusion on a more quantitative basis, we have evaluated the Hildebrand solubility parameters δ at room temperature for cellulose and CA from the sum[3] $\delta = \rho(\sum F_i/M_0)$ over the molar attraction constants F_i of all chemical groups in the repeating unit. The latter are tabulated by various authors.[18] The results indicate that for cellulose δ_2 = 15.0 ± 0.5 and for CA δ_3 = 10.5 ± 0.5. Application of the method of Hansen[18] (based on the contribution from dispersion, polarity, and hydrogen bonds, which may be evaluated by using values tabulated by Van Krevelen[18]) yielded δ_2 = 15.6 and δ_3 = 10.0. Calculation of χ_{23} from the difference $(\delta_2 - \delta_3)$,[2] as indicated in part 1,[1] yielded $\chi_{23} \sim 3.0$ for the pair cellulose (I or L)/CA (B). Finally, the critical χ_{23}^c was calculated from the degrees of polymerization as indicated in part 1[1] yielding $\chi_{23}^c = 4.2 \times 10^{-3}$ (DP = 290) and 3.2×10^{-3} (DP = 460). Since $\chi_{23}^c < \chi_{23}$, the two polymers should demix at some value of the composition in the undiluted state. In solution, assuming the $\chi_{12} = \chi_{13}$ (cf. seq.), compatibility is expected when the polymer volume fraction is below ~0.005, which is somewhat smaller than the value of ~0.028 deduced from Figures 3 and 4 with mixtures of CA and cellulose I or L.

The inclination of the tie lines experimentally observed has an opposite sign with respect to the theoretical prediction in Figure 5. Hsu and Prausnitz[19] have calculated binodals in ternary systems based on the Flory–Huggins equation. They show that a change of sign of tie lines can occur by alteration of the χ_{12} and χ_{13} parameters describing the interaction of the solvent with the two polymers. In a particular case (their Figure 6), the situation $\chi_{12} > \chi_{13}$ corresponds to slopes having the same sign as those observed here ($\chi_{12} < \chi_{13}$ reverses the slope). We have therefore tried to evaluate the latter parameters by calculating the value of δ_1 for the diluent. Having no available data to estimate the contribution of LiCl, we have determined that for pure DMAc $\delta_1 \sim 9 \pm 0.5$. Following the approach indicated above we obtained $\chi_{12} \sim 5.0$ and $\chi_{13} \sim 0.5$, which would be in line with Hsu and Prausnitz data assuming that LiCl played a comparable salting-in role on the two polymers. The assumption $\chi_{12} > \chi_{13}$ would tend to reduce the difference between the critical concentration for incompatibility evaluated above.

A final comment concerns the comparison of the present results with those obtained[4,5] for systems composed of two rigid polymers and a solvent. The latter systems exhibited a coexistence of three phases within the region corresponding to the biphasic gap of the two polymers. When above $v_2' = 0.065$ (0.08) the mesophase of cellulose I (L) in DMAc + 7.8% LiCl appears (Figures 3 and 4), we would have expected a region of coexistence of an isotropic and an anisotropic cellulose solution. The width of the biphasic gap was estimated in ref 14 to be $v_2''/v_2' \sim 1.32$ for a sample of regenerated cellulose II with DP = 288. However, it was also shown[14] that the solubility line encroached the biphasic gap, particularly when DP increased. Therefore, we believe that the anisotropic phase of cellulose observed here is not a pure phase. The separation of its components would require more extensive equilibration and problematic[14] centrifugation. Recognition of the biphasic nature of the anisotropic "phase" might not pose the same constraints to the variance of the system, as observed with the systems composed of two rigid polymers.[4,5] Here, in fact, the diluent is strictly a two-component system, although a large LiCl disproportion was not observed. For a truly three-component system, invariant compositions should prevail within the region of coexistence of three phases[4,5] (shadowed area in Figure 4). The data for the low molecular weight cellulose sample (Figure 4) are not inconsistent with this expectation, but a large deviation is exhibited by the system illustrated in Figure 3. Failure to achieve complete equilibration might be involved.

The observation that a mesogenic and a flexible polymer are incompatible not only by virtue of the entropy effect considered in Flory's theory[1,2] but also by virtue of the unfavorable interaction evidenced here enormously complicates the possibility of preparing desirable composites of the two polymers. The copolymerization route would appear a more promising approach.

Acknowledgment. This investigation was supported by the Italian Research Council, project "Chimica Fine e Secondaria".

References and Notes

(1) Bianchi, E.; Ciferri, A.; Conio, G.; Marsano, E.; Tealdi, A. *Macromolecules* 1984, *17*, 1526. Bianchi, E.; Ciferri, A.; Tealdi, A. *Ibid.* 1982, *15*, 1268.
(2) Flory, P. J. *Ibid.* 1978, *11*, 1138. Matheson, R. R.; Flory, P. J. *Ibid.* 1981, *14*, 954.
(3) Paul, D. R.; Newman, S., Eds. "Polymer Blends"; Academic Press: New York, 1978; Vol. I.
(4) Marsano, E.; Bianchi, E.; Ciferri, A. *Macromolecules* 1984, *17*, 2886.
(5) Marsano, E. *Polymer*, in press.
(6) Abe, A.; Flory, P. J. *Macromolecules* 1978, *11*, 1122.
(7) Bianchi, E.; Ciferri, A.; Conio, G.; Lanzavecchia, L.; Terbojevich, M. *Macromolecules*, following paper in this issue.
(8) Kamide, K.; Miyazaki, Y.; Abe, T. *Polym. J. (Tokyo)* 1979, *11*, 523.
(9) Kamide, K.; Saito, M. *Ibid.* 1962, *14*, 517.
(10) Kamide, K.; Saito, M.; Abe, T. *Ibid.* 1981, *13*, 421.
(11) Terbojevich, M.; Cosani, A.; Conio, G.; Ciferri, A.; Bianchi, E. *Macromolecules* 1985, *18*, 640.
(12) Marx, M. *Makromol. Chem.* 1955, *16*, 157. Marx-Figini, M.; Schulz, G. V. *Ibid.* 1962, *54*, 102. Brandrup, J.; Immergut, E. M., Eds. "Polymer Handbook"; Wiley: New York, 1975; V-107.
(13) Turbak, A. F.; El-Kafrawy; Snyder, F. W.; Auerbach, A. B. UK Pat. Appl. GB 2055-107 A, 1981.
(14) Bianchi, E.; Ciferri, A.; Conio, G.; Cosani, A.; Terbojevich, M. *Macromolecules* 1985, *18*, 646.
(15) Yamakawa, H.; Fujii, M. *Ibid.* 1974, *7*, 128.
(16) Brant, D. A.; Goebel, K. D. *Ibid.* 1972, *5*, 536.
(17) Flory, P. J. *Adv. Polym. Sci.* 1984, *59*, 1.
(18) Barton, A. "Handbook of Solubility Parameters and Other Cohesion Parameters"; CRC Press: Boca Raton, FL, 1983.
(19) Hsu, C. C.; Prausnitz, J. M. *Macromolecules* 1974, *7*, 320.

Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 5. Cellulose Acetate in *N*,*N*-Dimethylacetamide

E. Bianchi, A. Ciferri,* G. Conio,[†] L. Lanzavecchia,[‡] and M. Terbojevich[§]

Istituto di Chimica Industriale, Università di Genova, Genoa, Italy. *Received June 5, 1985*

ABSTRACT: The critical volume fraction for mesophase formation, v_2', was determined in *N*,*N*-dimethylacetamide for fractions of a cellulose acetate with DS = 2.3. The triacetate and the monoacetate did not exhibit a mesophase. The occurrence of a biphasic region was demonstrated. v_2' attains a limiting value of 0.33 at room temperature and increases with temperature, but encroachment with the solubility line prevents the observation of the $T_{NI}{}^0$ temperature for the pure polymer. Diluted solution data allow an evaluation of the persistence length, q, of the diacetate, which is 70 Å at 25 °C, and $d \ln q/dT = -7.8 \times 10^{-3}\ \text{deg}^{-1}$. Light-scattering data reveal the occurrence of a small degree of association in moderately concentrated solutions. These results, and those previously obtained with other systems, are analyzed to derive final conclusions concerning the molecular interpretation of mesophase formation. v_2' and the thermotropic effects are definitively correlated with chain rigidity, and association effects play only a minor role. Almost all features of the limiting behavior of semirigid mesogens are described by theory. However, a discrepancy on the absolute value of the limiting v_2' remains, for which, however, several justifications can be advocated. A successful theory for the overall behavior of semirigid mesogen is not yet available.

The first two papers of this series dealt with the relationship between chain rigidity and mesophase formation for hydroxypropyl cellulose (HPC) in *N*,*N*-dimethylacetamide (DMAc)[1] and in dichloroacetic acid (DCA).[2] In parts 3 and 4 we investigated the relationship between aggregation and mesophase formation for cellulose in DMAc + LiCl.[3,4] In the final part of this series, we study chain rigidity and mesophase formation for cellulose acetates, with varying degrees of substitution, in DMAc.

Several investigations have dealt with the mesophase

[†] Centro Macromolecole Sintetiche e Naturali, CNR, Genoa, Italy.

[‡] Thesis submitted to the University of Genoa for the Doctoral degree in Chemistry.

[§] Centro Studi Biopolimeri, CNR, Padua, Italy.

0024-9297/86/2219-0630$01.50/0