

Responsive Chiral Hydrogen-Bonded Polymer Composites

P. V. Shibaev,^{*†,‡,§} K. Schaumburg,[‡] and V. Plaksin[§]

Chiral Photonics Inc., 115 Industrial East, Clifton, New Jersey, 07012, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark, and Department of Physics, Moscow State University, 119899 Moscow, Russia

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Hydrogen-bonded thermotropic and lyotropic liquid crystals as well as hydrogen-bonded supramolecular structures are of considerable current scientific and technological interest because they are readily fabricated and may form a variety of structures with a broad range of new properties.^{1–3} Recently, the spontaneous chiral ordering in achiral alkylcyclohexanecarboxylic acids was discovered by Torgova et al.⁴ and the formation of cubic phases in new hydrogen-bonded mesogens was revealed by Nishikawa and Samulski.⁵ The temperature range displayed by mesophases consisting of hydrogen-bonded liquid crystals is broad and may be tuned by changing the geometry of mesogens via simple nonchemical methods.⁶ In a series of papers Kato et al.^{7–9} and Kresse et al.¹⁰ have shown the importance of hydrogen bonding for the stabilization and formation of the mesophase in low molar mass compounds and polymers.

The interest paid to hydrogen-bonded ordered compounds is primarily associated with the promising potential applications of these materials¹¹ especially as temperature- and light-responsive networks, gels, and filters. Among hydrogen-bonded materials, the chiral materials have attracted special attention because of their unique optical properties, in particular, the selective reflection of light. The unique property of selectively reflected circularly polarized light combined with the possibility to shift the selective reflection band in response to external fields presents a huge potential for new optical applications,¹² which require a stabilization

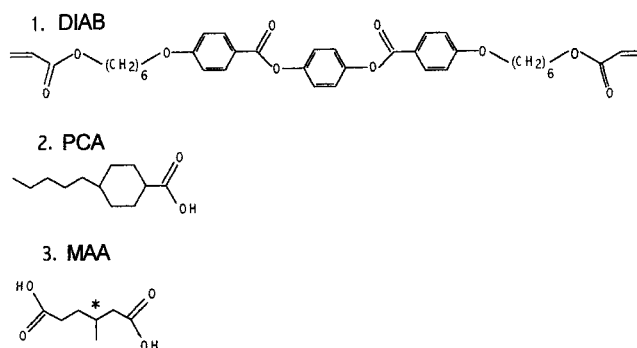


Figure 1. Chemical structure of low-molar mass compounds.

of cholesteric properties in a solid state.¹³ It may be achieved through the cross-linking of monomers existing in a prescribed cholesteric state or by the synthesis of side- or main-chain polymers which may form a glassy state with a frozen cholesteric structure. The first approach was used for cross-linking of the acrylate or methacrylate monomers and is described in a number of publications.^{14–16} The synthesis of side-chain and main-chain polymers is also a well-developed technique described in numerous publications. See, for example, ref 17 and references therein.

In this paper we report, for the first time, the hydrogen-bonded chiral polymer composites with a frozen cholesteric structure able to respond to changes of pH.

All nonreactive compounds were purchased from Aldrich Chemical Co. and used as received. The pentylcyclohexanecarboxylic acid (PCA) had a crystal–nematic transition near 55 °C and a nematic–isotropic transition at 108 °C. The methyladipic acid (MAA) had a melting point at 82 °C.

The synthesis of the difunctional monomer 3, 1,4-bis(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzene (DIAB), was performed as described elsewhere.^{14–16} The synthesis of (6-hexanoxy-4-benzoic acid) acrylate (HBA) was made in accordance with the procedure described in.^{18,19} Chemical structures of the compounds used in this work are presented at Figure 1.

The mixtures of PCA, MAA, DIAB, and HBA were studied at different compositions. Double mixtures of the pentylcyclohexanecarboxylic acid (PCA) and methyladipic acid (MAA) form cholesteric phases when the concentration of MAA do not exceed 30% (Figure 2). It may be explained in terms of the formation of molecular aggregates: PCA forms a liquid-crystalline state because its molecules form hydrogen-bonded mesogenic dimers.

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- * To whom correspondence should be addressed.
 † Chiral Photonics Inc.
 ‡ University of Copenhagen.
 § Moscow State University.
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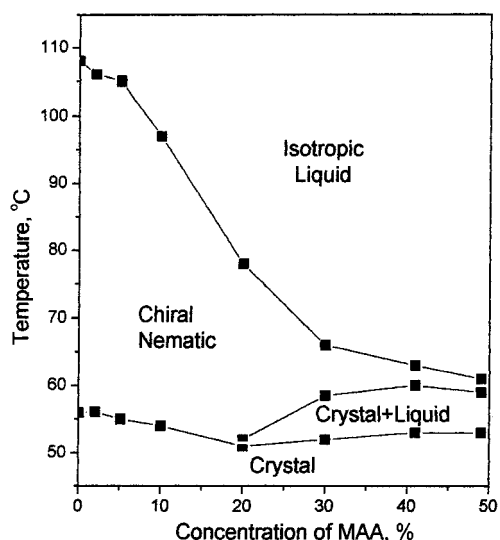


Figure 2. Phase behavior of the MAA-PCA mixture.

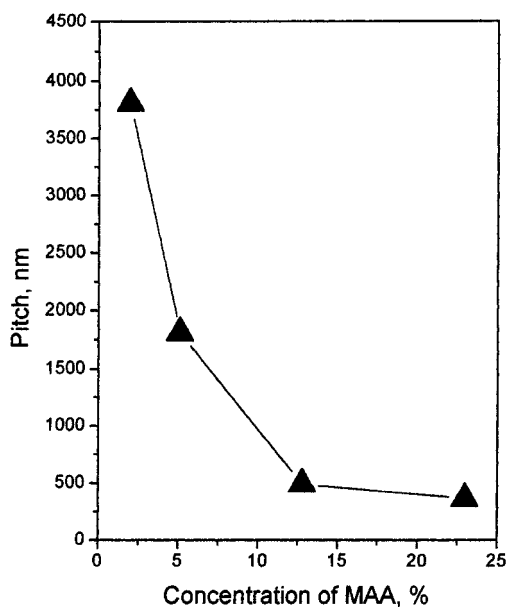


Figure 3. Position of the selective reflection band as a function of concentration of MAA.

Nonmesogenic hydrogen-bonded aggregates containing PCA and MAA are also formed in a mixture. When their concentration rises to a certain level, the mesophase is destroyed. At higher concentrations of MAA the liquid crystalline state does not exist. The selective reflection band of low molar mass mixtures containing PCA and MAA lies in a visible spectral region when the concentration of MAA reaches 12% (Figure 3). At higher concentrations the selective reflection band shifts toward shorter wavelengths and, at concentrations higher than 23%, leaves the visible region. The twisting power of MAA in the visible region was found to be about $12 \mu\text{m}^{-1}$ and was calculated on the basis of the following equation,

$$\beta = \frac{1}{pc}$$

where β is the helical twisting power of the chiral dopant which is inversely proportional to the molar concentration of dopant c and to the cholesteric pitch p .

It was found that the addition of DIAB and HBA to the mixture does not significantly change the twisting power of chiral MAA. Moreover, the mixtures of DIAB/HBA, MAA, and PCA do not exhibit any phase separation for all concentrations of the components at temperatures higher than 60 °C. Thus, the concentration of 12.5% of MAA was used in all mixtures subject to subsequent polymerization to obtain samples with the selective reflection band lying in the visible region of the spectrum. The concentration of HBA was about 10%.

The photopolymerization of the mixtures was initiated by a high-pressure Hg lamp. The polymerization was carried out in thin glass cells filled with the liquid-crystalline composition forming a planar texture at 60 °C. The selective reflection band could be shifted toward shorter wavelengths of visible spectrum by increasing the temperature. Concentrations of the cross-linker (DIAB) varied from 4 to 45%. The polymer materials with different optical and physical properties were obtained depending upon the concentration of the cross-linker.

For the mixtures with the concentration of DIAB about 10–15% the polymerization resulted in the slightly cross-linked cholesteric phase with a practically unchanged selective reflection band observed at 60 °C. Under cooling, the sample did not retain the color and crystallized at room temperature because of the crystallization of MAA and PCA. At concentrations higher than 20–25% DIAB the changes of the selective reflection band were more pronounced: it became broader and slightly shifted toward the longer wavelengths. The cholesteric structure could be preserved at room temperature for several hours without any crystallization of MAA or PCA.

At concentrations of DIAB higher than 35% the selective reflection band became broader but the sample still retained the same color even at room temperature. For these samples the crystallization did not occur for several days at room temperature but even when it did, after a few days, the sample retained the color and the selective reflection band.

The morphology of freshly prepared samples consists of domains with the size of 5–25 μm and with varying orientation of the cholesteric helix that leads to a higher degree of light scattering and broadening of the selective reflection band. This effect is more pronounced in the samples containing a smaller amount of DIAB in which the crystallization of MAA and PCA occurs faster. In all samples studied the crystallization does not destroy the cholesteric structure, partially because of the good miscibility between the network molecules and free PCA and MAA molecules entrapped in the network. An additional reason for retaining the cholesteric structure is the formation of the cholesteric network formed from DIAB. The attempts to remove the free MAA and PCA molecules from the matrix without disrupting the cholesteric properties of the material by exposing it in a number of organic solvents were not successful. Organic solvents easily removed free molecules and immediately destroyed the cholesteric structure of the material.

In contrast to the organic solvents, basic water solutions were able to change gradually the selective reflection properties of the material. Contrary to the

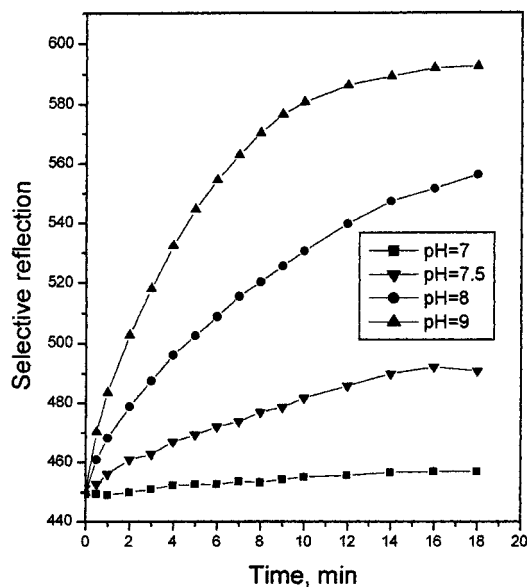


Figure 4. Changes in the selective reflection with time at different pH.

expectations, the neutralization of MAA and PCA did not result in the removal of the cholesteric properties.

The samples prepared on one glass surface were dipped into a water solution of NaOH or HCl at different pH. The thickness of the samples was about 40–50 μm . At pH = 9 the selective reflection band changed its position from 450 to 550 nm, typically after 3–5 min; this was accompanied by color changes. The time required to achieve the shift of selective reflection band of about 100 nm varied a little from sample to sample and depended on sample thickness. The shift of the wavelength of the selective reflection band as a function of time at different solution pH is shown in Figure 4.

No immediate changes were observed in mild acidic solutions. The changes observed in basic solution were not reversible: the cholesteric structure could not be restored after exposing the films to acidic solutions.

The time required to achieve significant color changes is smallest for the highest pH value. The breakage of hydrogen bonding in the films exposed to basic solutions was confirmed by IR spectroscopy. The bands at 2750–3250 cm^{-1} , which are characteristic for hydrogen-bonded carboxylic acids, gradually disappear with time.

The following explanation is proposed for chemically induced changes in color: After polymerization, an oriented cholesteric polymer network is formed. It contains free PCA and MAA molecules able to crystallize and molecules confined in much smaller volumes that inhibit crystallization. PCA and MAA molecules form an oriented cholesteric structure together with polymerized DIAB molecules. The effect of exposing the polymer to basic water solution is two-fold. First, it leads to the neutralization of the acid groups of chiral MAA molecules and, therefore, to the disruption of hydrogen bonding and the separation of molecules from the polymer matrix. Consequently, the chiral molecules cannot serve as effective chiral dopants. Second, PCA and DIAB molecules change the mechanical properties of the whole polymer matrix that results in pitch changes. The volumetric changes accompanying the neutralization of acid groups are also an important factor imposing mechanical stress on the polymer matrix and, therefore, is also a possible cause of pitch increase.

A detailed study of the mechanisms of pitch changes in polymer composites affected by water solution with different pH is the subject of work in progress in our laboratories.

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