Heterogeneous network polymers: 7. Cholesteric liquid crystal structure of poly(glutamic acid) fixed by crosslinking

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The phase structure of the heterogeneous network polymers prepared from poly(glutamic acid) (PGA) and poly(oxyethylene glycol) (PEG, $\bar{M}_n$ = 302) was investigated by polarizing microscopy. The solid films had a layered structure comprising cholesteric liquid crystal domains. In each domain α-helices of PGA are aligned nearly parallel to the film surfaces. The cholesteric liquid crystal structure was not destroyed even when the films were heated in dimethylformamide (DMF) at 100°C for a week in spite of the fact that DMF can easily dissolve PGA and PEG at 50°C. This suggests that the cholesteric liquid crystal structure formed in the concentrated solutions of PGA, PEG and DMF is perpetuated by crosslinking.

INTRODUCTION

Synthetic polypeptides such as poly(γ-benzyl-L-glutamate) (PBLG) and poly(γ-methyl-L-glutamate) form cholesteric liquid crystals in concentrated solutions[1-5]. Tobolsky *et al.*[6-10] showed that the liquid crystal structure was retained in solid films of PBLG and in plasticized PBLG prepared by evaporating the concentrated solutions. The films were composed of layered cholesteric domains, and in each domain the PBLG α-helices lay parallel to the film surfaces. Furthermore, some anisotropic order was preserved in the PBLG films moderately crosslinked in the solid state by γ-irradiation and the plasticized films may be crosslinked to perpetuate the cholesteric structure. Aviram[11] obtained solid films with a permanent homeotropic nematic texture by crosslinking PBLG with 1,6-hexanediamine in a magnetic field. In the absence of the magnetic field, however, a cholesteric phase arose in the solid gel. We have been studying the heterogeneous network polymers from poly(glutamic acid) (PGA) and poly(oxyethylene glycol) (PEG)[12,13]. In the previous papers[14,15] of this series, we showed that mere mixing of PGA with an appropriate proportion of PEG in dimethylformamide (DMF) gave rise to a cholesteric liquid crystal structure, and that such structure was retained when the mixture was heated to effect crosslinking in order to obtain the heterogeneous network polymers.

In this paper the phase structure of the heterogeneous network polymers was investigated in more detail by the polarizing microscopic observations of the swollen sections cut normal and parallel to the film surfaces.

EXPERIMENTAL

The specimens for polarizing microscopic observations were taken from the same heterogeneous network polymers as were used in the preceding paper[16]; that is, the heterogeneous network polymers containing 70 and 40 wt % of PGA were prepared from PGA and PEG (M_n = 302) with three different evaporation rates of DMF. The polymers are abbreviated as PGA–PEG300(70/30)-s, PGA–PEG300(70/30)-m, PGA–PEG300(70/30)-f, PGA–PEG300(40/60)-s, PGA–PEG300(40/60)-m and PGA–PEG300(40/60)-f.

A thin section (~ 0.5 mm × ~ 0.5 mm × ~ 0.05 mm) cut normal or parallel to the film surfaces was placed on a slide glass and was sandwiched with a cover glass. Then DMF or dichloroacetic acid (DCA) was added to swell it. The changes in the phase structure and the dimensions were observed by a Nikon polarizing optical microscope type LFG-KE between crossed polarizers.

RESULTS AND DISCUSSION

Figures 1 and *2* show the polarizing photomicrographs of vertical sections of the heterogeneous network polymers, unswollen or swollen in DMF for 2 h at room temperature. Optical retardation lines characteristic of a cholesteric liquid crystal structure were observed in PGA–PEG300(70/30)-s, PGA–PEG300(40/60)-m, and PGA–PEG300(40/60)-f. Cholesteric colours were observed in every unswollen section under crossed polarizers and, in addition, they appeared brightest and darkest when the section was placed at angles of 45° and 0° to the crossed polarizers, respectively. This suggests that the cholesteric domains were oriented. In PGA–PEG300(70/30)-s (*Figures 1a* and *1b*) the directions of the retardation lines were nearly parallel to the film surfaces while the directions of the retardation lines in the horizontal sections were random as shown in the preceding paper[16]. This indicates that the cholesteric domains are aligned parallel to the film surfaces and that each cholesteric domain is composed of PGA α-helices with their long axes lying parallel to the film surfaces. Moreover, the distance S between the retardation lines is smaller in the upper layers of the film. A reasonable explanation for this may be that

the crosslinking reaction occurs after the cholesteric liquid crystal domains have been formed. That is, during the course of crosslinking the concentration of PGA becomes higher near the surface of the reaction mixture because the evaporation of DMF occurs almost entirely around the upper surface of the reaction mixture.

Robinson[2] reported that S decreased as the PBLG concentration increased in the anisotropic phase. According to this experimental rule, S in the upper parts is smaller than in the lower parts. This cholesteric structure of the concentrated solution was frozen by crosslinking when the DMF evaporated thoroughly.

In PGA–PEG300(70/30)-m the layered domains exhibited irridescent colours although the retardation lines were not observed. This is also an indication of layered cholesteric structure of the film in this case.

In PGA–PEG300(70/30)-f and PGA–PEG300(40/60)-f there was no distinct difference between the polarizing photomicrographs of horizontal sections shown in the preceding paper[16] and vertical sections shown in *Figures 1e* and *2e*. However, the PGA α-helices are considered to be still aligned (on the whole) parallel to the film surfaces because the anisotropic swelling was observed as will be mentioned subsequently.

In PGA–PEG300(40/60)-s shown in *Figure 2a*, the vertical section exhibited cholesteric colours when it was placed at an angle of 45° to crossed polarizers and bright spots were finely dispersed when it was placed parallel to the crossed polarizers.

In PGA–PEG300(40/60)-m shown in *Figures 2c* and *2d*,

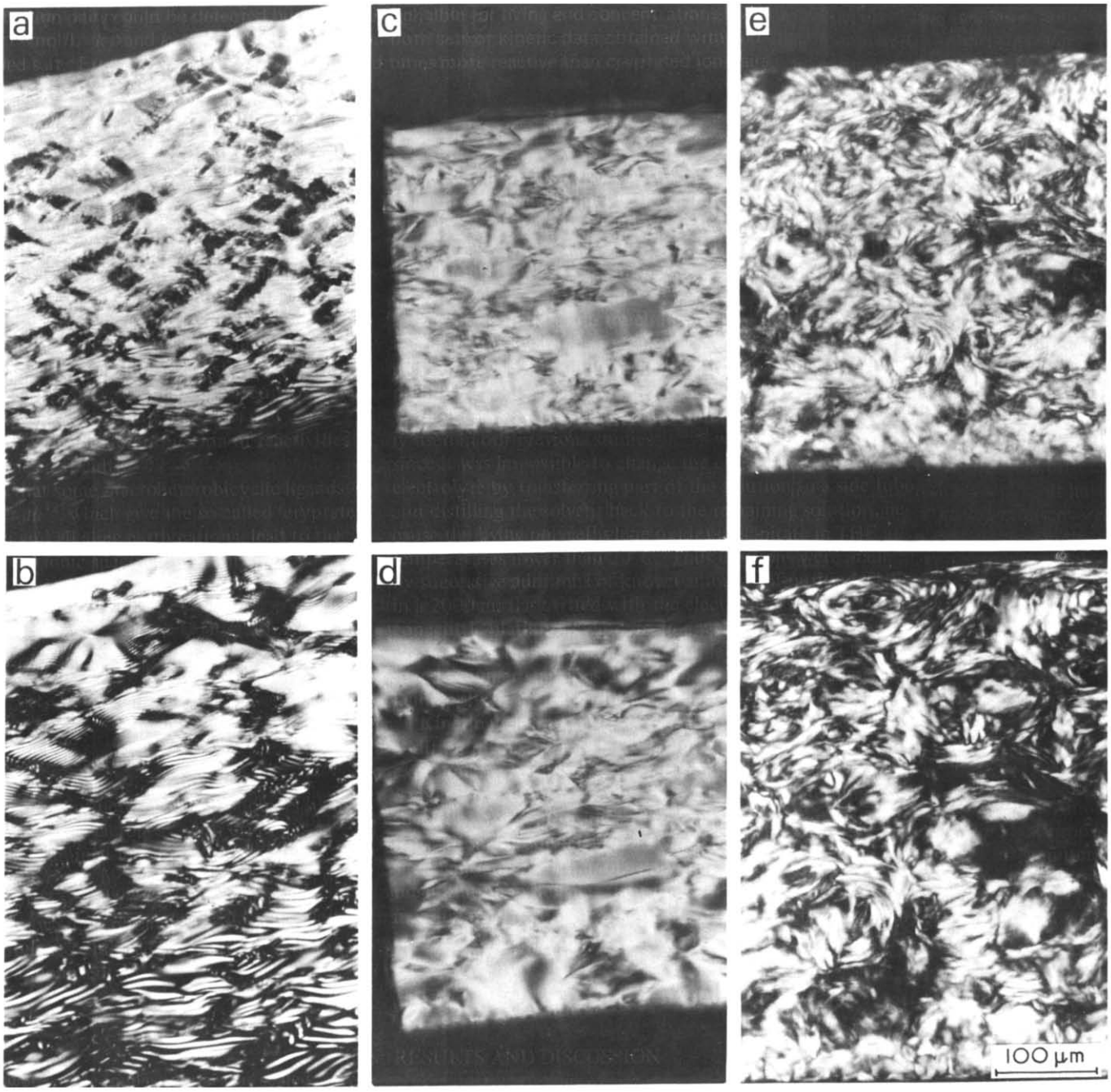

Figure 1 Polarizing photomicrographs of vertical sections of PGA–PEG300(70/30), unswollen or swollen in DMF for 2 h at room temperature: (a) PGA–PEG300(70/30)-s (unswollen); (b) PGA–PEG300(70/30)-s (swollen); (c) PGA–PEG300(70/30)-m (unswollen); (d) PGA–PEG300(70/30)-m (swollen); (e) PGA–PEG300(70/30)-f (unswollen); (f) PGA–PEG300(70/30)-f (swollen)

the cholesteric structure in the upper and lower layers of the film were similar to those of PGA–PEG300(40/60)-f and -s, respectively. These results can be explained as follows. At the PGA content of 40 %, PEG is apt to separate out when the evaporation rate of DMF is small, and the anisotropic domains are, therefore, finely dispersed[16]. When the evaporation rate of DMF is large, on the other hand, PEG constituting the cholesteric liquid crystals together with PGA cannot effectively separate. Therefore the cholesteric domains become large and the retardation lines were observed because of low concentration of PGA. Polarizing photomicrographs of vertical sections of the samples swollen in DMF for 2h at room temperature were shown in *Figures 1b, 1d, 1f, 2b, 2d,* and *2f.* Apparent equilibrium of swelling was attained in approximately 10 min. Clearly, the distance *S* increased with swelling and the layered cholesteric structure was very distinct. The cholesteric liquid crystal structure was not destroyed even when the thin samples were heated in DMF – a solvent that can dissolve easily both component polymers, PGA and PEG, at 50°C – at 100°C for a week.

In contrast, DCA, a random-coil solvent for PGA, caused some changes in the phase structure of PGA–PEG300(40/60)-f; the polarizing photomicrographs of the horizontal section appeared almost dark when the sample was swollen in DCA for 30 min at room temperature (*Figure 3b*). To our surprise, the original cholesteric structure was perfectly regained when the DCA was extracted by immersing the sample in ethanol (*Figure 3c*).

Gennes[17] described the possibility that when a polymer

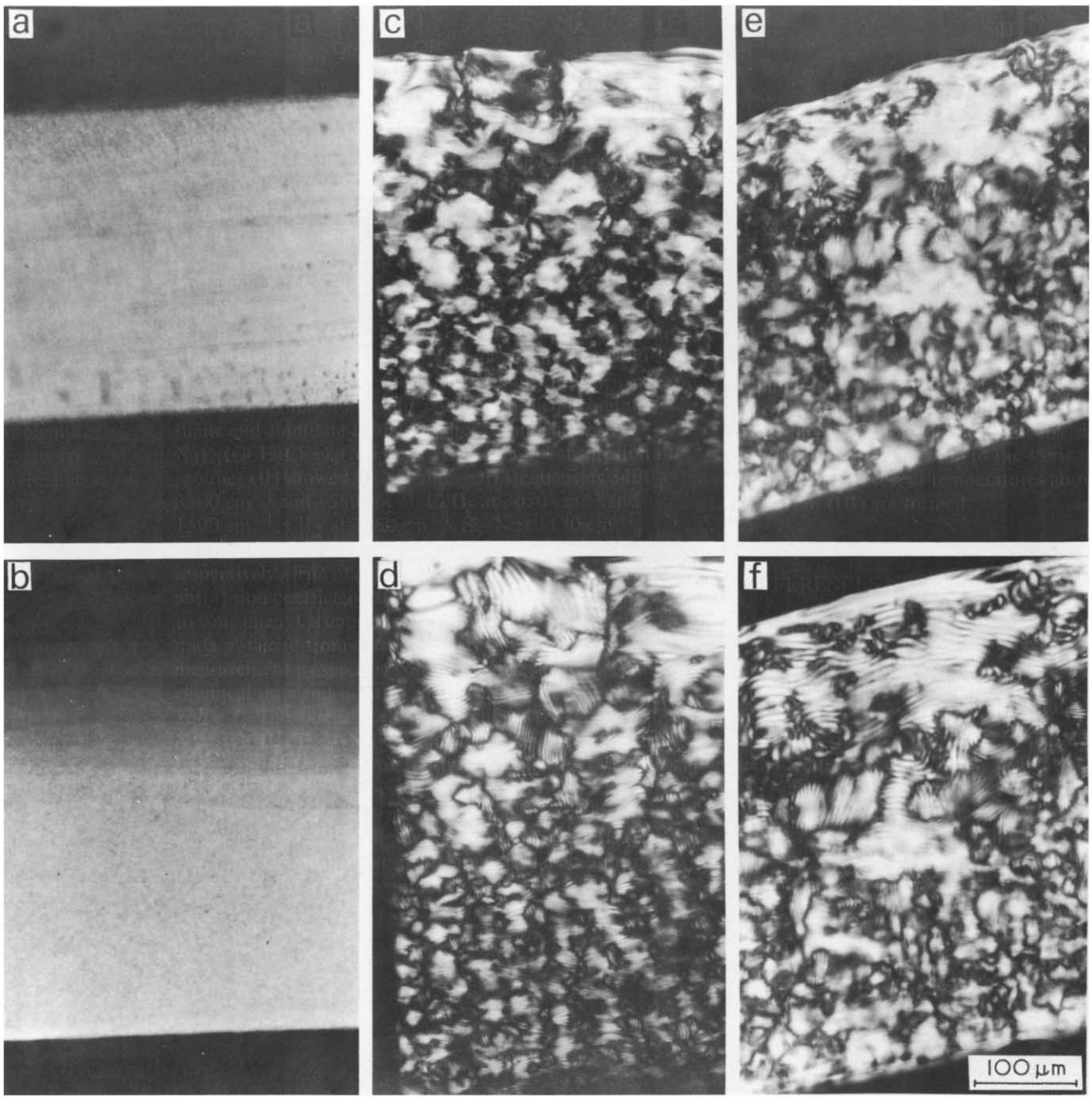

Figure 2 Polarizing photomicrographs of vertical sections of PGA–PEG300(40/60), unswollen or swollen in DMF for 2 h at room temperature: (a) PGA–PEG300(40/60)-s (unswollen); (b) PGA–PEG300(40/60)-s (swollen); (c) PGA–PEG300(40/60)-m (unswollen); (d) PGA–PEG300(40/60)-m (swollen); (e) PGA–PEG300(40/60)-f (unswollen); (f) PGA–PEG300 (40/60)-f (swollen)

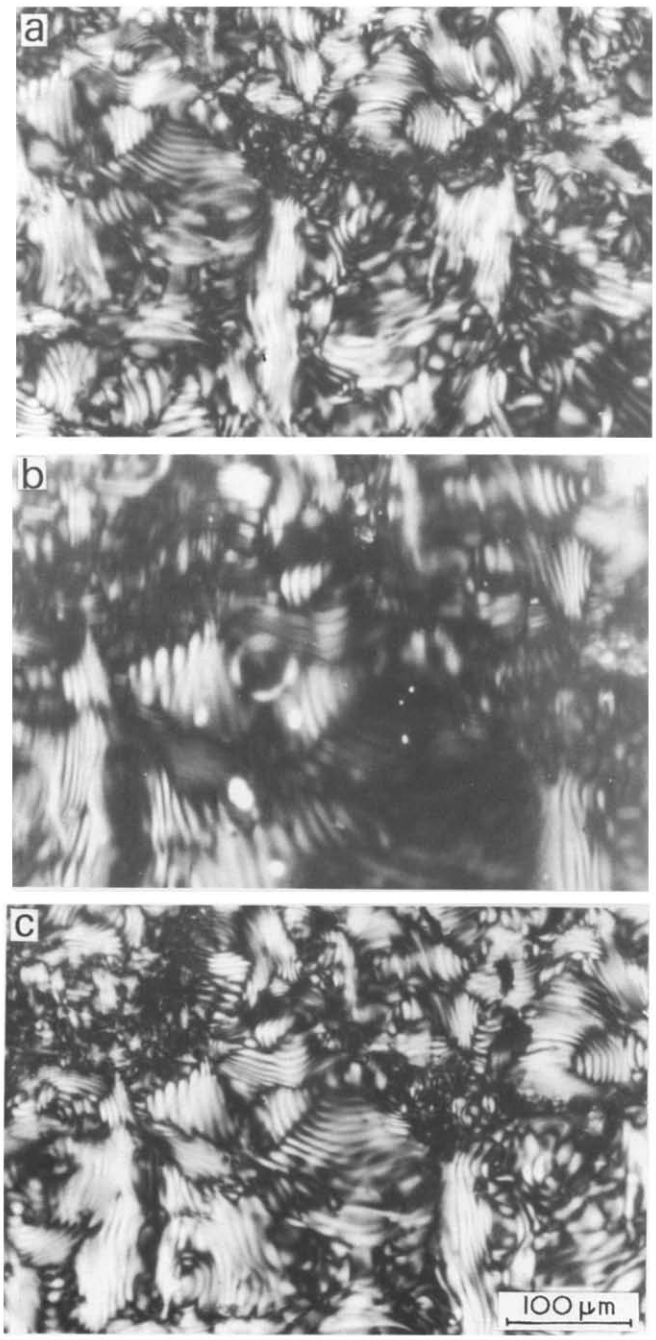

Figure 3 Changes of the phase structure of PGA–PEG300(40/60)-f (horizontal section) by swelling in DCA at room temperature: (a) unswollen; (b) swollen for 30 min; (c) immersing (b) in ethanol for 30 min

solution was crosslinked in a mesomorphic solvent, the anisotropic properties of the solvent persisted in the network polymer. Our heterogeneous network polymer system is a similar system except that it is the polymer that constitutes a liquid crystal structure.

Table 1 shows the changes in dimensions of vertical sections after swelling in DMF for 2 h at room temperature. A marked increase in the dimension was observed in the N direction. In PGA–PEG300(70/30), the ratio of N to P increased as the layered cholesteric liquid crystal structure became prominent, i.e. -f < -m < -s. This suggests that the PGA α-helices move more easily in the lateral direction than in the direction of long axes of the α-helices. Also in PGA–PEG300(40/60), N/P increased as the cholesteric

Table 1 Changes in the dimensions of vertical sections by swelling in DMF for 2 h at room temperature. N and P are the directions normal and parallel to the film surfaces, respectively

	N^* (%)	P^* (%)	N/P
PGA–PEG300(70/30)-s	37	8	4.6
PGA–PEG300(70/30)-m	39	10	3.9
PGA–PEG300(70/30)-f	26	14	1.9
PGA–PEG300(40/60)-s	33	11	3.0
PGA–PEG300(40/60)-m	24	12	2.0
PGA–PEG300(40/60)-f	26	14	1.9

* Changes are represented by $100(l-l_0)/l_0$, where l_0 is the initial dimension and l is the dimension of a swollen section

domains became small, i.e., -f < -m < -s. This can be explained similarly as above based on the polarizing photomicrographs of PGA–PEG300(40/60)-m shown in *Figures 2c* and *2d*, which indicate that the retardation lines are nearly parallel to the film surfaces when the cholesteric domains are small and, on the other hand, the retardation lines are relatively random when the cholesteric domains are large.

CONCLUSIONS

In conclusion, (a) the cholesteric liquid crystal structure of our heterogeneous network polymers was frozen by crosslinking, and (b) the heterogeneous network polymers had layered cholesteric domains which comprised PEG and PGA α-helices lying nearly parallel to the film surfaces.

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