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Composition and Fractionation within Conjugated Isotropic and Anisotropic Phases of Lyotropic Liquid Crystals

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ABSTRACT: The composition of conjugated isotropic and anisotropic phases occurring for solutions of poly(*p*-benzamide) in *N,N*-dimethylacetamide–LiCl was investigated. The phases were separated by ultracentrifugation, preferably following the nucleation of the isotropic phase by dilution of a pure anisotropic solution. The study included the determination of the molecular weight (through intrinsic viscosity) of the solute within the two phases. A selective enrichment of high and low molecular weight species occurred in the anisotropic and isotropic phases, respectively. The solute molecular weight in the anisotropic phase increased as the volume fraction of the isotropic phase was increased. The efficiency of a refractionation process performed by diluting a pure anisotropic phase isolated from the biphasic region was demonstrated. The compositions of isolated isotropic and anisotropic phases were found to decrease with the volume fraction of isotropic phase. The above results are discussed in terms of recent theoretical treatments of polydisperse rodlike molecules. Extremely clear patterns of the nematic order were obtained as a result of fractionation and separation of the isotropic phase.

In a solution of rodlike particles above a critical solute concentration C_p^*, a transformation from an isotropic to an anisotropic phase is experimentally observed.[1-6] However, the two phases coexist in a discrete range of solute concentration. The amount of anisotropic phase grows at the expense of the isotropic one when the concentration is increased from C_p^* to a value C_p^{**}, above which only the anisotropic phase is stable.

A theory developed for monodisperse particles[7] produced a composition–temperature phase diagram which indicates the boundaries of the biphasic region for a given axial ratio x. According to this theory, the C_p^* and C_p^{**} values are the limiting compositions of the pure isotropic and anisotropic phases, respectively, and also the compositions of the coexisting phases within the biphasic region, irrespective of the relative amount of the two phases. Calculations show that this theory yields an approximate expression for the critical volume fraction of the solute in terms of the axial ratio, $v_2^* \simeq (8/x)(1 - 2/x)$. However, this approximation is satisfactory only in athermal solvents.

The experimental determination of C_p^* and C_p^{**} has been performed[1-6] by techniques supposedly sensitive to the first appearance of the anisotropic phase and to the complete disappearance of the isotropic one, respectively. However, reservations about the reliability of some techniques (particularly the viscometric one)[5,6,8] and about the attainment of true equilibrium[5] have recently been made. In particular, Matheson[8] has analyzed theoretically the steady flow viscosity of solutions of rodlike macromolecules in the entire range of polymer concentration. His results indicate that the nucleation of the anisotropic phase occurs at a lower concentration than that indicated by the maximum in the viscosity–concentration plot. This result is in line with recent experimental findings.[5,6] Moreover, all studies performed so far have involved polydisperse rigid polymers. For the latter, preliminary experimental results, as well as theory,[9] indicate a selective partitioning of low and high molecular weight components between the coexisting phases. Actually, the latter theory[9] predicts boundaries of the biphasic region which are strikingly different from the ones predicted by the earlier theory[7] valid for monodisperse systems.

Thus, from both the experimental and theoretical point of view, the need arises for a renewed and more sophisticated attempt to determine the parameters affecting the boundaries of the biphasic region. In this paper we have followed the approach of isolating the coexisting phases and determining their equilibrium composition and molecular weight partition. It will be shown that both parameters are strongly affected by the ratio of phase volumes. We have used the poly(*p*-benzamide)–*N,N*-dimethylacetamide/LiCl systems used in previous investigations.[5]

Experimental Section

Materials and Solutions. The poly(*p*-benzamide) (PBA) sample used in this investigation was kindly supplied by Dr. J.

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Table I
Composition and First Fractionation Data for PBA-DMAc/3% LiCl Solutions Prepared by Direct Mixing

bulk solution			isotropic phase				nematic phase			
C_p, g/dL	$\rho^{25°C}$, g/mL	ϕ	C_p', g/dL	$\rho^{25°C}$, g/mL	$[\eta]$, dL/g	$\bar{M}_v$	C_p'', g/mL	$\rho^{25°C}$, g/dL	$[\eta]$, dL/g	$\bar{M}_v$
7.56	0.9874	0.71	6.27	0.9840	0.985	8900	10.29	1.0000	1.64	12 020
8.45	0.9919	0.45	7.49	0.9888	0.940	8670	10.20	0.9988	1.68	12 200
9.36	0.9949	⟨0.68⟩	7.55	0.9892	0.855	8200	12.36	1.0059	1.62	11 950

Sacco of the Rhône Poulenc Co. It was synthesized at low temperature (−10 to −30 °C) following the technique described by du Pont investigators.[3,10] This sample (sample A) was also used in previous work.[5] Its intrinsic viscosity, $[\eta]$, in 96% H_2SO_4 at 25 °C was 1.21 dL/g, corresponding to a molecular weight of $\simeq$10 000 in terms of the $[\eta]$-$\bar{M}_w$ relationship reported by Schaefgen et al.[11] The solvent was analytical grade *N,N*-dimethylacetamide (DMAc) containing 3 g of LiCl/dL of DMAc. Polymer concentration, C_p, is given as grams of PBA per *deciliter* of solution. For its determination from the weight of the solution, use was made of the density of the solutions, which was determined pycnometrically at 25 °C. C_p generally denotes the overall (bulk) composition, while the symbols C_p' and C_p'' are used for the composition of the isotropic and anisotropic phases, respectively. Biphasic solutions were prepared, as described elsewhere,[5] under moisture-free conditions by adding DMAc/LiCl diluent to a weighed amount of polymer and agitating for 3 months in sealed tubes at room temperature. Alternatively, biphasic solutions were prepared by dilution with a weighed amount of diluent, starting from a single anisotropic phase. For the conjugated isotropic and anisotropic phases, which were separated by ultracentrifugation, C_p's were determined from the weight of the dried polymer, following precipitation with H_2O.

Ultracentrifugation. An analytical ultracentrifuge (Spinco, Model E), operated at 44 770 rpm at 20 °C, was used for determining the volume fraction, ϕ, of the isotropic phase. A schlieren optical system was used. During centrifugation separation of the two phases occurs and the boundary becomes visible on transmitted light. Equilibrium required from 20 to 70 h of centrifugation. Periods of centrifugation of about 8 h were alternated with periods of rest of about 15 h to prevent sedimentation of the polymer. ϕ could be determined from the micrographs, and the known parameters of the cell. Measurements were repeated 3–4 times with a reproducibility of ~3%. The sensitivity for the determination of ϕ was evaluated at ~0.04. The separation of the isotropic phase from the anisotropic phase was performed by using a preparative ultracentrifuge (Spinco, Model L2-65B) operated at 44 000 rpm and 20 °C. Polyallomer tubes were used. No satisfactory separation of the two phases could be achieved without centrifugation. Values of ϕ, determined by calibration of the volumes of the two supernatant phases following centrifugation with the preparative ultracentrifuge, were found to agree with those determined with the analytical centrifuge.

Viscosity. Intrinsic viscosity was determined for diluted PBA solutions at 25 °C in 96% H_2SO_4 by using Ostwald or Ubbelhode capillary viscometers. The relationship of Schaefgen et al.[11] used for determining the molecular weight is $[\eta] = 1.9 \times 10^7 \bar{M}_w^{1.7}$ and is valid for $\bar{M}_v < 12000$. Optical microscopy was performed with polarized light using a Reichert Zetopan microscope.

Results and Discussion

The determination of the volume fraction of the isotropic phase was first performed on solutions which were prepared (as previously done[5]) by direct mixing of PBA and diluent at C_p values of 7.56, 8.45, and 9.36 g/dL. These compositions were chosen because they are within the biphasic region of the phase diagram previously[5] determined. In the latter diagram the limiting compositions of conjugated phases for the DMAc/3% LiCl diluent were $C_p' = 6.6$ g/dL and $C_p'' = 9.8$ g/dL, corresponding, respectively, to $\phi = 1$ and $\phi = 0$ (values of C_p given in ref 5 as grams per deciliter of solvent have been converted to grams per deciliter of solution). In Figure 1 we report (black points) the values of ϕ determined for the solutions with $C_p = 7.56$, 8.45, and 9.36 and include also the limiting values, indicated above, deduced from the previous work. It is seen that the value of ϕ measured at $C_p = 9.36$ g/dL lies considerably above the line defined by the other points. From this and similar unreported deviations we concluded that the direct mixing of PBA and diluent often produces biphasic solutions having a nonequilibrium value of ϕ. This fact, of course, casts some doubts on the realiability of the limiting C_p' and C_p'' values determined, for instance, with the viscometric technique.[5] In spite of these limitations, we report in Table I the results of the determination of polymer concentration, density, intrinsic viscosity, and molecular weight performed on the isotropic and anisotropic phases for the three solutions at $C_p = 7.56$, 8.45, and 9.36 g/dL following separation of the phases by ultracentrifugation. The data show that the anisotropic phase is enriched with the high molecular weight component of the original distribution. The indication of a similar trend was also observed in previous work.[3,5] We also note that the C_p' and C_p'' values may not be constant and appear to depend upon the value of ϕ, in line with the prediction of the recent Flory–Frost[9] theory and in contrast to the original treatment for monodisperse systems.[7]

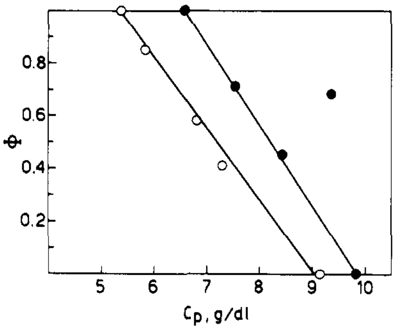

Figure 1. Variation of the volume fraction of the isotropic phase with the overall composition of the biphasic solution of PBA in DMAc/3% LiCl. $T = 20$ °C. Black points: Solutions prepared by direct mixing of PBA and diluent (values at $\phi = 0$ and $\phi = 1$ derived from previous work[5]). Open points: Solutions prepared by dilution of a pure anisotropic phase which was isolated from a biphasic solution having $C_p = 8.45$ g/dL and $\phi = 0.45$.

In order to derive a more precise dependence of the various parameters upon ϕ, we refined our method for determining the latter. Eventually, we concluded that reliable and equilibrium values of ϕ were obtained starting from a pure nematic phase and forming the isotropic phase by diluting the former. A considerable amount of anisotropic solution was obtained by centrifugation of a biphasic solution having $C_p = 8.45$ g/dL and $\phi = 0.45$ (cf. Table I). We used this solution, rather than one formed directly at $\phi = 0$, since it allowed an examination of a second fractionation process during the subsequent dilution (the first fractionation occurred (cf. Table I) during the formation of the biphasic solution at $C_p = 8.45$ g/dL). Small amounts of diluent (0.2 mL of diluent to a 10-mL solution) were gradually added to the anisotropic solution. The solution was stirred for 1–2 days after each addition of diluent, allowed to rest for an additional 2 days, and finally ana-

Table II
Composition and Second Fractionation Data for PBA-DMAc/3% LiCl Solutions Prepared by Dilution of an Anisotropic Phase

bulk solution		isotropic phase			nematic phase		
C_p, g/dL	ϕ	C_p', g/dL	$[\eta]$, dL/g	$\bar{M}_v$	C_p'', g/dL	$[\eta]$, dL/g	$\bar{M}_v$
5.40	1	5.40	1.68	12 200			
5.83	0.85	5.55	1.55	11 600	7.4		
6.80	0.58	5.65	1.45	11 200	8.02	1.92	13 200
7.29	0.41	6.20	1.27	10 350	7.85	1.86	12 950
9.15	0				9.15	1.68	12 200

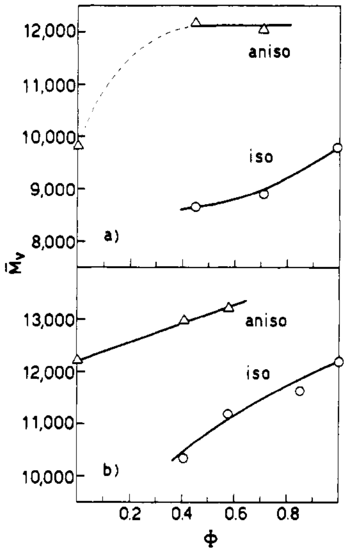

Figure 2. Variation of solute molecular weight with the volume fraction of the isotropic phase. Determinations made on isotropic and anisotropic phases isolated from biphasic solutions. (a) First fractionation; (b) second fractionation.

lyzed with the ultracentrifuge to detect if the first isotropic phase had nucleated. The latter appeared when $C_p'' = 9.15$ g/dL, which was taken to correspond to the lower limit of C_p'' for $\phi = 0$. (It is likely that a still more refined approach to the detection of the first isotropic phase might have increased the latter C_p'' value. Note, however, that the initial concentration of the anisotropic phase was $C_p'' = 10.2$ g/dL (cf. Table I).)

The technique of diluting the pure anisotropic phase was also applied to the determination of the limiting concentration C_p', at which the anisotropic phase is barely detectable. C_p' at $\phi = 0$ was found to be 5.4 g/dL. The latter value was confirmed with optical microscopy. Next, compositions between C_p'' and C_p', namely, $C_p = 5.83$, 6.80, and 7.29 g/dL, were prepared, always by dilution of the anisotropic solution. After these biphasic solutions had reached equilibrium ϕ was determined, and a plot of ϕ vs. C_p is included in Figure 1 (open points). The five ϕ values determined with the dilution technique fall nicely on a single tie line.

Coexisting anisotropic and isotropic phases for the latter solutions were then separated by ultracentrifugation and the corresponding polymer concentration, intrinsic viscosity, and molecular weight were determined. The data are collected in Table II (data for the anisotropic phase at $\phi = 0.85$ are incomplete due to the small amount of solution). The variation of $\bar{M}_v$ with ϕ is illustrated in Figure 2. It is seen that while the same molecular weight is exhibited by pure anisotropic ($\phi = 0$) and pure isotropic ($\phi = 1$) phases, the $\bar{M}_v$ value increases regularly when the amount of the anisotropic phase in the biphasic region is decreased. Simultaneously, the molecular weight of the isotropic phase decreases as the amount of the latter phase is decreased. Thus, even during the second fractionation process of the original PBA sample, the high molecular weight continues to be selectively partitioned in the anisotropic phase, the low molecular weight component is partitioned in the isotropic one, and the efficiency of both processes increases as the amount of the corresponding phases is decreased.

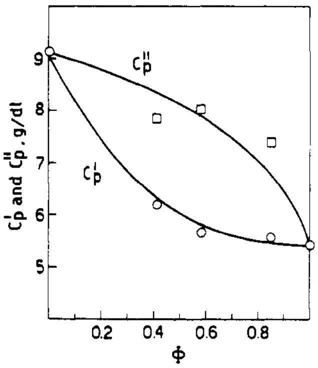

Figure 3. Variation of the composition of the isotropic (C_p') and anisotropic (C_p'') phases isolated from biphasic solutions prepared with the dilution technique.

The data in Table II also reveal a clear dependence of the concentrations C_p' and C_p'' upon ϕ, which is also illustrated in Figure 3. Thus, it is confirmed that the boundaries of the biphasic region are not unequivocally defined as in the original treatment of monodisperse rods.[7] A dependence of C_p' and C_p'' upon the ratio of phase volume is predicted by a more recent theory which considers biphasic equilibria for rodlike particles having a most-probable distribution.[9] The trend of the theoretical prediction corresponds to the experimental trend of C_p' and C_p'' upon ϕ observed here. The latter theory also predicts a fractionation effect of the type illustrated in Figure 2. However, this theory would predict a much broader biphasic region and a more efficient fractionation effect than observed. Our C_p''/C_p' ratio does not appear to be much larger than 2, somewhat greater than the ratio predicted for a monodisperse system, but considerably smaller than expected for a most-probable distribution.[9] We note, however, that our C_p'' value for $\phi = 0$ (9.15 g/dL) cannot be regarded as the upper limit available to the present system. In fact, as indicated above, problems of detection of the first appearance of the isotropic phase lower the reported C_p'' (problems of detection of the early appearance of phases have also been discussed by Flory and Frost[9]). More importantly, the starting anisotropic solution was isolated from a biphasic solution having $\phi = 0.45$ (cf. above). Thus not only the starting C_p'' was lower than for an anisotropic solution prepared directly as a one-phase system but the distribution of the sample subjected to the second fractionation process was narrower than the most-probable one. The large biphasic gap expected for a most-probable distribution should not be expected for a narrower distribution. In fact, Frost and Flory[12] have analyzed the partitioning of solute species between the two phases for the case of a Poisson distribution, which has a much narrower breadth than the most-probable one. The results obtained for the Poisson distribution conform closely to those expected for monodisperse systems.[12]

Thus, while the results obtained during our second fractionation process may not be in disagreement with theoretical predictions, an ambiguity remains in that the

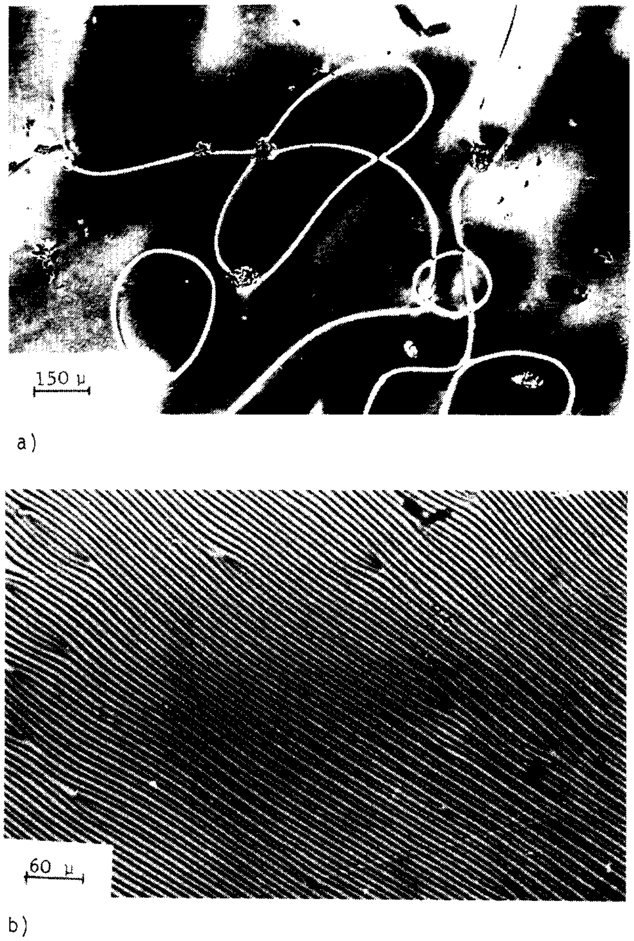

Figure 4. Micrographs of a pure fractionated anisotropic phase: (a) thickness of the layer about 50 μm; (b) same sample at a lower thickness.

biphasic gap observed for the unfractionated polymer is smaller than expected. Indeed, as pointed out elsewhere,[5] all the experimental phase diagrams so far reported for polydisperse polymers appear to conform more closely to the predicted phase diagram for monodisperse system than to the diagram for polydisperse systems.

Several causes of disagreement between theory and experiment can be considered. As pointed out before[5] aggregation occurring for the PBA-DMAc/LiCl system would tend to broaden the molecular weight distribution of unfractionated PBA, which should otherwise be of the most-probable type. Aggregation should not, therefore, explain the deviations observed. Nonconformity of the PBA molecule with the rigid-rod model could be considered. However, the persistence length of PBA in 96% H_2SO_4 was found[13] to be close to 400 Å, a value also indicated by conformational analysis[14] calculation. It is easy to verify that the contour length of our PBA sample is close to the persistence length, so that the molecule can be regarded as rodlike. LiCl disproportion could alter the solvent quality for the isotropic and anisotropic phases and introduce a net charge on the polymer. The problem of LiCl disproportion has been discussed elsewhere.[5] Very slight differences on the LiCl concentration of the two phases may indeed occur.

We believe that a more quantitative assessment of the differences between theory and experiments must await the results of experiments similar to those reported above, but for another polymer system. Such an analysis is currently in progress.

Finally, we present the results of the direct observation of the phases under the polarizing microscope. Micrographs of the pure anisotropic phase, after the first fractionation and separation of the conjugated isotropic phase (C_p = 8.45 g/dL, ϕ = 0.45; cf. Table I) are reported in Figure 4. The typical treadlike pattern of the nematic phase is seen with great clarity. (Some solid inclusions observed in some instances are not surprising in view of the theoretical considerations and experimental results regarding crystallization in lyotropic liquid crystals.[5,15]) We wish to point out that in our previous work with biphasic or anisotropic solutions of PBA, we were unable to detect patterns having such clarity. We attribute this result to the fractionation process and to the complete elimination of the isotropic phase.

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