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Mechanical and Optical Anisotropies of Nematic and Cholesteric Hydrogels of Poly(L-glutamic acid)[1)]

Yoshiki MATSUOKA, Ryoichi KISHI, and Masahiko SISIDO*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

Cross-linked gels of poly(L-glutamic acid) (PGA) possessing cholesteric or nematic liquid-crystalline (LC) order were prepared from the corresponding LC gels of poly(γ-benzyl L-glutamate). Optical anisotropy measured by transmitted light intensity through cholesteric LC hydrogels between crossed polarizers showed reversible changes with the alternation of pH values. Mechanical anisotropy was also found in the nematic LC hydrogels.

Polymer gels have been attracting interest of many workers as materials that are responsible to external stimulus. Swelling and shrinking of gels have been controlled reversibly by electric field[2)] and photoirradiation.[3)] In usual cases, these gels posses no supramolecular structure and respond isotropically to stimulus. If gels with anisotropic structures were prepared, anisotropic responses, such as a swelling toward one direction and a switch of linear or circular polarization of transmitted light, may be expected. Polymer gels with liquid-crystalline order [liquid-crystalline (LC) gels] have been reported recently from our[4-8)] and other laboratories.[9-12)] In our case, lyotropic LC solution of poly(γ-benzyl L-glutamate) (PBLG) was cross-linked with appropriate diamino compounds to form a gel possessing original cholesteric or nematic LC order.[4)] The LC gels showed optical anisotropy as exemplified by strong induced circular dichroism from dye-doped cholesteric LC gels.[6,7)] Recently, we found that the LC gels of PBLG can be hydrolyzed to give <u>hydro</u>gels of poly(glutamic acid) (PGA) that hold the original cholesteric or nematic LC order.[8)] In this letter we will report reversible swelling and shrinking of the LC hydrogels and optical and mechanical anisotropies that are controlled reversibly by the pH values of external solution.

Preparation of PBLG gels with cholesteric LC order has been described.[4)] PBLG gels of nematic LC order were prepared by setting a mixture of PBLG (20 wt%) and cross-linker (triethylenetetramine) (10 mol% with respect to glutamate units) in dioxane under a magnetic field (21 kG) for 7 days at 25 ^{o}C and by heating the mixture

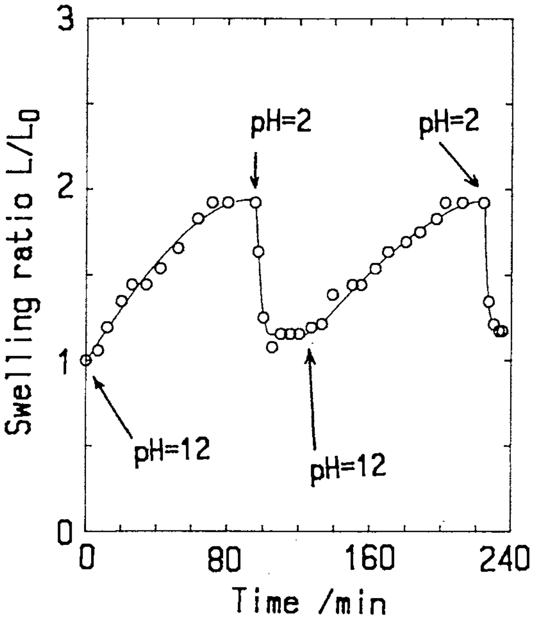

Fig.1. Dimensional changes of cholesteric LC hydrogels of PGA by pH.

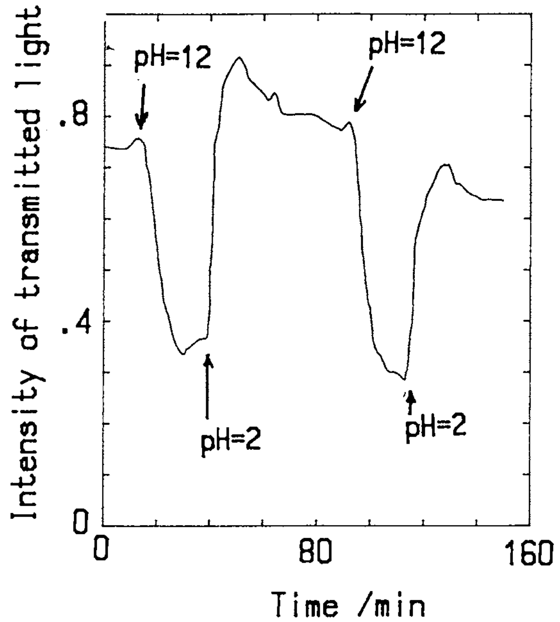

Fig.2. Intensity of transmitted light during cholesteric-isotropic phase transitions of cholesteric LC hydrogel of PGA.

at 70 °C for 7 days.[5] The gels of cholesteric or nematic order were immersed in acetic acid containing 25 wt% of HBr at room temperature for 4 h to remove benzyl esters and then rinsed with distilled water. The resulting hydrogels of poly(glutamic acid) (PGA) kept the original cholesteric or nematic order as observed by optical microscopy. Details of the preparation of LC hydrogels will be described elsewhere.[8] Swelling experiments were carried out in aqueous solution on samples of about 2 mm x 2 mm size. The pH values were regulated by adding appropriate amount of hydrochloric acid or NaOH to external solution. The size of gels was measured under Olympus BH-2 microscope.

Swelling behavior of cholesteric LC hydrogels of PGA was measured under alternating pH values. The change of the distance between two points marked on the gel was followed after adding acid or alkaline solution as shown in Fig. 1. The length expanded twice the original length after adding NaOH solution (pH=12) in about 70 min. Addition of acid to the swollen gel induced a rapid shrinking to the original shape within a few minutes. The slower response in the expansion process may be explained in terms of slower diffusion of alkaline solution and slower rate of unfolding of PGA chains inside the shrinked gel.

The shape change is associated with a phase change that could be observed optically when the LC hydrogel was placed between crossed polarizers. When the gel is in a cholesteric phase (lower pH), light can pass through the polarizers because of the optical anisotropy of the gel, and when it is in an isotropic phase (higher pH), the light cannot pass through. The intensity of transmitted light is plotted against

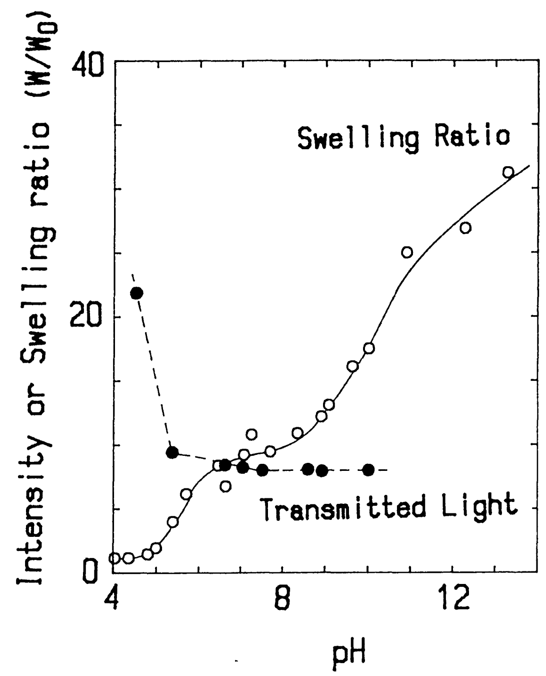

Fig.3. pH Dependence of the swelling ratio (W/W_0) and the intensity of transmitted light.

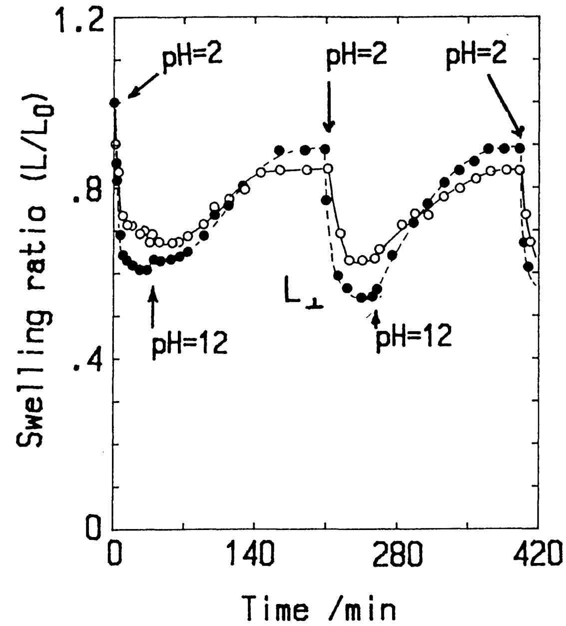

Fig.4. Swelling ratio of nematic LC hydrogel. $L_{/\!/}$ and $L_\perp$ are lengths parallel and perpendicular to magnetic field.

the pH of external solution in Fig. 2. A reversible change of the transmitted light intensity is observed. A marked difference between Figs. 1 and 2 is that the optical anisotropy disappears much earlier than the swelling becomes completed in alkaline solution, indicating that the hydrogel looses the LC structure earlier than it becomes swollen.

The swelling ratio calculated from a wet weight of a gel divided by a dry weight(W/W_0) is shown in Fig. 3 as a function of pH values of external solution (open circles). It is evident that the swelling consists of two stages. The first stage of swelling occurs at pH = 5 and the second stage starts at pH = 9. From a detailed consideration on the dissociation behavior of PGA inside the gel, the first stage has been attributed to a partial expansion of the gel due to the repulsions of partially ionized helical PGA chains and the second stage has been attributed to a full expansion of ionized PGA chains accompanied with the helix to coil conformational changes.[8] Fig. 3 also shows the transmitted light intensity at different pH values. The optical anisotropy disappeared already at pH = 5, indicating that the cholesteric phase virtually diminished at the onset of the first stage of swelling. The early disappearance of the optical anisotropy can explain the fast responses in Fig. 2.

LC hydrogels of nematic order were also prepared from the nematic LC gels of PBLG cross-linked under magnetic field. PBLG solution was cross-linked in an nmr tube of 5 mm diameter. Therefore, a rod-like gel was obtained initially. The rod was sliced to obtain symmetrical disks. After hydrolysis of benzyl esters by acid treatment, the disk-like gel was immersed in a buffer (pH = 3.4, ionic strength = 0.2). The nematic gel shrinked to an oval with a short axis perpendicular to the magnetic field. The long axis/short axis ratio, that is a ratio of dimension parallel to the magnetic field to that perpendicular to magnetic field, was 1.60. Since PBLG helices are known to orient parallel to the magnetic field,$^{13)}$ the above result indicates that PGA helices preferably shrink perpendicular to the magnetic field.

Anisotropic swelling and shrinking of the nematic LC hydrogel was studied by changing pH values alternately (Fig. 4). Swelling and shrinking were more significant to the direction perpendicular to the magnetic field or to the helix axis of PGA. If we define a swelling ratio as (length after full swelling/length after complete shrinking), the ratio is 1.64 for the perpendicular direction and 1.35 for the parallel direction. The mechanical anisotropy was not large as has been observed for the swelling and shrinking of nematic LC gels of PBLG in organic solvents.$^{5)}$ Possible reasons for the small mechanical anisotropy are that the cross-linking density was fairly high in the present samples (10 mol % with respect to the glutamate units) and that the initial concentration of PBLG in the cross-linking reaction (20 mol%) was too high. Although these conditions were selected to obtain tight gels that are tractable in mechaincal and optical measurements, higher mechanical anisotropy wil be attained by using hydrogels of lesser cross-linking densities.

To conclude, reversible changes in optical and mechanical anisotropy were first attained in cholesteric and nematic LC hydrogels of PGA by changing pH values alternately. Hydrogels of supramolecular structure will be a promising approach toward functional devices for micromachines and for other areas.

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