Articles

Color Changing Cholesteric Polymer Films Sensitive to Amino Acids

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ABSTRACT: Chiral hydrogen-bonded polymer films that respond to the presence of some amino acids (arginine, lysine, histidine) in water by changing the color and shifting the wavelengths of the selective reflection band (SRB) were synthesized and studied. The kinetics of the film's response depends on the concentration of donor/acceptor groups in the polymer matrix. A higher concentration of hydrogen-bonded groups results in a faster shift of the SRB and color changes. This effect is explained in terms of structural changes and the breakage of hydrogen bonds that occurs between the components of a cholesteric polymer, immersed in various aqueous solutions of amino acids. Optical pumping of cholesteric films doped with laser dyes leads to lasing. The changes in the selective reflection induced by amino acids in water solutions result in a shift of the lasing wavelength.

Introduction

The design and development of novel responsive polymers that are able to change their optical and electrical properties due to changes in the chemical environment have become a subject of significant interest in the scientific community.[1−4] In recent years, the area of responsive polymers has been developing rapidly, due in part to the progress in the synthesis of sophisticated block copolymers and multilayered ionic and hydrogen-bonded polymers.[1,2] In these systems, the mechanical or optical response of the material is related to changes in the local molecular ordering, which in turn is sensitive to environmental agents. However, the correlation between the responsive properties of the polymers and their structural changes is often masked by the high complexity of these changes. The pioneering works of Abbott et al.[3,4] suggested a new approach to sensing biologically active molecules by detecting orientational changes of low molar mass nematic molecules. In their approach, the response of the material is found by measuring changes in optical birefringes and is amplified by the cooperative rearrangement of liquid crystals (LC). However, the majority of modern thermotropic liquid crystals, including LC polymers, are hydrophobic and therefore are not able to respond to water solutions. One of the promising ways to increase hydrophilicity of LC polymers is to increase concentration of hydrogen-bonded groups.

Hydrogen-bonded thermotropic liquid crystals and supramolecular structures are promising candidates for a variety of sensors because they are readily fabricated and have the potential to form a variety of structures with a broad range of new properties.[5,6] Hydrogen bonding is achieved through the complexation of two or more molecules containing proton donor and proton acceptor groups. The temperature range of mesophases displayed by hydrogen-bonded liquid crystals is broad and may be tuned by changing the geometry of mesogenic fragments via simple nonchemical methods.[7] In hydrogen-bonded cholesteric polymer films containing donor/acceptor side groups, one can expect much higher sensitivity of the helical supramolecular structure toward molecules disrupting hydrogen bonds.

The hydrogen bonding is highly sensitive to the chemical environment and can be easily "turned off" and/or replaced by ion bonding if the hydrogen-bonded polymers are immersed in aqueous solutions of amino acids. Under the action of amino acids or other environmental agents the pitch of the cholesteric helix might change. This is a challenging task that is being dealt with in our article. The preliminary studies and the design of cholesteric polymers able to respond to pH changes of aqueous solutions containing inorganic bases were described by the authors[8] without revealing a mechanism of the response.

Cholesteric liquid crystals (CLC) are self-organized materials capable of forming planar helical structures when placed between glass plates coated with rubbed polyimide. Planar CLCs are one-dimensional, photonic band-gap (PBG) structures for light with the same sense of polarization as the cholesteric helix. The selective reflection band (SRB) is centered at the wavelength $\lambda = nP$. The width of the band is $\Delta\lambda = (\Delta n/n)\lambda$, where P is the pitch of the chiral liquid crystal,[9] and $n = (n_e + n_o)/2$ is the average refractive index of the cholesteric planes with a birefringence of $\Delta n = n_e - n_o$.

In this paper we report, for the first time, CLC polymers capable of responding to the presence of basic amino acids in surrounding aqueous solutions by changing color and shifting the SRB. A broad range of chemical compositions of the

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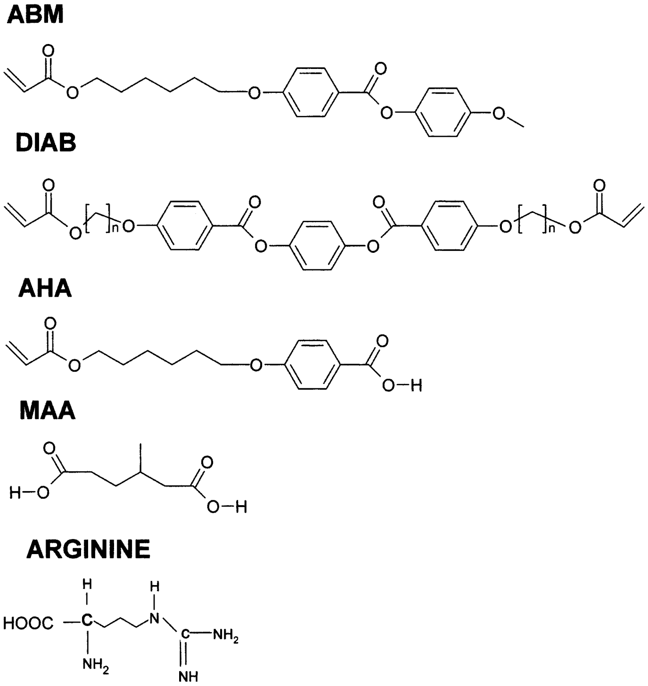
Scheme 1. Chemical Structure of the Monomers Used To Synthesize CLC Polymer (in DIAB $n = 6$) and Amino Acid



responding polymer is considered, and the mechanism of the amino acid-induced changes of the cholesteric helix is revealed.

It is also shown that narrowing of spontaneous emission and lasing may occur in the responsive polymer films. Optically pumped lasing in dye-treated CLCs occurs in long-lived modes at the edge of the optical stop band.[10−14] This enhancement leads to a low lasing threshold for CLCs used as an optical resonator in lasing experiments. This opens new possibilities for creating responsive lasing materials with tunable lasing wavelengths[14] as a result of the sensitivity of the helical pitch to external stimuli.

Methods and Materials

Nonracemic methyladipic acid (MAA) was purchased from Aldrich Chemical Co. and was used as a chiral dopant in cholesteric mixtures. It had a melting point at 84 °C. The synthesis of the monofunctional 4-(6-acryloyloxyhexyloxy)benzoic acid (AHA), difunctional monomers 1,4-di(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzene (DIAB), and monofunctional monomer 4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)methoxybenzene (ABM) was performed as described elsewhere.[8,15] The chemical structures of the arginine and compounds used for the design and synthesis of polymer matrices are shown in Scheme 1. All the monomers were mesogenic compounds and formed a nematic state at elevated temperatures. Laser dyes (pyrromethene 597) were supplied by Exciton Co. The mixture of AHA, DIAB, and ABM formed a LC state at elevated temperatures. The cholesteric liquid crystal was placed between two glass plates with a rubbed polyimide layer. This arrangement provided an almost planar cholesteric layer, with planarity determined by the wedge between the two glass plates. Photopolymerization of the mixtures was initiated by a high-pressure Hg lamp (intensity 10 mW cm^{-1} at 366 nm) with a 2% w/w photoinitiator (benzophenone) added to the mixtures. After polymerization, one of the glass plates was removed, releasing the film surfaces for treatment in aqueous amino acid solutions. Phase transitions in monomer mixtures were controlled by differential scanning calorimetry; no glass transition was detected after polymerization, although the melting peak of MAA was still present. The polymers responded to three amino acid water solutions (arginine, lysine, and histidine). Their response was monitored by in situ spectroscopy in a visible spectral range. Polymer films with a width of ca. 0.5 cm and thickness of ca. 30 μm were put in a quartz cuvette. The volume of the cuvette was ca.10 mL, the volume of the polymer film was at least 10^4 times smaller so that any reaction occurring in polymer film could not significantly change the concentration of amino acid in water solution. Optical spectra were recordered by fiber-optics spectrometer (Ocean Optics 2000) collecting the light passing through the film and solution. The response of CLC polymers to the treatment in lysine and histidine solutions is similar to that in the arginine solution, but slower, and will be discussed in detail in a separate publication.

The IR spectra were collected on a Perkin-Elmer FT-IR spectrometer, Spectrum RX 1. The samples treated in amino acid solutions were taken from the solutions, wiped out, and dried in a vacuum oven. The optical microscopy observations were made with a Van Guard microscope equipped with a hot stage. The second harmonic of a Q-switched Nd:YAG laser (5 ns pulse duration) was used in order to pump the cholesteric samples and excite the laser dyes that were dissolved in the CLC samples. The pH of the amino acid/water solutions was determined by a glass electrode connected to a pH meter (pH209, Hanna Instruments). In the following section the results of arginine solution studies are given the most attention.

Results and Discussion

The mixtures of AHA, DIAB, ABM, and MAA form a left-handed cholesteric phase at temperatures above 60 °C when the mixtures melt. The inert, non-hydrogen-bonded mixture of DIAB and ABM has a broad temperature interval for the LC state, which can be cooled and remains in a LC state at room temperature for some time. The mixture of AHA, DIAB, and ABM has a narrower temperature interval of LC state. Increasing concentration of AHA results in narrowing the temperature interval of the LC state. The nematic mixtures containing AHA, DIAB, and ABM can be twisted by adding a chiral dopant (MAA) to form a cholesteric liquid crystal (CLC) phase. The cholesteric state can also be formed by adding some inert chiral dopants (for example ZLI 4572, supplied by Merck Co.) which are incapable of forming strong hydrogen bonds. The helical pitch of the mixture decreases with an increased concentration of MAA.[8] At concentrations of MAA above 30% the liquid crystalline state does not exist.

The SRB of low molar mass mixtures lies in a visible spectral region when the concentration of MAA reaches ca. 13%. At higher concentrations the SRB shifts toward shorter wavelengths and, at concentrations higher than 24%, leaves the visible region. The position of the SRB nonlinearly depends on the concentration of chiral dopants.

The twisting power of MAA for the visible region of the spectrum was found to be about 10−14 μm^{-1} and was calculated on the basis of the following equation:

$$\beta = 1/pc \qquad (1)$$

where β is the helical twisting power (HTP) of a chiral dopant, which is inversely proportional to the molar concentration of dopant c and to the cholesteric pitch p. The magnitude of β for different solutes in a given solvent is a characteristic property of the chiral solute and its interaction and ordering within the liquid crystalline matrix. The change of the helical twisting power of chiral dopants in low molar mass liquid crystals results in changes in the helical pitch of the cholesteric helix and a subsequent shift in the selective reflection band. In tightly cross-linked CLC networks, the interaction of chiral solutes with the matrix does not have much impact on the ordering of the molecules and the helical pitch.

The helical pitch may change either in response to the disruption/weakening of the hydrogen bonds between the chiral dopants and the components of the liquid crystalline matrix or in response to the disruption/weakening of the hydrogen bonds between components of polymer matrix. The question “What part of a polymer film, the matrix or the chiral dopants, has a greater effect on polymer response to the amino acids?” should be answered in order to understand the mechanism of response of polymer films to the presence of amino acids in the surrounding aqueous media.

A variety of the polymer films with inert matrix (not able to form hydrogen bonds) and active matrix (able to form hydrogen bonds due to the presence of donor/acceptor groups) synthesized by the authors fall into the following four categories: (1) inert chiral dopant/inert matrix, (2) inert chiral dopant/active matrix, (3) active chiral dopants/inert matrix, or (4) active dopant/active matrix. The response of the films belonging to each type to different amino acids was studied in order to understand the mechanism of helical changes and the role of the interactions between chiral dopants and polymer matrix. Polymers of first three categories did not display any response in a pure water. Polymers of fourth category did show a small shift (5−10 nm) of the SRB toward shorter wavelengths after being immersed in water for an hour.

The polymers belonging to the first category (inert chiral dopant, ZLI 4572/inert matrix, monomers DIAB, ABM) have the best quality of the SRB. However, they do not respond to the presence of basic molecules and amino acids at all.

The polymers belonging to the second category (inert chiral dopant, ZLI 4572/hydrogen-bonded matrix, DIAB, ABM, AHA) have very weak response to the presence of amino acids. The maximum shift of the selective reflection band in the polymer films with high concentration of AHA (60%) and concentration of arginine in water ca. 10% does not exceed 15−20 nm. If a concentration of AHA molecules in polymer matrix decreases, the shift of the SRB becomes undetectable at concentration of AHA molecules as small as 30% (even after 1 h of polymer treatment in 10% arginine solution).

The polymers of third category (hydrogen-bonded chiral dopant, MAA (15−20%)/inert matrix DIAB, ABM) displayed the highest light scattering and very distinct areas of phase separation. Phase separation occurs because of incompatibility of hydrophilic MAA and hydrophobic molecules composing the polymer matrix (DIAB, ABM). The SRB is practically invisible due to the light scattering. It was impossible to detect any response of polymers belonging to this category to amino acids−water solutions.

The polymers of fourth category (hydrogen-bonded chiral dopant, MAA/hydrogen-bonded matrix DIAB, ABM, AHA) were found to be the most responsive to amino acids. The polymer films belonging to this category are discussed hereafter. The most stable monomer composition with the SRB lying in the visible part of the spectrum corresponds to the ratio DIAB:ABM:AHA:MAA = 24:18:39:19 (these ratios show the actual concentrations, i.e., 24% of DIAB, 18% of ABM, 39% of AHA, etc.). With the increasing concentration of a difunctional monomer, the melting temperature of the monomer mixture increases, and the composition displays a tendency to undergo a phase separation. In the experiments described below the ratio DIAB:ABM = 4:3 was kept constant. The increase in concentration of AHA in the aforementioned composition results in higher sensitivity of the CLC polymer to amino acids. The use of the monomer mixture RMM34 purchased from Merck instead of the mixtures containing DIAB and ABM produces similar experimental results. The optical spectra of the sample with composition DIAB:ABM:AHA:MAA = 24:18:41:17 treated in a 10% arginine solution are shown in Figure 1 as a function of time. All spectra are taken in left circularly polarized light. There are no any bands in all spectra taken with right circularly polarized light (Figure 2), which proves that bands in Figure 1 result from the selective reflection of light. Before the treatment, the center of the selective reflection band lies at 600 nm. The magnitude of the SRB shift toward longer wavelength is about 170 nm, and it occurs within 15 min of treatment in arginine solution. The shift of the SRB occurs as follows. The depth

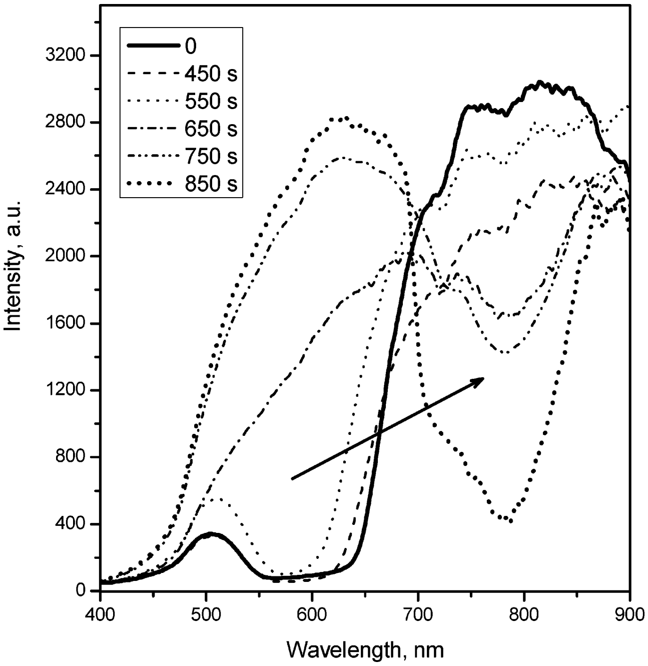


Figure 1. Spectra of the sample with the hydrogen-bonded chiral dopant (composition DIAB:ABM:AHA:MAA = 24:18:41:17) immersed in a 10% aqueous solution of arginine as a function of time (left-handed circularly polarized light).

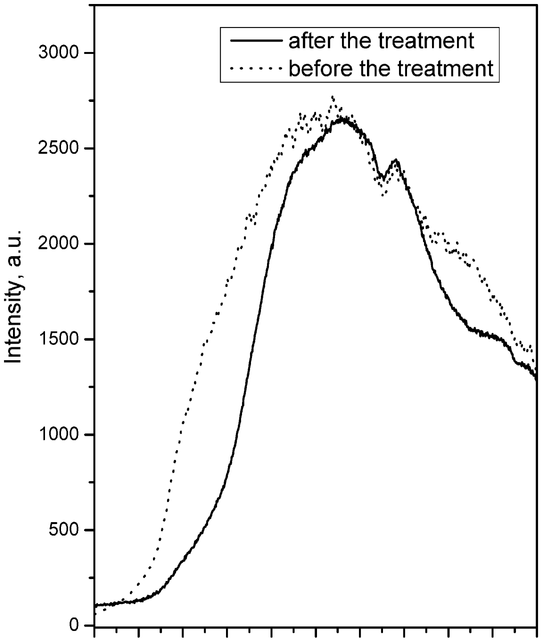


Figure 2. Spectra of the sample with the hydrogen-bonded chiral dopant (composition DIAB:ABM:AHA:MAA = 24:18:41:17) before and after the treatment in 10% aqueous solution of arginine (right-handed circularly polarized light).

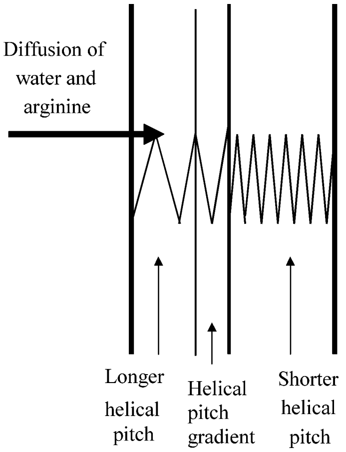


Figure 3. Diffusion of amino acids and water ions into a polymer and formation of structures with longer helical pitch.

and width of the SRB at 600 nm start to decrease while the new SRB with increasing depth and width appears at 770 nm. Almost all spectral lines intersect around the same point at ca. 700 nm (Figure 1). In general, such a point (isosbestic point) appears in spectra of light-absorbing materials at the wavelengths at which molar absorption coefficients are the same. This point is often an indication of the reaction between two phases. In our films the role of absorption is played by the selective reflection of light due to the presence of two cholesteric layers with different pitch. The diffusion of water and arginine molecules into the film results in the formation of two areas inside the film separated by the front of diffusion (Figure 3). The increase in the width of the SRB could be explained either in terms of increased birefringence and molecular order of cholesteric layers or in terms of the formation of a refractive index gradient across the sample due to the propagation of the diffusion front. However, the increase in the order and birefringence cannot be of such magnitude and cannot happen in a cross-linked structure due to limited molecular mobility. It is most likely the gradient of refractive index induced by the diffusion of dissociation products of amino acids and OH ions inside the polymer film that results in widening the SRB.

An increase in the concentration of AHA molecules in polymer composition leads to a faster and larger shift of the SRB toward longer wavelengths (Figure 4). For example, for polymer with concentration of MAA about 16%, the maximum shift of the SRB is achieved at concentration of AHA groups about 65%. However, the quality and stability of the SRB at high concentration of AHA groups deteriorate. The shift of the SRB monitored as a function of time for the samples with different concentrations of hydrogen donor/acceptor groups is shown in Figure 5. The change of the position of the SRB for the films of thickness ca. 40 μm occurs within 200 s for the film with 68% of AHA and 850 s for the film with 36% of AHA. An increased rate of response can also be achieved by increasing the concentration of the amino acid in water solution. At low concentrations of the amino acid the response slows down significantly; for example, for concentrations of arginine about 0.8% only minor shift (15−20 nm) in the spectral position of the SRB was observed over the course of 15 min.

The hydrophilicity of the polymer increases with a rise of concentration of −COOH groups in polymer films. The hydrophilicity of polymer films was estimated by measuring the contact angles of water droplets put on the polymer films. The contact angle decreases from ca. 85° to ca. 65° when concentration of AHA groups in polymers of second category rises from 5% to 68%. Contact angle decreases to ca. 25° in polymers of fourth category with 60% of AHA and 18% of MAA molecules. Thus, the addition of MAA molecules leads to significant increase in hydrophilicity.

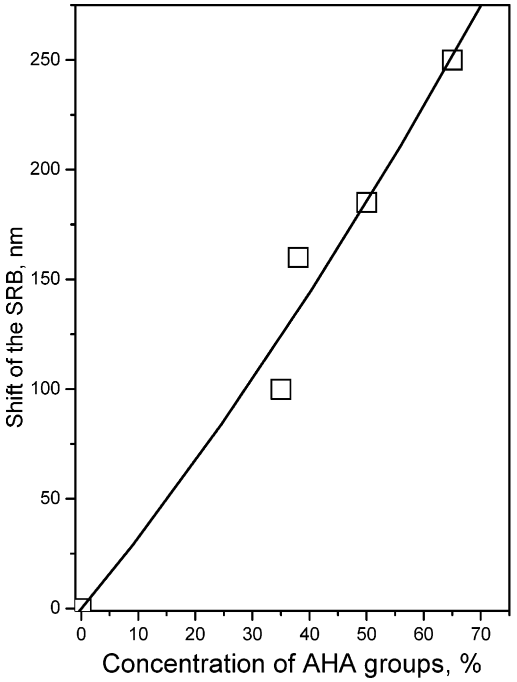


Figure 4. Shift of the SRB vs time in the samples with an increasing concentration of AHA.

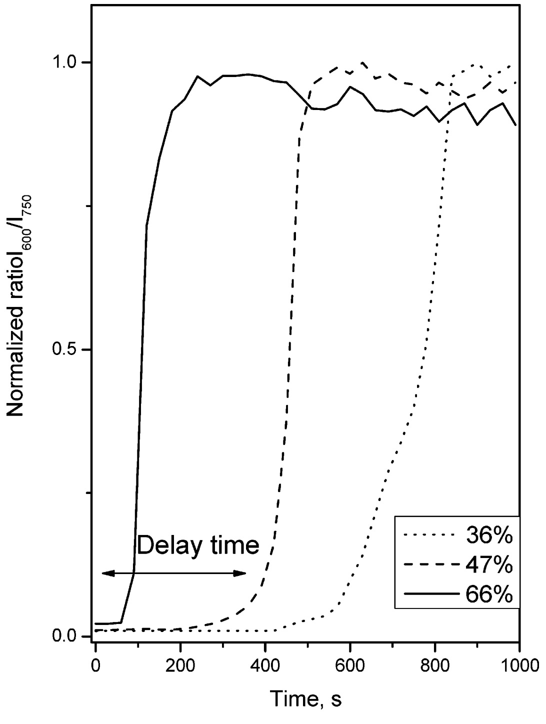


Figure 5. Kinetics of the SRB shift during the treatment: I_{600} is a light intensity at 600 nm (position of the SRB before the treatment), and I_x is a light intensity at new position of the SRB.

After treatment in the solution of arginine for about 20 min, the sample thickness was measured under the microscope. The wet samples swelled and increased their thickness by a factor of 1.2−1.8. The swelling depends on the concentration of AHA and MAA molecules. For concentrations of MAA molecules about 14% and AHA molecules of about 30% the swelling factor

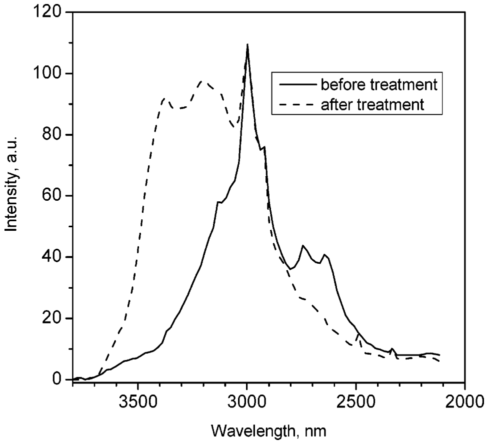


Figure 6. IR spectra (3800−2000 cm^{-1}) of polymer films before (a) and after (b) treatment in a 10% water solution of arginine.

is about 1.2, whereas for a concentration of AHA molecules about 65% the swelling factor increases to ca. 1.8. This correlates well with the shift of the SRB at different concentrations of AHA molecules. However, the swelling factor does not directly proportional to the shift of the SRB. If swelling was the only factor contributing to the shift of the SRB, then the dry samples should restore their shape and the position of the SRB. However, the drying of cholesteric films treated in amino acid solutions for a prolonged period of time always results in some shift of the position of the SRB with respect to the position of the initial SRB in untreated film. Typically, the polymer samples with a concentration of hydrogen donor/acceptor groups AHA of about 40% displayed a shift of about 40−60 nm toward longer wavelength with respect to the initial position of the SRB. In samples with higher concentration of AHA groups the aforementioned shift reaches 60−90 nm. These facts can be explained in terms of the disruption of hydrogen bonds of polymer samples and their replacement by ion bonds formed between the residues of amino acids and AHA/MAA molecules attached to the polymer matrix. This leads to significant changes in the molecular interactions, a decrease of the free volume of the polymer matrix, and changes in the helical pitch.

The IR spectrum (Figure 6) of polymer films recorded before the treatment has peaks at 2850−2980 cm^{-1} associated with CH_2 stretching and two peaks at 2600 and 2740 cm^{-1} associated with OH stretching of hydrogen-bonded dimers between −OH and C═O groups of polymer matrix. This type of spectrum is typical for hydrogen-bonded polymers and fatty acids. After the treatment in arginine the spectrum of the dried sample broadens, and two new peaks at ca. 3360 and 3174 cm^{-1} appear. The position of these peaks almost coincides with the position of NH stretching bands (3366 and 3184 cm^{-1} in butyramide).[16,17] Significant decrease of intensity of peaks at 2600 and 2740 cm^{-1} after the treatment means the breakage of hydrogen bonds between −OH and C═O groups of MAA and the matrix. The analysis of the IR spectra in spectral interval 1800−1400 cm^{-1} also confirms the presence of amino acid residues in polymer films (Figure 7). Before the treatment there are strong absorption peaks by the C═O group at 1740 cm^{-1} and absorption of benzene ring at 1600 cm^{-1}. After the treatment the overlapping bands appear in the range 1600−1660 cm^{-1}. These are strong NH bending superimposed with strong NH_2 scissoring absorption (often occurring in the range 1550−1650 cm^{-1}) and absorption by the reacted −COOH groups (band at 1660 cm^{-1}).[16,17] Thus, IR data strongly suggest that the diffusion of amino acid residues inside a polymer occurs during a treatment in amino acid solution.

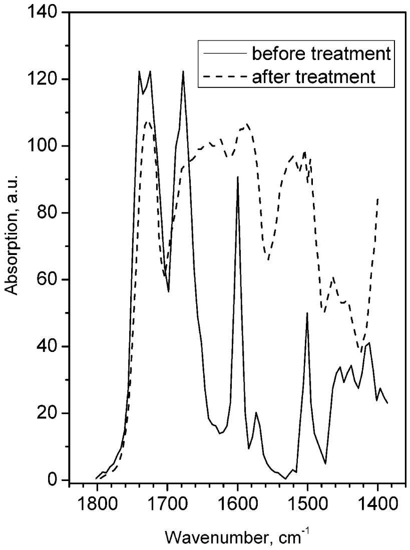


Figure 7. IR spectra (1800−1400 cm^{-1}) of polymer films before (a) and after (b) treatment in a 10% water solution of arginine.

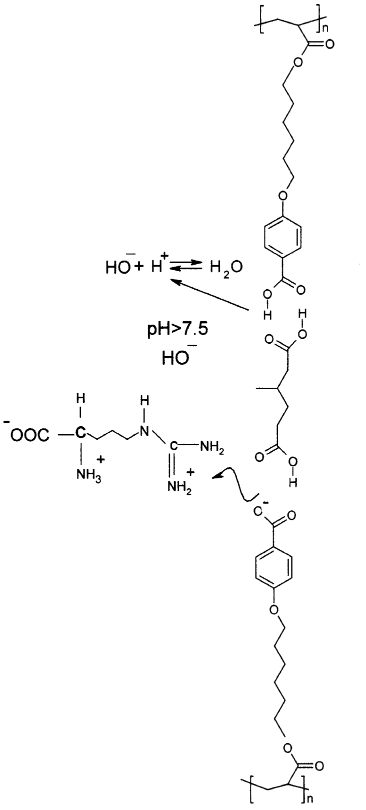


Figure 8. Breaking hydrogen bonds between components of polymer matrix.

We propose the following mechanism of supramolecular helical structure changes in hydrogen-bonded CLC, responding to the presence of amino acids in water (Figure 8). In concentrated water solution of amino acids the pH is determined by the concentration of amino acid ions. They and −OH^{-} ions are able to diffuse into the polymer. The diffusion coefficient depends on concentration of matrix hydrogen-bonded acid groups in MAA and AHA which are hydrophilic and able to react with diffusing molecules. Diffusion of amino acid residues and OH ions into the polymer matrix leads to the reaction between −COOH groups and ions and to increase of the local

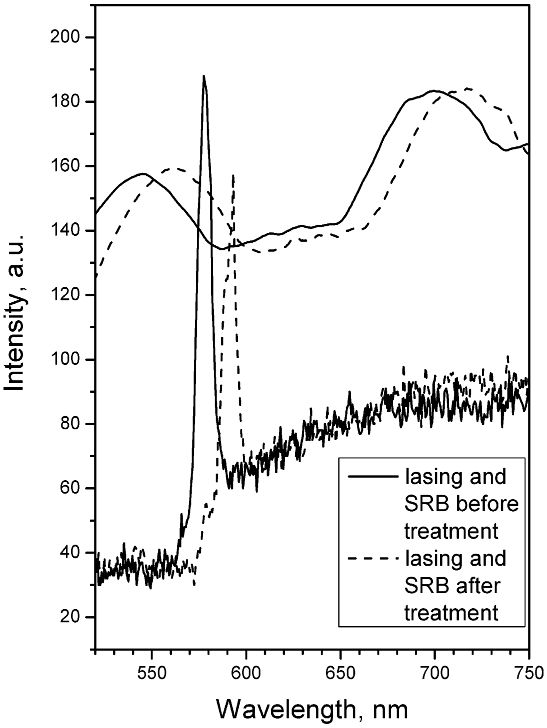


Figure 9. Shift of the lasing wavelength of the sample with low concentration of AHA (DIAB:ABM:AHA:MAA = 36:27:20:17) immersed in 10% arginine solution before (a) the treatment and 40 min after (b) the beginning of treatment.

volume occupied by $-$COOH groups. This reaction also increases the hydrophilicity of the polymer matrix that in turn results in an increased diffusion of water solutes.

The concentration of acid groups depends on concentration of AHA and MAA molecules in polymer matrix. Since MAA has two $-$COOH groups, its contribution to total concentration of acid groups in polymer film is 2 times higher than contribution of AHA molecules. This explains the much higher sensitivity of polymers of fourth category to amino acid solution. All of these factors play a major role in the increase of polymer swelling that leads to the extension of helical pitch. The compact size of MAA and its reaction with amino acids result in changes of HTP and rearrangement in a polymer matrix. This also contributes to the changes of helical pitch. Since the position of the SRB depends on a refractive index (n) and helical pitch (p) through the equation $\lambda = pn$, the position of the SRB changes. Structural changes of polymer matrix and its swelling have a more profound effect on the helical changes than HTP changes of noncovalently bonded MAA.

CLC polymers described here may find applications as simple pH and amino acid sensors, responding to environmental agents by changing their color. Another possible application of polymer films is related to their use as light emitters and lasers sensitive to changes in chemical environment.

Light emission was studied from the samples doped with laser dyes (pyrromethene 597) before, during, and after treatment in amino acid solutions in accordance with the procedure described in refs 10−14. All samples before the treatment displayed optically pumped lasing at the edge of the SRB when dye emission band overlapped with the SRB. Less sensitive samples (with low concentration of AHA groups and therefore small shift of the SRB) placed in water solutions of amino acids displayed lasing at the beginning of the treatment when the SRB started to shift toward a longer wavelength and still overlapped the dye emission band (Figure 9). The shift of the lasing wavelength was easily detectable and was observed even when there were no visible color changes. Thus, a lasing from CLC polymer is an ideal tool to monitor the initial stage of the SRB shift. While the shift of the SRB progresses with increasing concentration of AHA groups, the lasing is turned off, and only narrowing of spontaneous emission could be observed with increased pumping energy of the Nd:YAG laser. This is a result of the smaller overlap between the SRB and the emission band of a laser dye and formation of the refractive index gradient. In polymers with low concentration of AHA groups the lasing occurred during longer time than in polymers with high concentration of AHA groups and approximately corresponded to the delay times (Figure 5). The shift of lasing wavelength also correlates with the shift of the SRB and therefore with type and concentration of amino acids used in experiments. Laser dyes were not affected by the treatment in amino acid solutions.

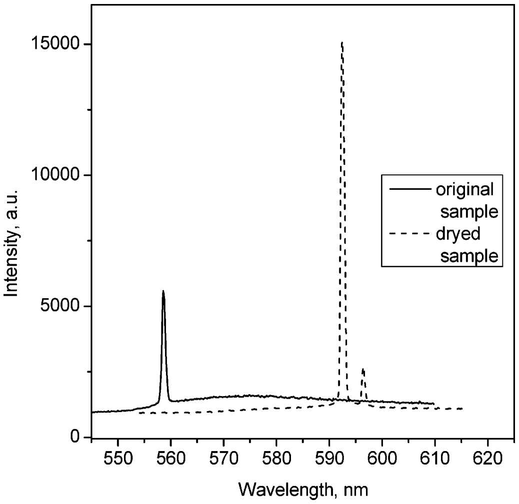


Figure 10. Transmission and lasing from dry polymer films.

The lasing emission from dried polymer samples treated in amino acid solutions was observed from almost all the samples (Figure 10), except those with a very high concentration of AHA molecules (more than 68%). There is always a shift in the positions of the SRBs in the samples immediately after the treatment and dried samples. Lasing always occurred close to the edge of the SRB (Figures 9 and 10) when the emission band still overlaps the edge of the SRB. Typical lasing spectra are sometimes characterized by several lasing peaks, thus indicating that the inhomogeneity of the samples and their multidomain structure still persist in the samples after the treatment.

Conclusions

Polymer cholesteric liquid crystals containing hydrogen donor/acceptor groups in chiral dopants and polymer matrices respond to the amino acid water solutions by changing the color of the matrix and shifting the selective reflection band. The increase in concentration of donor/acceptor groups, especially methyladipic acid (MAA) in a polymer matrix, results in faster color changes. The structural changes in a polymer matrix and its swelling in water solutions were found to be the major factor contributing to changes of helical supramolecular structure. Polymers doped with the laser dyes and pumped by an external laser display lasing at the edge of the selective reflection band. The duration of lasing depends on the concentration of AHA groups in polymer matrix as well as type and concentration of amino acid used. The shift of lasing wavelength also correlates with the concentration of amino acid. The observation of color changes in the polymer CLCs and the related optical effect, the shift of the selective reflection band, and lasing, which are described in this article, open new possibilities for the creation of effective biological sensors and lasers sensitive to the presence of biological molecules.

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