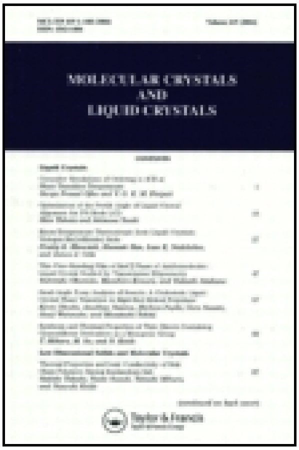

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The Region of Coexistence of Isotropic and Anisotropic Solutions in Polymer Liquid Crystals

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The Region of Coexistence of Isotropic and Anisotropic Solutions in Polymer Liquid Crystals

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The width of the biphasic gap separating the pure isotropic and anisotropic phases has been investigated for samples of poly(*p*-benzamide), poly(γ-benzyl-L-glutamate), and poly(*n*-hexyl isocyanate). The determination was performed by studying the variation of the volume fraction of isotropic phase, ϕ with polymer volume fraction, v_2, particular emphasis being placed on the behavior at low values of ϕ. The dependence of ϕ upon v_2 is more complex than previously reported. Still the biphasic gap, defined by the ratio of the limiting compositions of anisotropic $(v_2'')_{\phi=0}$ and isotropic $(v_2')_{\phi=1}$ phases, is a rather narrow one. $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ does not exceed 1.9 for the polymer investigated. By contrast, theoretical predictions which account for the polydispersity of chain length suggest ratios at least one order of magnitude larger. The behavior of polydisperse system is close to the prediction for a monodisperse one. The origin of the discrepancy is not known.

A thermodynamic requirement, common to all theories of liquid crystallinity[1–3] in the presence of a non nematic solvent (lyotropic systems) is the occurrence of a biphasic gap separating the region of stability of isotropic and anisotropic phases. Within this gap, one can define a volume fraction of isotropic phase, ϕ, and solute fractions v_2' and v_2'', respectively for the isotropic and the anisotropic solution. For a monodisperse rodlike molecule, the conjugated compositions stay constant within the biphasic gap. Only the relative amount of phases changes upon increasing solute concentration between the limit $\phi = 1$ (pure isotropic) and $\phi = 0$ (pure anisotropic). Considering, for instance, Flory's lattice theory[2] for monodisperse rods having axial ratio X, the v_2''/v_2' ratio assumes typical values of 1.20 and 1.55 as X increase from 10 to 100, indicating a rather narrow gap.

The width of the gap is also affected by the quality of the solvent, becoming much wider in poor solvents, a case which we shall not be considering here.

Considerable alterations to the situation described above occur when a distribution of axial ratios is considered. In a series of papers, Flory and coworkers considered the cases of two solutes with different axial ratios,[4] of a most probable[5] and of a Poisson distribution.[6] The small biphasic gap is now considerably widened and a partitioning of the components with larger (smaller) axial ratios in the anisotropic (isotropic) phase is expected. In fact, the compositions v_2' and v_2'' should no longer be independent of ϕ. The *maximum* breath of the gap, for a given $\overline{X}_n$, is characterized by the ratio of the *limiting* compositions $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$, smaller v_2''/v_2' ratios occurring at compositions between those of the pure isotropic and pure anisotropic solutions. These results were also confirmed by Moscicki and Williams[7] who extended the above calculations to a Gaussian distribution of rod lengths.

On the experimental side attention has been focused on methods for determining the width of the gap and the fractionation effect. Early attempts were based on the optical determination of the appearance of anisotropic droplets in isotropic solutions (yielding v_2'), and on the viscosity-concentration behavior exhibiting a maximum and minimum. However, the attribution of these extrema respectively to v_2' and v_2'' was later proven to be incorrect.[9,10,11] Conio *et al.*[12] proposed an analitical technique based on the extrapolation of the variance of ϕ with the overall v_2 within the gap. The extrapolated values of $(v_2')_{\phi=1}$ and $(v_2'')_{\phi=0}$ were also confirmed by the extrapolation of the individual compositions v_2' and v_2'' at $\phi = 1$ and $\phi = 0$, respectively. The $(v_2')_{\phi=1}$ values thus obtained were shown to be in agreement with optical determination. However no independent, reliable determination of $(v_2'')_{\phi=0}$ was available. The results for poly(*p*-benzamide) (PBA), $\overline{M}_v \sim 12{,}000$, in N-N-dimethylacetamide (DMAc) yielded a $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ ratio of ~1.6 somewhat greater than expected (1.55) for a monodisperse system with $X = 100$, but considerably smaller than predicted (cf. seq.) for a most probable distribution having $\overline{X}_n = 100$. Fractionation was observed, but not as efficient as expected, in line with the small gap width.

Results obtained with other systems have been generally in line with the above results. Flory[13] postulated that the failure to observe a widening of the gap for polydisperse systems reflects a failure to achieve equilibrium conditions. In this note we present new data showing that the gap may be wider than so far reported, although still smaller than theoretically predicted.

EXPERIMENTAL

PBA was synthetized following the procedure of Yamazaki *et al.*,[4] described in more detail elsewhere.[15] The sample had intrinsic viscosity, $|\eta|$ = 1.19 dL/g in 96% H_2SO_4 at 25°C, corresponding[12,16] to $\overline{M}_w$ ~ 10,000. Solutions in DMAc + 3% LiCl were prepared as described elsewhere.[12] Poly(γ-benzyl-L-glutamate) was obtained from Sigma Chemicals (Lot 111 F-5102) and had a reported $\overline{M}_w$ ~ 120,000. Solutions were prepared in dioxane stirring at room temperature for about one month.[17] Poly(*n*-hexyl isocyanate) was synthetized as previously described[18] following the procedure of Shashoua *et al.*[19] $|\eta|$ in toluene was 5.42 dL/g corresponding to $\overline{M}_w$ ~ 120,000. Solutions were prepared as previously described.[18] Separation of the conjugated phases was achieved by centrifugation, usually at 6000 rpm for a time up to ~100 hrs. Determination of the volume of each phase was performed at room temperature by calibration of the centrifuge tube. The polymer volume fractions were calculated from the composition in g polymer/dL diluent using the partial specific volume of the polymers determined as previously described.[9,18] The values of $(v_2')_{\phi=1}$ were determined microscopically as previously described.[9]

RESULTS AND DISCUSSION

As noted above, Conio *et al.*[12] proposed a determination of the limiting gap width by extrapolation of v_2 *vs.* ϕ plots. Their data are included in Figure 1 (black points). The long extrapolation of $(v_2'')_{\phi=0}$ from ϕ ~ 0.4 cannot be regarded as an accurate one. In fact, any upward curvature, leading to larger $(v_2'')_{\phi=0}$, would not be detected. We present in the same Figure 1 (open circles) data for a new PBA sample covering a rather wide range of ϕ values. (The axial ratio of the present sample is smaller than the one used by Conio *et al.*).[12] These extensive data clearly show an upward curvature in the v_2 *vs.* ϕ plot when $\phi \lesssim 0.4$. The extrapolated $(v_2'')_{\phi=0}$ is ~0.10, whereas a linear extrapolation of the data would have suggested $(v_2'')_{\phi=0}$ ~0.09. The extrapolation at ϕ = 1 yields $(v_2')_{\phi=1}$ = 0.55 very close to the value determined microscopically. Thus, the revised $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ value is ~1.8, only slightly larger than reported by Conio *et al.*[12]

Other data in Figure 1 include those obtained with poly (γ-benzyl-L-glutamate) (PBLG) in dioxane. In this case, the data can be represented by a straight line down to ϕ ~0.05. The slope is characterized by a $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ ~1.3. Still in Figure 1 we include the data

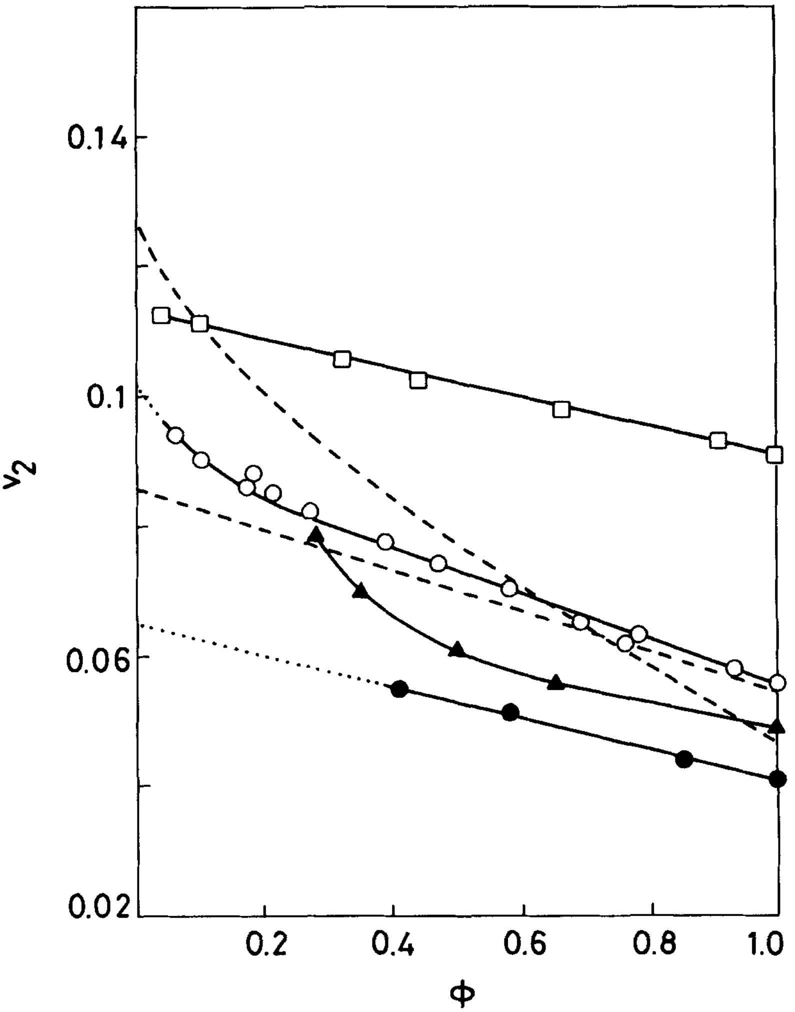

FIGURE 1 Variation of the volume fraction of the isotropic phase with the overall polymer volume fraction in the biphasic region. (●) Data of Conio *et al.*[12] for PBA ($\overline{M}_w$ ~12,000); (○) New data for PBA ($\overline{M}_w$ ~10,000) in DMAc + 3% LiCl; (□) New data for PBLG ($\overline{M}_w$ ~120,000) in dioxane; (▲) Data of Bianchi *et al.*[16] for a PBA/PABH-T (sample A) copolymer in DMAc + 3% LiCl. Broken lines are theoretical curves calculated[7] for (1) $X = 150$; $\overline{X}_w/\overline{X}_n = 1.00$; (2) $\overline{X}_n = 150$; $\overline{X}_w/\overline{X}_n = 1.08$.

recently reported by Bianchi *et al.*[15] for a block copolymer of PBA and the polyterephthalamide of *p*-aminobenzydrazide (PABH-T). A strong upward curvature in the v_2 *vs.* ϕ plot is exhibited in this case. The finding is surprising since the length of the PBA block in the copolymer is similar to that of the PBA homopolymers in Figure 1, while the PABH-T blocks were much shorter.

Data for poly(*n*-hexyl isocyanate) (PHIC) are presented in Figure 2. The full points reproduce the data already published by Conio *et al.*[18] for PHIC in dichloromethane (DCM). These data extend down to ϕ ~0.2 and can be represented by a straight line yielding[18] $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ ~1.9. The data for the newly synthesized PHIC in benzene show a strong upturn when $\phi < 0.2$. In fact, the extrapolation of $(v_2'')_{\phi=0}$ is rather problematic, a lower limit being ~0.40. Thus the ratio $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ for the new PHIC sample would appear to be ~1.9, quite similar to that reported by Conio *et al.*[18] The similarity of these results is primarily due to the smaller slope exhibited by PHIC in benzene with respect to PHIC in DCM when $\phi > 0.4$ (the lower $(v_2')_{\phi=1}$ exhibited by the present data reflects a larger persistence length of PHIC in benzene than in DCM).[18]

The comparison of the experimental data with theoretical expectations based on polydispersity is illustrated by the broken lines in Figures 1 and 2. We have used the theoretical curves for the Gaussian distribution[7] due to simplicity and flexibility of calculation with respect to the most probable distribution.[5] For the latter, in fact, the axial ratio $\bar{X}_n$ and the polydispersity index $\bar{X}_w/\bar{X}_n$ cannot be independently assigned since they are related by the well known relationships[5,20] $\bar{X}_n = 1/1 - p$ and $\bar{X}_w/\bar{X}_n = 1 + p$, where p is the extent of conversion. The actual distribution for our PBA should be of the most probable type, but occurrence of aggregation in DMAc + 3% LiCL[21] might have widened it. For PHIC, an analysis performed in Ref. 18 suggested $\bar{M}_w/\bar{M}_n$ ~8. It is however clear that there is no need to introduce such large polydispersities since indexes as small as $\bar{X}_w/\bar{X}_n = 1.08$ (Figure 1) produce already significant deviations between theory and experiments. In the latter case, $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ is seen to be ~2.3 when $\bar{X}_n = 150$, as opposed to the ratio of ~1.8 measured for PBA. Assuming $\bar{X}_n = 50$, we calculated $(v_2'')_{\phi=0}/(v_2')_{\phi=1}$ ~24 and 8, respectively for the most probable ($p = 0.98$) and gaussian distribution ($\bar{M}_w/\bar{M}_n = 1.30$).

One should note that these deviations between theory and experiment are particularly severe since it is ratio of the limiting compositions $(v_2'')_{\phi=0}$ and $(v_2')_{\phi=1}$ which is considered. Theory predicts much smaller figures for the v_2''/v_2' ratio at intermediate ϕ values. For in-

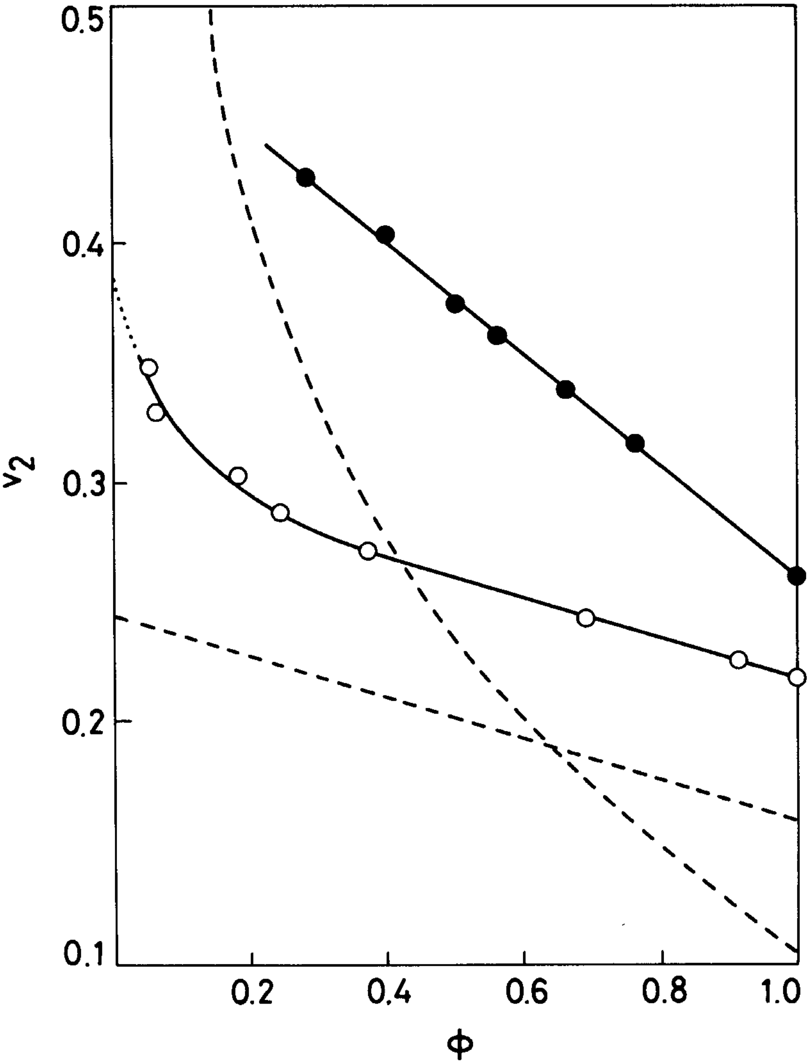

FIGURE 2 Overall composition, v_2, *vs*. volume fraction of isotropic phase for PHIC. (●) Data of Conio *et al.*[18] in DCM ($\overline{M}_w$ = 79,000); (○) New data in benzene ($\overline{M}_w$ = 72,000). Broken lines are theoretical curves calculated[7] for (1) $X = 50$; $\overline{X}_w/\overline{X}_n = 1.00$: (2) $X = 50$; $\overline{X}_w/\overline{X}_n = 1.30$.

stance, the ratios mentioned above for $\overline{X}_n = 50$ decrease to ~3 and ~2, respectively, when $\phi = 0.5$. These ratios have not been measured in this work, but published data indicate values of ~1.3 for both PBA[12] and PHIC.[18]

While the experimental dependence of v_2 upon ϕ does not show the large slopes and upturns theoretically expected, there are still some noteworthy features of the present results. A small upturn is exhibited by the data for PBA and PHIC when $\phi < 0.2$, a considerably larger effect being evident for the PBA/PABH-T copolymer. For PBA and PHIC, the very low molecular weight components of the distribution may be reluctant in entering the mesophase due to their very small axial ratios. Fractionation is, in fact, occurring in both systems.[12,18] Therefore, not all the features theoretically predicted are suppressed. In connection with the fractionation behavior of PHIC, it should be noticed that the sample considered here (similar to the A-I and D-II samples previously considered)[18] has a relatively low molecular weight so that the semirigid behavior[18,22] is not yet manifested. Fractionation was not evident at larger chain length when v_2' is only a function of persistence length, and it is not affected by contour length.[18]

For the PBA/PABH-T copolymer in Figure 1, we believe that the large upturn reflects the occurrence of a PABH-T component (homopolymer or oligomers)[15] which is prevented from entering the mesophase, even when v_2 is increased, due to its flexible conformation. Such exclusion is theoretically predicted[22] and experimentally proven.[23]

The present results confirm that the behavior within the biphasic gap is a major unexplained feature of liquid crystallinity for solutions of rodlike molecules. The predicted widening of the gap, and efficient fractionation, is a natural consequence of the fundamental postulate common to virial and lattice theories[1-3] that the critical concentration is inversely proportional to the axial ratio. For instance, according to Flory[2]

$$v_2' \sim \frac{8}{X} \qquad (1)$$

Future studies may investigate the origin of the discrepancy. There seems to be an unexpected compatibility or interaction between rodlike molecules preventing their separation or efficient fractionation. Possibly, orientational order may occur at a faster rate than back diffusion of shorter rods into the isotropic phase.[13] There is, however, a feature of the present results which Flory might have regarded with sympathy. In the limit of $\phi = 1$, the theoretical curves in Figure 1 reveal that, at given X or $\overline{X}_n$, the occurrence of a distribution will lower v_2'. Since the experimental critical concentrations are usually smaller[18,24,25] than those calculated from Eq. (1), it appears that an account of polydispersity will reduce the latter discrepancy, favoring the lattice over the viral theory.

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References

1. L. Onsager, *Ann. N. Y. Acad. Sci.*, **51**, 627 (1949).
2. P. J. Flory, *Proc. Roy. Soc. London*, **A234**, 73 (1956).
3. D. E. Martire, G. A. Oweimreen, G. J. Agren, S. G. Ryan and H. T. Peterson, *J. Phys. Chem.*, **64**, 1456 (1976).
4. A. Abe and P. J. Flory, *Macromolecules*, **11**, 1122 (1978).
5. P. J. Flory and R. S. Frost, *ibid.*, **11**, 1126 (1978).
6. R. S. Frost and P. J. Flory, *ibid.*, **11**, 1134 (1978).
7. J. K. Moscicki and G. Williams, *Polymer*, **23**, 558 (1982).
8. C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
9. C. Balbi, E. Bianchi, A. Ciferri, A. Tealdi and W. R. Krigbaum, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2037 (1980).
10. S. M. Aharoni, *Macromolecules*, **12**, 94 (1979).
11. R. R. Matheson, Jr., *Macromolecules*, **13**, 643 (1980).
12. G. Conio, E. Bianchi, A. Ciferri and A. Tealdi, *Macromolecules*, **14**, 1084 (1981).
13. P. J. Flory, *Adv. Polym. Chem.*, **59**, 1 (1984).
14. N. Yamazaki, M. Matsumoto and F. Higashi, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1373 (1975).
15. E. Bianchi, A. Ciferri, G. Conio, A. Tealdi and W. R. Krigbaum, submitted.
16. J. R. Shaefgen, V. S. Foldi, F. M. Logullo, V. H. Good, L. W. Gulrich and K. L. Killan, *Polym. Preprints Am. Chem. Soc. Div. Polym. Chem.*, **17**, 69 (1976).
17. L. Sartirana, E. Marsano, E. Bianchi and A. Ciferri, *Mol. Cryst. Liq. Cryst.*, **144**, 263 (1987).
18. G. Conio, E. Bianchi, A. Ciferri and W. R. Krigbaum, *Macromolecules*, **17**, 856 (1984).
19. V. E. Shashoua, W. Sweeney and R. F. Tiez, *J. Am. Chem. Soc.*, **82**, 866 (1960).
20. M. N. Berger and B. M. Tidswell, *J. Polym. Sci., Polym. Symp.*, **42**, 1603 (1973).
21. B. Millaud and Ch. Strazielle, *Macrom. Chem.*, **179**, 1261 (1978).
22. P. J. Flory, *Macromolecules*, **11**, 1141 (1978); R. R. Matheson and P. J. Flory, *ibid.*, **14**, 954 (1981).
23. E. Bianchi, A. Ciferri, G. Conio, E. Marsano and A. Tealdi, *Macromolecules*, **17**, 1526 (1984).
24. A. Ciferri in "Polymer Liquid Crystals", A. Ciferri, W. R. Krigbaum and R. B. Mayer (eds.), Academic Press, N.Y. 1981.
25. E. Bianchi, A. Ciferri, G. Conio, L. Lanzavecchia and M. Terbojevich, *Macromolecules*, **19**, 630 (1986).