Preparation of Chiral Nematic Gels by Radiation Cross-Linking

Solid polymeric films with chiral nematic (cholesteric) order may be prepared from cellulose and its derivatives by solvent evaporation from lyotropic mesophases[1-4] or by slow precipitation from solution.[2] Cross-linked chiral nematic films have been prepared by photo-cross-linking thermotropic mesophases of cellulose derivatives containing unsaturated side chains[5] and by chiral cross-linking of lyotropic mesophases.[6,7] Cross-linking reactions have also been used to prepare deformable rubbers[8] and gels[9] with chiral nematic structure. (Hydroxypropyl)cellulose is a readily available polymer that forms chiral nematic phases in water and in many organic solvents,[10] so it seems a suitable starting point for gel formation. Recently, Suto and Tashiro[7] succeeded in cross-linking preformed liquid-crystalline solutions of (hydroxypropyl)cellulose in water and alcohols by adding formaldehyde, and Song et al.[11] photoinitiated the cross-linking of HPC mesophases in *N,N*-dimethylacetamide. In this paper, we describe the cross-linking of HPC liquid-crystalline phases by exposure to γ radiation and show that the chiral nematic structure is at least partially retained after cross-linking, swelling, and drying, thus providing a potential route to stable water-swellable chiral nematic gels.

When polymers are irradiated, cross-linking or scission may occur, depending on the chemical nature of the material. Both processes take place simultaneously; the predominant process depends on the substrate and radiation conditions. The formation of a swollen gel in solvents in which the polymer normally dissolves is an indication that cross-linking has occurred.

Little is known about the γ-irradiation of liquid crystals. Studies of the selective reflection properties of some liquid-crystalline cholesterol derivatives[12] and of biological systems that are analogues of cholesteric liquid crystals[13] indicate that γ-rays cause a decrease in the phase-transition temperatures of those systems, suggesting that scission may occur. Irradiation of cellulosic material at relatively high doses is known to create mainly scission products.[14-16] Surprisingly, we find that both HPC films exhibiting chiral nematic order and HPC mesophases are cross-linked by γ-rays.

Chiral nematic mesophases were prepared by dissolving commercially available HPC (Aldrich Chemical Co., nominal molecular weight M_w = 100 000) in distilled water and in methanol. All solutions were allowed to stand for a minimum of 2 months at room temperature. The concentrations ranged between 50% and 52% HPC (w/w) for methanol solutions and 55% to 66% HPC (w/w) for water solutions. HPC films were prepared from the aqueous mesophase.[1] A small quantity of the anisotropic solution was placed between two polyethylene sheets (permeable to water vapor) and allowed to dry in room conditions for a few weeks. The film thickness, controlled with Teflon spacers placed between the plastic sheets, was 75–80 μm.

The samples were irradiated in a SLOWPOKE nuclear reactor.[17] The core of this small pool-type reactor is made of highly enriched ^{235}U and is surrounded by a beryllium reflector. Samples, sealed in polyethylene vials, were introduced to the irradiation sites in the beryllium reflector by means of a pneumatic system. The solid HPC films were irradiated at maximum power (20 kW, neutron flux = 10^{12} n·cm^{-2}·s^{-1}) where the γ dose rate is 1700 rad·s^{-1} and the temperature reaches 55 °C.[17] The liquid-crystalline solutions were irradiated at low power (2 kW, γ dose rate = 170 rad·s^{-1}) to keep the temperature at about 25 °C in order to avoid thermal distortion of the liquid-crystalline texture and incipient phase separation.[18]

The cast and irradiated HPC films were initially transparent and colorless. When immersed in water or methanol, they did not dissolve but became swollen and slightly iridescent. After drying they displayed a faint blue iridescence. The apparent circular dichroic (CD) spectrum of the film, measured with a Jasco J-500C spectropolarimeter, showed a negative reflection peak, indicating that some chiral nematic order has been trapped in the gel structure. However, the wavelength of the peak varied from one sample to another and was often outside the visible range.

During irradiation, the iridescence of the HPC mesophase was maintained although the original viscous fluids were progressively transformed into rubbery solids. When immersed in water or methanol, the iridescence of the cross-linked mesophase became progressively fainter as the gel became swollen. After immersion for several days, the samples did not dissolve but remained as distended gels. Upon drying, the iridescent colors reappeared, and for all our samples, the final colors were in the blue range. Circular dichroism measurements showed a negative peak, as for cross-linked chiral nematic films. However, the CD peak for the cross-linked mesophases always appeared at wavelengths above 300 nm. The maximum intensity was of the same order of magnitude as for the original cross-linked mesophase before swelling, with typical values for the ellipticity of about 1000 mdeg. Thus, the cross-linked material appears to maintain, at least partially, the right-handed helicoidal structure that is characteristic of HPC chiral nematic solutions.

The cross-linked chiral nematic films were observed in a Leitz optical microscope under polarized light. The films were first swollen in water for 20 min, placed on a clean glass slide, and allowed to dry in room conditions under the optical microscope. Figure 1a shows a cross-linked HPC film irradiated at a total dose of 34.5 Mrad before swelling in water. It exhibits the typical birefringent texture of a polygonal focal conic organization in the anisotropic film. Cross-linking did not change the texture. After the film was swollen in water, the birefringence could still be detected, but with difficulty (Figure 1b). Figure 1c shows the same area of film after complete drying. The general appearance of the birefringent texture is similar to that in Figure 1a, but the size of domains is reduced and their shape is more elongated, possibly due to strains caused by drying of the film on a solid support (a glass slide). Similar micrographs were obtained by Suto et al. for chemically cross-linked HPC films.[7]

The chiral nematic order of the cross-linked liquid-crystalline phase was also examined by transmission electron microscopy. Small pieces of an aqueous HPC mesophase that had been irradiated with a 5.7 Mrad dose were embedded in a fresh preparation of Araldite after exchanges in the same resin. Sections of different thicknesses, ranging from 70 to 300 nm, were cut from the embedded samples with a diamond knife mounted on a Reichert Ultracut E microtome. The resulting sections were collected on carbon-coated electron microscope grids and examined with a Philips EM 400T instrument operated at 120 keV. An electron micrograph of a section of the cross-linked HPC/water mesophase is shown in Figure 2. It shows a striking whorled pattern, where the dark and light lines correspond to sample areas with high and low electron densities, respectively. The line spacings range from 590 to 1000 nm and are thought to be related

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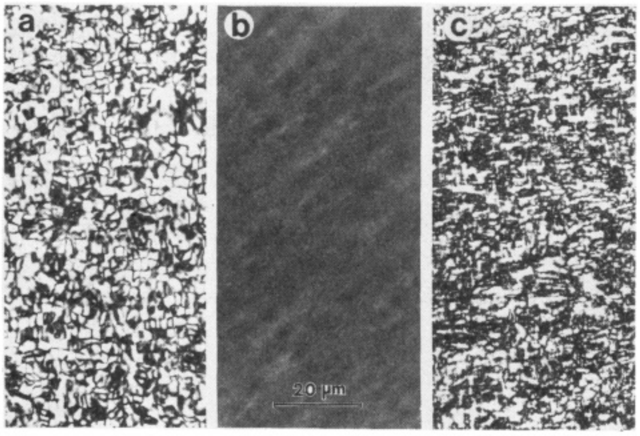

Figure 1. Cross-polarized optical micrographs of a γ-ray cross-linked HPC film cast from and HPC/water mesophase: (a) directly after irradiation, (b) after swelling in water, and (c) after complete drying on a glass slide.

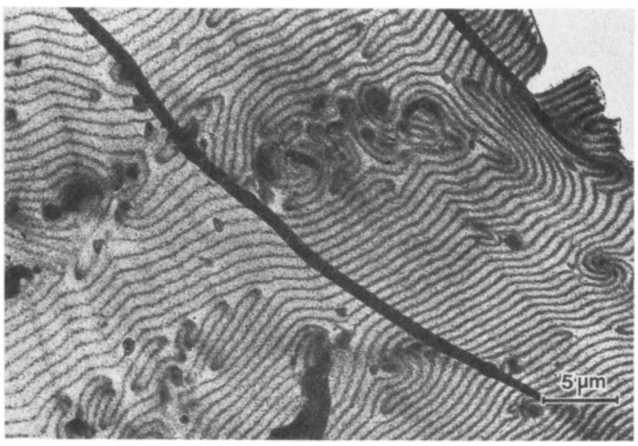

Figure 2. Transmission electron micrograph of a γ-ray cross-linked HPC/water mesophase. The section is 300-nm thick.

to the periodicity of the helicoidal supramolecular arrangement of the chiral nematic structure, where the axis of the helicoid is in the plane of the electron micrograph and orthogonal to the direction of the lines. (The very dark areas are introduced during sample preparation.) Similar electron micrographs, but with much smaller periodicities, were recently obtained with films of cellulose acetate and regenerated cellulose.[3] The reasons for density fluctuations in sections of chiral nematic films and gels will be discussed in a future paper.

The present results show clearly that HPC chiral nematic mesophases and films can be cross-linked by high-energy radiation. However, the experiments were conducted in a nuclear reactor in which the γ-radiation is a side product of neutron generation. To make sure that neutrons are not responsible for the cross-linking of the HPC samples, another series of experiments were conducted in a ^{60}Co reactor, with γ-ray doses of the same order of magnitude as those produced in the SLOWPOKE reactor. Again, cross-linked samples were obtained. This finding is contrary to what is known for γ-radiation of cellulosic material, where scission reactions predominate.[14-16] The reason is not clear, but it might be that cross-linking the extended molecular chains in the ordered cholesteric arrangement leads to efficient intermolecular bonds, whereas coiled conformations lead to some intramolecular cross-linking. Preliminary estimates of gel fraction, measured by Soxhlet extraction with water, support this explanation. When HPC powder is γ-irradiated (16.7 Mrad dose), no cross-linking can be detected; the irradiated sample remains soluble in water. For the irradiated chiral nematic films, gel fractions ranging from 25% to 57% were obtained with γ-ray doses between 23 and 57.5 Mrad. However, a gel fraction of about 90% was obtained for cholesteric gels of HPC/methanol that had received a dose of only 2.9 Mrad. The efficiency of the cross-linking is evidently very different for powder, film, and mesophase samples.

The preliminary results show some promise, but, as pointed out recently by Kishi and co-workers,[19] chiral nematic gels with *multidomain texture* will swell virtually isotropically. By cross-linking a poly(γ-benzyl L-glutamate) mesophase under a magnetic field, they succeeded in generating a nematic gel with anisotropic swelling properties. How would a well-ordered *planar-textured* chiral nematic respond to swelling? Consider a long narrow cylinder of cross-linked chiral nematic, cut with the cylindrical axis along the cholesteric axis. By analogy with a nematic gel,[19] the swelling will be predominantly in the long direction, but since the equilibrium twist angle drops sharply with concentration, the swelling may also generate a torque about the long axis, in a direction opposing the decrease in chiral nematic pitch. In other words, swelling may produce an extension along the cholesteric axis and also rotation about the cholesteric axis. This has not yet been observed for a chiral nematic gel, but an analogous chiral mechanical deformation has been observed when wood pulp fibers are immersed in water. The crystalline cellulose microfibrils in the major part of the wood cell wall are wound in a right-handed helix,[20] so that straining or swelling causes the fiber to twist about the fiber axis[21] and can result in readily observable chiral deformations in paper made from wood pulp.[22]

On a less speculative vein, this work shows that irradiation cross-linking may be used to prepare ordered aqueous samples for direct observation by transmission electron microscopy. The structure in the thin cross-linked sections of HPC was maintained despite the fact that the samples became swollen by contact with water during microtome sectioning; un-cross-linked HPC microtome sections dissolve immediately on contact with water. Without cross-linking, more complicated indirect methods such as freeze-fracturing and replication are required.[23]

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