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THE CHOLESTERIC MESOPHASE IN POLY-L-GLUTAMIC ACID—POLY(ETHYLENE OXIDE)—DIMETHYLFORMAMIDE SYSTEM

Tetsuo TSUTSUI and Takehide TANAKA
Department of Materials Science and Technology, Faculty of
Engineering, Kyushu University, Hakozaki, Fukuoka 812

The cholesteric mesophase of poly-L-glutamic acid which incorporated poly(ethylene oxide) chains was found. The polarizing micrographs of the cholesteric phases, the phase diagram of poly-L-glutamic acid—poly(ethylene oxide)—dimethylformamide ternary system, and the effect of molecular weight of poly(ethylene oxide) on the stability of the cholesteric phases, suggested the importance of the intermolecular interactions between constituent polymers for the stabilization of the cholesteric mesophases.

The cholesteric mesophases of several synthetic polypeptides in organic solvents have been known and their optical properties,[1)] thermodynamic properties,[2)] and electric- and magnetic-field effects on them [3),4)] have been investigated. This paper stresses the importance of the intermolecular interactions in the cholesteric mesophases of polypeptides.

The polymers with pendant carboxylic acid groups, such as poly(acrylic acid), poly(methacrylic acid), and poly-L-glutamic acid, form intermolecular polymer complexes with the polymers which possess hydrogen bond acceptor sites.[5)] Poly-L-glutamic acid (PLGA) is known to give cholesteric mesophases in dimethylformamide (DMF)—H_2O system.[6),7)] A natural question would then be how the cholesteric mesophases of PLGA-DMF system are affected in the presence of a polymer that can form a intermolecular complex with PLGA. In this work, we chose poly(ethylene oxide) (PEO) as a potential hydrogen bond acceptor polymer and examined the nature of PLGA-DMF-PEO ternary system.

PLGA was obtained by the saponification of poly-γ-methyl-L-glutamate (Ajinomoto Co., Ltd.) in aqueous ethanol.[8)] The molecular weight determined from solution viscosities was 5.0×10^4. 9) The optical rotation of 0.2 M NaCl aqueous PLGA solution at pH 7.3, $[\alpha]_D^{20}$ was $-105 \pm 5°$. 10) Commercial PEO ($M_v = 1.5 \times 10^4$) was used after drying under vacuum at room temperature. Tetraethylene glycol and three polyoxyethylene glycols with M_n = 360, 950, and 1900 were used as the low molecular weight analogues of PEO. Cholesteric mesophases were observed by using a Nikon polarizing microscope under crossed polarizers. Sample cells, 0.15 mm thick, were constructed on slide glasses by use of cover glasses and a cyanoacrylate adhesive. The phase diagram of the ternary system was determined by the observation of phase separation behaviors on the solutions with various compositions in 5 ml stoppered bottles. All concentrations were expressed by wt/wt %.

Fig. 1 shows the polarizing micrographs of 15 % polymer (PLGA+PEO) DMF solutions 24 hrs and 7 days after they were loaded in the cells. All samples, irrespective of their polymer compositions, gave spherulitic structures at first, and then the

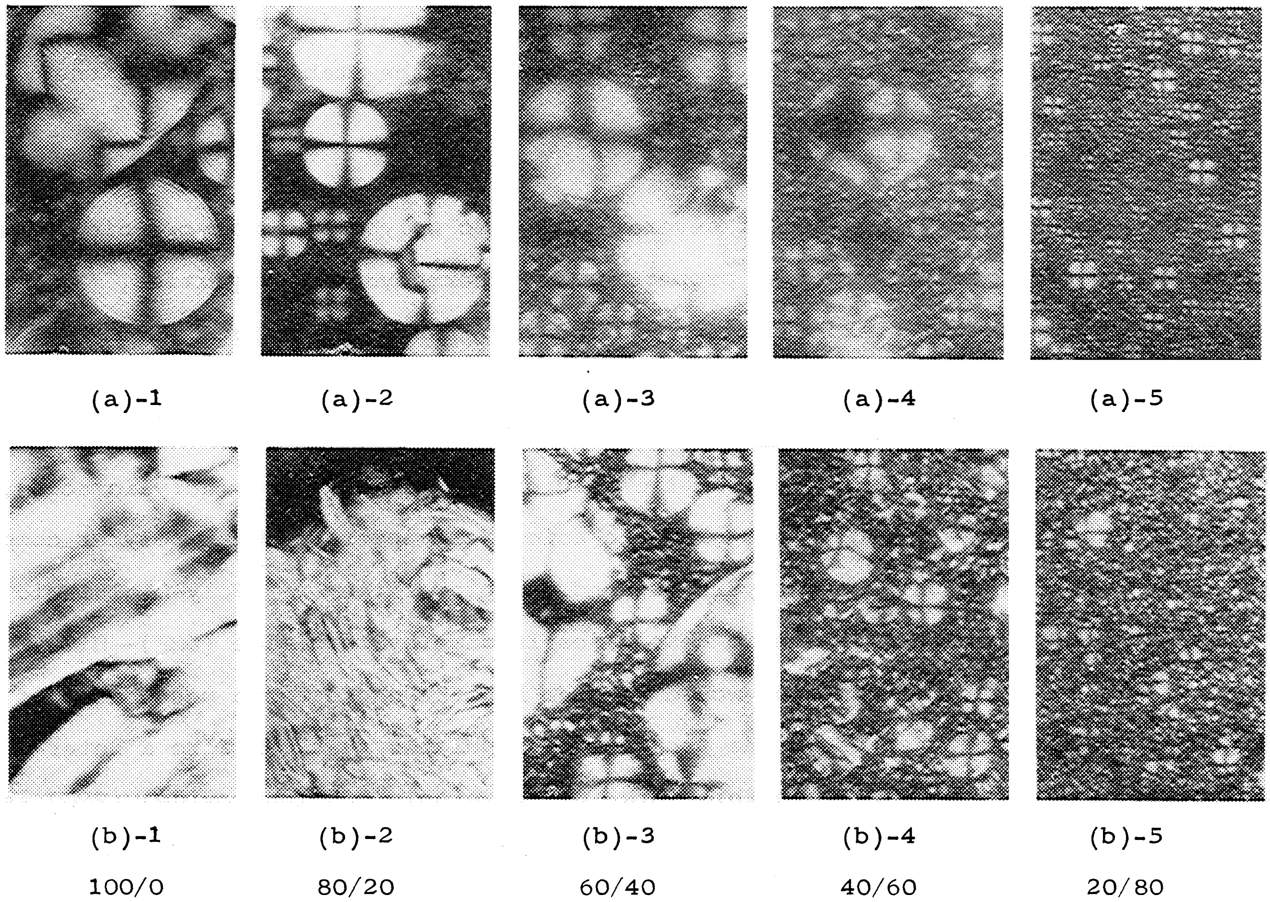

Fig. 1 Polarizing micrographs of 15 % solutions after (a) 24 hrs and (b) 7 days. Numericals below the micrographs indicate PLGA/PEO compositions. Under crossed polarizers, magnification ×250.

continuous layers that gave brilliant cholesteric colors, grew gradually. The rates of transformation from spherulites to continuous layers were slower in the samples rich in PEO than in those with little PEO. The periodical lines which represented cholesteric pitches,$^{1)}$ were clearly observed during the certain periods of the transformation in each sample, though the lines can be distinguished only in PLGA sample in Fig. 1. The pitches were between 0.5 and 2 μ, and they tended to decrease with the increase of polymer concentration or PEO contents. We were not able to obtain the quantitative information between the pitches and sample compositions, because they were delicately dependent on their thermal histories.

Fig. 2 shows the phase diagram of the ternary system at 30°C. In a PLGA-DMF binary system, A point below which only a isotropic phase is present and B point above which only a cholesteric phase is present were 12.3 % and ca. 18 %, respectively. The two-phase region between A and B points broadens in the ternary system.
The existence of the single phase (cholesteric) region in the ternary system should be emphasized; for this provides the evidence of the incorporation of PEO chains in the cholesteric mesophases. The broken line in Fig. 2 indicates the composition of the 1:1 mole repeat unit ratio of PLGA and PEO. No singularity on this line was found. Then it should be concluded that the formation of 1:1 hydrogen bonding between PLGA and PEO does not play an important role in the PLGA-PEO-DMF ternary system.

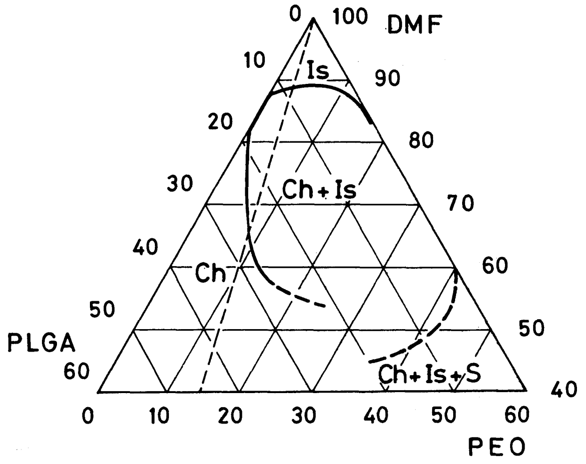

Fig. 2 The phase diagram of PLGA-PEO-DMF system at 30°C. Ch: cholesteric phase; Is: isotropic phase; S: solid phase.

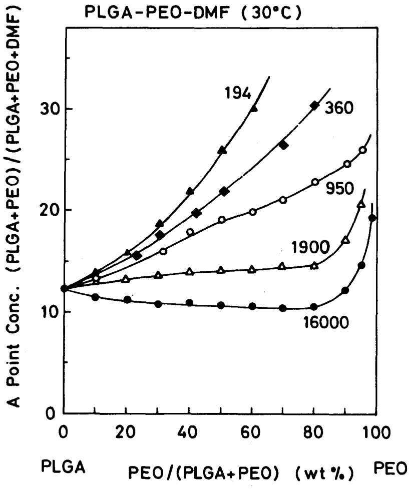

Fig. 3 The variation of A point concentration with the molecular weight of PEO. Numericals in the figure indicate the molecular weight of PEO.

In the high polymer concentration region above 50 %, the solutions were very viscous and turbid, and the observation of state of the solutions was difficult. In a PEO rich region, the crystallization of PEO was recognized.

Fig. 3 shows the variation of A point concentration with a polymer composition at 30°C. In the systems with low molecular weight PEO (less than 950), the A point concentration increased with the increase of PEO content. On the other hand, PEO of high molecular weight acts to depress the A point concentration. This phenomenon suggests the presence of a kind of co-operative interaction between PLGA and PEO chains. Therefore, the PLGA-PEO-DMF system should be discliminated from common polypeptide-solvent-nonsolvent systems.

The concentrated aqueous solutions of DNA and RNA are known to take cholesteric mesophases,11),12) but no cholesteric mesophase that involves inter-polymer complexes of synthetic polymers, has been known. Although we possess no concrete image on the structure of inter-polymer complexes through hydrogen bonding between PLGA and PEO, this ternary system may be one of the first findings of cholesteric mesophases which are composed of inter-polymer complexes.

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