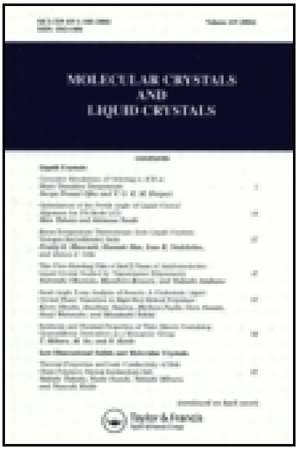

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Novel Color Changing pH Sensors Based on Cholesteric Polymers

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Color changing cholesteric hydrogen bonded polymer films responding to pH changes induced by basic amino acids or inorganic bases were synthesized and studied. The films with a higher concentration of donor/acceptor groups display a larger shift of the selective reflection band and faster response. This effect is explained in terms of the breakage of hydrogen bonds that occurs between the components of a cholesteric polymer, immersed in various basic aqueous solutions including amino acids.

Keywords: amino acids; chiral; cholesteric; color sensors; hydrogen bonds; selective reflection; water

INTRODUCTION

In recent years, the area of responsive polymers has been developing rapidly, due in part to progress in the synthesis of sophisticated block-copolymers and multilayered ionic and hydrogen bonded polymers [1–4]. In these systems, the mechanical or optical response of the material is related to changes in the local molecular ordering, which is sensitive to environmental agents. The pioneering works of

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Abbott *et al.* [3,4] suggested a new approach to sensing biologically active molecules by detecting orientational changes of low molar mass nematic molecules deposited on a top of a sensitive layer. This approach has been proven to be very successful in detecting biological molecules adsorbed on the surface from water solutions. However, the detection of molecules may be affected by surface contamination. Thus, the systems able to respond to environmental agents not only by changing their surface properties, but also by changing the bulky properties seem to be more advantageous. However, the majority of modern thermotropic liquid crystals, including LC polymers, is hydrophobic and, therefore, is not able to respond to water solutions of biologically active molecules. Here we suggest a new approach aiming to increase a sensitivity of thermotropic liquid crystals to a variety of biological solutions and to environmental pH changes by incorporating hydrogen bonded nematic molecules and chiral dopants into thermotropic LC polymers.

Hydrogen bonding is achieved through the complexation of molecules containing proton donor and proton acceptor groups. The temperature range and physical properties of mesophases displayed by hydrogen-bonded liquid crystals may be tuned by changing or disrupting hydrogen bonds [5]. The preliminary studies and the design of cholesteric polymers able to respond to pH-changes of aqueous solutions containing inorganic bases [6] and amino acids [7] by shifting the selective reflection band and lasing wavelength were described by the authors in previous publications. Here we discuss some new results and suggest a model describing kinetics of chemical reactions in responsive polymer films.

METHODS AND MATERIALS

Chiral methyladipic acid (MAA) was purchased from Aldrich Chemical Co. and was used as a dopant inducing cholesteric state. 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 [6–8]. The mixture of AHA, DIAB and ABM formed a LC state at elevated temperatures (Figure 1). The cholesteric liquid crystal was placed between two glass plates with a rubbed polyimide layer. This arrangement provided a planar cholesteric layer. Photopolymerization of the mixtures was initiated by a high pressure Hg lamp (intensity 10 m Wcm^{-1} at 366 nm) with a 2 wt.% of photoinitiator (benzophenone) added to the mixtures. The glass plates were removed

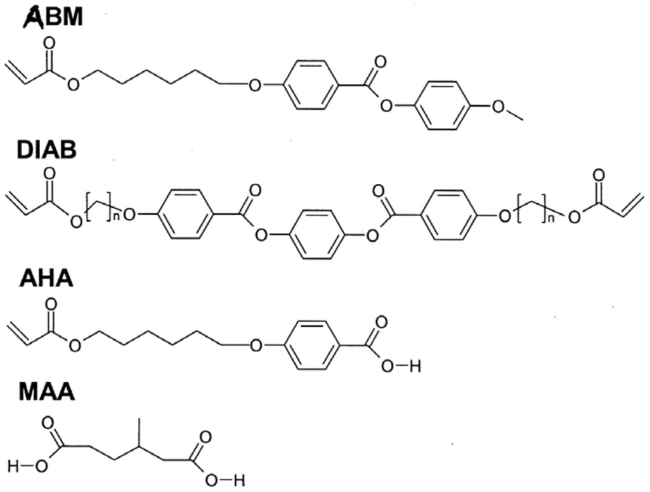

FIGURE 1 Monomers used to synthesize responsive polymer.

after polymerization, releasing free standing films ready for treatment in aqueous basic solutions. The polymers responded to inorganic bases (KOH, NaOH, CsOH) and three amino acid water solutions (arginine, lysine and histidine). Their response was monitored by *in situ* spectroscopy in a visible spectral range.

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 selective reflection band (SRB) of the mixture shifts towards shorter wavelengths with increasing concentration of MAA [6–7]. The SRB of low molar mass mixtures lies in a visible spectral region when the concentration of MAA reaches ca. 13% (everywhere in the article the weight percentage is used). At higher concentrations the SRB shifts towards shorter wavelengths and, at concentrations higher than 24%, leaves the visible region.

The helical pitch may change in response to the disruption/weakening of the hydrogen bonds in polymer matrix. Here we discuss films displaying the highest response to basic solutions. 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.). The increase in concentration of AHA in the

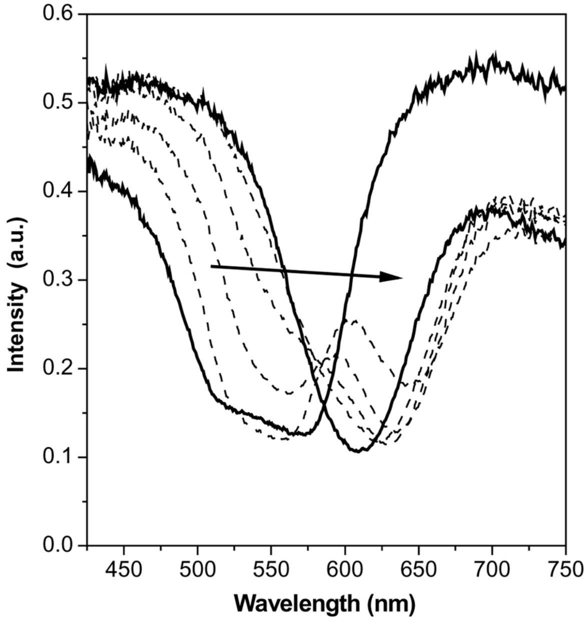

FIGURE 2 Shift of the selective reflection band in responsive chiral polymers with 26% of AHA groups (spectra are shown for every 180 s, thick black lines are initial and final positions).

aforementioned composition results in higher sensitivity of the CLC polymer to basic solutions and 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 typical optical spectra of the sample with composition DIAB:ABM:AHA:MAA = 32:24:26:18 before and during the treatment in 5% KOH solution is shown in Figure 2. Before the treatment, the center of the selective reflection band is at ca. 550 nm. After 900 s of the treatment, the SRB shifts to ca. 620 nm and the sample changes the color from green to red. Two bands are seen in Figure 2 in the middle of the transition. The positions of these bands correspond to the position of the selective reflection band in untreated sample and in a sample after 900 s of the treatment. The presence of these intermediate bands indicates that the polymer film consists of treated and untreated areas with a sharp border between them. This is also confirmed by the fact that almost all spectra intersect around one point analogous to isosbestic point in two phase alloys. The magnitude of the SRB shift depends on concentration of hydrogen bonded groups in the sample (Fig. 3). Higher concentrations

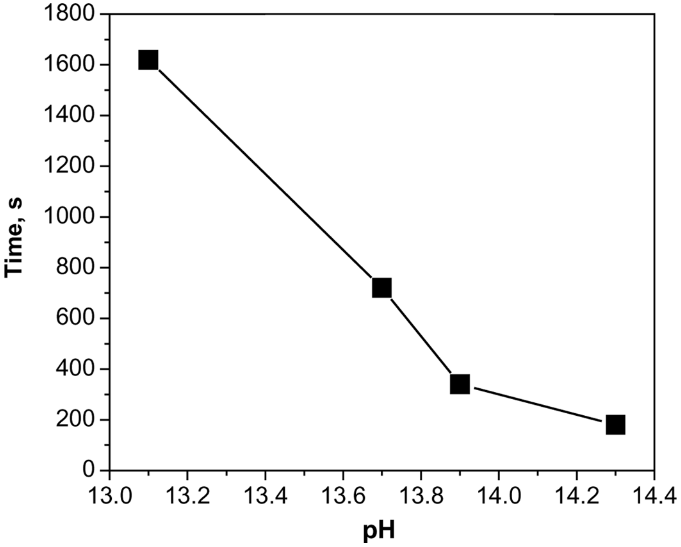

FIGURE 3 Time needed to shift the selective reflection band as a function of pH.

of hydrogen bonded AHA groups lead to a faster and larger shift of the SRB. At higher pH the SRB moves towards longer wavelengths much faster. For example, in samples with thickness of c.a. 30 microns and concentration of AHA groups of about 35% the shift of the SRB occurs during 700 s, while in samples with higher concentration of AHA groups (c.a. 65%) it takes only 150 s.

The Infra Red spectra of the samples after the treatment in diluted solutions of strong inorganic bases show the presence of –COOM groups (M=K, Na, Cs). The band at 1740 cm^{-1} (–C=O) changes its shape and additional bands appear between 1500 cm^{-1} – 1300 cm^{-1} and around 950 cm^{-1}. The positions of these bands in spectra depend on the mass of the metal ion; ions with the higher mass (for example Cs) move bands towards smaller wavenumbers. In case of amino acids, the IR spectra indicated on the presence of their residues in polymer film after the treatment.

We propose the following mechanism of supramolecular helical structural changes in hydrogen bonded chiral liquid crystals, responding to the presence of different bases in water. In case of strong inorganic bases (MOH), metal ions (M^+) and –hydroxyl (OH^-) ions diffuse into the polymer along with water molecules. In case of amino acids the diffusing agents are OH^- ions and ionized amino acids. The diffusion induces structural changes in polymers increasing their helical pitch [6,7]. The diffusion coefficient depends on concentration of hydrogen-bonded acid groups in the polymer which are hydrophilic and are able to react with penetrating molecular ions.

The process of diffusion can be described by a simple equation:

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} \tag{1}$$

where c(x,t) is a concentration of diffusing ions and molecules able to disrupt hydrogen bonded –COOH groups. The diffused molecules then react with –COOH groups inside the polymer matrix. The rate of this reaction depends on concentration of already reacted –COOH groups (m(x,t)):

$$\frac{\partial m(x,t)}{\partial t} = k(m_0 - m(x,t))c(x,t) \tag{2}$$

where m_0 is an initial concentration of non-reacted –COOH groups, k is a rate constant of the reaction. Both equations (1) and (2) can be greatly simplified if we assume that the diffusion coefficient does not depend on time and position. We solved Eqs. (1) and (2) by means of numerical methods for different concentrations of –COOH s in the matrix. The exact value of the diffusion coefficient is unknown, so calculations were made for D ranging from $10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ to $10^{-6}\,\mathrm{cm}^2/\mathrm{s}$. The best fit to experimental data was achieved for $D = 1.5 * 10^{-8}\,\mathrm{cm}^2/\mathrm{s}$ and $k = 3.5 * 10^{-3}\mathrm{cm}^{-3}\mathrm{s}^{-1}$. The calculated concentrations allow to monitor spectral changes by taking into account the positions of the selective reflection band before, during and after the treatment in basic solutions. The kinetics is totally determined by the diffusion coefficient and the rate constant; the selective reflection spectra were calculated on the basis of standard equations incorporating only refractive index and birefringes [9]:

$$R(\lambda) = \frac{Q^2}{(e^2 + (Q^2 - e^2))\coth(\nu\sqrt{Q^2 - e^2})^2} \tag{3}$$

where $Q = \pi|n_o - n_e|/n$, $e = 2\pi(\lambda - \lambda_0)/\lambda$; n_o, n_e are ordinary and extraordinary indexes of refraction, $\lambda_o = nP$ is a center of the selective reflection band, ν is a number of layers in cholesteric structure. Indexes of refraction were measured and birefringes was found from the width of the selective reflection band proportional to the birefringes ($n = 1.6, |n_0 - n_e| = 0.28$).

The results of the calculations are shown in Figure 4 along with experimental data. The excellent agreement between experimental

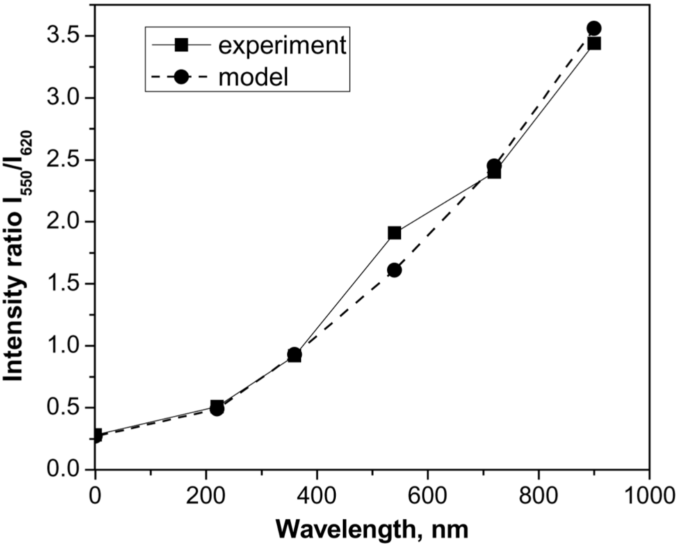

FIGURE 4 Calculated spectral changes and their comparison with experimental data.

data and model calculations indicates that suggested model can be used to describe helical pitch changes in responsive cholesteric polymers.

Cholesteric polymers described here may find applications as simple pH and amino acid sensors, responding to environmental agents by changing their color. Some modifications of chemical structure of these polymers can make them sensitive to a wider variety of chemicals. This work is underway in the laboratory of the authors.

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