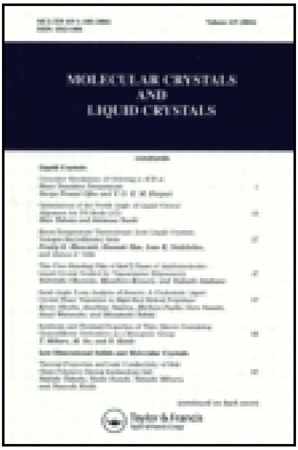

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Measurement of the Anisotropic Refractive Indices of Polybenzylglutamate Liquid Crystals. Molecular Factors and Dispersion

Donald B. Dupré [a] & Fu-Mei Lin [a]
[a] Department of Chemistry, University of Louisville, Louisville, Kentucky, 40292

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Measurement of the Anisotropic Refractive Indices of Polybenzylglutamate Liquid Crystals. Molecular Factors and Dispersion

DONALD B. DUPRÉ and FU-MEI LIN

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

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The ordinary and extraordinary refractive indices have been measured for lyotropic liquid crystal solutions of poly-γ-benzyl-*L*-glutamate. The onset of the liquid crystal formation is noted as an abrupt jump in the sample birefringence in the biphasic region. The concentration dependence is otherwise unremarkable. The polymer is found to add a small, anisotropic increment to the refractivity of the supporting solvent. Both n_o and n_e can thus be measured in an ordinary Abbé refractometer for the low refractive solvents common to these liquid crystal solutions. The optical birefringence does not depend significantly on polymer molecular weight. Data is also included for the wavelength dependence (dispersion) of n_o, n_e, and Δn.

INTRODUCTION

In the course of a study of polymer liquid crystals, we have found it necessary to make accurate measurements of the ordinary (n_o) and extraordinary (n_e) refractive indices of concentrated solutions of poly-γ-benzyl-*L*-glutamate (PBLG). These indices are required in the interpretation of quasielastic light scattering spectra[1] and the Frederik's distortion[2] of liquid crystals. Optical and laser spectroscopic methods of this sort yield quantitative information on the viscoelastic properties of the material: namely, the three major elastic constants (K_{ii}: $i = 1, 2, 3$) or ratios thereof and an assortment of viscosity coefficients. Data on refractive indices of lyotropic liquid crystals is scant in the literature. We report here our results for a range of concentrations and molecular weights of the PBLG polymer dissolved in a number of frequently used solvents that support the liquid crystal phase. The wavelength dependence of the anisotropic refractivity and birefringence is also included for possible future use with different light sources.

EXPERIMENTAL METHODS

A number of procedures[3-9] have been reported in the literature for measuring the refractive index or birefringence of liquid crystals. The birefringence of the common thermotropic liquid crystals is usually large, precluding a direct measurement of both n_o and n_e in an ordinary laboratory refractometer. We have found, however, that the birefringence of the PBLG polymer is quite small and amounts to a small increment to the refractivity of the larger solvent contribution in the liquid crystal solution. As the solvents of interest have an (isotropic) refractive index, n_s, less than that of glass ($n_g = 1.7100$), a conventional Abbé refractometer can be used to measure both n_o and n_e. Two critical angles corresponding to n_o and n_e appear as two boundaries (sometimes diffuse) in the eyepiece of the refractometer. The use of the Abbé refractometer thus considerably simplifies the determination of liquid crystal refractive indices. In most cases these boundary edges can be resolved to ±0.0001 index units. Reproducibility of the results among liquid crystal specimens prepared with the intent of identical experimental conditions was found to be within ±0.008 units.

The refractometer was a Bausch and Lomb Abbé-3L with a measurement range of 1.3000 to 1.7100. The temperature of the prisms and sample stage was stabilized at 25°C with the use of a constant temperature circulator. No specific surface orientation of the liquid crystal was attempted. Samples were transfered and measurements made rapidly to preclude solvent evaporation. The light source for these measurements was either a 2mW He-Ne laser (6328 Å) or an incandescent lamp used with a set of narrow band-pass (50 Å) filters.

PBLG samples of the study were obtained from Sigma Chemical Co. and had molecular weights, based on viscosity determinations, of 70,000, 240,000 and 296,000.

Solvents employed have all been previously shown to support PBLG liquid crystals and were chosen to give as broad a range of n_s as possible. PBLG forms a cholesteric liquid crystal, at the appropriate concentrations, in *p*-dioxane, $CHCl_3$, and *m*-cresol.[10-12] A mixture of 1:4 by volume of CH_2Cl_2 and dioxane has been shown to yield a nematic liquid crystal through compensation of opposite pitch senses in the binary solvent.[12] Benzene was also examined as it has been thought to induce a smectic organization of this polymer.[15-19]

Concentrations are reported as volume fractions ($\emptyset$) of polymer, which were calculated on the basis of a polymer density of 1.3gm/cc.[11]

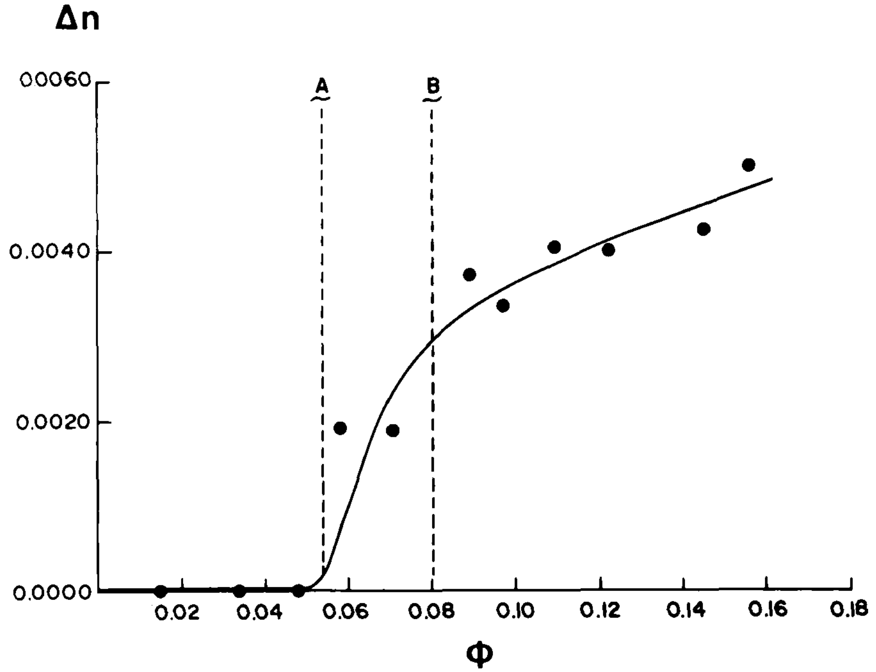

FIGURE 1 Concentration dependence of the birefringence of PBLG (molecular weight = 240,000) solutions in *p*-dioxane. The vertical line labelled *A* indicates the volume fraction (ϕ) at which phase separation just begins; the line labelled *B*, the volume fraction after which the medium is totally anisotropic. In between *A* and *B*, the solution is biphasic and the liquid crystal has not fully formed.

LIQUID CRYSTAL FORMATION AND THE PRETRANSITIONAL STATE

The formation of lyotropic liquid crystals from concentrated solutions of rod-shaped macromolecules proceeds in several identifiable stages.[10-14] As the concentration of polymer increases from zero, a point is reached beyond which randomness of orientation is no longer possible. Above a critical concentration, referred to as the *A* point, the solution separates into two phases: a dilute phase, isotropic in the arrangement of solute particles, and a more concentrated phase which is anisotropic. The polymer rich phase is birefringent and departs from the more dilute medium initially in the form of spherical droplets. The appearance and optical rotatory properties of these spherulites were recently discussed in detail for PBLG solutions.[13,14] If the two phase solution is further concentrated in polymer, the droplets grow in size and coalesce to form a continuously birefringent fluid at what is known as the *B* point.

In Figure 1, we plot the birefringence versus volume fraction of polymer for a PBLG (molecular weight = 240,000) solution in *p*-dioxane. The birefrin-

TABLE I

Anisotropic refractive indices of PBLG liquid crystals in various solvents. Molecular weight = 240,000; volume fraction of polymer in all preparations = 0.122, except as noted. λ = 6328Å. $T = 25°C$.

Solvent	n_{solvent} (±0.0001)	n_e (±0.0001)	n_o (±0.0001)	Δn (±0.0002)
p-dioxane	1.4210	1.4481	1.4440	0.0041[a]
		1.4535	1.4496	0.0039
		1.4501	1.4464	0.0037[b]
$CHCl_3$	1.4433	1.4665	1.4627	0.0038
m-cresol	1.5390	1.5457	1.5420	0.0037
CH_2Cl_2/ *p*-dioxane (1:4 by volume)	1.4206	1.4483	1.4437	0.0046
C_6H_6 + 2% TFA	—	1.4960	1.4931	0.0029

[a] volume fraction, 0.145

[b] molecular weight = 70,000; volume fraction, 0.122

gence is, of course, zero below the *A* point but rises in the *A-B* biphasic region. The value of the birefringence, $\Delta n = n_e - n_o$, which is apparently constant, in this intermediate region is not as large as that of the fully formed liquid crystal. As the isotropic component of the solution in this region should not contribute to the overall birefringence, we attribute this smaller value to morphological differences in the spherulitic structures of the anisotropic component in the *A-B* region. Above the *B*-point, Δn increases slowly with concentration of polymer in this totally uniform and single phase, anisotropic region.

SOLVENT EFFECTS

Table I summarizes the results for the solvents examined in this study. The first three solvents are known to produce a cholesteric (spontaneously twisted) texture in the liquid crystal of this polypeptide. The CH_2Cl_2/*p*-dioxane mixture was selected because it presents a nematic texture as a result of pitch compensation.[12] The individual solvents of this binary mixture support opposite twist senses. At a 1:4 mixture, competitive chiral influences are balanced resulting in an infinite pitch. A smectic like organization of this polymer in benzene solution has been suggested[15-18] but recently shown not to be the case.[19] Retardation lines characteristic of cholesteric mesophases appear in the polarization microscope with this solvent as well.

In general, we find that addition of PBLG polymer to a solvent to form an anisotropic phase adds a small increment to the supporting solvent refractivity. The value of the birefringence imparted to the solution is $\Delta n \simeq 0.004$ for the cholesteric texture solvents. This changes little from the low (1.4210) to

TABLE II

Molecular weight dependence of the anisotropic refractivity of PBLG liquid crystals. Volume fraction, 0.122 in *p*-dioxane. $T = 25°\text{C}$. $\lambda = 6328\text{Å}$.

Molecular weight	n_e	n_o	Δn
70,000	1.4476	1.4437	0.0039
240,000	1.4452	1.4420	0.0032
296,000	1.4447	1.4415	0.0032

high (1.5390) of solvent refractivity and among the different liquid crystal preparations in these solvents. The birefringence of the nematic mixture is slightly higher at $\Delta n \simeq 0.005$. The benzene solution for which there is evidence of unusual macromolecular associations[15–18] gives a slightly lower value of $\Delta n \simeq 0.003$.

MOLECULAR WEIGHT DEPENDENCE

We find no significant molecular weight dependence of n_o, n_e or Δn at constant concentration of polymer in the liquid crystal phase. Three polymer samples of molecular weight, 70,000, 240,000, and 296,000 were examined. Results in the solvent *p*-dioxane are listed in Table II. Discrepancies in the absolute values of n_o and n_e with those quoted in Table I for the solvent dioxane are due to variations mentioned in sample preparation. Values of the birefringence, Δn, remain roughly the same.

DISPERSION

The measurements above were made at 6328Å, the wavelength of the red line of the He-Ne laser that we have used most in our optical studies. Other common laser excitations occur in the blue-green region of the spectrum (Ar^+ laser major lines, for example, at 4880Å and 5145Å). We include, therefore, in this study the wavelength dependence (dispersion) of the ordinary and extraordinary refractive indices. Values reported here are for PBLG solutions of molecular weight 296,000 at a volume fraction of 0.150 in *p*-dioxane. In the use of this data for other preparations one should recall the solvent and concentration dependence of n_e and n_o discussed above.

The ordinary, extraordinary, and root-mean-square average refractive indices are plotted as a function of wavelength in Figure 2. n_e and n_o have been fitted (solid lines) to an equation of the form:[20]

$$n^2 = a + \frac{b}{\lambda^2 - \lambda_o^2}$$

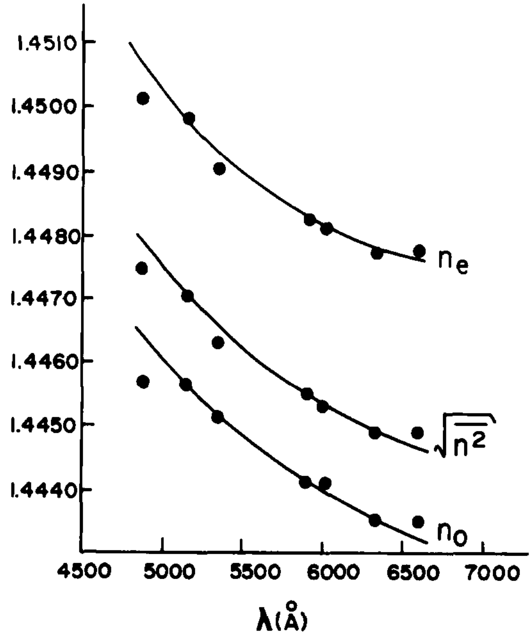

FIGURE 2 Dispersion of the ordinary (n_o), extraordinary (n_e), and root-mean-square average ($\sqrt{\overline{n^2}}$) refractive indices. PBLG (molecular weight = 296,000) in *p*-dioxane ($\phi = 0.150$). $T = 25°C$. The solid lines are the best fits to the equation in the text.

For n_e, $a = 2.0924$, $b = 83568$, and $\lambda_o = 4208.0$Å. For n_o, $a = 2.0735$, $b = 372720$, and $\lambda_o = 1896.0$Å. The dispersion of the birefringence is shown in Figure 3. The above equation is used for curve fitting purposes only and does not mean to imply an absorption maximum at λ_o.

TABLE III

Wavelength dependence of the anisotropic refractive indices. PBLG (molecular weight = 296,000) in *p*-dioxane ($\phi = 0.150$). $T = 25°C$.

λ(Å)	n_e	n_o	Δn	$\sqrt{\overline{n^2}}$*
4880	1.4509	1.4456	0.0053	1.4474
5145	1.4498	1.4456	0.0042	1.4470
5338	1.4490	1.4450	0.0040	1.4463
5896	1.4482	1.4441	0.0041	1.4455
6000	1.4481	1.4441	0.0040	1.4454
6328	1.4478	1.4435	0.0043	1.4449
6600	1.4479	1.4435	0.0044	1.4450

*$\sqrt{\overline{n^2}} = \sqrt{1/3(2n_o^2 + n_e^2)}$

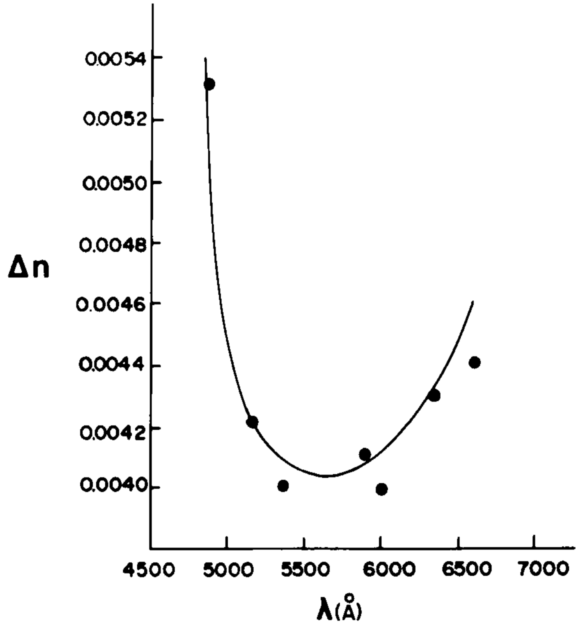

FIGURE 3 Birefringence (Δn) versus wavelength for same preparation as in Figure 2. The solid line is calculated from the equation given in the text.

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