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Lyotropic Liquid Crystalline Structures of Synthetic Polypeptides I: Molecular Weight Dependence of the Cholesteric Pitch on Poly(γ-benzyl L-glutamate) Solutions

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A study has been made of the effects of the molecular weight of polymer on the liquid crystalline structures of poly(γ-benzyl L-glutamate) solutions. The cholesteric pitch of poly(γ-benzyl L-glutamate) solution depends on the molecular weight in dioxane and 1,2-dichloroethane (EDC), but is independent of that in dimethyl formamide (DMF). More detailed experiments show that the nematic temperature, at which the cholesteric pitch becomes infinite, varied with molecular weight in dioxane and EDC, but was unchanged in DMF. The relationship between the aggregation states and the molecular weight dependence of the nematic temperature is discussed.

Keywords: cholesteric liquid crystal, nematic temperature, poly(γ-benzyl L-glutamate)

INTRODUCTION

Poly(γ-benzyl L-glutamate) (PBLG) solutions form lyotropic liquid crystals in sufficiently high concentrations of polymer. The liquid crystals have a high-form optical rotation and a striation pattern characteristic of cholesteric mesophases.[1] The spacing of the striation pattern corresponds to half the cholesteric pitch. The cholesteric pitch p varies with physical parameter, i.e., temperature,[2–4] polymer concentration,[2,5] the nature of the solvent.[6,7] Many workers have reported relations of p with temperature and polymer concentration in PBLG solutions. The temperature and concentration dependence of p has been well explained by Kimuras' theory, which assumed an intermolecular force as the sum of the Maier-Saupe-Gooseens type dispersion forces and the hard-core repulsion of twisted rod shapes and used the scaled particle theory for hard-rod fluids.[8,9] The structure of PBLG liquid crystals is strongly influenced by solvents.[7] The relations between the liquid crystalline structures and the properties of solvents, however, are not clear at present.

There are few papers which have reported on the influence of the macromolecular weight of the cholesteric pitch. Robinson *et al.* reported that the p of PBLG-dioxane

was independent of the molecular weight M_v of PBLG in the range of M_v, 6 – 27.5 × 10^4, at room temperature.[1]

The purpose of this study is to examine the influence of the molecular weight of PBLG on the cholesteric pitch of PBLG liquid crystals. The values of p for different molecular weight PBLG were determined as functions of temperature and concentration in three solvents.

EXPERIMENTAL

Samples of PBLG were synthesized by the N-carboanhydride method.[11] The average molecular weights of PBLG were calculated from the values of $[\eta]$ in dichloroacetic acid and N,N-dimethylformamide (DMF) by using Norisuye's $[\eta]$-M_v relations as follows[12]:

$$[\eta] = 1.02 \times 10^{-4} M_v^{0.76} \text{ in dichloroacetic acid} \quad (1)$$

$$[\eta] = 5.82 \times 10^{-8} M_v^{1.45} \text{ in DMF} \quad (2)$$

The numerical values are summarized in Table I.

N,N-dimethylformamide was distilled under a dry nitrogen atmosphere (bp 39.9°C, 10 mmHg). Dioxane (bp 101.3°C) was dried and fractionally distilled over metallic sodium. Ethylene dichloride (EDC, bp 85.5°C) was dried and fractionally distilled over calcium hydride.

Polymer concentrations were determined gravimetrically. The concentration v_2 expressed in volume fraction of PBLG at 25°C was calculated by assuming the specific volume of PBLG to be 0.786 $cm^3\ g^{-1}$. The necessary data for the densities of the solvents were taken from the literature.[13]

The concentrated solution of PBLG became transparent within two days and appeared viscous. Polling glass cells (thickness = 2.0 mm) with a thin inlet tube were used for both microscopic observation and laser light diffraction. A cell was filled with an appropriate amount of the solution, sealed off at the inlet tube, and stored at 50°C for at least one week before examination. In order to determine the equilibrium pitch, the solution was maintained at each temperature for more

TABLE I

Molecular weights of the PBLG samples studied

Code	$M_v \times 10^{-4}$	Degree of polymerization
s-1	1.8	80
s-2	2.2	100
s-3	3.9	180
s-4	5.6	260
s-5	16.2	740
s-6	24.1	1100
s-7	25.6	1170
s-8	33.7	1540

than 20 hours in a thermostated oven. The cholesteric pitch was measured with a polarizing microscope inserted in a thermostatic cell holder by the photographic recording method. The optical diffraction technique with a Ne-He gas laser was employed in some cases for the pitch measurement.

Optical rotatory dispersion (ORD) measurements were made on a Shimazu QV-50 spectrometer with accessories attached for the ORD measurement. Data were obtained at wavelengths of 400 to 700 nm by the use of a cell of optical pathlength 0.2 mm.

RESULTS AND DISCUSSION

The cholesteric pitch is a function of temperature and concentration. So, we examined the molecular weight dependence of p under the condition that temperatures and concentrations were constant. Figure 1 shows plots of the reciprocal of cholesteric pitch p^{-1} versus the degree of polymerization N for PBLG-dioxane at 40, 80, 90°C at a volume fraction of polymer v_2, 0.33. The cholesteric pitch clearly depended on the molecular weight of PBLG. When the degree of polymerization (DP) was lower than 260, the value of p^{-1} decreased with the lowering of DP at each temperature. The p^{-1} became negative values at 80 and 90°C, where the sign p was positive for the right-hand cholesteric structure and negative for the left-hand one. The p^{-1} were independent of DP by more than DP 260. As mentioned above, Robinson *et al.* reported that the pitch was independent of the molecular weight of PBLG over the range DP 270 to 1255.[1] Our result is consistent with Robinsons'.

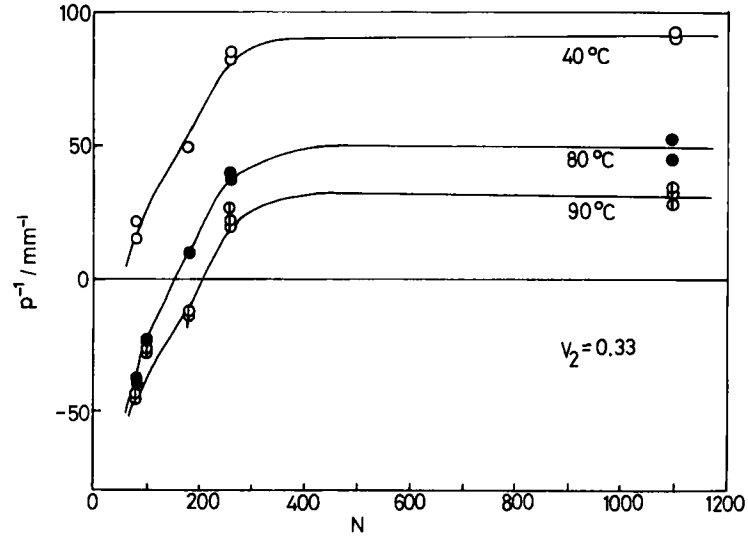

FIGURE 1 Degree of polymerization dependence of the cholesteric pitch for PBLG-dioxane at each temperature.

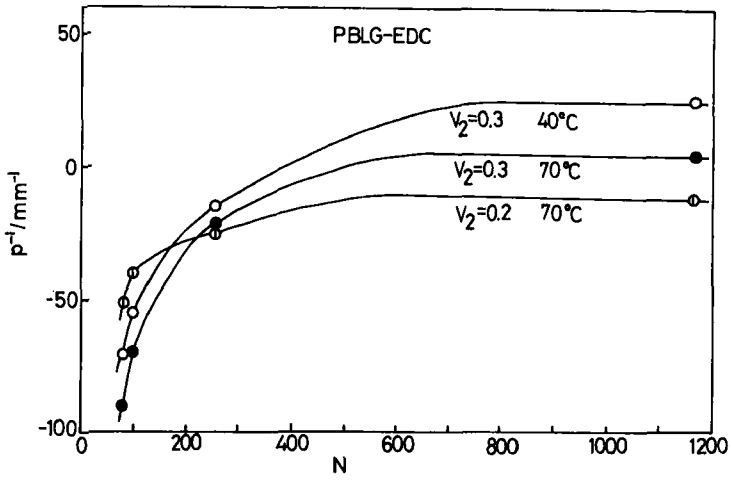

FIGURE 2 Degree of polymerization dependence of the cholesteric pitch for PBLG-EDC at each temperature.

Figure 2 shows plots of p^{-1} versus N for PBLG-EDC at v_2 0.3 and 0.2 at 40 and 70°C. The cholesteric pitch depended on the molecular weight of PBLG. When DP was lowered to less than 260, the values of p^{-1} decreased with the lowering of DP in all cases of Figure 2.

We could not examine the relationship between the cholesteric pitch and molecular weight in DMF under the condition of a fixed concentration. The concentrations of B-point in DMF were very high for low molecular weight samples. On the other hand, experiments in high concentrations for high molecular weight samples are difficult because the concentrated solutions of high molecular weight samples are very viscous. Figure 3 shows double-logarithmic plots of p versus concentration at two temperatures for five molecular weight samples. The data points for all molecular weight samples at each temperature were placed on a straight line. This agreement shows that the cholesteric pitch for the PBLG-DMF system is independent of molecular weight in the range of DP 80 to 1540.

The cholesteric pitch depended on the molecular weight of PBLG in dioxane and EDC, but the pitch in DMF was independent of that of PBLG. In order to investigate the molecular weight dependences of the cholesteric pitch in more detail, the pitches were examined as functions of the temperatures and the concentrations of PBLG for each molecular weight sample in dioxane, EDC, and DMF. The results are shown in Figures 4, 5, 6, and 7. Figures 4 and 5 show plots of p^{-1} versus the reciprocal of temperature T^{-1} in dioxane for DP 1100 and 80, respectively. Kimura *et al.* proposed p^{-1} versus T^{-1} plots by use of the statistical theory of cholesteric ordering in hard-rod fluids.[8,9] The real temperature dependence seems to be more like p^{-1} versus T^{-1} plots than the trial p^{-1} versus T one.[2,8,9,14] The concentrations of PBLG, v_2 are 0.336, 0.241, and 0.214 in Figure 4 and 0.214,

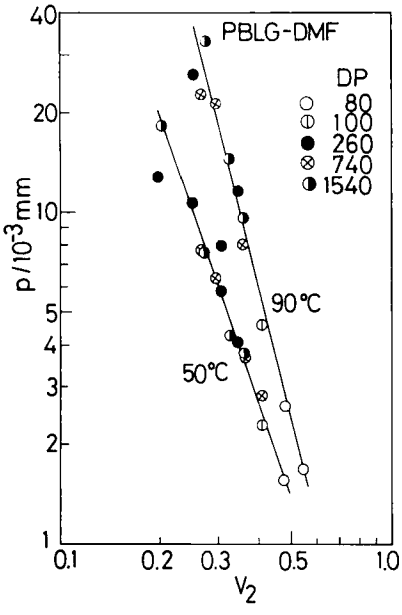

FIGURE 3 Double-logarithmic plot of p versus v_2 for PBLG-DMF.

0.231, and 0.339 in Figure 5, from top to bottom. The data points for each solution were fitted to a straight line.

Figure 6 shows plots of p^{-1} versus T^{-1} in EDC for DP 1170 and 80 at the indicated concentrations. The data points above 40°C ($T^{-1} = 3.19 \times 10^{-3}$) for each solution were fitted to a straight line. Below 40°C the value of p^{-1} remained constant in each solution. For the constants of the pitch at low temperatures, a

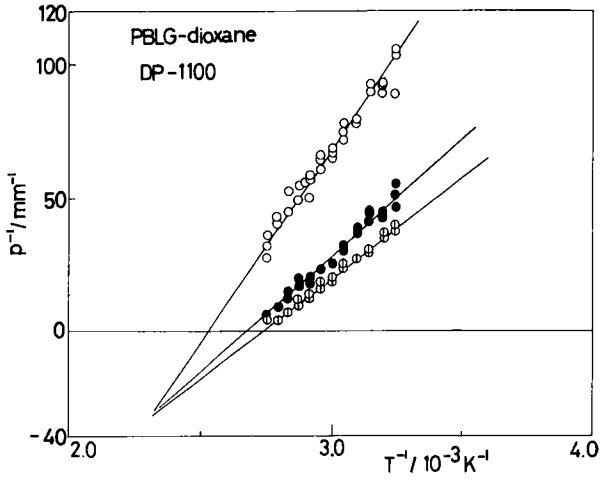

FIGURE 4 Plots of p^{-1} versus T^{-1} for PBLG(DP 1100)-dioxane v_2: ○: 0.336; ●: 0.231; ◑: 0.214.

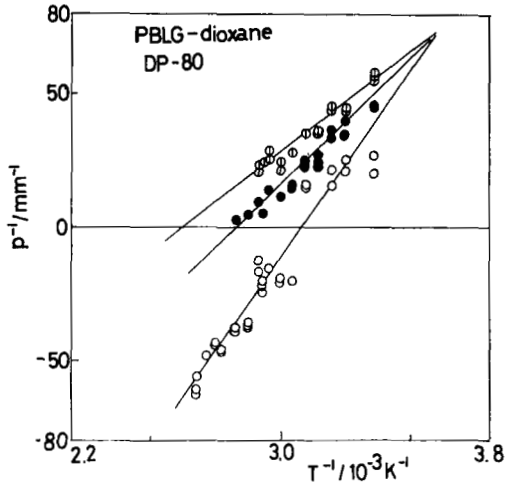

FIGURE 5 Plots of p^{-1} versus T^{-1} for PBLG(DP 80)-dioxane v_2: ○: 0.339; ●: 0.231; ⊕: 0.214.

possible explanation is that the cholesteric structure was fixed by gelation and the cholesteric pitch could not change within the time scale of our experiments. Similar behavior was observed already in another solvent system.[4] Figure 7 shows plots of p^{-1} versus T^{-1} in DMF, the non aggregation solvent, for DP 1540, 100, and 80 at the indicated concentrations.

Summarizing all experimental results, the data points of plots of p^{-1} versus T^{-1} at each concentration fell on a straight line in all solvents. The slopes of the plots in dioxane and DMF increased with the concentration. These properties of p^{-1} versus T^{-1} plots, which were independent of the molecular weight of PBLG, were well known,[2,4,5] and were explained satisfactorily by Kimuras' theory.[8,9]

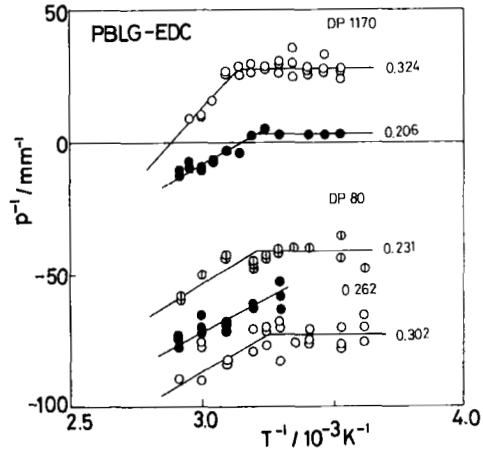

FIGURE 6 Plots of p^{-1} versus T^{-1} for PBLG(DP 1170 and 80)-EDC.

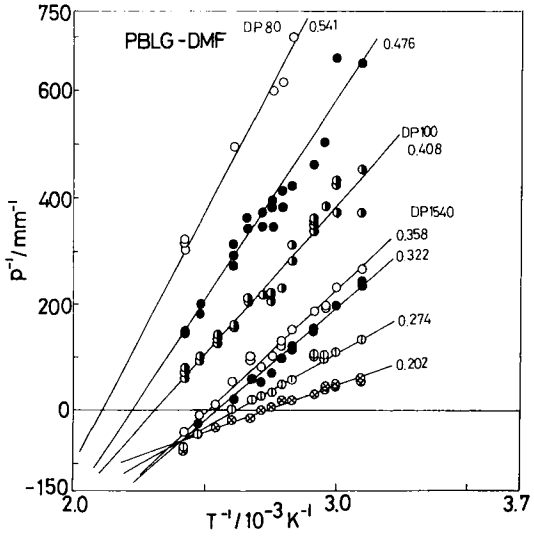

FIGURE 7 Plots of p^{-1} versus T^{-1} for PBLG(DP 1540, 100, and 80)-DMF.

For the sample of DP 1100 in dioxane (Figure 4), that of DP 1170 in EDC (Figure 6), and all samples in DMF (Figure 7), as the concentration was higher, the nematic temperature T_N, which is the temperature at $p^{-1} = 0$, rose. This behavior is similar to that of PBLG-*m*-cresol and $CHCl_3$.[2,4,6] On the other hand, for the sample of DP 80 in dioxane (Figure 5), the T_N rose with a decrease in concentration. This concentration dependence of the T_N was newly observed evidence. The values of p^{-1} of PBLG (DP 80)-EDC in Figure 6 could not become zero, so the nematic temperatures were evaluated by the extrapolation of the plots of p^{-1} versus T^{-1} above 40°C to $p^{-1} = 0$. The results of the extrapolation suggest that the T_N of PBLG (DP 80)-EDC was also lowered with the increasing of the concentration.

From the results of plots of p^{-1} versus T^{-1} in Figures 4 through 7, the concentration dependences of the T_N in dioxane and EDC have molecular weight dependences. Figure 8 shows double-logarithmic plots of T_N versus v_2 in dioxane for PBLG of DP 1100, 260, 180, 100, and 80. For the samples of DP 1100 and 260 the slopes of the plots were positive, that is, the T_N rose with the increasing of the concentration. On the other hand, for the sample of DP 180, 100, and 80, the slopes were negative, that is, the T_N rose with the decreasing of the concentration.

The DP dependence of p^{-1} shown in Figure 1 could be explained in terms of the molecular weight dependences of the concentration dependence of the T_N in Figure 8. In the condition of v_2 equals 0.33, Figure 8 shows that the nematic temperature was lowered with the lowering of the molecular weight. Generally, the lowering of the T_N results in the decreasing of the values of p^{-1} at a fixed temperature. Consequently, at v_2 equals 0.33 and a fixed temperature the values of p^{-1} decreased with the decreasing of the molecular weight. In analogy with PBLG-dioxane, the DP dependence of p^{-1} shown in EDC resulted from the molecular weight dependence of the T_N.

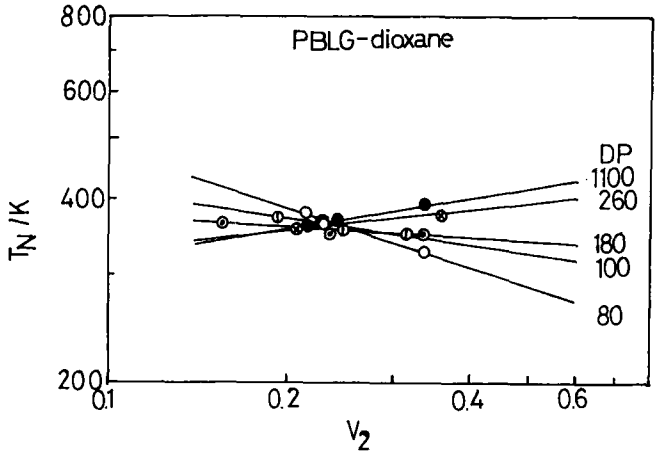

FIGURE 8 Double-logarithmic plots of T_N versus v_2 for PBLG-dioxane.

Figure 9 shows double-logarithmic plots of the T_N versus the concentration in DMF for each molecular weight sample. The data points were fitted to a straight line for all samples. The results show that the concentration dependence of the T_N was independent of the molecular weight of PBLG. Consequently, the cholesteric pitch in DMF was independent of the molecular weight of PBLG (see Figure 3). The behavior of the T_N on molecular weight was quite different from that of PBLG-dioxane and EDC.

In dioxane the concentration dependences of the T_N had molecular weight dependence and in DMF that of the T_N was independent of molecular weight. The molecules of PBLG in dilute solutions aggregated in dioxane and were dispersed

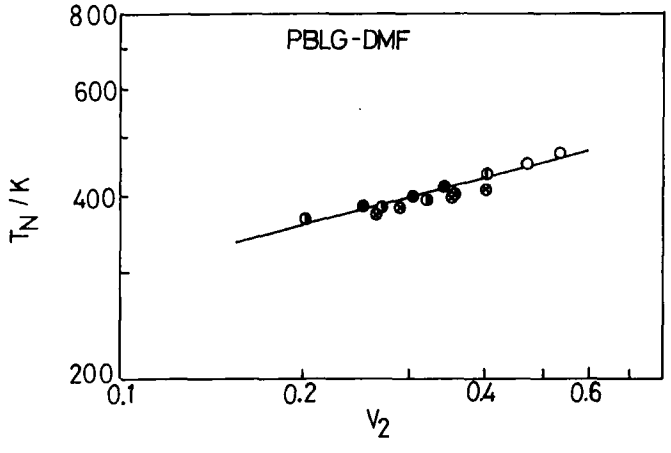

FIGURE 9 Double-logarithmic plots of T_N versus v_2 for PBLG-DMF DP: ○: 80; ⊕: 100; ●: 260; ⊗: 740; ◑: 1540.

molecularly in DMF.[10,15-23] This fact suggests that the concentration dependence of the T_N was affected by aggregation states of PBLG in dilute solutions and not by the molecular weight of PBLG. Gupta *et al.* reported that the maximum length for aggregates of PBLG in dioxane was equivalent to the PBLG length of a molecular weight of about 210,000 (DP = 1,000).[16-18] The PBLG molecules of a molecular weight above 210,000 could not aggregate with each other. This suggests that the states of PBLG of DP 1100 in dioxane are similar to those of the molecular dispersal system, i.e., DMF. In fact, the slope of plots of T_N versus v_2 for DP 1100-dioxane was positive and was nearly equal to that of the DMF system (see Figures 8 and 9). On the other hand, as the molecular weight of PBLG was lower, the slope of the double logarithmic plot of T_N versus v_2 decreased and became negative depending on the degree of polymerization under 180 in dioxane. Gupta *et al.* reported that, as the molecular weight is lower, the aggregation number of PBLG is larger in dilute solutions.[16-18] Thus the slopes of plots of T_N versus v_2 decreased with the increase of the aggregation number. Our results showed that the slopes of plots of T_N versus v_2 were independent of the molecular weight of PBLG and depended on the aggregation states of PBLG in dilute solutions. The relationship between the aggregation states of PBLG in dilute solutions and those in concentrated solutions was discussed by several researchers.[21,22,24] A clear relationship, however, was not obtained, because the size of the aggregates of PBLG in concentrated solutions could not be estimated.

We conclude that the values of the cholesteric pitch in dioxane and EDC solutions depended on the molecular weight of PBLG, but those in DMF solutions were independent of the molecular weight of PBLG. The molecular weight dependences of the cholesteric pitch resulted from the molecular weight dependence of the concentration dependence of the T_N.

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