Network polymers with cholesteric liquid crystalline order prepared from poly(γ-butyl L-glutamate)–butyl acrylate liquid crystalline system

Tetsuo Tsutsui and Ryuichi Tanaka
Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Fukuoka 812, *Japan*
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Polymer composites consisting of poly(γ-butyl L-glutamate) (PBuLG) and crosslinked poly(butyl acrylate) (PBuA) have been prepared by causing butyl acrylate (BuA) to polymerize in PBuLG–BuA cholesteric liquid crystalline states. The composites exhibited cholesteric organizations in bulk and in swollen states. Microscopic as well as macroscopic swelling behaviour of the composites was examined and was discussed in relation to their crosslink densities. About two-thirds of the PBuLG component could be eliminated from the composites by extraction with either chloroform or dichloroacetic acid (DCA), and the extracted composites still possessed cholesteric organizations. Practically complete removal of the PBuLG component from the composites was achieved by hydrolytic extraction with a DCA–HCl mixture. The PBuA polymer networks thus obtained exhibited no cholesteric organization, but once again the cholesteric organizations emerged when the networks were swollen in solvents. This observation was interpreted in terms of the topology of the networks constructed in cholesteric liquid crystalline states.

INTRODUCTION

Liquid crystalline organizations can be immobilized by the polymerization of vinyl monomer incorporated in systems[1-4]. Satisfactory immobilization of liquid crystalline organizations is attained only in the case when the polymerization of vinyl monomers is accompanied by either rapid solidification of the system or formation of crosslinkage among polymer chains. Only in the latter case, the immobilized liquid crystalline textures are expected to endure heat, solvents, and mechanical deformations.

Of particular interest is the network polymers that are constructed in a cholesteric liquid crystalline environment; for such networks may possess topologically peculiar characteristics[5]. We previously demonstrated the feasibility of reticulation in cholesteric liquid crystalline states in a few synthetic polypeptide–vinyl monomer systems by causing the solvents (vinyl monomers) to polymerize[6-8]. In the present study, we focus our attention on the network polymer systems prepared from poly(γ-butyl L-glutamate)–butyl acrylate (PBuLG–PBuA) liquid crystals and discuss their fixed liquid crystalline features.

The cholesteric organizations of those network polymers (PBuLG–PBuA composites) cannot only withstand swelling in solvents and mechanical deformations, but also persist even after the PBuLG component, the only mesogenic element in the original PBuLG–BuA liquid crystalline systems, is eliminated from the composites. A special mention is, therefore, worthwhile concerning the steric structure of these particular PBuA networks, which, peculiarly enough, do not lose the cholesteric organizations even in the absence of any mesogens.

EXPERIMENTAL

Materials

PBuLG was prepared by *trans*-esterification of poly(γ-methyl L-glutamate) (Ajicoat A-2000, Ajinomoto Co. Inc.) with butyl alcohol using *p*-toluene-sulphonic acid as a catalyst[9]. The degree of substitution of the methyl group by the butyl group was found, from the n.m.r. spectra measured in a trifluoroacetic acid solution, to be 96%. BuA, methyl acrylate (MeA), and 2-ethylhexyl acrylate (OcA) were distilled under reduced pressure before use. Ethylene glycol dimethacrylate (EGDM), triethylene glycol dimethacrylate (TGDM), benzoyl peroxide (BPO), dichloroacetic acid (DCA), chloroform, and dimethylformamide (DMF) were reagent-grade chemicals and were used without further purification.

Preparation of network polymers

PBuLG (0.6 g) was dissolved in BuA (1.4 g) which contained 0.5–10.0 wt % EGDM as a crosslinking agent. The viscous solutions were stirred vigorously to ensure homogeneous mixing and allowed to stand overnight at room temperature. After addition of 2.0 wt % BPO (with respect to the amount of BuA), the solutions were charged in 2 mm diameter capillaries and sealed. The capillaries were kept at 60°C for 48 h, cooled to room temperature, and broken. Five varieties of flexible, rod-shaped polymer composites comprising PBuLG and crosslinked PBuA were obtained as given in *Table* 1. The composites were dried under vacuum at 100°C for 24 h. The weight losses with this procedure were less than 3% in all the composite samples.

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Partial elimination of the PBuLG component from the composites was performed by extracting it with chloroform or DCA; the composites (~0.4 g) were immersed in 100 ml of chloroform or DCA and allowed to stand at room temperature for 7–10 days. Complete elimination of the PBuLG from the composites was accomplished by hydrolytically extracting it with a DCA–concentrated HCl (4:1) mixture at room temperature. The PBuLG contents of the treated samples could be determined from their nitrogen contents, because only the PBuLG component contained nitrogen atoms.

Swelling ratios of the original composite samples in chloroform or DMF were calculated from their weight increases after swelling, their densities, and the density of chloroform or DMF.

Table 1 Properties of PBuLG–PBuA composites

No.	EGDM content (wt %)	Crosslink density[a] (mol/cm^3)	Density[b] (g/cm^3)	Swelling ratio (vol/vol)	
				Chloroform	DMF
1	0.5	0.20×10^{-4}	1.076	7.94	3.63
2	1.0	0.40×10^{-4}	1.080	7.60	3.47
3	2.0	0.77×10^{-4}	1.081	7.60	3.10
4	5.0	1.93×10^{-4}	1.087	3.85	2.32
5	10.0	3.87×10^{-4}	1.096	2.77	1.97

[a] Average crosslink density calculated from EGDM content
[b] Measured by a flotation method in $CaCl_2$ aq. soln. at 25°C

Microscopic observation

Thin sections were cut out of the untreated or treated sample rods, perpendicularly to their long axes, and were observed through a Nikon polarizing optical microscope under crossed polarizers. To observe them in their swollen states through a microscope, they were placed between a glass slide and a cover glass, and a few drops of chloroform or DMF were added. Observations were made after about 15 min, when their equilibrium swelling was attained. The values S, one-half the cholesteric pitch, were determined by measuring the distances between the retardation lines on the photomicrographs. The average values were based on measurements made on at least five different photomicrographs of the same samples.

RESULTS AND DISCUSSION

Effect of crosslink density on properties of polymer composites

In *Figure* 1, the cholesteric organizations of the PBuLG–PBuA composites were compared with the cholesteric liquid crystalline states of the PBuLG–BuA systems at 60°C. No effect of the difference in EGDM contents was found on the liquid crystalline states before polymerization. In contrast, the fine textures of the polymerized PBuLG–PBuA composites depended markedly on the amounts of the crosslinking agent. Since we have already discussed elsewhere the effect of a crosslink-

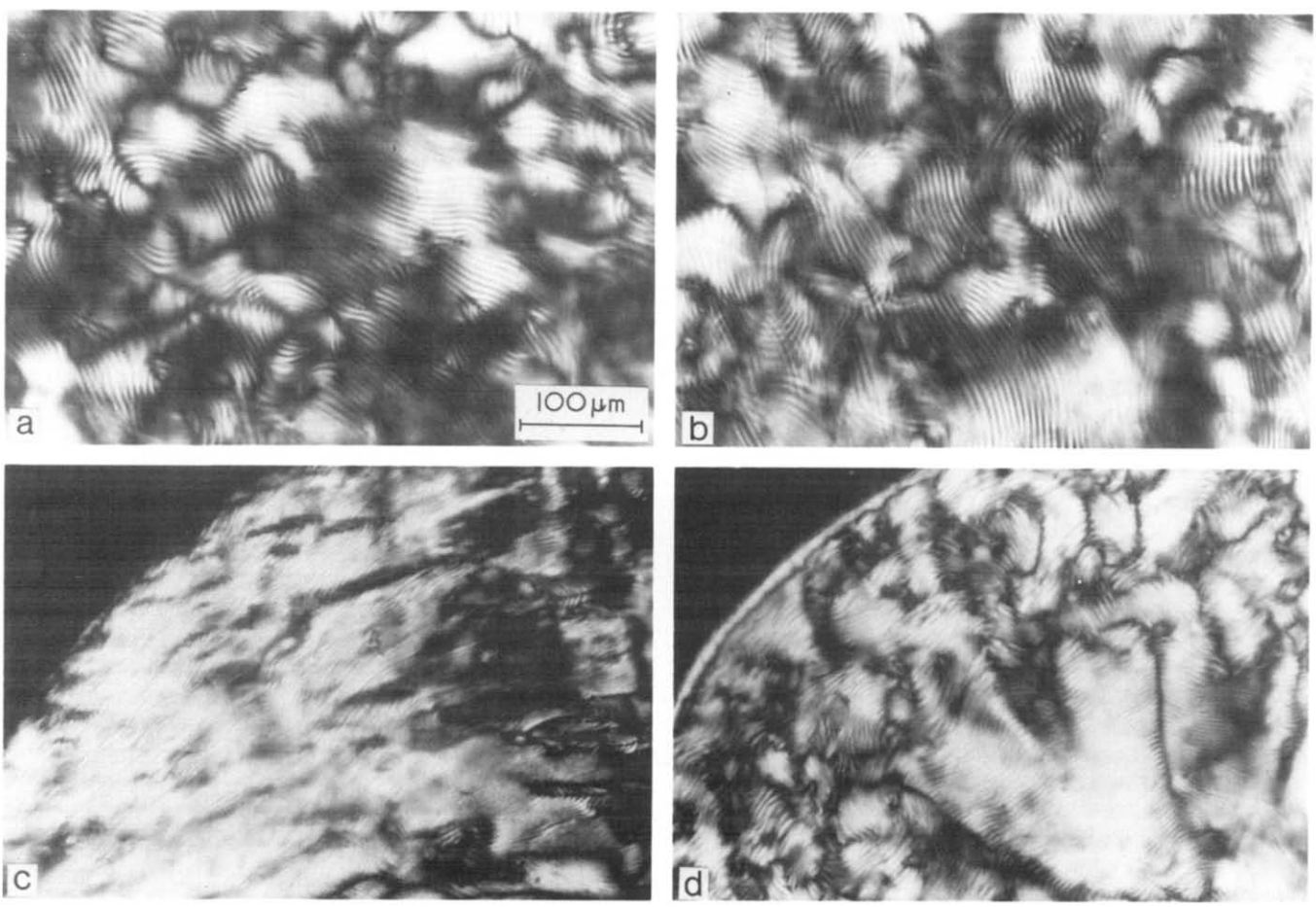

Figure 1 Polarizing micrographs of PBuLG–BuA liquid crystalline systems at 60°C and PBuLG–PBuA composites: (a) PBuLG–BuA solution (1.0% EGDM); (b) PBuLG–BuA solution (10% EGDM); (c) PBuLG–PBuA composite (1.0% EGDM); (d) PBuLG–PBuA composite (10% EGDM)

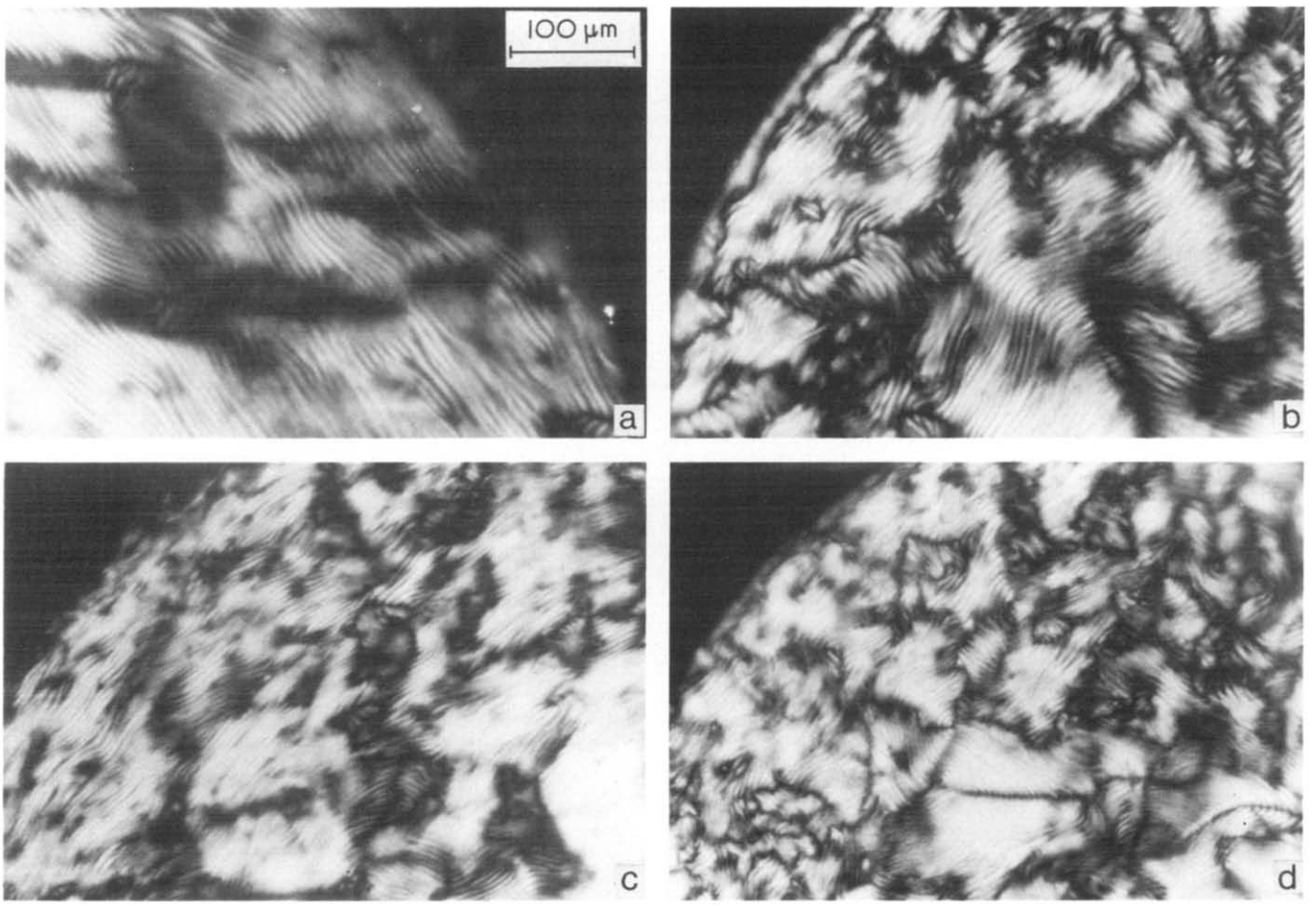

Figure 2 Polarizing micrographs of swollen PBuLG–PBuA composites: (a) PBuLG–PBuA (1.0% EGDM) in chloroform; (b) PBuLG–PBuA (10% EGDM) in chloroform; (c) PBuLG–PBuA (1.0% EGDM) in DMF; (d) PBuLG–PBuA (10% EGDM) in DMF

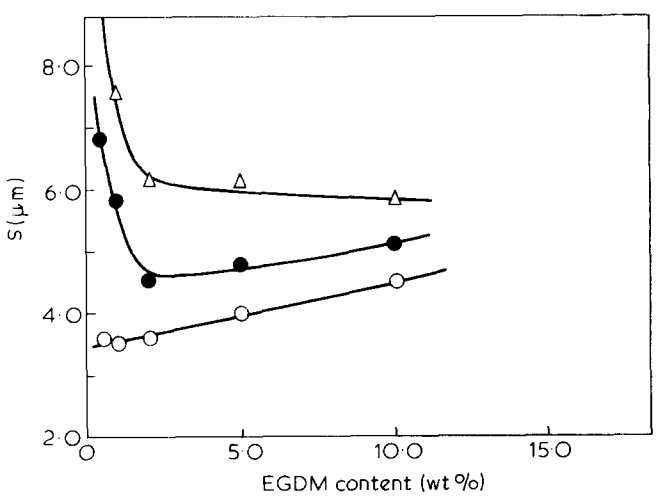

Figure 3 One-half of a cholesteric pitch, *S*, plotted against EGDM content: ○, unswollen; △, swollen in chloroform; ●, swollen in DMF

ing agent on immobilization of cholesteric organizations by polymerization, here we only point out that a scarcity of the crosslinking agent resulted in the occurrence of disordered cholesteric textures (*Figure* 1*c*)[8].

The PBuLG–PBuA composites swelled in organic solvents such as chloroform, DMF, and benzene, but not in methanol and cyclohexane. The swelling ratios (vol/vol) in chloroform and DMF are summarized in *Table* 1. The cholesteric pitch of each composite invariably increased with swelling; however, the original pitch was restored when the solvent was allowed to evaporate from the sample. *Figure* 2 shows the polarizing micrographs of the composites swollen in both choloroform and DMF. The cholesteric pitches of the swollen composites were dependent on the crosslink densities and solvents. Therefore, the change of the cholesteric pitch with swelling was expected to be expressed in terms of the macroscopic swelling ratio. In *Figure* 3, one-half the cholesteric pitch, *S*, of both the unswollen and the swollen composites was plotted against the EGDM content. From this plot, one can calculate the change of cholesteric pitch with swelling, S/S_0, and plot it against a swelling ratio Q (*Figure* 4).

S can be expressed in terms of the interplanar spacing between α-helix layers, d, and the cholesteric twist angle per adjacent layers, ψ:

$$S = \pi \cdot \frac{d}{\psi} \tag{1}$$

Then,

$$\frac{S}{S_0} = \frac{d}{d_0} \cdot \frac{\psi_0}{\psi} \tag{2}$$

where S_0, d_0 and ψ_0 respectively denote S, d, and ψ for an unswollen state. If three-dimensional uniform swelling is assumed, $d/d_0 = Q^{1/3}$. One can also assume two-dimensional anisotropic swelling; swelling along the chain

axis of the α-helix of rigid PBuLG molecules may be much smaller than that in the directions perpendicular to that axis. In this case, $d/d_0 = Q^{1/2}$.

Then,

$$\frac{S}{S_0} = \frac{\psi_0}{\psi} \cdot Q^{1/3} \quad \text{(uniform)} \tag{3a}$$

$$\frac{S}{S_0} = \frac{\psi_0}{\psi} \cdot Q^{1/2} \quad \text{(two-dimensional)} \tag{3b}$$

Putting $\psi = \psi_0$ for simplicity, one can draw equations (3a) and (3b) in *Figure* 4. The experimental points for the composites with the EGDM contents larger than 2% dropped near the curve expressing the three-dimensional uniform swelling. The small increase of the twist angle, ψ, accompanying the increase of d must be taken into account for better agreement between experimental values and estimates from equation (3a). The experimental point for the composite with 0.5% EGDM fell on the curve for two-dimensional swelling, indicating the easier expansion of the networks in the direction perpendicular to the axis of the PBuLG helix.

These facts reveal that the crosslink density determines the cholesteric pitches of the swollen composites. In other words, the PBuA networks, which envelop the PBuLG

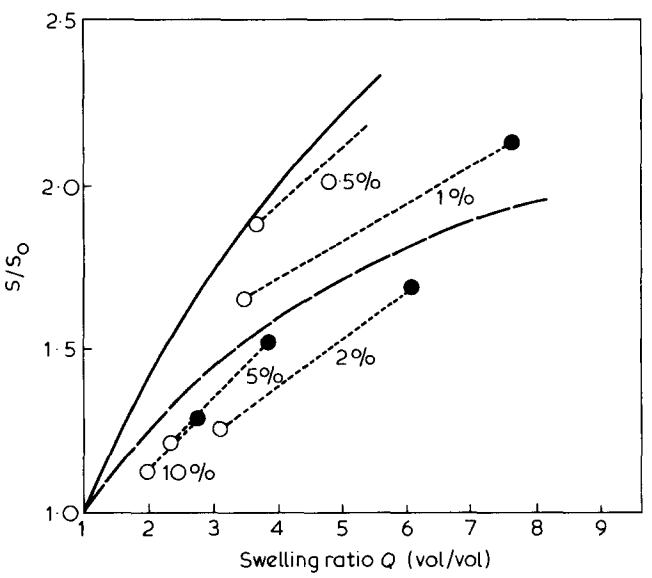

Figure 4 S/S_0 plotted against swelling ratio, Q: ●, swollen in chloroform; ○, swollen in DMF. Numerals indicate the EGDM contents of the composites. The broken and the solid lines represent three-dimensional (isotropic) and two-dimensional (anisotropic) swelling, respectively

α-helices, dominate the swelling behaviour of the PBuLG–PBuA composites. The PBuLG component, the mesogen, which originally gives rise to the PBuLG–BuA liquid crystalline states before polymerization, no longer plays an important role in the PBuLG–PBuA composites; it merely contributes to the optical properties of the composites as the origin of optical anisotropy.

Extraction of PBuLG component from composites

Since the PBuLG molecules in the composites are not chemically bound to the PBuA networks, the PBuLG component can be eliminated from the composites by solvent extraction. The composites were extracted with chloroform, DCA, and a DCA–HCl mixture. *Table* 2 summarizes the weight losses after extraction together with the PBuLG contents of the treated composites. About one-third of the PBuLG component could be extracted with chloroform in 10 days. It was difficult, however, to completely eliminate the PBuLG from the composites with a simple solvent extraction procedure. To overcome this difficultly, we employed the hydrolytic extraction of PBuLG with DCA–HCl mixture; namely, the PBuLG skeletal chains were hydrolysed into fragments under acid catalysis (HCl), and the fragments were extracted with DCA. The PBuLG contents of the DCA–HCl treated composites, which were estimated from their nitrogen contents, were found to be less than 3%. All the composites treated with a DCA–HCl mixture can be regarded as PBuA network polymers, even though some of them include small amounts of the residual PBuLG.

Despite the drastic decrease in the PBuLG contents, all the composites extracted with chloroform or DCA retained the cholesteric liquid crystalline organizations. *Figure* 5 shows the polarizing micrographs of some DCA extracted composites. The cholesteric textures were clearly observed in those composites, though the optical contrasts were considerably diminished.

As is exemplified by the open circles in *Figure* 6, the cholesteric pitch of the composite (10% EGDM) decreased as its PBuLG content was reduced by extraction. The decrease of the cholesteric pitch was uniform throughout the observed sample sections, indicating the uniform removal of PBuLG molecules from the composite. The observed decrease in the cholesteric pitches in the crosslinked composites can be explained as the result of decrease in the interplaner spacing, d, due to partial disappearance of PBuLG molecules. It is, on the other hand, peculiar that the cholesteric pitch decreases as the mesogen (PBuLG) is removed. In fact, the above results were in sharp contrast with the relationship between S and the PBuLG content of the 'as polymerized' PBuLG–PBuA composites, which are illustrated with the filled circles in *Figure* 6. In the latter case,

Table 2 Extraction of PBuLG–PBuA composites

		Chloroform		DCA		DCA–HCl mixture	
No.	EGDM content (wt %)	Weight loss (wt %)	PBuLG content (wt %)	Weight loss (wt %)	PBuLG content (wt %)	Weight loss (wt %)	PBuLG content (wt %)
1	0.5	15.5	–	20.1	–	44.1	3.2
2	1.0	12.4	–	20.4	–	37.7	0
3	2.0	13.9	21.6	20.7	14.8	38.4	1.2
4	5.0	16.8	23.7	26.2	13.6	35.5	2.4
5	10.0	16.0	22.3	26.5	12.7	34.0	2.8

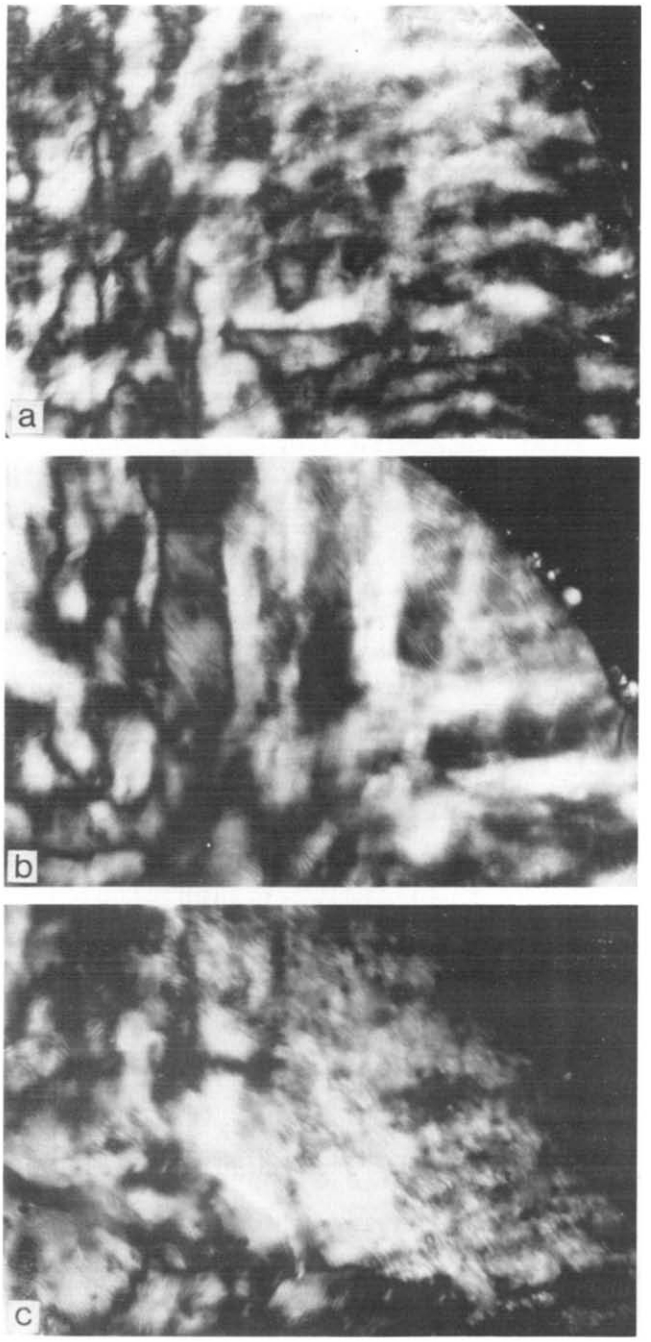

Figure 5 Polarizing micrographs of the composites extracted with DCA: (a) EGDM content 0.5%; (b) EGDM content 2.0%; (c) EGDM content 10%. Scale as in *Figure 2*

the trend agrees with our usual expectation; a higher mesogen (PBuLG) content in BuA monomer resulted in a cholesteric solution with a smaller pitch before polymerization, and that structure of the solution was fixed and carried over to the 'as polymerized' sample. Hence, *Figure* 6 collectively demonstrates that the detailed cholesteric texture in the PBuLG–PBuA composites is not determined by the current mesogen content, but is predetermined by the PBuLG content when the networks are constructed.

Properties of PBuA networks

All the thin sections cut out of the DCA–HCl treated samples were completely dark under crossed polarizers irrespective of their crosslink densities. The cholesteric organizations emerged under crossed polarizers, however, when the sample crosslinked with 10% EGDM was swollen in solvents. Whereas the swollen section with 5% EGDM still showed faint optical anisotropy, the swollen sections with EGDM contents less than 5% exhibited no optical anisotropy. *Figure* 7 shows the polarizing microg-

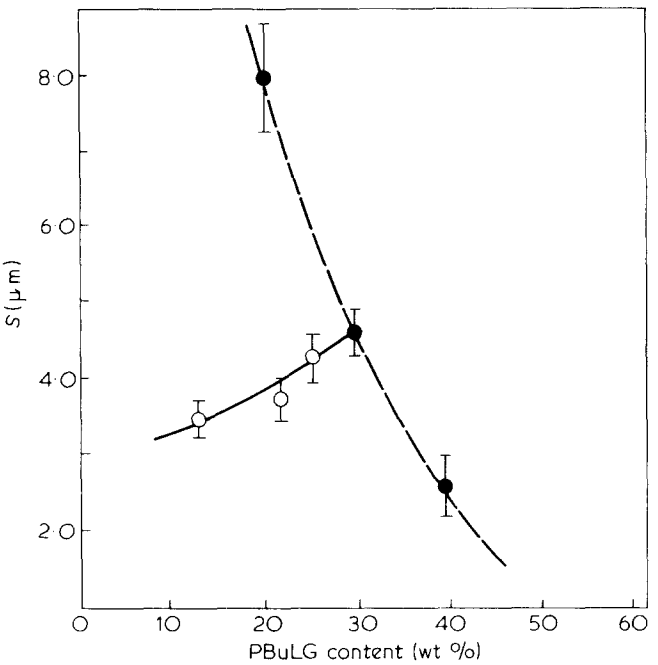

Figure 6 One-half of a cholesteric pitch, *S*, plotted against PBuLG content; ●, 'as polymerized' composites; ○, composites derived from the 'as polymerized' composite with 30% PBuLG

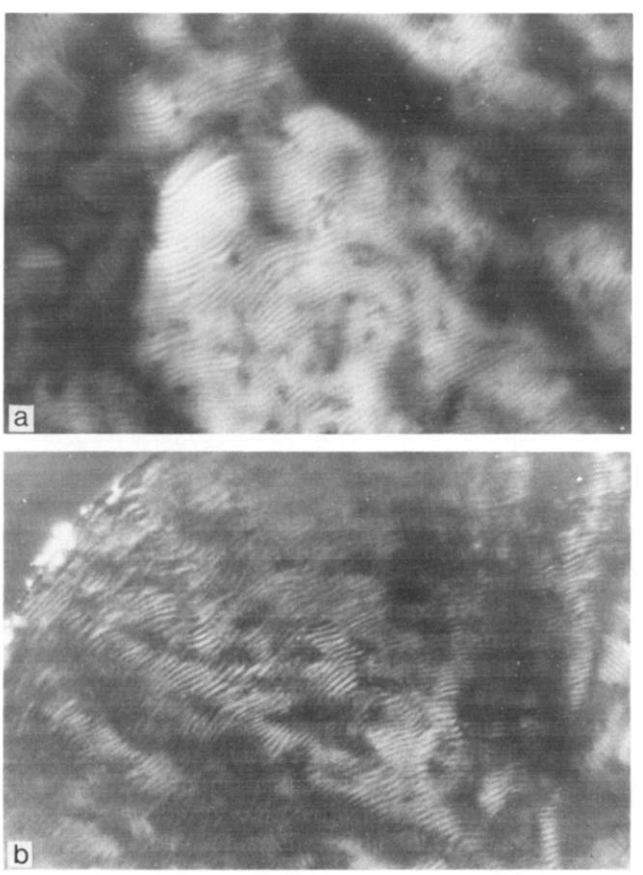

Figure 7 Polarizing micrographs of the DCA–HCl treated sample (10% EGDM) swollen in (a) chloroform and (b) DMF. Scale as in *Figure 2*

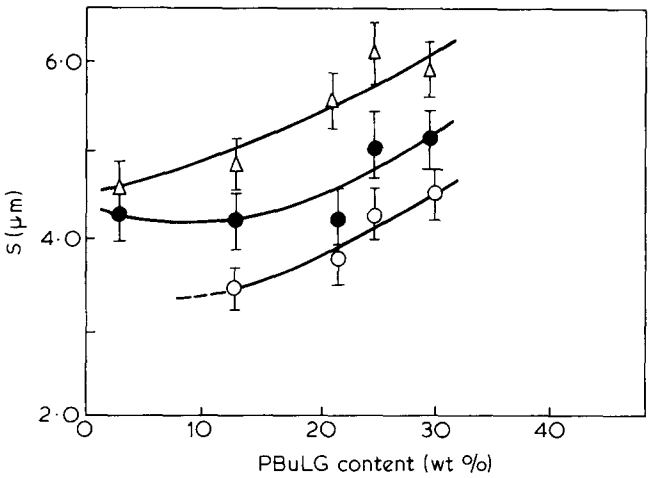

Figure 8 One-half of a cholesteric pitch, *S*, plotted against PBuLG content of the composites derived from the 'as polymerized' composite with 30% PBuLG: ○, unswollen; △, swollen in chloroform; ●, swollen in DMF

raphs of the DCA–HCl treated sample with 10% EGDM swollen in chloroform and DMF.

In *Figure* 8, *S* values of the extracted composites (10% EGDM) in both unswollen and swollen states were plotted against PBuLG contents. The *S* values for the swollen, DCA–HCl treated sample (2.8% PBuLG) came close to the extrapolation of the *S* vs. PBuLG content curves for partly extracted composites. Consequently, the cholesteric textures observed in the DCA–HCl treated samples are surely attributable to the same origin as that of the unextracted PBuLG–PBuA composites.

The cholesteric organization became observable even in the unswollen DCA–HCl treated sample (10% EGDM), provided that a large deformation was added to it. *Figure* 9 shows the polarizing micrograph of a section deformed between two pieces of glass slide.

These observations lead us to the conclusion that the cholesteric organizations can be induced in the PBuA networks by the aid of the cholesteric arrangement of PBuLG, and that the organization can survive even after the mesogen (PBuLG) is totally eliminated, once a dense crosslinkage is formed. Two fundamental questions may arise. First, what kind of mechanism can one assume that brings the cholesteric organizations into the PBuA networks, which include no cholesteric mesogens? Second, what is the origin of optical anisotropy in the cholesteric texture in the swollen PBuA networks?

The former question will be solved if one consults the theoretical consideration of de Gennes[5]. He discussed the topological aspect of polymer networks and predicted that the polymer network which is constructed in a cholesteric liquid crystalline state should possess anisotropy with cholesteric order and should never lose it even after mesogens are completely eliminated from the system, whereas the anisotropic networks which are constructed in either nematic or smectic states should relax when freed from mesogens. The polymerization of BuA in the PBuLG–BuA cholesteric liquid crystalline system exactly substantiates this idea of reticulation in cholesteric liquid crystalline states.

The origin of the optical anisotropy in the cholesteric textures of the PBuA networks should be ascribed to either the oriented PBuA chains or oriented solvent molecules among the PBuA chains. The fact that the cholesteric textures were observable both in the unswollen PBuA networks under deformation and in the PBuA networks swollen in non-polar solvents such as benzene and carbon tetrachloride supports the former interpretation.

As was mentioned before, high crosslink densities are one of the principal factors for the appearance of the cholesteric textures in the PBuA networks. To elucidate other principal factors, the effect of the structure of crosslinking points and the pendant groups of the vinyl monomer units was examined. *Table* 3 lists the network polymers that exhibited the cholesteric textures without mesogen. Neither the introduction of long (OcA) or short (MeA) side chains nor the use of TGDM as a crosslinking agent, which produced looser crosslink points, gave any substantial difference in the optical anisotropy of the polymer networks. Consequently, the most essential cause of the cholesteric textures in the polymer networks is deduced to be the effective extension of the skeletal chains which constitute the topologically unique polymer networks.

CONCLUSIONS

A generalized scheme for the preparation of network polymers in cholesteric liquid crystalline states is shown in *Figure* 10. First, a polypeptide as mesogen, a vinyl monomer as solvent and a crosslinking agent were mixed to form homogeneous lyotropic cholesteric liquid crystals. Second, the vinyl monomer was caused to polymerize in the presence of a crosslinking agent without destruction of cholesteric organization. The resulting polypeptide–vinyl polymer composite swelled in organic solvents. The swollen composite also exhibited cholesteric organization. Finally, the polypeptide component was elim-

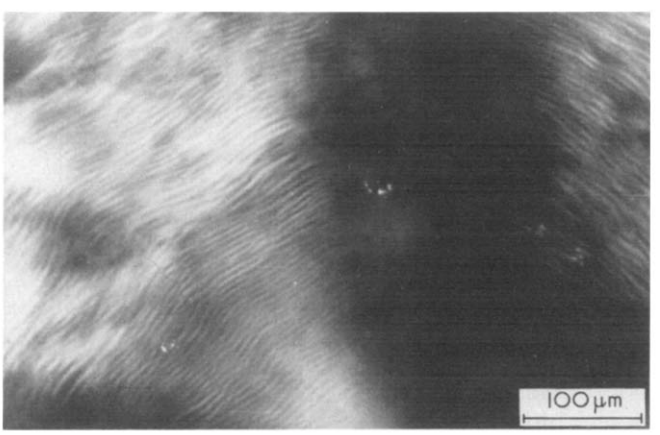

Figure 9 Polarizing micrograph of the DCA–HCl treated sample (10% EDGM) under deformation

Table 3 Some examples of network polymers exhibiting cholesteric organizations without mesogen

Monomer	Crosslinking agent	Content of crosslinking agent
BuA	EGDM	5%, 10%, 20%
BuA	TGDM	10%, 16%
MeA	EGDM	10%
OcA	EGDM	10%

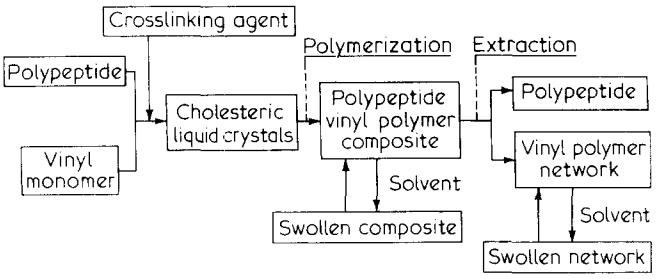

Figure 10 A schmatic diagram for the preparation of polypeptide–vinyl polymer composites and vinyl polymer networks

inated from the composite by hydrolytic extraction with a DCA–HCl mixture. The extracted vinyl polymer networks, which no longer contained polypeptide, did not exhibit cholesteric organization. However, the cholestric organization was restored when the networks were swollen in organic solvents.

Crosslinkage in the vinyl polymers played a key role in preserving cholesteric organization in the polypeptide–vinyl polymer composites. Further, the presence of dense crosslinkage was essential for the manifestation of cholesteric organization in the swollen vinyl polymer networks without polypeptide as mesogen. Finally, the occurrence of transfer of topologically specific cholesteric geometry from the original cholesteric liquid crystals to the vinyl polymer networks should be emphasized.

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