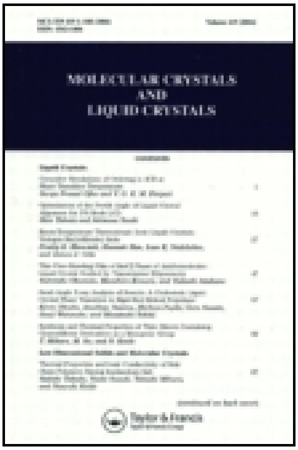

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Order Parameter in Polymer Liquid Crystal 2. Poly(γ-Benzyl-L-Glutamate) in Dioxane

M. Luisa Sartirana [a] [b] , Enrico Marsano [a] , Estella Bianchi [a] & Alberto Ciferri [a]

[a] Istituto di Chimica Industriale, Università di Genova, 16100, Genoa, Italy

[b] Part of M. L. Sartirana's thesis for the Research Doctoral Degree in Chemistry

Version of record first published: 21 Mar 2007.

To cite this article: M. Luisa Sartirana , Enrico Marsano , Estella Bianchi & Alberto Ciferri (1987): Order Parameter in Polymer Liquid Crystal 2. Poly(γ-Benzyl-L-Glutamate) in Dioxane, Molecular Crystals and Liquid Crystals, 144:5, 263-274

To link to this article: http://dx.doi.org/10.1080/15421408708084220

Mol. Cryst. Liq. Cryst., 1987, Vol. 144, pp. 263–274
Photocopying permitted by license only

Printed in the United States of America

Order Parameter in Polymer Liquid Crystal 2. Poly(γ-Benzyl-*L*-Glutamate) in Dioxane

M. LUISA SARTIRANA,† ENRICO MARSANO, ESTELLA BIANCHI and ALBERTO CIFERRI

Istituto di Chimica Industriale, Università di Genova, 16100 Genoa, Italy

We report a study of the order parameter, S, for nematic solutions of poly(γ-benzyl-*L*-glutamate) (PBLG) in dioxane. The homeotropic alignment evolved naturally in thin NaCl cells and was improved by a magnetic field. i.r. spectroscopy was used for determining the ratio of the band intensity in a rather wide composition range and for two different molecular weight PBLG. Bands at 3294 (amide A, N-H stretching) and at 1549 cm^{-1} (amide II vibration) were used for both isotropic and anisotropic solutions. Angles between the transition moment of the vibrations and the chain axis were selected from the literature. S was found to increase with both polymer concentration and molecular weight, approaching the value of 1 characteristic of perfect orientation. Comparison of the results with the predictions of virial and lattice theories indicates that the former offers the closest representation at rather low polymer volume fraction v_2, while the latter is to be preferred at a somewhat larger v_2.

Keywords: Order parameter, lyotropic polymer, PBLG, nematic alignment, I.R. spectroscopy

INTRODUCTION

The molecular order in the liquid crystalline state of polymers has been the subject of intense investigations in recent years from both the experimental[1–17] and the theoretical[18,19] standpoint. The order parameter

$$S = 1 - 3/2 \langle \sin^2 \theta \rangle \qquad (1)$$

is the single quantity necessary to specify completely the degree of the order in nematics; θ being the angle that the molecule main axis

---

†Part of M. L. Sartirana's thesis for the Research Doctoral Degree in Chemistry.

makes with the direction of the preferred orientation (the director) in the liquid crystal, the brackets indicating average over the orientation of the molecules.

Several quantitative studies of the order parameter have been reported for nematic thermotropic polymers,[1-14] but only few measurements were carried out for lyotropic systems.[15-17, 20] In a previous paper[20] we have determined the order parameter for poly(*p*-benzamide) (PBA), *N*-*N*′-dimethylacetamide (DMAc) + 3% LiCl in a planar alignment. S was obtained using polarized i.r. spectroscopy. The concentration dependence of S was investigated in the range extending from the volume fraction v_2'' above which a pure anisotropic phase exists, to the solubility limit of the polymer. This range was very narrow because for this system the solubility limit is only slightly larger than v_2''. S was found to increase from 0.76 to 0.83 with increasing polymer concentration.

For rodlike molecules the lattice theory[18] predicts an increase of the order parameter with concentration. S attains the value ~ 1 at $v_2 = 1$ and, at fixed compositions, is expected to increase with the axial ratio x. The virial theory[19,21] predicts the same concentration dependence, but smaller values of S.

In the present paper we report i.r. data allowing a determination of the order parameter for the system poly(γ-benzyl-*L*-glutamate) (PBLG)/dioxane. The high solubility of the PBLG in dioxane allows the exploration of a composition range considerally wider than for PBA. We also report the effect of the molecular weight of PBLG on S. Perfect homeotropic alignment appears to be easily obtained for the present system in contrast to the planar orientation achieved with the PBA/DMAc system previously investigated.[20] Studies of the order parameter of PBLG reported in the literature appear to yield conflicting results. Murthy *et al.*[15] using x-ray diffraction reported rather low, concentration-dependent, S values in dioxane. On the other hand, Volchek *et al.*,[17] using i.r. spectroscopy and CH_2Cl_2 as a solvent, reported rather large, concentration-independent, order parameters.

EXPERIMENTAL SECTION

Two samples of PBLG having molecular weight 120000 and 210000 were supplied by the Sigma Chemical Company and used without further purification. Molecular weights ($\overline{M}w$) were determined by the producer. In order to remove traces of water, the polymer was dried at room temperature under vacuum for 24 h, and then held over P_2O_5. The solvent was analytical grade dioxane dried over molecular sieves and used without purification. PBLG solutions were prepared by dissolving weighed amounts of the polymer in the diluent and by stirring the components for about one month at room temperature in a sealed tube. The polymer volume fraction, v_2, was calculated from the polymer concentration C_p (w/w) using 0.7900 mL/g for the partial volume ($\bar{v}_2$) of PBLG and 1.0282 mL/g for the specific volume of diluent. These values were determined pycnometrically.[22] The minimum polymer volume fraction, v_2'', for the stability of the pure anisotropic phase was calculated from the experimental value of the critical volume fraction, v_2', at which the anisotropic phase first appears. v_2' values were determined with a polarizing microscope (Reichert Zetopan) as previously described.[23] The cholesteric pitch of the solution was evaluated from the calibration reported by Robinson.[24] i.r. measurements were performed at room temperature using a Perkin Elmer model 983 spectrometer with a relative noise of 0.2% transmittance. Due to the homeotropic arrangement polarized radiation was not necessary. The intensity at 3294 cm^{-1} (I_1) and 1549 cm^{-1}(I_2) was measured for both isotroic and anisotropic solutions, and the ratios $B_{an} = (I_2/I_1)_{an}$ and $B_{iso} = (I_2/I_1)_{iso}$ determined. Occasionally, the dicroic ratio for the anisotropic solutions was determined using polarized radiation. The former band has been assigned to the N-H stretching (amide A) and the latter one to the amide II vibration of the peptide group.[25] For these measurements the solutions were put in i.r. cells consisting of two NaCl windows, separated by a 15 μm Teflon spacer, held together by an aluminium frame and sealed with silicone. The evolution of the nematic texture was followed with the polarizing microscope. A magnetic field (15 KG) normal to the cell surface, was applied before i.r. measurements for a time ranging from 1 h to 30 h. Duplicate measurements after the cell was removed from the magnet gave similar results, revealing a very slow relaxation of the alignment.

RESULTS AND DISCUSSION

The critical volume fraction v_2' was equal to 0.092 and to 0.084, respectively for the samples with $\overline{M}w = 120000$ and 210000. The conjugated composition of the pure anisotropic phase was obtained using the relationship) $v_2''/v_2' \sim 1.4$ reported by Flory[26] (experimental data[26] for other polymers support this relationship). v_2'' was equal to 0.129 and 0.117 respectively for the lower and higher molecular weight samples.

Cholesteric solutions of polypeptide are expected to undergo a phase transition to an uniform nematic texture when specimens are confined in very thin cells with separation between the plates equal or less than the undisturbed pitch.[27,28] The resulting texture (homeotropic) is probably favored by electrostatic interactions between the chain terminals and the surface, and in this respect NaCl seems to play an important role.[17] A magnetic field can improve this alignment by promoting the formation of a large monodomain.

The evolution of the texture from the initial cholesteric finger print pattern to an homeotropic nematic structure, followed with the polarizing microscope for our system, is shown in Figure 1. We observed that, after about 10 h, the specimens, viewed vertically between crossed polarizers, extinguished the light completely (Figure 1c). However, using convergent light we did not detect the characteristic conoscopic image due to the thickness of the NaCl windows.

It should be pointed out that the homeotropic alignment obtained from the break down of the cholesteric structure is not easily distinguishable, under the polarizing microscope, from the cholesteric planar texture.[29] However, consideration of the thickness of the cell and dicroic measurements on the amide II and amide A bands confirm that the texture of our sample is nematic homeotropic. The dicroic ratio in the case of homeotropic alignment must be equal to 1 when the incident beam is perpendicular to the cell surface, and become <1 and >1 for amide II and amide A vibration, respectively, when the surface of the cell is inclined to the incident beam.[30] These expectations were fully verified by our determination of the dicroic ratio.

Typical anisotropic and isotropic spectra for the system PBLG-dioxane are shown in Figure 2. As ascertained from unreported spectra of the pure components, the bands at 3294 and 1549 cm^{-1} are spectrally isolated from the diluent bands and therefore can be used for the evaluation of intensity ratio in isotropic (B_{iso}) and anisotropic (B_{an}) solutions. B_{iso} was determined as an average of 45 independent measurements on our samples at different concentrations below v_2'. No concentration dependence was observed and the resulting value was 1.205 ± 0.03. Values of B_{an} at different concentrations for the two samples are reported in Table I. Average values of B_{an} were evaluated from at least four measurements. The scatter of these determinations is reflected by the reported indetermination.

Figure 3 illustrates the variation of B_{an} with the reduced volume fraction v_2/v_2' for two molecular weights. The curves represent the calculated best line fitting the experimental data.

The order parameter, S, for a system of this kind may be obtained from the equation[30]

$$S = \frac{B_{\text{iso}} - B_{\text{an}}}{B_{\text{an}}(1.5 \sin^2 \alpha_2 - 1) - B_{\text{iso}}(1.5 \sin^2 \alpha_1 - 1)} \qquad (2)$$

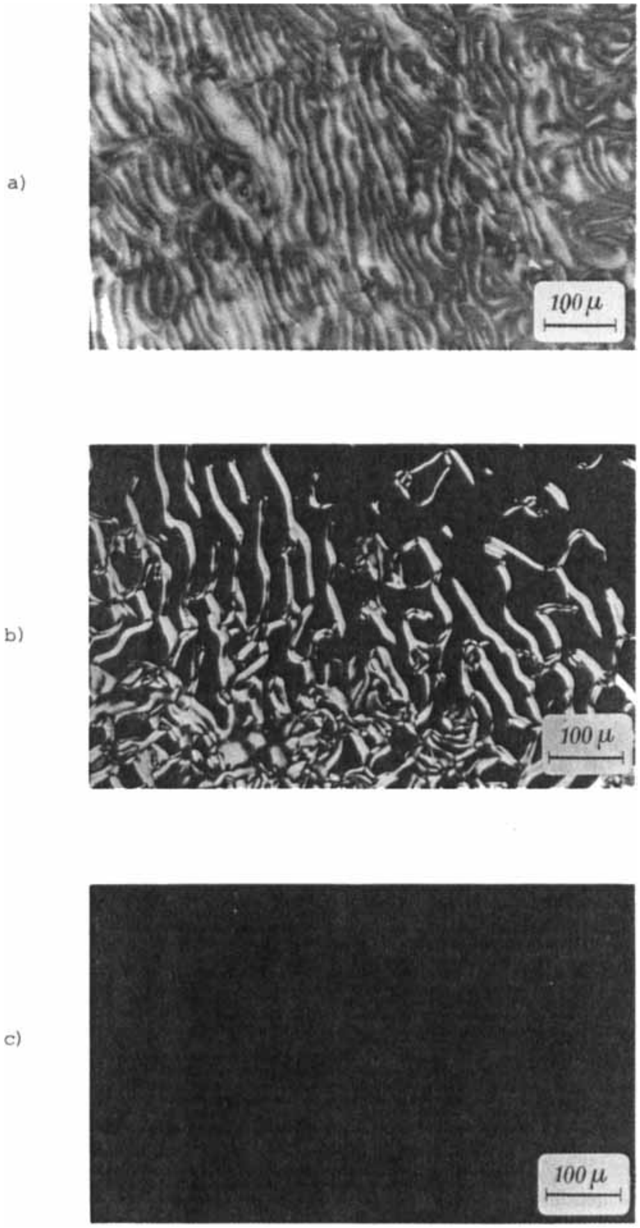

FIGURE 1 Photographs of PBLG/dioxane solution ($\overline{M}_w$ 120000; $\nu_2 = 0.187$) under polarizing microscope.
a) cholesteric finger print pattern; 10 min after filling of the cell.
b) disclination lines in homeotropic structure; 1h after filling of the cell.
c) homeotropic nematic texture; sample aligned in a H field (~15 KG) for 10h.

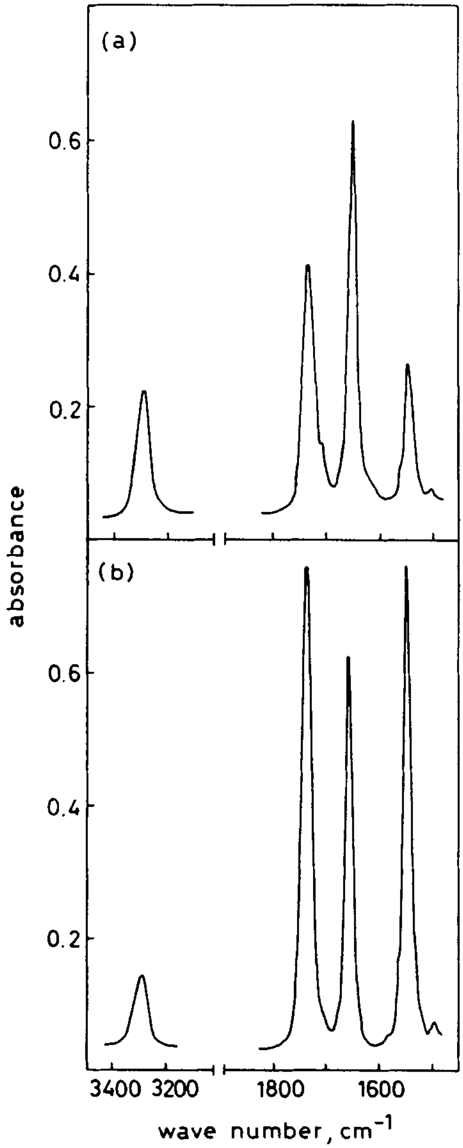

FIGURE 2 i.r. absorption spectra of PBLG/dioxane solutions ($\overline{M}_w$ = 120000)
a) isotropic solution $\nu_2 = 0.08$
b) anisotropic solution $\nu_2 = 0.275$

where α_1 and α_2 are the angles for the transition moments of the vibration with the chain axis. Evaluation of the order parameter, S, according to equation (2), requires the angle values of amide II and

TABLE I

Order parameter for PBLG/dioxane solutions

$\overline{M}_w$	v_2	v_2/v_2'	B_{an}	$S_{exp.}$	$S^a_{theor.}$	$S^b_{theor.}$
120.000	0.145	1.576	4.34 ±0.06	0.84	0.954	0.888
	0.167	1.815	4.95 ±0.15	0.91	0.970	0.921
	0.187	2.032	5.82 ±0.15	0.94	0.978	0.940
	0.229	2.489	6.565±0.50	0.98	0.988	0.972
	0.275	2.989	6.56 ±0.22	0.99	0.992	0.974
	0.349	3.793	6.93 ±0.16	0.999	0.997	0.984
210.000	0.123	1.464	4.35 ±0.10	0.84	0.939	0.867
	0.152	1.809	5.52 ±0.20	0.94	0.968	0.921
	0.186	2.21	6.93 ±0.30	0.99	0.980	0.950

[a] Theoretical values derived from lattice theory.[18]
[b] Theoretical values derived from virial theory.[21]

amide A vibrations, $\alpha_{am\ II}$ and $\alpha_{am\ A}$ respectively. Unfortunately, literature reports[17, 31–36] a large scatter of these values which vary from 19° to 30° for the amide A band, and from 60.5° to 87° for the amide II band. The scattering reflects the fact that some of these values are calculated from atomic models,[34] while others are experimentally observed. Furthermore, the experimental values are de-

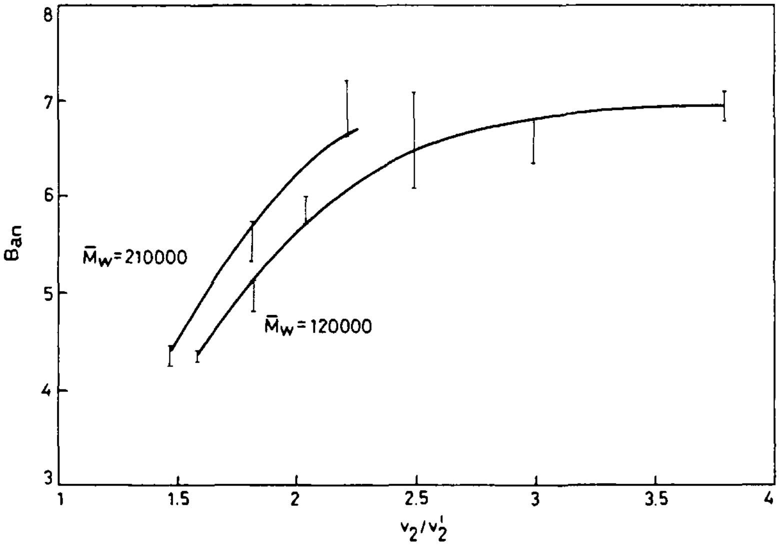

FIGURE 3 Experimental change of the ratio between the optical densities of amide II and amide A bands B_{an} with the reduced polymer volume fraction v_2/v_2' for PBLG/dioxane solutions. $\overline{M}_w$ of PBLG is indicated.

termined for films or solutions in different solvents, and, as known, the solvent may affect the molecular conformation. Since spectroscopic studies of PBLG in the dioxane solvent are not reported, we followed the suggestion by Volchek *et al.*[31] to use the pair

$$\alpha_{\mathrm{am\ A}} = 23^\circ \qquad \alpha_{\mathrm{am\ II}} = 69.5^\circ$$

In fact this is the only pair which allows values of S smaller than 1.

Values of S, calculated from Eq. (2) using the smoothed B_{an} data in Figure 3, are collected in the fourth column of Table I, and are plotted *vs* v_2/v_2' in Figure 4. Assuming an uncertainty of ~ 5% on α, the S values estimated could be affected by an error not larger than 5%. Figure 4 includes, for comparison, the experimental data reported by Volchek[17] and Murthy,[15] and also the theoretical prediction of lattice[18] and virial[19] theories. S values are plotted starting from the v_2'' composition (corresponding to ~1.3 – 1.5 on the v_2/v_2' scale depending upon the value of x or the particular theory).

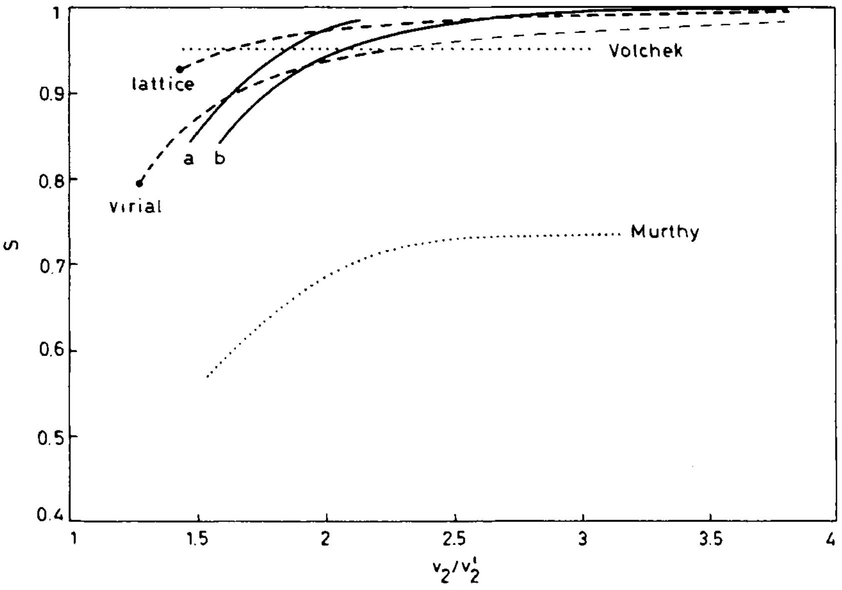

FIGURE 4 Order parameter for the system PBLG/dioxane as a function of the reduced polymer volume fraction v_2/v_2'
a) $\overline{M}_w$ = 210000
b) $\overline{M}_w$ = 120000
dotted lines experimental data from: Murthy *et al.* for PBLG/dioxane solutions, $\overline{M}_w$ = 300000; Volchek *et al.* for PBLG/CH_2Cl_2 solutions, $\overline{M}_w$ = 120000. Broken lines are the prediction from lattice and virial theories.

The prediction of the lattice theory was calculated, as previously described,[20] from Eq. (1) using[18] $\langle \sin^2\theta \rangle = f_3/f_1$ where

$$f_n = \int_0^{\pi/2} \sin^n \theta \exp(-\beta \sin \theta)\, d\theta$$

$$\beta = -\left(\frac{4}{\pi}\right) \times \ln\left[1 - v_2\left(1 - \frac{\bar{y}}{x}\right)\right]$$

$$\bar{y} = \left(\frac{4}{\pi}\right) \times f_2/f_1$$

$$n = 1, 2, 3$$

The prediction of the virial theory was assessed using the data of Lee and Meyer.[21]

Our experimental S values are quite high for both samples, and increase with polymer volume fraction approaching the value $S \sim 1$. As shown in Figure 4, stabilization of the pure anisotropic phase at $v_2 = v_2''$ occurs at values of the order parameter lower than the lattice prediction but remarkably close to the prediction of Onsager theory. However, when the polymer volume fraction is slightly increased, the experimental S values approach the values predicted by the lattice theory (cf. Figure 5 and Table I for more detailed illustration of the concentration range at which the lattice theory represents the experimental data). The more successful performance of the virial and lattice theory, respectively in the low and high concentration range has been postulated,[26] but never until now verified. In our previous work on PBA/DMAc +3% LiCl[20] we also observed that the experimental data were in better agreement with the lattice theory than with the Doi's[37] elaboration of the virial theory. However, the difference between the experimental values and those predicted by the lattice theory was larger than that shown by the system here investigated. We attribute the larger discrepancy previously observed to the difficulty in obtaining large planar monodomains for the PBA/DMAc + LiCl system.

The results of Volchek[17] *et al.* and of Murthy *et al.*[15] are also schematized in Figure 4. The former, obtained using i.r. spectroscopy on homeotropically aligned PBLG/CH_2Cl_2 are more in line with present results than those of Murthy *et al.* who used x-ray diffraction and

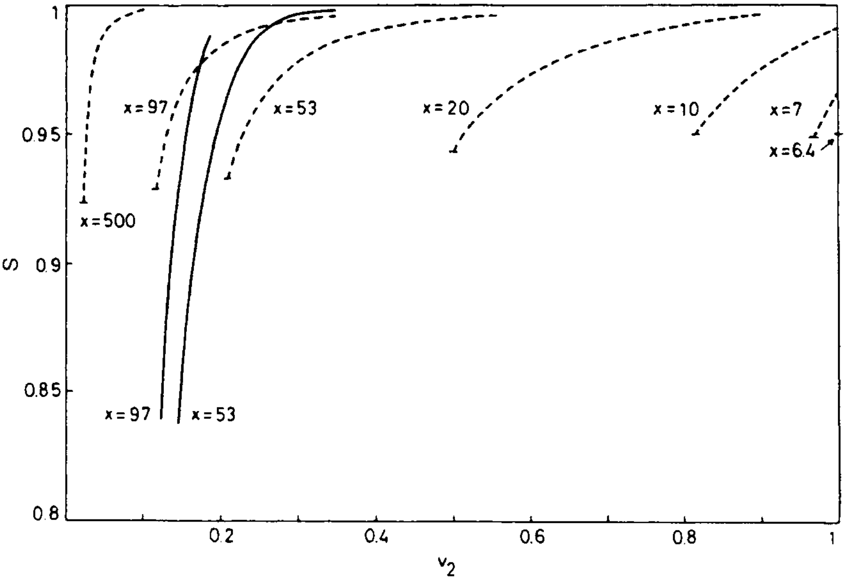

FIGURE 5 Order parameter as a function of the polymer volume fraction. Dashed lines calculated from the lattice theory for different axial ratios. Full lines our experimental results for PBLG/dioxane solutions.

the PBLG/dioxane system. However, Volchek *et al.*[17] data fail to show the increase of S with concentration which we have observed. The data of Murthy *et al.*[15] refer to planar orientation (the magnetic field was parallel to the capillary axis). The lower values of S they reported should be attributed to the lower sensitivity of the x-ray technique or to poorer alignment. Kirov *et al.*[38] also observed that the orientation in homeotropic sample is better than in the case of planar alignment.

The dependence of S upon molecular weight predicted by the lattice theory[18] is compared with our results in Figure 5. Theoretical curves for axial ratio ranging from $x = 6{,}4$ (the smallest axial ratio which stabilizes the mesophase due to geometrical asymmetry) to $x = 500$ are reported. We observe that the theoretical S value at v_2'' slightly decreases with increasing the axial ratio, while at fixed composition S is higher for larger x. The axial ratio of our samples, derived from the relationship $x = \mathrm{DP} \times 1.5/15$[39] where DP is the degree of polymerization, was $x = 53$ for $\overline{M}_w = 120000$ and $x = 97$ for $\overline{M}_w = 210000$. The agreement between the theoretical and experimental dependencies is fairly good, although the experimental dependence of S upon molecular weight is somewhat more pronounced than predicted.

Acknowledgment

We would like to thank Dr. S. Lee for helpful suggestions on computation of Onsager theory.

This work was carried out with the financial support of Ministero Pubblica Istruzione of Italy.

References

1. K. Muller, B. Hisgen, H. Ringsdorf, R. W. Lenz and G. Kothe, "*Recent Advances in Liquid Crystal Polymers*," L. Chapoy Ed., Elsevier, London (1984).
2. C. Noel, "*Recent Advances in Liquid Crystal Polyers*," L. Chapoy Ed., Elsevier, London (1984).
3. C. Noel, F. Laupetre, C. Friedrich, B. Fayolle and L. Bosio, *Polymer*, **25**, 808 (1984).
4. R. B. Blumstein, E. M. Stickles, M. M. Gauthier and A. Blumstein, *Macromolecules*, **17**, 177 (1984).
5. A. F. Martins, J. B. Ferriera, F. Volino, A. Blumstein and R. B. Blumstein, *Macromolecules*, **16**, 279 (1983).
6. F. Volino, M. M. Gauthier, A. M. Giroud-Godquin and R. B. Blumstein, *Macromolecules*, **18**, 2620 (1985).
7. F. Volino, A. M. Giroud, R. B. Blumstein and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **127**, 103 (1985).
8. A. Blumstein, S. Vilasagar, S. Ponrathnam, S. B. Clough and R. B. Blumstein, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 877 (1982).
9. A. Blumstein and O. Thomas, *Macromolecules*, **15**, 1264 (1982).
10. A. Blumstein, M. M. Gauthier, O. Thomas and R. B. Blumstein, *Faraday Discuss. Chem. Soc.*, **79**, 3 (1985).
11. R. Campasso, P. Ianelli, A. Roviello and A. Sirigu, *Macromolecules*, **18**, 2773 (1985).
12. G. Sigaud, D. Y. Yoon and A. Griffin, *Macromolecules*, **16**, 875 (1983).
13. D. Y. Yoon, S. Bruckner, W. Volksen, J. C. Scott and A. C. Griffin, *Faraday Discuss. Chem. Soc.*, **79**, 4 (1985).
14. S. Bruckner, J. C. Scott, D. Y. Yoon and A. C. Griffin, *Macromolecules*, **18**, 2709 (1985).
15. N. S. Murthy, J. R. Knox and E. T. Samulski, *J. Chem. Phys.*, **65**, 4835 (1976).
16. R. W. Duke, D. B. Duprè and E. T. Samulski, *J. Chem. Phys.*, **66**, 2748 (1977).
17. B. Z. Volchek, A. V. Gribanov, A. T. Kol'Tsov, A. V. Purkina, G. P. Vlasov and L. A. Ovsyannikova, *Vysokomol. Soyed.* **A19**, 3, 519 (1977).
18. P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 289 (1979).
19. L. Onsager, *Ann. N. Y. Acad. Sci.*, **51**, 627 (1949).
20. M. L. Sartirana, E. Marsano, E. Bianchi and A. Ciferri, *Macromolecules*, **19**, 1176 (1986).
21. S. Lee and R. B. Meyer, *J. Chem. Phys.*, **84**, 3443 (1986).
22. E. Marsano, E. Bianchi and A. Ciferri, *Macromolecules*, **17**, 2886 (1985).
23. C. Balbi, E. Bianchi, A. Ciferri, A. Tealdi and W. R. Krigbaum, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 883 (1981).
24. C. Robinson, *Tetrahedron*, **13**, 219 (1961).
25. T. Miyazawa, T. Shimanouchi and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956).
26. P. J. Flory, *Adv. Polym. Sci.*, **59**, 1 (1984).
27. Y. Uematsu and I. Uematsu, *Polym. Prep. Am. Chem. Soc. Div. Polym. Chem.*, **20**, 66 (1979).
28. D. B. Duprè, "*Polymer Liquid Crystals*," A. Ciferri, W. R. Krigbaum, R. B. Meyer Eds., Academic Press N.Y. (1982).

29. A. Saupe, "*Liquid Crystal and Plastic Crystal I*," G. W. Gray, P. A. Winsor Ellis Horwood Eds., Chichester (1974).
30. R. Zbiden "*Infrared Spectroscopy of High Polymers*," Academic Press, Inc., N.Y. (1964), p. 201.
31. B. Z. Volchek, A. V. Purkina, L. A. Ovsyannikova and G. P. Vlasov Vjsokomol, *Soyed*, **A21**, 1037 (1979).
32. E. Iizuka, *Advances in Polymer Science*, **20**, 79 (1976).
33. M. Tsuboi, *J. Polym. Sci.*, **59**, 139 (1962).
34. C. H. Bramford, A. Elliot and W. F. Hanby, "*Sinthetic Polypeptides*," Academic Press, N.Y. (1956), p. 124.
35. E. Iizuka, *Polym. J.*, **7**, 650 (1975).
36. R. T. Ingwall, C. Gilon and M. Goodman, *J. Am. Chem. Soc.*, **97**, 4356 (1975).
37. M. Doi, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 229 (1981).
38. N. Kirov, P. Simova and H. Ratajczak, *Mol. Cryst. Liq. Cryst.*, **58**, 285 (1980).
39. P. J. Flory, *J. Polym. Sci.*, **49**, 105 (1961).