Liquid Crystal Solutions. Ternary Systems Involving a Nematogenic and a Nonnematogenic Polymer

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ABSTRACT: The ternary diagram involving a rigid polymer (unfractionated poly(*p*-benzamide), PBA), a more flexible polymer (unfractionated polyterephthalamide of *p*-aminobenzhydrazide, X-500), and a diluent composed of dimethylacetamide plus 3% LiCl was investigated. Isotropic ternary solutions were monophasic below the critical concentration at which the binary PBA/diluent system formed a mesophase. At this point, an increase of X-500 content produced an increase of the overall PBA + X-500 concentration at which a nematic phase appeared. At still greater concentrations, the system always remained biphasic, and in no case was a single anisotropic phase observed. Isolation of conjugated phases by centrifugation, analysis of their composition and relative volumes, separation of X-500 from PBA, and determination of the molecular weight of the species partitioned in each phase were performed. A peculiarity of the diagram is that the binodal for the anisotropic solution lies on the PBA composition axis, indicating complete exclusion of X-500 from the mesophase. X-500 is found only in the conjugated isotropic phase; thus the tie lines are strongly inclined with respect to the line describing solutions with a constant X-500/PBA ratio. The molecular weight of PBA fractionated in the conjugated isotropic phase is considerably lower than that segregated into the mesophase. This effect is more pronounced the larger the X-500/PBA ratio at a given overall composition or the larger the overall composition at a constant X-500/PBA ratio. The X-500 persistence length is intermediate between that of a typical rigid polymer and a conventional random coiling polymer. Still, most of the above results are in excellent agreement with theoretical predictions valid for ternary systems involving rodlike and random coiled polymers.

Anisotropic solutions of rigid and semirigid polymers have been extensively investigated in recent years. Detailed phase diagrams describing the field of stability and coexistence of isotropic and anisotropic phases have been reported for binary solutions of poly(*p*-benzamide) (PBA),[1-3] or poly(γ-benzyl L-glutamate) (PBLG).[4] Phase relationships have also been reported for solutions of poly(*p*-phenyleneterephthalamide) (PPDT),[5] polyisocyanates,[6] cellulose,[7] cellulose derivatives,[8-11] and poly(*p*-phenylenebenzobisthiazole (PBT).[12] Interest in these types of studies is due to new developments in the fundamentals of liquid crystals[13] and to new technologies leading to ultrahigh modulus polymers.[1,5]

The experimental investigations quoted above[1-12] refer to binary solutions involving one polymer and one solvent system (a two-component solvent is often approximated as a one-component system[3,14]). The fact that each of the polymers investigated was actually a mixture of species differing in chain length was not adequately accounted for in the above investigations. Only recently, the problem of partitioning of rodlike molecules between isotropic and anisotropic phases according to their molecular length has been the subject of detailed experimental investigation.[15,16] On the theoretical side, the role of a difference in length of two rodlike solutes on the biphasic equilibria was described by Abe and Flory.[17] Ternary diagrams involving two monodisperse rodlike solutes differing in their axial ratio, x, and not necessarily possessing the same chemical structure show that a single anisotropic phase should occur at high enough concentration. When the concentration is decreased, a biphasic region is expected. The width of this region is greater than for monodisperse systems and the anisotropic phase is richer in the high molecular weight polymer than the isotropic one. Volchek et al.[18] and Aharoni[19] investigated mixtures of two chemically different rodlike polymers in a common solvent and confirmed that the well-known compatibility principle is verified. In fact, at high enough polymer concentration the two polymers entered a single anisotropic phase. The theory was extended to the case of rodlike particles having a most probable[20] or a Poisson[21] distribution of molecular lengths. These theoretical predictions were partly verified by two experimental studies quoted above.[15,16] Mixtures of two mesogenic polymers in the solid state may possibly have technological relevance.[18]

Consideration of the behavior of a mixture of rodlike molecules differing in length or in composition was followed by the analysis of the behavior of mixtures involving polymers differing also in their conformational rigidity. Actually, from a technological standpoint, there is a great deal of interest in mixed systems including a rigid and flexible polymer as a way to produce composite materials based on ultrahigh modulus polymers.[22] Fragmentary results have been published concerning the behavior of mixture of poly(*n*-hexyl isocyanate) (PHIC)–polystyrene,[19,23] PTB–poly[2,5(6)-benzimidazole],[24] PPDT–nylon 6,[25] PBA–polyterephthalamide of *p*-aminobenzhydrazide (X-500),[26] and a series of aromatic polyamides with greater flexibility than PBA.[27] A theoretical guideline is offered by the calculation of the ternary system comprising a monodisperse rodlike polymer, a random coiled polymer, and a solvent.[28] According to this theory, the flexible polymer is essentially excluded from the anisotropic phase. The isotropic phase exhibits a somewhat greater tolerance for the rodlike polymer. None of the fragmentary results quoted above[19,23-27] represents a comprehensive quantitative study of the partition of rodlike and flexible solutes between isotropic and anisotropic phases, although the prevailing incompatibility of the two polymers was demonstrated.[19,27]

In the present paper we analyze the phase diagram involving polydisperse PBA, polydisperse X-500, and a solvent composed of *N*,*N*-dimethylacetamide (DMAc) + 3% LiCl. The boundaries of the biphasic regions have been determined by isolating the coexisting phases and determining their equilibrium composition and molecular weight partition. Interest in this particular system arises from the fact that both PBA and X-500 form separately

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ultrahigh modulus fibers.[5,29] However, X-500 does not form a mesophase at rest[29] and its conformation, as judged by the persistence length,[30,31] is intermediate between that of a rodlike polymer and that of a random coiled polymer.

Experimental Section

Materials and Stock Solutions. The X-500 sample used in this investigation was prepared by Dr. J. Preston according to the method described in the literature.[32] Its intrinsic viscosity in dimethyl sulfoxide (Me_2SO) at 25 °C was 1.36 dL/g, corresponding to a molecular weight of about 8200.[31] The PBA sample was synthesized by us following the method described by Yamazaki et al.[33] Its intrinsic viscosity in 96% H_2SO_4 at 25 °C was 1.94 dL/g, corresponding to a molecular weight of about 13 300.[34] The solvent was analytical grade DMAc containing 3 g of LiCl/dL of DMAc. The samples were separately dissolved in the solvent by slow stirring at room temperature (ca. 20 °C) for about 2 months. The solutions were then filtered with an extrusion apparatus equipped with a polypropylene filter. The concentration of the filtered solutions was determined by precipitating the polymer with water. LiCl was eliminated during the same operation. Polymer concentration, C_p, is given as weight of polymer per 100 g of solution. The stock solutions of X-500 and PBA prepared in this way had C_p values of 7.77 and 8.77 g/100 g, respectively. Additional stock solutions of X-500 (C_p = 6.18 and 3.16%) and of PBA (C_p = 6.88 and 4.30%) were prepared by diluting the most concentrated stock solution. Concentrations are alternatively expressed as polymer volume fraction. These were calculated from the coresponding C_p by using the partial specific volumes of X-500 and PBA, using the specific volume of the diluent, and assuming additivity.

Phase Diagram. Ternary mixtures of X-500, PBA, and solvent were prepared by mixing weighed amounts of the above pairs of stock solutions as to obtain about 10 mL of total volume (see Table I). The overall composition of the ternary systems was calculated from the weight and composition of the corresponding stock solutions. Mixtures were stirred by slow rotation (1 rpm) at room temperature (~20 °C) for about 1 month to reach equilibrium. Mixtures showing biphasic separation were then centrifuged at 3000 rpm for 2–3 h. Under these conditions a good separation of the two phases was obtained, and the boundary between them could easily be determined. The volume of the two phases was determined by calibration of the centrifuge tube, and the volume fraction of isotropic phase (volume of isotropic phase/total volume) was calculated. The composition of the two phases was determined by using weighed aliquots of each phase. The aliquot was diluted with the solvent (DMAc + 3% LiCl) and the polymer precipitated with water. The precipitate was washed with hot water (to extract completely LiCl), dried under vacuum at 60 °C, and weighed. To determine which part of the precipitate was X-500 and which PBA, an extraction with Me_2SO was performed. The latter is a good solvent for X-500[31] but does not dissolve PBA. Optical anisotropy of solutions was determined with a Reichert Zetopan polarizing microscope.

Viscosity. Intrinsic viscosities were determined at 25 °C (±0.1) by means of Ostwald and Ubbelohde viscometers with flow time for the solvent greater than 100 s. The relationship of Schaefgen et al.,[34] used for determining the molecular weight of PBA, is $[\eta] = 1.9 \times 10^{-7} M_w^{1.7}$ and is valid in 96% H_2SO_4 for $\bar{M}_v < 12000$.

LiCl Partition. The amount of LiCl in the coexisting isotropic and anisotropic phases was determined by atomic absorption spectrophotometry on the waters used for washing the polymer precipitated from each phase.

Specific Volumes. The partial specific volume of X-500 in DMAc + 3% LiCl solutions was determined pycnometrically at 25 °C and found to be $\bar{v}_{\text{X-500}} = 0.6968$ mL/g. The partial specific volume of pBA in the same solvent was found to be $\bar{v}_{\text{PBA}} = 0.7542$ mL/g. The specific volume of the solvent was found to be 1.0356 mL/g.

Results and Discussion

Data regarding the composition of the various solutions are collected in Table I. Under the heading "binary solutions" are indicated the concentration and the phase

Table I
Summary of Data for the X-500/PBA/DMAc + LiCl System

binary solutions			ternary systems									
	amount mixed		overall composition,[a] % C_p			composition iso,[a] % C_p			composition aniso,[a] % C_p			
solution	g of A, B, or C	g of A', B', or C'	X-500	PBA	X-500 / X-500 + PBA	X-500	PBA	X-500 + PBA	X-500	PBA	ϕ	observations
A (X-500), C_p = 7.77% iso; A' (PBA), C_p = 8.77% aniso	6.9719	3.0179	5.42	2.65	0.67		na		na		0.81	biphasic
	4.3008	6.1514	3.20	5.16	0.38	5.31	1.09	6.40	0	11.2	0.57	biphasic
	2.4260	7.4236	1.91	6.61	0.22	3.93	2.1	6.03	0	10.0	0.40	biphasic
	1.0150	8.8700	0.80	7.87	0.09		na		na		0.23	biphasic
B (X-500), C_p = 6.18% iso; B' (PBA), C_p = 6.88% aniso	6.6414	2.9931	4.26	2.14	0.66		na		na		0.85	biphasic
	3.6994	5.6015	2.46	4.14	0.37	3.3	2.0	5.3	0	9.3	0.67	biphasic
	2.4903	7.1580	1.59	5.1	0.24	2.14	3.13	5.27	0	8.12	0.62	biphasic
	0.9560	8.6950	0.61	6.20	0.09		na		na		0.42	biphasic
C (X-500), C_p = 3.16% iso; C' (PBA), C_p = 4.30% iso	6.5393	3.0983	2.14	1.38	0.61	2.14	1.38	3.52				iso + gel
	3.9190	5.9366	1.26	2.59	0.33	1.26	2.59	0.33				iso
	2.5140	7.4681	0.79	3.22	0.20	0.79	3.22	4.01				iso
	1.0329	8.7993	0.33	3.85	0.08	0.33	3.85	4.13				iso
	0.5227	0.5472	2.82	0.46	0.85	2.82	0.46	3.28				iso + gel

[a] Percent compositions are grams of polymer per 100 g solution. na = not analyzed.

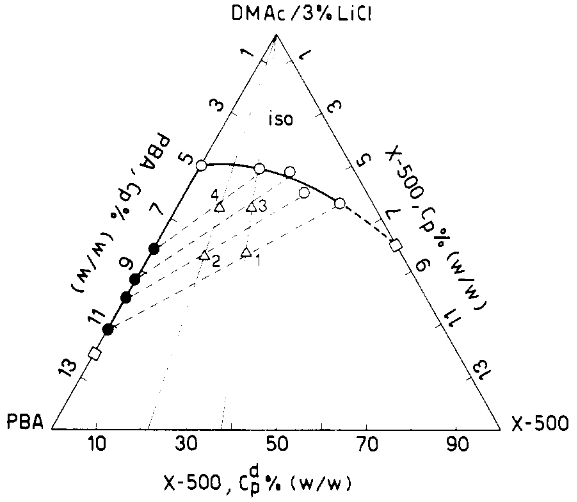

Figure 1. Ternary phase diagram for the system PBA/X-500/DMAc–3% LiCl at 20 °C: (○ and ●) composition of conjugated isotropic and anisotropic phases, respectively; (□) concentration at which a crystalline phase appears; (△) overall composition of biphasic mixtures (1, X-500 3.20%, PBA 5.16%; 2, X-500 1.91%, PBA 6.61%; 3, X-500 2.46%, PBA 4.14%; 4, X-500 1.59%, PBA 5.1%). (Cf. Table I.)

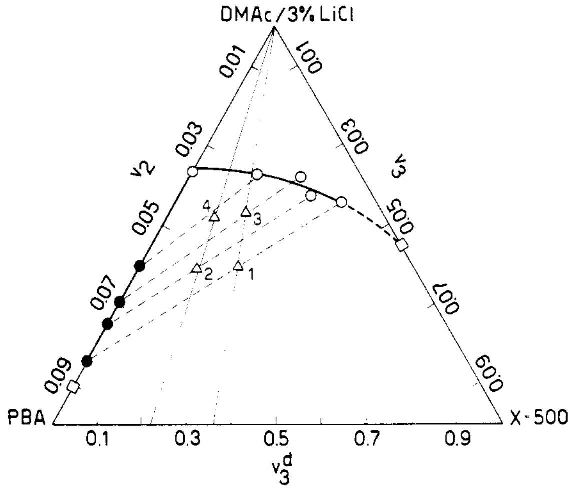

Figure 2. Same data appearing in Figure 1, with concentration expressed as volume fraction.

of the stock solutions, and the amount of these that was mixed for preparing the ternary systems. Under the heading "ternary systems" we indicate, in columns 3–5, the corresponding overall composition given as grams of X-500 or of PBA per 100 g of ternary system. The overall ratio (w/w) of X-500 to the total solid (X-500 + PBA) is also given. In columns 6–10 we give compositions of isotropic and anisotropic phases (separated by centrifugation) as grams of X-500 and of PBA per 100 g of isotropic or anisotropic solution. The total solid in the isotropic phase per 100 g of solution is given in column 8. The total solid in the anisotropic phase coincides with the value in column 10, since no X-500 was detected in the latter phase. Also, in the case of mixtures prepared from the isotropic stock of PBA—which yielded only isotropic solutions—the overall composition and the composition of the isotropic phase obviously coincide. The volume fraction of the isotropic phase, ϕ, and a specification of the phase of the system are given in the last two columns of Table I. In no case did the compositions investigated yield a single anisotropic phase. Formation of a small amount of insoluble gel was observed for the isotropic solutions having the largest X-500/(X-500 + PBA) ratio.

We note that the two phases separated by centrifugation appeared homogeneous and stable, and the ϕ value was not altered by prolonging the time used to reach equilibrium. Moreover, the separation of the two phases was obtained with relatively short times and speed of rotation. These findings are at variance with the behavior of binary PBA–DMAc/LiCl solutions previously reported.[15]

Optical determinations on the binary PBA systems yielded $C_p^* = 5.0\%$ as the critical concentration above which an anisotropic phase starts growing at the expense of the isotropic one. The anisotropic solutions of PBA crystallized at $C_p = 12\%$. The X-500 solution was isotropic up to $C_p = 8.0\%$ when crystallization of polymer was noticed. Within the experimental errors, the LiCl concentration in the isotropic and anisotropic phases was found to be the same. The addition of LiCl was necessary in order to solubilize PBA in DMAc. In fact, an increase of solubility (salting in) occurs up to ~3.5% LiCl, followed by a salting out at still greater LiCl concentration.[3] X-500, instead, is soluble in pure DMAc, and 3% LiCl does not increase its solubility.[35] These salting in–salting out effects have been adequately described[36-38] and are primarily due to binding of LiCl to the amide bond, followed by saturation (no net charge is built up at these high salt concentrations).

The above data were used to construct the ternary diagrams illustrated in Figures 1 and 2. The diagram of Figure 2, based on compositions expressed as volume fraction, will be preferentially used to facilitate comparison with theory.[28] The indexes 1, 2, and 3 refer to diluent, PBA, and X-500, respectively. Binary mixtures PBA/diluent ($v_2 = 1 - v_1$), X-500/diluent ($v_3 = 1 - v_1$), and PBA/X-500 are represented by the left-hand side, the right-hand side, and the base axis, respectively. The composition along the base axis is given as $v_3^d = 1 - v_2^d$ (volume of X-500 divided by the combined volumes of X-500 and PBA); the superscript d signifies that no solvent is present. Composition within the ternary diagrams is $v_2 + v_3 = 1 - v_1$. Straight lines from the vertex to the base represent solutions with constant X-500/PBA ratio (or constant v_3^d).

The mixtures made from binary isotropic solutions (last five entries in Table I) yielded isotropic ternary solution. When the binary PBA/diluent system was an anisotropic one, biphasic ternary mixtures were obtained. Beginning with the binary PBA/diluent system at its critical concentration v_2^* (cf. Figure 2), an increase of X-500 concentration produces an increase of the combined PBA + X-500 concentration at which an anisotropic phase appears, as indicated by the downward trend of the $(v_2 + v_3)^*$ line. The slope of the latter line increases with X-500 content. From the last experimental point the curve is extrapolated (dotted line) to the solubility limit of the binary X-500/diluent system. In the absence of crystallization, $(v_2 + v_3)^*$ would hit the left-hand side axis at a greater v_3 value (cf. seq.). In previous determinations of ternary diagrams of this type, the position of the $v_2 + v_3$ line separating the isotropic from the biphasic solutions was determined by tracing a somewhat arbitrary boundary between the composition of isotropic and biphasic solutions. This is strikingly at variance with the present determination, in which the $(v_2 + v_3)^*$ are the experimentally determined compositions of the pure isotropic solutions *separated* from the pure anisotropic ones. In this way, not only is the boundary between isotropic and biphasic solution established with greater precision but the composition of each isotropic solution—given in terms of both v_2^* and v_3^*— is easily related to the composition of its

Table II
PBA Fractionation Data

C_p, %			isotropic solution		anisotropic solution	
overall	X-500 / (X-500 + PBA)	ϕ	$[\eta]$,[a] dL/g	$\bar{M}_v$	$[\eta]$,[a] dL/g	$\bar{M}_v$
8.36	0.38	0.57	0.76	7 600	2.07	13 800
8.51	0.22	0.40	0.88	8 300	2.07	13 800
6.60	0.37	0.67	1.17	9 900	2.01	13 600
6.69	0.24	0.62	1.31	10 500	2.23	14 400

[a] $[\eta]$ in 96% H_2SO_4 at 25 °C. Original PBA: $[\eta]$ = 1.94 dL/g, $\bar{M}_v$ = 13 200.

conjugated anisotropic phase. This is represented by the tie lines linking the composition of the conjugated phases on the binodals for the isotropic and the nematic phases (dashed lines). The overall composition for the four mixtures for which tie lines are given is indicated by the triangles (1, 2, 3, and 4) lying on the lines connecting the vertex to the base at the particular v_3^d composition. The strong inclination of the tie line with respect to the vertex-to-base line is a quantitative representation of the disproportion of PBA and X-500 in the two phases. With respect to the overall composition, the isotropic solution is invariably richer in X-500, while the anisotropic solution is richer in PBA. Actually, the binodal for the anisotropic phase essentially coincides with the binary PBA axis, illustrating the total exclusion of X-500 from the pure nematic phase of PBA. We also note that for a given v_3^d (or v_2/v_3 ratio), the enrichment of X-500 in the isotropic solution increases with decreasing diluent content. At still larger polymer concentration, crystallization of the binary and of the ternary systems occurred.

All of the observations reported above are in line with the theoretical prediction[28] for the phase diagram for mixtures of monodisperse rodlike and random coiled molecules. Our system, however, includes two polymers having, likely, a most probable distribution. Therefore, in terms of the results for polydisperse systems discussed in the introductory section, we expect that a fractionation based on molecular length is *superimposed* on the disproportion of the polymers due to chain conformation. The effect of this fractionation should be evident for PBA, since this is the only polymer present in both phases. Previous work[15] showed that, in line with theoretical predictions,[20] the solute molecular weight in the anisotropic phase increased as the volume fraction of the isotropic phase increased. In the binary system,[15] ϕ was varied by changing the overall composition C_p. In the present system, ϕ is affected by the overall composition and also the X-500/PBA ratio, as illustrated in Figure 3. In the latter, the volume fraction of the isotropic phase is plotted against the weight fraction of X-500, using the data for the eight biphasic mixtures appearing in Table I. The data fall on two curves, one characterized by an overall (X-500 + PBA) C_p = 6.6 ± 0.2% and another by an overall C_p = 8.37 ± 0.3%.

Intrinsic viscosities were determined for PBA occurring in the conjugated isotropic and anisotropic phases of the mixtures included in Table I (in the case of the isotropic phase, X-500 was previously extracted with Me_2SO). The corresponding molecular weights were calculated and are collected in Table II. In analogy with the results presented in previous work,[15] $\bar{M}_v$ in the anisotropic phase is consistently larger than in the isotropic one. The enrichment of the high molecular weight component in the anisotropic phase is not greatly affected by the variables affecting the system. However, the molecular weight of PBA that goes into the isotropic phase is lower, at a given overall C_p, the higher the weight fraction of X-500. At a given weight fraction of X-500, an increase of the overall C_p causes a reduction of the molecular weight of PBA in the isotropic phase. These relationships are more complicated than in the previously investigated binary systems[15] due to the combined effect on ϕ of the overall composition and of the X-500 weight fraction.

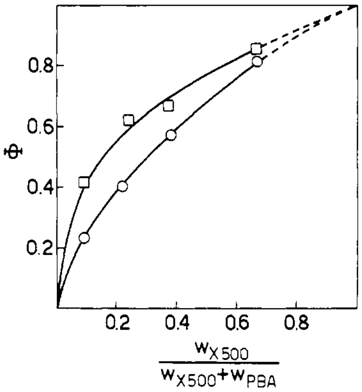

Figure 3. Variation of the volume fraction of isotropic phase with the weight fraction of X-500: (□) overall composition C_p = 6.6 ± 0.2; (○) overall composition C_p = 8.37 ± 0.3. (Cf. Table I.)

As indicated in the introductory section, X-500 has a persistence length on the order of 50 Å,[30,31] intermediate between those of typical random coils and of molecules that are rigid enough to form a mesophase at rest. On the basis of this persistence length, X-500 would be expected[29] to form a mesophase at $v_3^* \sim 0.8$, but this expectation cannot be verified due to earlier occurrence of crystallization. However, it has been suggested that a nematic phase may form when X-500 solutions are subjected to a flow field.[29,39] In previous work it was indicated that X-500 tends to random coil behavior at a molecular weight of about 40 000.[30,31] The present sample has $\bar{M}_v \sim 8200$, corresponding[31] to a contour length of ~450 Å, which is about 10 times the value of the persistence length. Its overall conformation may be at a border line between that of a wormlike chain and that of a random coil. By contrast PBA, which forms a mesophase at $v_2 < 0.1$, has a persistence length[40] of ~400 Å. Our PBA sample has $\bar{M}_v \simeq$ 13 000, corresponding[29] to no more than two persistence lengths. Obviously, there is a considerable difference between the conformations of our PBA and X-500 samples. However, in view of the above considerations, it is perhaps surprising that X-500 conforms to the theoretical predictions[28] valid for a random coil in a ternary mixture with a nematic polymer. The theoretical basis for incompatibility,[28] the interference of the random coil with the mutual orientation of the rodlike sections of a rigid polymer, may nevertheless be fullfilled in the present system. However, it is interesting to speculate about the hypothetical possibility X-500 would form a mesophase at $v_3^* \sim 0.8$ if earlier crystallization did not occur. In this case, the phase diagram might assume characteristics typical of those expected for two rodlike polymers.[17] In particular, the binodal for the isotropic phase would be extended to $v_3^* \sim 0.8$, and the composition range of biphasic solutions would be limited by a line below which a single anisotropic phase would occur. One could possibly treat such a diagram in terms of the Abe and Flory[17] theory of two rodlike polymers having axial ratios in the ratio 8:1, corresponding to the ratio of persistence lengths of PBA and X-500. Such a diagram is also expected[17] to show considerable inclination of tie lines with respect to the vertex-to-base line.

It will be interesting to explore in future work if these speculations can be put to a more stringent test in the case of pairs of mesogenic polymers exhibiting significant differences in their critical concentration before crystallization occurs. Also, quantitative determination of tie lines for systems involving PBA and a more flexible polymer than X-500 should be of interest, as well as a consideration of the possible role of actractive interactions between two polymers. The latter may occur for some special systems.

The above results and considerations should offer useful guidelines for the identification of conditions under which one could prepare technologically relevant composites based on these types of polymers.[22]

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References and Notes

(1) Panar, M.; Beste, L. F. *Macromolecules* **1977**, *10*, 1401.
(2) Kulichiklin, V. G.; Vasil'eva, N. V.; Serova, L. D.; Platanov, V. A.; Mil'kova, L. P.; Andreyeva, L. N.; Volkohina, A. V.; Kudryavtsev, G. I.; Papkov, S. P. *Polym. Sci. USSR* (*Engl. Transl.*) **1976**, *18*, 672.
(3) Balbi, C.; Bianchi, E.; Ciferri, A.; Krigbaum, W. R. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2037.
(4) Miller, W. G., Jr.; Ray, J. H.; Wee, E. L. "Liquid Crystals and Ordered Fluids"; Porter, R., Johnson, I., Eds.; Plenum Press: New York, 1974; Vol. II.
(5) Kwolek, S. L. U.S. Patent 3 671 542 (du Pont), 1972.
(6) Aharoni, S. M. *Macromolecules* **1979**, *12*, 94.
(7) Chanzy, H.; Pegny, A. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1137.
(8) Werbowyj, R. S.; Gray, D. *Macromolecules* **1980**, *13*, 69.
(9) Aharoni, S. M. *Mol. Cryst. Liq. Cryst.* **1979**, *56*, 237.
(10) Novard, P.; Haudin, J.; Dayan, S.; Sixou, P. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 379.
(11) Conio, G.; Bianchi, E.; Tealdi, A.; Ciferri, A.; Aden, M. M., submitted to *Macromolecules*.
(12) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules* **1981**, *14*, 915.
(13) For a review see: Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds. "Polymer Liquid Crystals"; Academic Press: New York, 1982.
(14) Rajagh, L. V.; Puett, D.; Ciferri, A. *Biopolymers* **1965**, *3*, 421.
(15) Conio, G.; Bianchi, E.; Ciferri, A.; Tealdi, A. *Macromolecules* **1981**, *14*, 1084.
(16) Bianchi, E.; Ciferri, A.; Conio, G.; Tealdi, A., in preparation.
(17) Abe, A.; Flory, P. J. *Macromolecules* **1978**, *11*, 1122.
(18) Volchek. B. Z.; Puzkina, A. V.; Ovsyannikova, L. A.; Vlasov, G. P. *Vysokomol. Soedin., Ser. A* **1979**, *21*, 1037.
(19) Aharoni, S. M. *Polymer* **1980**, *81*, 26.
(20) Flory, P. J.; Frost, R. S. *Macromolecules* **1978**, *11*, 1126.
(21) Frost, R. S.; Flory, P. J. *Macromolecules* **1978**, *11*, 1134.
(22) Prevorsek, D. C. In "Polymer Liquid Crystals"; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1982.
(23) Gupta, A. K.; Benoit, H.; Marchal, E. *Eur. Polym. J.* **1979**, *15*, 285.
(24) Hwang, W. F.; Wiff, D. R.; Helminiak, T. *Org. Coat. Plast. Chem., Prepr.* **1981**, *44*, 32.
(25) Takayanagi, M.; Ogata, T.; Morikawa, M.; Kai, T. *J. Macromol. Sci., Phys.* **1980**, *B17*, 591.
(26) Asrar, J.; Preston, J.; Ciferri, A.; Krigbaum, W. R. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 373.
(27) Aharoni, S. M. *J. Appl. Polym. Sci.* **1980**, *25*, 2891.
(28) Flory, P. J. *Macromolecules* **1978**, *11*, 1138.
(29) Ciferri, A.; Valenti, B. In "Ultra-High Modulus Polymers"; Ciferri, A., Ward, I. M., Eds.; Applied Science Publishers: London, 1979.
(30) Bianchi, E.; Ciferri, A.; Tealdi, A.; Krigbaum, W. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2091.
(31) Bianchi, E.; Ciferri, A.; Preston, J.; Krigbaum, W. R. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 863.
(32) Preston, J.; Black, W. B.; Hoffenbert, W. L., Jr. *J. Macromol. Sci., Chem.* **1973**, *A7*, 67.
(33) Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1373.
(34) Schaefgen, J. R.; Foldi, V. S.; Logullo, F. M.; Good, V. H.; Gulrich, L. W.; Killian, K. L. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1976**, *17*, 69.
(35) Krigbaum, W. R.; Sasaki, S., unpublished results.
(36) Orofino, T. A.; Ciferri, A.; Hermans, J. J. *Biopolymers* **1967**, *5*, 773.
(37) Ciferri, A. In "Treatise on Skin"; Elden, H. R., Ed.; Interscience: New York, 1971.
(38) Bianchi, E.; Ciferri, A.; Tealdi, A.; Torre, R.; Valenti, B. *Macromolecules* **1974**, *7*, 495.
(39) Valenti, B.; Alfonso, G. C.; Ciferri, A.; Giordani, P.; Marrucci, G. *J. Appl. Polym. Sci.* **1981**, *26*, 3693.
(40) Arpin, M.; Strazielle, C. *Polymer* **1977**, *18*, 597.

Influence of External Field on the Liquid-Crystalline Ordering in Solutions of Stiff-Chain Macromolecules

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ABSTRACT: Using the Onsager method, we consider the influence of external fields of the dipole and quadrupole types on the liquid-crystalline ordering in solutions of completely stiff macromolecules (rigid rods), freely jointed semiflexible macromolecules (chains of freely jointed rods), and persistent semiflexible macromolecules. We construct the corresponding phase diagrams in the variables strength of the external field–concentration. A sufficiently strong orientational field of either type suppresses effectively the liquid-crystalline phase transition—this leads to the existence of the critical point on the phase diagrams. At the same time, when a sufficiently strong "disorientational" field of the quadrupole type is applied, the liquid-crystalline phase transition becomes of the second order. The realization of the phase transition induced by the field is generally possible, the case of the macromolecule with a persistent flexibility mechanism in the dipole field being most favorable for its observation.

1. Introduction

It is well-known that in sufficiently concentrated solutions of stiff-chain macromolecules the liquid-crystalline phase can appear.[1] Polymeric materials prepared from liquid-crystalline solutions have remarkable mechanical properties;[1,2] this is mainly due to high orientational order

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