SHORT COMMUNICATIONS

Deuterium NMR Studies of the Orientational Order Parameter of Poly(γ-benzyl L-glutamate)s in the Lyotropic Liquid Crystalline State

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Chapman *et al.*[1] have reported a deuterium NMR spectrum of α-helical poly(γ-benzyl L-glutamate) (PBLG) whose amide hydrogen is selectively deuterated. A well-resolved quadrupolar splitting $\Delta\nu_N$ was observed for a liquid crystalline solution (though the concentration is not specified) of PBLG in dichloromethane. We adopted this technique in our study of the orientational order parameter s of PBLG in the lyotropic mesophase.

$$s=(2/3)(\Delta\nu_N/q_{zz}) \qquad (1)$$

where q_{zz} is the component of the field gradient tensor along the molecular axis: Chapman *et al.* estimated a value of $q_{zz}=192.9\,\text{kHz}$ on the basis of the D-NMR data reported for the single crystal of urea-d_4.[2] In this communication, we wish to report our preliminary results obtained for PBLG solutions in dichloromethane (DCM) and in 1,4-dioxane (DOX). Measurements were carried out at several concentrations including those in the immediate vicinity of the phase transition point.

The order parameters determined in this manner may be readily compared with those derived from appropriate theories. Flory[3] proposed his well-known phase diagram for the two component system solvent-rodlike particle

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based on a lattice model in 1956. Experiments on equilibria between an anisotropic liquid crystalline and a dilute isotropic phase in mixtures comprising α-helical polypeptides or *p*-phenylene polyamides in suitable solvents have confirmed the main predictions of the theory. An expression for the orientational order parameter has been explicitly derived in a more recent work with Ronca.[4] For an athermal mixture of rodlike particles with axial ratio x, the orientational distribution function can be defined for the state of equilibrium disorder. For a given angle ψ of inclination to the preferred axis of the domain, the probability of finding the particle with such an orientation is expressed as

$$f(\psi)=f_1^{-1}\sin\psi\exp(-\alpha\sin\psi)\,d\psi \qquad (2)$$

where

$$f_p=\int_0^{\pi/2}\sin^p\psi\exp(-\alpha\sin\psi)\,d\psi \qquad (3)$$

with $p=1$,
and

$$\alpha=-(4/\pi)x\ln[1-v_x(1-\bar{y}/x)] \qquad (4)$$

At a given concentration v_x, the equilibrium value of the disorder index

$$\bar{y} = (4/\pi)x\langle\sin\psi\rangle$$

$$= (4/\pi)x(f_2/f_1) \qquad (5)$$

can be calculated by an iterative process using eq 3, 4, and 5. The order parameter s can then be easily evaluated[5] from the higher moment ($p = 3$) of distribution:

$$s = 1 - (3/2)(f_3/f_1) \qquad (6)$$

Recently, Teramoto et al.[6] examined the applicability of the Flory theory in their phase equilibrium studies on the PBLG/N,N-dimethylformamide system. They noted some sizeable discrepancy in the isotropic-liquid crystal phase boundary concentrations from the theory for low molecular weight samples ($x < 50$). An attempt was made to revise the theory by introducing an interaction energy term, which involves an orientation-dependent interaction and a negative χ-parameter. Inclusion of such an empirical modification gave rise to an improvement in the agreement with observed concentrations. Teramoto's expression can be easily accomodated by adopting revisions in eq 4.

On the other hand, Ballauff[7] examined the effect of flexible side chains within the framework of the Flory theory.[3] Inclusion of the side chain leads to a revised expression for the polymer concentration such that $v_p = v_x(1 + zm/x)$, where z represents the number of side chains per rod, and m the number of segments involved in a side chain. Accordingly, the effective value of the axial ratio is given by $x(1 + zm/x)^{1/2}$. Some narrowing of the biphasic gap with increasing volume fraction of the side chain is predicted.

RESULTS AND DISCUSSION

A sample of PBLG-N-d, deuterated at the amide group, was prepared by treating PBLG ($\bar{M}_w = 2.75 \times 10^5$, or $x = 121$) with trifluoroacetic acid-d_1.[1] D-NMR measurements were carried out by using a JEOL JNM-GX-500 spectrometer. The order parameters s esti-

Table I. Observed values of the quadrupolar splitting $\Delta\nu_N$ and the order parameters s estimated therefrom

Solvent	v_x[a]	$\Delta\nu_N$/kHz	s
Dichloromethane[b]	0.15	240.0	0.829
	0.21	249.2	0.861
	0.28	256.1	0.885
	0.30	258.5	0.893
1,4-Dioxane[c]	0.20	247.1	0.854
	0.25	249.3	0.861
	0.30	254.3	0.879

[a] Volume fraction of PBLG in the liquid crystalline phase.
[b] Observed at 21°C.
[c] Observed at 30°C.

mated from the observed quadrupolar splittings $\Delta\nu_N$ are listed in Table I. Values of s tend to decrease gradually as the concentration of PBLG-N-d is lowered. The lowest concentration employed in DCM ($v_x = 0.15$) is close to the critical value, the B-point, of the system. The difference between the two solvents, DCM and DOX, was found to be trivial at given concentrations.

Comparison with theory was shown in Figure 1. The order parameter s calculated according to Flory–Ronca theory is plotted against the polymer concentration v_x in Figure 1a. Computations were carried out for several discrete values of x as indicated by the numerical figures given to each curve. The variations of s in the anisotropic phase are illustrated by the solid curves, and the broken curves indicate the results of calculations extended over the concentration range where the biphasic equilibrium should be expected. The values of s at the boundary between these curves define s_{crit}. For the system comprising rodlike molecules with a large axial ratio (e.g., $x \geq 100$), the theory predicts that the orientational order should remain high over a wide range of concentration, and it departs from unity only in the vicinity of the critical (B) point. Experimental values of s obtained in DCM are shown by the circles in Figure 1a. The agree-
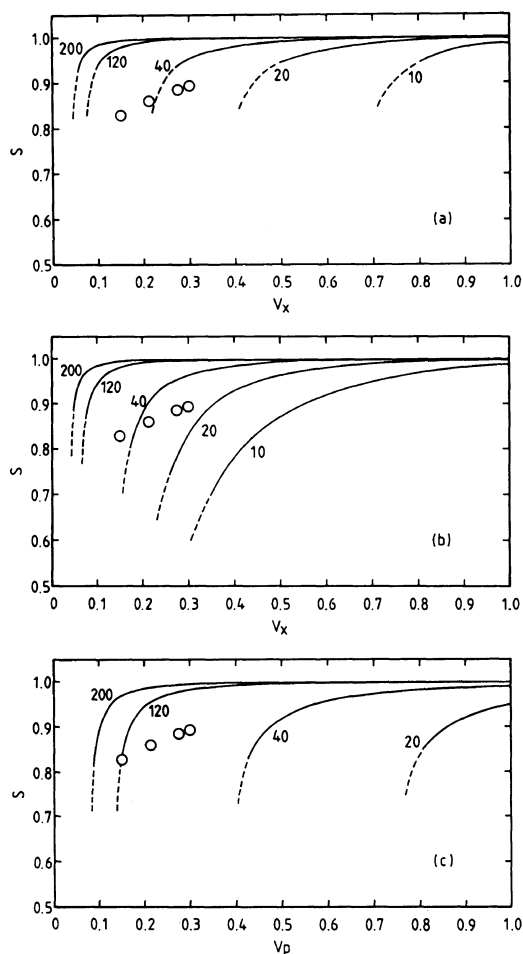
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Figure 1. Variation of the order parameter s with polymer concentration (volume fraction). The results of theoretical calculations are shown by the solid curves. Values of the axial ratio x used in these calculations are given to each curve. The broken curves indicate the results of calculations extended over the concentration range where the biphasic equilibrium should be expected. The junction between the solid and broken curves corresponds to the nematic-isotropic phase boundary: the value of s at this point defines the critical order parameter (s_{crit}). Theoretical curves were estimated according to (a) Flory-Ronca theory. (b) Teramoto theory, and (c) Ballauff theory (the notation v_p is used for the volume fraction in accordance with the original paper[7]). In Figure (c), the value of zm/x ($=0.96$) was so chosen as to reproduce the observed value of s at $v_p=0.15$ for $x=120$. Indicated by open circles in each diagram are the experimental values of s observed for the PBLG-N-d/DCM system at 21°C.

ment between theory and experiment is only qualitative: the experimental observations can not be reproduced by the theoretical curve drawn for $x=120$.

As stated earlier, the revisions introduced by Teramoto yielded an improvement in the agreement for the critical concentrations in the lower range of x. The s vs. v_x plot calculated according to this scheme is indicated in Figure 1b. As may be shown by comparison with Figure 1a, the effect of the interaction energy term newly introduced is manifested in the shift of theoretical curves toward lower concentrations. Another characteristic feature of this scheme may be found in the lower values of s_{crit}. Experimental data included in Figure 1b are the same as those in the previous figure. The observed results can not be reproduced by theoretical curves calculated for reasonable axial ratios.

In Ballauff's scheme, z and m may be treated as adjustable parameters. In general, an increase in zm causes a decrease in the s value at a given concentration. In Figure 1c, the factor zm/x was so adjusted as to reproduce the observed value of s at $v_x=0.15$ (in DCM), x being set equal to 120. Calculations were carried out for the athermal mixture. The theoretical curve increases more rapidly than the experimental $s-v_p$ plot. The agreement is again only qualitative. A fairly large discrepancy is noted in the phase diagram, where calculations using $zm/x=0.96$ lead to an appreciable overestimate of the critical concentrations for lower values of x.

The Onsager theory[8] is also known to give an abrupt transition between a strongly-ordered nematic and an isotropic phase. The calculated value[8,9] of s_{crit} is found to be in a reasonable agreement with those observed. The theory, however, disagrees with experiment about the critical concentration.

In this analysis, the orientation of the N–D bonds situated along the α-helical PBLG provides the clue to elucidate the order parameter. The standard set of geometrical parameters[10]

is adopted for the α-helical arrangement of PBLG to correlate the direction of these N–D bonds to the molecular axis: an 18/5 helix has been suggested for the PBLG molecule in solution from the recent 2D-NMR studies by Mirau and Bovey.[11] The α-helical synthetic polypeptides exhibit certain flexibility in dilute (isotropic) solutions.[12] The depression of the order parameter due to such flexibility intrinsic to the PBLG molecule is difficult to assess, and has been entirely ignored. The polydispersity in the axial ratio of the rodlike component should affect the order parameter of the system as well.[13] The values of s determined in this work are somewhat higher than those reported by Murthy et al.[14] over the entire concentration range observed. They estimated the orientational order parameter from the broadening of the X-ray diffraction streaks of PBLG ($\bar{M}_w = 3.0 \times 10^5$) in dioxane. Sartirana et al.[5] reported values of $s = 0.76$ to 0.83 for a lyotropic liquid crystals of poly(p-benzamide) by applying polarized IR technique.

For a more critical examination of the theories, further accumulation of experimental data is needed. In this communication, we wish to emphasize the importance of the information obtained from the D-NMR technique regarding the orientational order of PBLG in the lyotropic liquid crystalline state.

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