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TOPOLOGICAL POLYMER NETWORKS RETAINING CHOLESTERIC LIQUID CRYSTALLINE ORDER WITHOUT MESOGEN

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Abstract: Crosslinked poly(butyl acrylate) which possesses cholesteric liquid crystalline order has been prepared. First, butyl acrylate was caused to polymerize in a poly(γ-butyl L-glutamate)—butyl acrylate liquid crystalline state. Then, the poly(γ-butyl L-glutamate) component was eliminated from the system by hydrolytic extraction. The network polymer thus obtained exhibited cholesteric liquid crystalline organization when it was swollen in solvents.

In 1969, de Gennes pointed out a possibility of preparation of a special type of network polymers, which were crosslinked in cholesteric mesophases (1). According to his consideration, the polymeric network that is constructed in a cholesteric liquid crystalline [Ch LC] state should possess anisotropy with Ch order and should never loose it even after mesogens are completely removed from the system, whereas the anisotropic networks that are constructed in either nematic or smectic states should relax when freed from mesogens.
No report seems to have been presented that substantiates his prediction experimentally, although some crosslinked polymer systems that were prepared in Ch LC states have been reported. Samulski and Tobolsky (2) and recently Mori et al. (3) have reported the crosslinking of polypeptides in Ch LC states. Strzelecki and Liebert have prepared some polymeric solids with Ch order by causing mesogenic vinyl monomer and bifunctional mesogenic monomer to copolymerize in bulk (4).
In those cases, however, the mesogenic elements were incorporated in the polymer networks with covalent bonds, and therefore, the mesogens could not be removed from the network polymers afterwards.

We have reported on the polymerization of vinyl monomers in polypeptide-vinyl monomer Ch LC systems. In this particular case, polymer networks can be formed in Ch LC states without the formation of crosslinkage between polypeptides as mesogen and network polymers (5,6). A previous paper dealt with the nature of poly(γ-butyl L-glutamate)—poly(butyl acrylate) [PBuLG-PBuA] composites which were prepared in Ch LC states. In that study, a preliminary experiment to eliminate the PBuLG component from the PBuLG-PBuA composites for the purpose of getting the crosslinked PBuA was unsuccessful, even though about a half of the PBuLG component was managed to be extracted with chloroform (6). In this letter, we will deal with the same system and wish to show that the PBuA network prepared in a Ch LC state really retains Ch LC order, even after the complete removal of the mesogenic component, PBuLG.

In butyl acrylate [BuA] which contained 10 wt% ethylene glycol dimethacrylate [EGDM] as a crosslinking agent, 30 wt% of PBuLG was dissolved, and the solution was caused to polymerize at 60°C in glass capillaries; the detail of experimental procedure was described in a previous paper (6). In order to eliminate the PBuLG component, the obtained PBuLG-PBuA composite was immersed in a dichloroacetic acid [DCA]-concentrated HCl (4:1) mixture and allowed to stand for a week at room temperature. The rod-shaped composite swelled in the DCA-HCl mixture about three fold, and the PBuLG component was hydrolyzed with HCl. The treated composite sample was washed with chloroform several times and dried. The weight loss after the treatment above was 34.0 %. The PBuLG content in the treated sample was found to be 2.8 % from its nitrogen content. More than 90 % of the PBuLG in the original sample turned out to be eliminated from the system. Consequently, the treated sample can be regarded as pure PBuA crosslinked with 10 % EGDM, in which negligible amount of the mesogen, PBuLG, is incorporated.

Thin sections were cut out from both the original and the treated sample rods perpendicularly to their long axes and were examined through a Nikon polarizing microscope under crossed polarizers. The original sample exhibited a well-defined Ch organization, but the treated sample was found to have no optical anisotropy. To our surprise, however, the treated sample, which was assumed to have no mesogen at all, revealed Ch order when it was swollen in dimethylformamide [DMF]. Fig. 1a shows the polarizing photomicrograph of the treated sample swollen in DMF. Ch pitches, which are aligned circularly, are clearly distinguished. For comparison, the

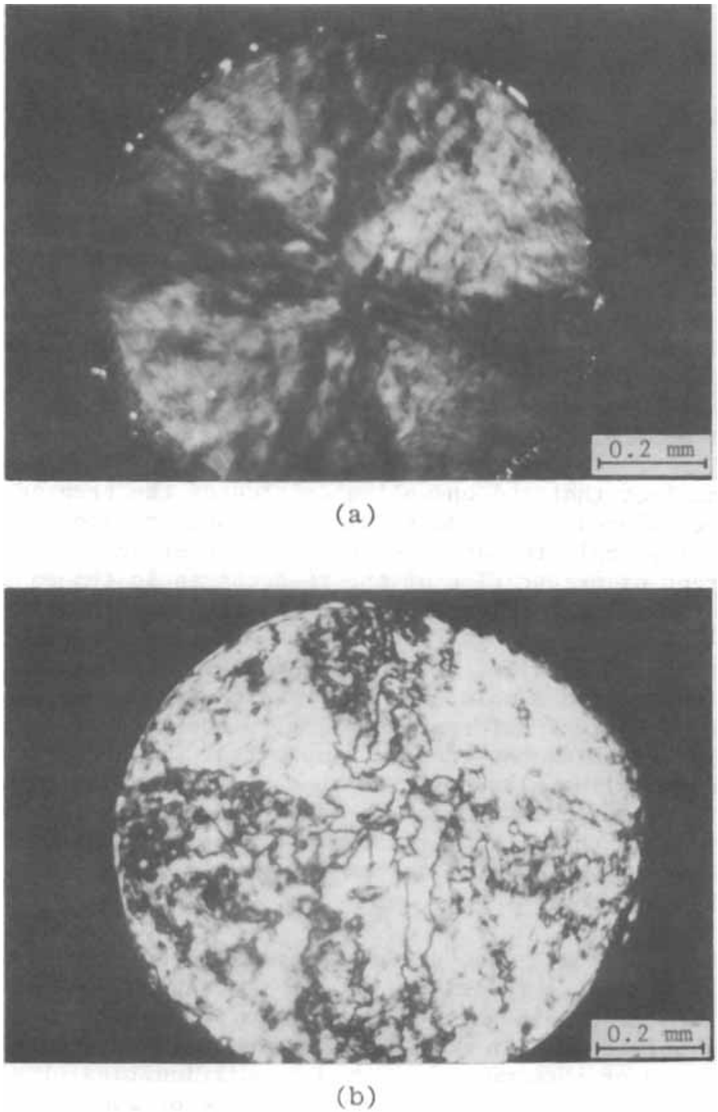

Figure 1 Polarizing photomicrographs of the treated (a) and the original (b) samples swollen in DMF. Under crossed polarizers.

polarizing photomicrograph of the original sample swollen in DMF is given in Fig. 1b.

The extent of optical anisotropy is considerably different between the original and the treated samples. Naturally, the origin of optical anisotropy in the original sample is the α-helix of PBuLG. In contrast, the PBuLG content in the treated sample seems to be too small to manifest clear optical anisotropy. Thus, the origin must be attributed to the orientation of either PBuA chains or DMF molecules. Judging from the fact that the treated sample revealed the optical anisotropy when it was swollen in non-polar solvents, such as carbon tetrachloride and benzene, the existence of oriented PBuA chains were recognized to be essential for the appearance of Ch order in the treated sample, even though the minor contribution from the orientation of solvent molecules might be present.

The fact that the unswollen section of the treated sample looked completely dark under crossed polarizers does not necessarily imply the absence of the Ch order in it. The extent of orientation of the PBuA chains in the sample can be too small to reveal optical anisotropy through a polarizing optical microscope, despite the presence of latent Ch order in it. Actually, the Ch pitches were observable in the unswollen treated sample when the PBuA chains were oriented through mechanical deformation. Fig. 3 shows the polarizing photomicrograph of the treated sample that was deformed between two slide glasses. The appearance and disappearance of the structure was completely reversible. This observation clearly demonstrates that the treated sample itself possesses the Ch order even when it is not observable through an optical microscope.

In this study, the "de Gennes' network polymer" was prepared through a relatively simple procedure. One may, in principle, propose a variety of ways to produce "de Gennes' network polymers". In most cases, however, experimental realization of them must face various difficulties. The key to our success can be attributed to the usage of lyotropic cholesteric liquid crystals.

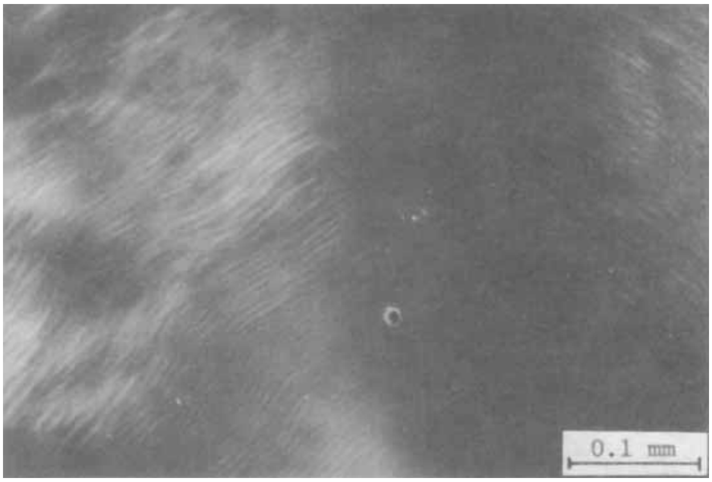

Figure 2 Polarizing photomicrograph of the treated sample under deformation. Under crossed polarizers.

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