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Kinetics of Helix Untwisting in Photosensitive Cholesteric Polymer Mixtures: Influence of Molecular Mass and Ordered Phase Formation

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ABSTRACT: Photooptical behavior of cholesteric mixtures based on two fractions of nematic polymer with different molar masses containing chiral-photosensitive dopant with C=C double was studied. UV irradiation of planarly oriented films of the mixtures leads to *E−Z* photoisomerization of dopant, helix untwisting and shift of selective light reflection peak to the longer wavelength spectral region. Kinetics of this process was studied at different temperatures. It was shown that a relative rate of helix untwisting for the mixture with the high molar mass fraction (DP ∼ 87) is 2 orders of magnitude less than for the mixture containing a low-molar-mass fraction (DP ∼ 22), whereas the activation energies of the helix untwisting for both mixtures have almost the same values. The formation of the ordered TDK* phase during annealing of the blend at 50 °C for 1 week completely prevents the helix untwisting. This fact is worthy of attention because it provides a possibility of fixing a helical structure even at temperatures above the glass transition; this advantage makes this system promising for optical data recording and storage.

Introduction

It is well-known that cholesteric mesophase is characterized by the helical supramolecular organization of mesogens which determines its unique optical properties.[1,2] One of these optical properties is the selective reflection of light with wavelength λ_{max} depending of helix pitch (P) of the cholesteric structure according to the equation:

$$\lambda_{max} = \bar{n}P \qquad (1)$$

where $\bar{n}$ is the average refractive index of liquid crystal.

The concrete value of the selective reflection wavelength depends on many internal and external factors. One of these factors is the structure and geometry of the chiral fragments responsible for the helical twisting of the whole system. The key parameter characterizing the ability of chiral groups for twisting cholesteric mesophase is so-called helical twisting power, expressed by the simple equation

$$\beta = dP^{-1}/dX = \bar{n}(d\lambda_{max}^{-1}/dX)_{X=0} \qquad (2)$$

where *X* is the concentration of the chiral fragments.

The first example of cholesteric low molar mass liquid crystal mixture with photovariable selective light reflection wavelengths was published in 1971 by Sackmann.[3] Since then, a number of new interesting approaches for photoregulation of selective light reflection wavelength were developed.[4−18] One of them is based on the introduction of combined chiral-photochromic fragments capable of photoisomerization into cholesteric or nematic matrix. Under the irradiation the helical twisting power of chiral-photochromic dopant decreases leading to reversible or irreversible shift of selective light reflection wavelength.

Synthesis of cholesteric polymers and preparation of the polymer-based mixtures allow one to create glass-forming materials with optical properties "frozen" in the glassy state

for a prolonged time.[5,11−18] This advantage is very significant for the creation of new materials for optical data recording and storage.

In this connection, it seems to be very important to study the kinetics of helix untwisting in such polymer materials in detail and evaluate an influence of different factors on this process. In particular, it would be essential to study an influence of molar mass of polymer on the rates and activation energies of helix rearrangement of irradiated polymer mixtures. It should be pointed out that up to now these processes have not been considered in the literature.

In this work we prepared cholesteric mixtures based on two fractions of nematogenic polymer **PAA** with different molecular masses:
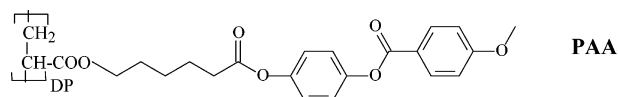

We have selected two fractions of **PAA** which are distinguished not only by degree of polymerization but also by phase behavior.[19] These fractions display the following phase transitions temperatures:

fraction I, DP∼22: g 18 N 99 I

fraction II, DP∼87: g 31 TDK 73 N 135 I

Fraction I forms only the nematic phase, but for high molar mass fraction II an additional formation of ordered two-dimensional crystal TDK phase is observed. The structure of this phase was studied and discussed in detail elsewhere.[20] A local order of mesogenic groups of the mesophase is similar to the smectic K phase (tilted monoclinic cell) but layer ordering is completely absent. Formation of the ordered phase is kinetically controlled: this phase is formed after one month storage at room temperature, at higher temperature (45−50 °C) the process proceeds faster and takes only several days.

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Scheme 1. *E-Z* Isomerization Process Taking Place under UV-Irradiation of Chiral Photochromic Dopant Sorb
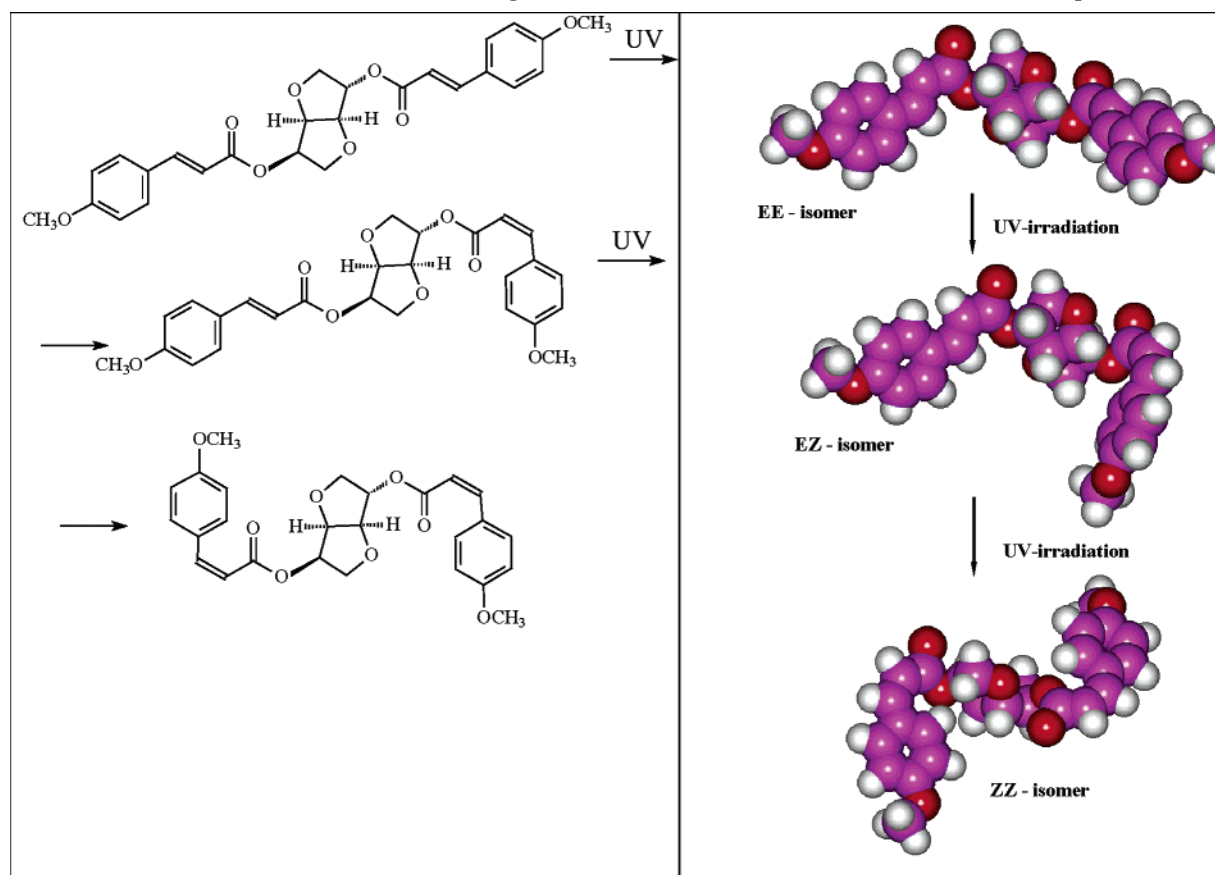
The cinnamoyl derivative of isosorbide (**Sorb**) we used as chiral-photochromic dopant is
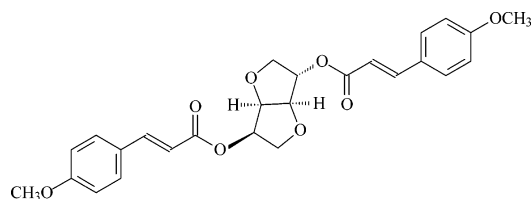
This right-handed chiral compound has a high twisting ability and can undergo *E−Z* isomerization, leading to a decrease in its helical twisting power due to reduction of the molecular anisometry (Scheme 1).[21,22] Introduction of chiral dopant into nematic and ordered TDK phases induces twisting of the both phases with helix formation. In our papers,[12,23,24] it was shown that in chiral copolymers with the same side phenylbenzoate fragments of **PAA** the formation of the TDK* phase does not lead to significant helix untwisting and has no influence on optical properties (selective reflection peak position and its width).

We have prepared the two mixtures based on two fractions I and II of PAA, containing 6 wt % of **Sorb**. One goal of the work is to study of kinetics of the helix untwisting in "pure" cholesteric phase before TDK phase formation; whereas another goal of this work is to study influence of formation of ordered TDK phase on possibility of helix untwisting and its kinetics.

Experimental Section

4-Phenyl-4′-methoxybenzoate monomer was synthesized according to the procedures described elsewhere.[19] Chiral dopant **Sorb** was synthesized according to the standard esterification method using dicyclohexylcarbodiimide.[21] The polymer **PAA** was synthesized by radical polymerization of monomer in benzene solution at 65 °C; AIBN was used as an initiating agent. The synthesized polymer was purified by the repeated precipitation with ethanol and dried in a vacuum.

High molar-mass fraction was obtained by the precipitation with ethanol from 1% solutions in THF.[19] Low-molar-mass fraction was separated using high performance liquid chromatography. Separation was carried out in THF (distilled in nitrogen atmosphere) on a semipreparative column (19 × 300 mm) packed with UltraStyragel (effective pore size 500 Å). The HPLC setup uses Knauer pump and Waters 440 UV detector operating at 254 nm, flow rate 5.3 mL/min, concentration of the oligomer solution 40 mg/mL, and batch volume 0.5 mL. The repetitive chromatographic cycles yielded about 300−600 mg of each narrow oligomer fraction.

High-molar-mass fraction has degree of polymerization (DP) 87 and polydispersity 1.15, whereas for low-molar-mass fraction DP = 23, and polydispersity 1.2.[19]

The phase transition temperatures of the polymer fractions and mixtures were studied by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min).

The polarizing microscope investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope.

Thin films of the mixture for photooptical experiments were obtained between two glass plates by melting of small amount of the mixture. Thickness of the films was predetermined by 11 μm glass beads. Before investigation all films were annealed during 30 min at temperature 10° below clearing point followed by slow cooling (1 °/min). For formation of TDK* phase, the films of mixture II (see below) were annealed during 1 week at 50 °.

The photochemical properties were studied using a special instrument equipped with a DRSh-250 ultrahigh-pressure mercury lamp. Light with wavelength 365 nm was selected using interference
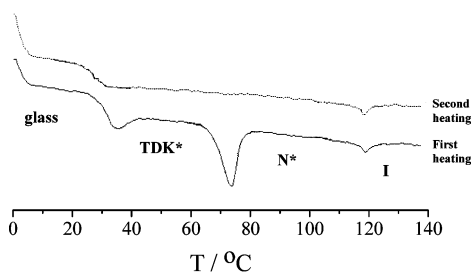
Figure 1. DSC curves of mixture **II** measured during heating with a rate of 10 °C/min. Before the first heating, the mixture sample was annealed at 50 °C during 1 week.

filters. To prevent heating of the samples due to IR irradiation of the lamp, water filter was used. The intensity of light was equal to 1.0 mW×cm^{-2}, as measured by LaserMate-Q (Coherent) intensity meter. Spectral measurements were performed using photodiode array UV/visible spectrometer (J&M). Before study of helix untwisting kinetics the samples were irradiated by UV light during 30 min at room temperature. After that temperature was increased and shift of selective light reflection peak was monitored by the spectrometer.

Results and Discussion

According to the data of polarizing optical microscopy and DSC (Figure 1) the obtained mixtures were characterized by the following phase transitions:

mixture **I**: g 17 N* 88 (1.3) I

mixture **II**: g 27 TDK* 73 (6.7) N* 118 (1.0) I

Enthalpies of phase transitions are presented in parentheses in J/g. Clearing temperatures of both mixtures are about 10 deg lower than ones for initial fractions of **PAA** (see above) that is explained by mesophase disruption induced by nonmesogenic chiral dopant **Sorb**.

For mixture **II** based on the high-molar-mass fraction of **PAA**, a formation of a highly ordered chiral TDK* phase is also observed similar to the pure polymer fraction. But as discussed above, formation of this phase has no effect on the optical properties of the cholesteric films: a position and width of selective light reflection peak remains the same.

Planar texture of mixtures selectively reflects the light with wavelength corresponding to the blue regions of the spectrum. The maximum of selective light reflection weakly depends on the temperature.[21]

Let us consider the kinetics of long-wavelength shift of selective light reflection maximum during annealing of irradiated films at different temperatures. Before measurements the films of mixtures were irradiated by UV-light (365 nm) at room temperature for 30 min. At ambient conditions no selective light reflection changes were found. After irradiation the films were heated to different temperatures and optical properties were monitored simultaneously by diode-array spectrometer. Figure 2 demonstrates the typical absorbance spectra for right-handed circularly polarized light during annealing. Helix untwisting has took place due to the low helical twisting power of *EZ* and *ZZ* isomers of chiral-photochromic dopant **Sorb** (Scheme 1) produced during photoreaction. The shift of the selective light reflection peak is accompanied by its significant widening and a reduction of its intensity. Such spectral changes reflect some distortion of the planar texture during the helix untwisting.

As is clearly seen from Figure 3, the rate of helix untwisting is strongly dependent on the temperature and molar mass of polymer matrix. For mixture **II** containing a high-molar-mass
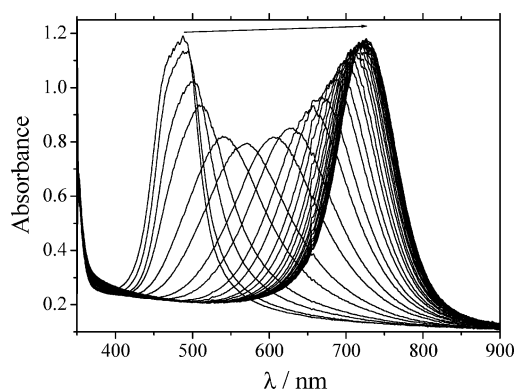

Figure 2. Absorbance spectra for right-handed circularly polarized light of mixture **I** during annealing at 60 °C. Before annealing the film was irradiated at room temperature by UV light (30 min). Spectra were recorded each 5 s of annealing; arrow indicates the direction of the peak shift.
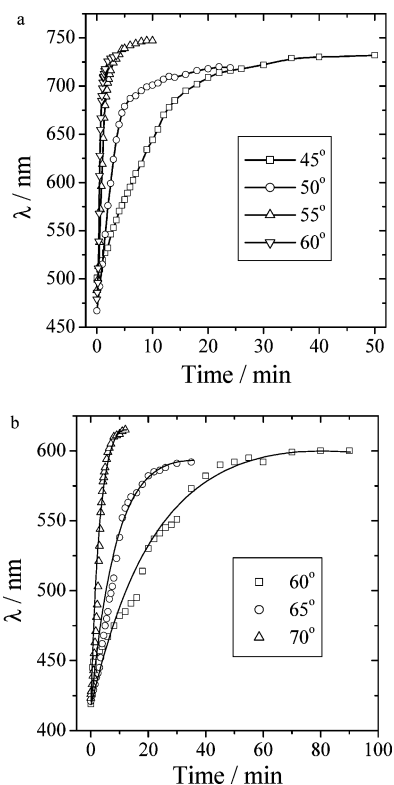

Figure 3. Kinetics of helix untwisting under annealing at different temperatures for mixture **I** (a) and **II** (b). Before annealing the mixture films were irradiated by UV light during 30 min.

polymer fraction the rate of helix untwisting is significantly lower. It is noteworthy that data presented in Figure 3b corresponds to "pure" cholesteric mesophase of mixture **II**, i.e., before TDK* phase formation.

We have estimated the relative rate of selective light reflection shift for both mixtures by approximation of time evolution of inverse λ_{max} using the monoexponential function. At the same temperatures the rate of selective reflection wavelengths shift is about 2 orders of magnitude higher for the mixture I based on low-molar-mass fraction of **PAA** in comparison with the mixture II.

The calculation of the activation energy of the helix untwisting was based on the Arrhenius equation and Figure 4 shows ln k as a function of inverse temperature. The calculated values of activation energy were equal to 208 ± 25 kJ/mol for mixture **I** and 228 ± 25 kJ/mol for mixture **II**.
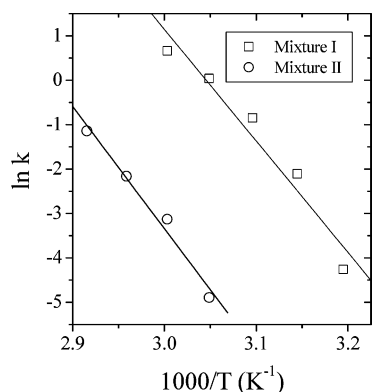
Figure 4. Arrhenius plot of the helix untwisting kinetics for the two mixtures.
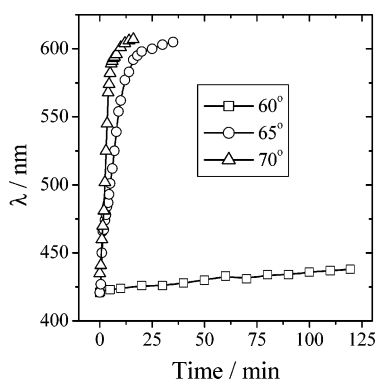

Figure 5. Kinetics of the helix untwisting of mixture **II** at different temperatures. Before measurements film was annealed at 50 °C during 1 week followed by UV irradiation at room temperature.

Let us consider the influence of the highly ordered TDK* phase formation on kinetics of helix untwisting. The behavior of planarly oriented films of the mixture II is completely different after annealing at 50 °C and irradiation at room temperature by UV light. At temperatures below 65 °C no shift of selective light reflection peak was found (Figure 5). This fact is explained by the formation of the ordered TDK* phase completely preventing any macroscopic mobility of mesogenic fragments. Most likely, a large number of small paracrystallites of ordered phase acts as a three-dimensional network which stabilizes the helical supramolecular structure. But under heating of the sample above 65 °C the rate of the process becomes the same as it was before annealing of the same sample during 1 week. This is in accordance with DSC data (Figure 1) showing the melting of TDK* phase at the temperature close to 65 °C.

In conclusion, an influence of molar mass of polymer matrix on kinetics of helix untwisting of photoactive cholesteric polymer mixtures was studied. It is shown that relative rate of helix untwisting for the high molar mass fraction (DP ∼ 87) is

2 orders of magnitude less than for the low-molar-mass fraction (DP ∼ 22), whereas the values activation energies are almost the same ones. The formation of ordered TDK* phase completely prevents helix untwisting. This fact is worthy of attention because provides a possibility of fixing a helical structure even at temperatures above glass transition; this advantage makes this system promising for optical data recording and storage.

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