

NOTES

Thermally Induced Cholesteric-to-Nematic-to-Cholesteric Transition of Poly(L-glutamic acid) Liquid Crystals

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It is well known that cholesteric liquid crystals are formed in concentrated solutions of polyglutamate.¹⁻³ The sense of twisting in the cholesteric structure of polyglutamate depends on the structures of side chains and solvents used. For instance, the twisting of cholesteric liquid crystals formed by poly(γ -benzyl L-glutamate) (PBLG) occurs in an opposite sense in dioxane and dichloromethane to each other.³ The other example is that in chloroform, poly(γ -butyl L-glutamate) and poly(γ -octyl L-glutamate) liquid crystals have different senses of twisting from each other.⁴ These show the important roles of interactions between side chains of polyglutamate and solvents in the determination of cholesteric sense. As to the effect of temperature on the twisting power of the cholesteric liquid crystals, Toriumi *et al.* have interpreted the thermally induced inversion of the cholesteric sense of PBLG liquid crystal in *m*-cresol in terms of the effect of hydrogen bonding between the side chains and the solvent.⁵ Most of the preceding studies of polypeptide liquid crystals, however, have been made on polyglutamates, and the behavior of poly(L-glutamic acid) liquid crystals in organic solvents is not fully clarified.

EXPERIMENTAL

Poly(L-glutamic acid) (PLGA) ($M_w = 4.8 \times$

10^4) was prepared by saponification of poly(γ -methyl L-glutamate). The solvents used were *N,N*-dimethylformamide (DMF), *N*-methylformamide (NMF) and formamide (FA). Concentrated solutions of PLGA were prepared with solvents having various solvent compositions: DMF-NMF (100:0, 70:30, 50:50, 0:100, v/v) and DMF-FA (90:10, 80:20, 70:30). The cholesteric pitch was measured using a Nikon polarizing microscope equipped with a Leitz microscope heating stage type 350. The temperature of the concentrated solution was raised at a rate of about 0.1 K min^{-1} up to the measuring temperature and was kept at this temperature for 1 h before measurements.

RESULTS AND DISCUSSION

PLGA formed a cholesteric liquid crystal in every solvent used in this study. When observed under crossed polarizers, the concentrated solutions of PLGA displayed equally spaced retardation lines as shown in Figure 1, in which the distance between parallel lines was equal to one half the cholesteric pitch (P). Figures 2 and 3 show that $1/P$ of these liquid crystals decreases linearly with increasing temperature in the range of relatively low temperature. The extrapolation of the plots to $1/P=0$ (*i.e.*, $P=\infty$) gives a nematic temperature (T_N).

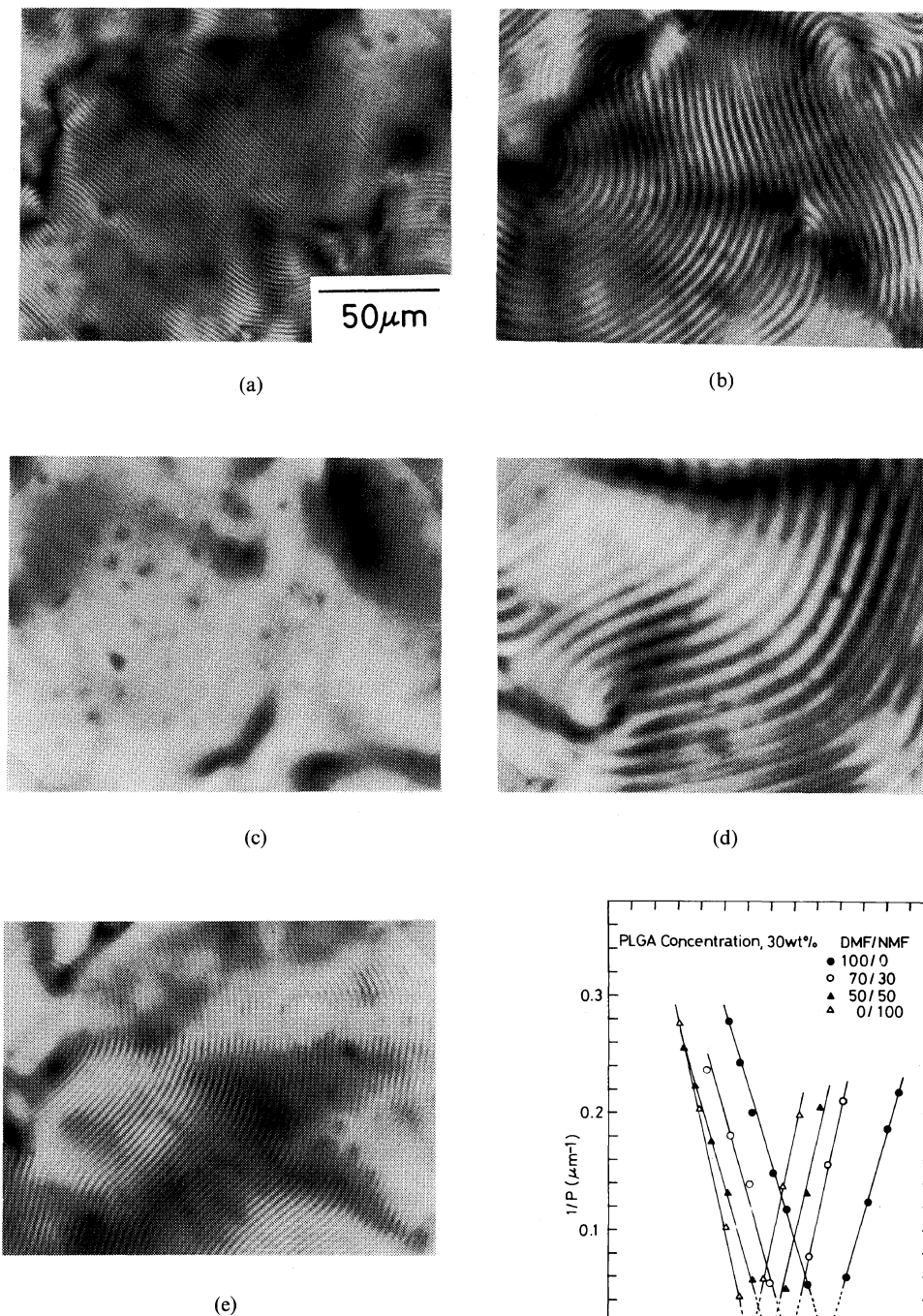


Figure 1. Polarizing micrographs of a 30 wt% PLGA solution in DMF at (a) 76.5°C, (b) 97.5°C, (c) 118°C, (d) 124°C, and (e) 141.5°C.

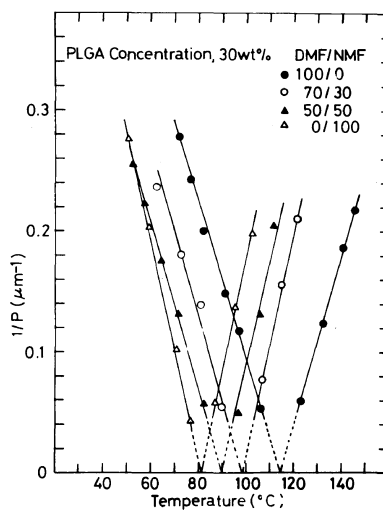


Figure 2. Temperature dependence of the reciprocal of the cholesteric pitch for PLGA liquid crystals in DMF/NMF mixed solvents.

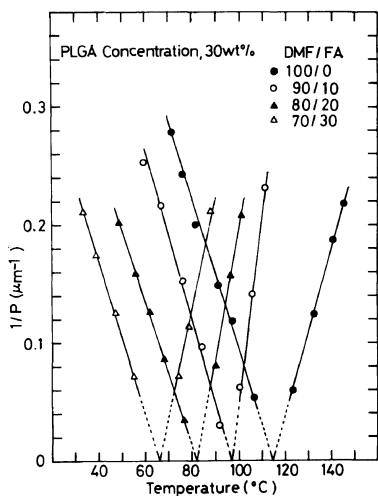


Figure 3. Temperature dependence of the reciprocal of the cholesteric pitch for PLGA liquid crystals in DMF/FA mixed solvents.

At temperatures above T_N , $1/P$ increased with an increase in temperature again linearly starting at temperature T_N . This indicates that a cholesteric-to-nematic-to-cholesteric liquid crystal transition takes place. In view of the results of poly(γ -alkyl L-glutamate),^{4,5} it is considered that the cholesteric structure of PLGA formed above T_N has an opposite sense of twist to that of the cholesteric structure formed below T_N . Such thermally induced phase transition of PLGA liquid crystals has not been found except in ethanol-water mixed

solvent⁶ and this is the first finding of a thermally induced transition of PLGA liquid crystals in a single solvent such as DMF or NMF. The cholesteric-to-nematic transition temperature was shifted toward a lower temperature with increasing content of NMF or FA in the mixed solvents. The origin of the cholesteric twist has been discussed and it is shown that the interaction between the side chains of polypeptides and solvents effects twisting power.^{3,5,7,8} In the case of PLGA liquid crystals, the COOH groups of PLGA would form hydrogen bonds both with the C=O groups of DMF, NMF, or FA and with the N-H groups of NMF or FA in DMF/NMF or NMF/FA mixed solvents. These hydrogen bonds may have an important effect on the cholesteric twisting power, the mechanism of which is still to be clarified.

REFERENCES

1. C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
2. C. Robinson, J. C. Ward, and R. B. Beevers, *Discuss. Faraday Soc.*, **25**, 29 (1958).
3. C. Robinson, *Tetrahedron*, **13**, 219 (1961).
4. N. Mori, *Nippon Kagaku Kaishi*, 864 (1978).
5. H. Toriumi, Y. Kusumi, I. Uematsu, and Y. Uematsu, *Polym. J.*, **11**, 863 (1979).
6. T. Mori, *Kobunshi Ronbunshu*, **40**, 767 (1983).
7. T. V. Samulski and E. T. Samulski, *J. Chem. Phys.*, **67**, 824 (1977).
8. N. Mori, *Nippon Kagaku Kaishi*, 117 (1979).