

LIQUID CRYSTALLINE STRUCTURES OF RANDOM COPOLYMERS OF L-LEUCINE
AND γ -BENZYL-L-GLUTAMATE¹⁾

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The cholesteric pitch of random copolymers of L-leucine and γ -benzyl-L-glutamate in solutions was measured as a function of temperature and the composition of the copolymer. It was found that the increase in leucine residue incorporated in the copolymer increased the temperature dependence of the cholesteric twisted angle.

The study on the liquid crystals of synthetic polypeptides has been so far confined to ones having polar side chains, such as poly(γ -benzyl-L-glutamate)²⁾ (PBLG) and a series of poly(γ -alkyl-L-glutamate)³⁾ (PALG)s, which form cholesteric liquid crystals respectively in concentrated solutions. It is of particular interest to compare the liquid crystalline structure and its thermal behavior of PBLG and PALGs with those of the other polypeptides having nonpolar side chains, such as polyleucine, if the latter forms liquid crystals in solutions.

Initially attempts were made to dissolve poly-L-leucine up to the concentration at which the liquid crystal phase appeared. However, this was unsuccessful, and instead, the random copolymer of L-leucine and γ -benzyl-L-glutamate was prepared. The purpose of this paper is to investigate the effect of nonpolar side chains incorporated in the copolymer on the cholesteric structure and its thermal behavior of polypeptides.

The copolymer was synthesized by the method of Nylund and Miller⁴⁾ with slight modification. L-Leucine N-carboxyanhydride (NCA) and γ -benzyl-L-glutamate NCA were copolymerized in 1,2-dichloroethane (EDC) by initiation with triethylamine. Five copolymers of varying leucine content were prepared in this manner and are characterized in Table 1. The glutamate content was determined from the absorption of phenyl group using an UV spectrometer.⁵⁾ The amount of leucine residue in the copolymer was obtained by difference. The five copolymers were dissolved in EDC and in 1,4-dioxane at a concentration of 0.1M.⁶⁾ Each of these solutions was transferred to a glass tube hermetically sealed to prevent solvent evaporation and aged about 7-20 days until the stable cholesteric pitch appeared. The cholesteric pitch was measured with polarizing microscope under a controlled temperature.

In Figs. 1 and 2 the value of $1/P$ (P : cholesteric pitch in micrometer) for each copolymer is plotted against temperature. The results are summarized as follows.

Table 1. Copolymerization of L-leucine NCA and γ -benzyl-L-glutamate NCA in 1,2-dichloroethane.

Mole fraction of glutamate in monomer mixture	copolymer	abbreviation
1.00	1.00	PBLG
0.91	0.98	COP1
0.81	0.91	COP2
0.72	0.84	COP3
0.62	0.76	COP4

(1) All the copolymers form cholesteric liquid crystals in both solvents. (2) The inverse pitch ($1/P$) varies approximately linearly with temperature for all the copolymers except in a range of high temperature for COP4. The similar relation has been already obtained in the case of PBLG⁷⁾ and PALGs³⁾ previously reported. (3) The values of $d(1/P)/dT$ obtained by the least-squares method are shown in Table 2. As the content of leucine residue increases, the values of $d(1/P)/dT$

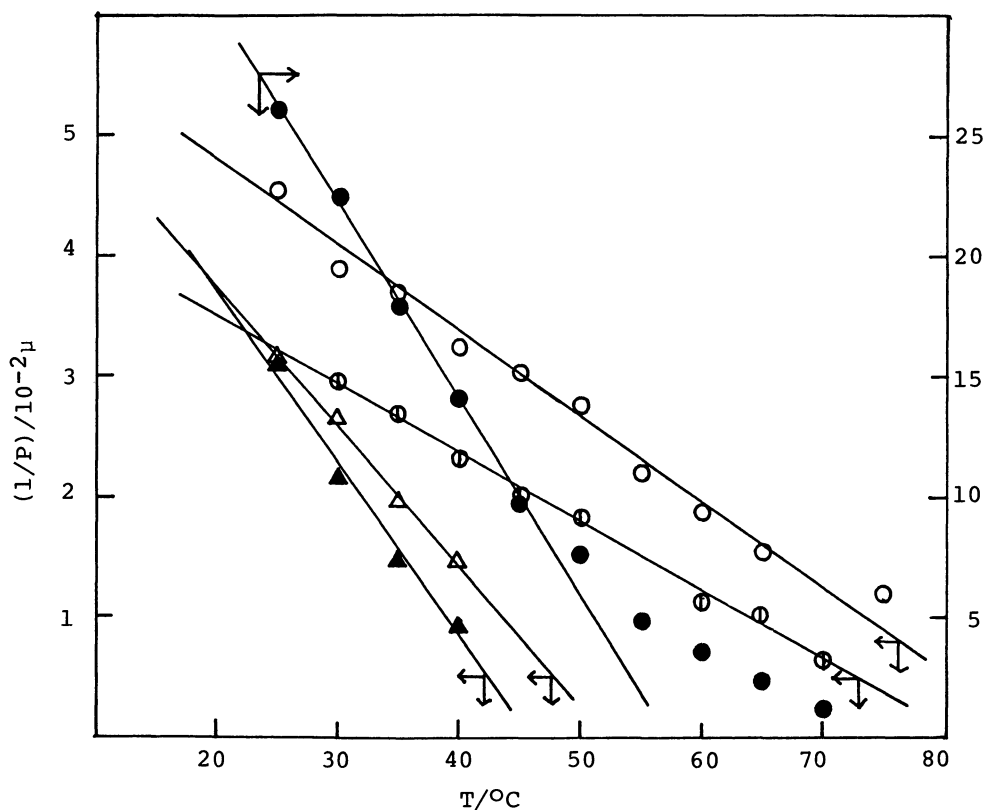


Fig. 1. Temperature dependence of $1/P$ of cholesteric liquid crystals in 1,2-dichloroethane solutions of PBLG(\circ), COP1(\odot), COP2(\blacktriangle), COP3(\triangle) and COP4(\bullet). P: cholesteric pitch in micrometer

Table 2. The value of $d(l/P)/dT$ obtained from Figs. 1 and 2 for each copolymers.

proportion of leucine	$d(l/P)/dT$ (EDC)	$d(l/P)/dT$ (dioxane)
0.00	-0.07	-0.04
0.02	-0.06	-0.04
0.09	-0.14	-0.06
0.16	-0.13	-0.09
0.24	-0.81	-0.42

gradually increase initially. At the proportion of leucine residue of 0.24 (COP4), the value of $d(l/P)/dT$ is larger by a factor of about 10 than that of PBLG. The result of (3) also does not depend on the solvent used in this study. However, the quantitative relationship between $d(l/P)/dT$ and the leucine content was not obtained in this experiment.

It is concluded from the above results that the increase in leucine content increases the temperature dependence of the twisted angle of the cholesteric liquid crystals.

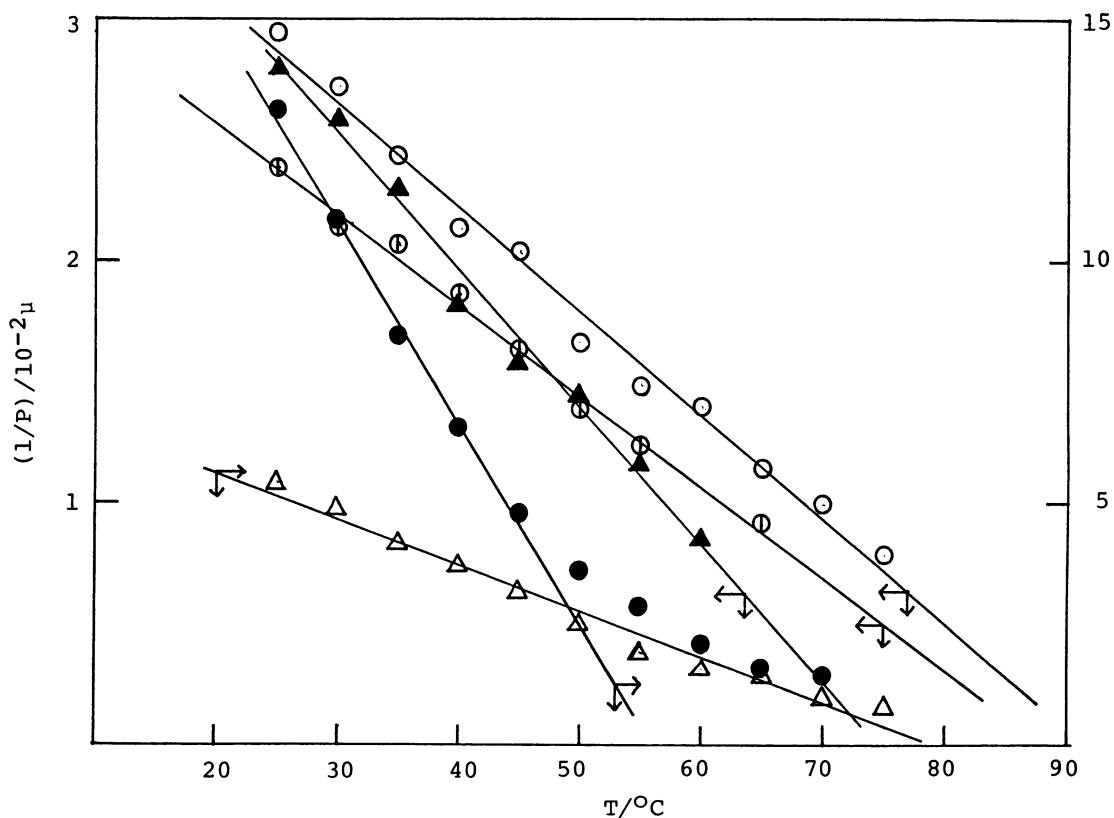


Fig. 2. Temperature dependence of l/P of cholesteric liquid crystals in 1,4-dioxane solutions of the copolymers.

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References and Notes

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- 5) The presence of leucine residue does not alter the absorption band of the benzyl group(See Ref. 4).
- 6) Concentration of the copolymers is expressed as residue mole of polymer per 1000ml solvent.
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