Colloid Polym Sci (2007) 285:681–686
DOI 10.1007/s00396-006-1593-5

SHORT COMMUNICATION

Photo-optical properties of photopolymerizable cholesteric compositions

Natalia Dadivanyan · Alexey Bobrovsky · Valery Shibaev

Received: 27 July 2006 / Accepted: 4 October 2006 / Published online: 19 January 2007

Abstract Compositions consisting of nematogenic diacrylate monomer and chiral dopants capable of forming the cholesteric mesophase and of photopolymerizing were obtained and studied. For the first time, the change of optical properties and cholesteric helix pitch during photocrosslinking of diacrylate under UV irradiation (365 nm) was investigated. The kinetics of photopolymerization was studied and several stages of this process were observed. Cholesteric photopolymerizable blends containing chiral photosensitive dopant capable of E–Z isomerizing under UV irradiation (313 nm) were studied. The decrease of the helix twisting power of the dopant during photoisomerization was observed resulting in untwisting of the helix and shift of the selective light reflection peak into the long-wavelength region of the spectrum. The possibility of the photoregulation of optical properties of such blends with following fixation of structure and of these properties by means of photopolymerization under UV irradiation (365 nm) was demonstrated.

Keywords Cholesteric photopolymerizing mixtures · Chiral-photochromic dopant · E–Z isomerization · Selective light reflection peak photoregulation

Introduction

Among liquid crystalline (LC) systems, cholesteric LC polymers, and blends are of great interest because of their unique optical properties. The first of these properties is the selective circularly polarized light reflection. This property gives one the opportunity to use such materials in polarizing filters and reflectors of light in different regions of the spectrum in optics and optoelectronics.

There are several ways to prepare polymer cholesteric LC systems [1–5]. One of them is the synthesis of comb-like copolymers containing nematogenic groups that form the mesophase and chiral groups responsible for cholesteric helix formation. Another possibility is related to obtaining blends consisting of the nematogenic polymerizable monomer and chiral dopant, which is responsible for the formation of the cholesteric helix. From such blends, not only linear polymers, but also polymer networks can be obtained. The advantage of such crosslinked systems is the fixation of the helix pitch (P). This method allows getting films with constant wavelength maximum (λ_{max}) of the selective light reflection.

One of the methods of network preparation is the photopolymerization of a blend containing a bifunctional nematogenic monomer which is a crosslinker and, at the same time, a chiral dopant. Such experiments are described by Broer et al. [6, 7], Lub et al. [8, 9], and others [10–13].

It is of practical interest to get from one blend cholesteric films samples with different values of λ_{max} which are related to $P : \lambda_{max} = \overline{n}P$, where $\overline{n}$ is the average refractive index. There are several methods of cholesteric helix pitch changing. The first method is based on the dependence of the helix pitch on temperature. Variation of the temperature allows one to obtain films with selective light reflection in different regions of the spectra. On the other hand, the P value can be changed by introducing photosensitive chiral groups into the cholesteric matrix. These groups can change their geometry under irradiation, which results in the change of P. This approach was used, for example, in [14–18]. In [14], the conformational transition in chiral

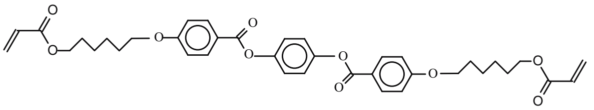
---

N. Dadivanyan · A. Bobrovsky (✉) · V. Shibaev
Department of Chemistry, Moscow State University,
Lenin Hills,
Moscow 119992, Russia
e-mail: bbrvsky@yahoo.com

azobenzene derivative fragments was described. In these substances, E–Z isomerization of N=N-bond under UV irradiation takes place. In [15–17], the analogous isomerization of C=C-bond is observed. In [18], the isomerization of a chiral dopant based on isosorbide derivatives was described. In all the above mentioned cases, E–Z isomerization leads to a decrease of the chiral fragments anisometry, helix untwisting, and shift of the selective light reflection to the long-wavelength region of the spectrum.

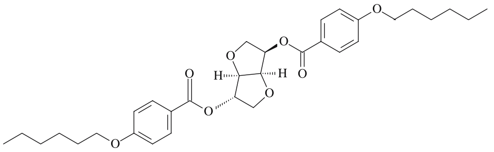
In this work, the combination of the two methods is presented: on one hand, photocrosslinking of blends containing bifunctional nematogenic monomer and chiral photochromic dopant; on the other hand, change of the helix pitch by photoisomerization of chiral photochromic dopant (Fig. 1). The changes of the optical properties during irradiation were studied in detail.

As objects for this study, two types of blends consisting of photopolymerizable bifunctional nematogenic monomer and low-molar-mass chiral dopant were chosen. In both cases, diacrylate monomer DA was used as nematogenic monomer.



DA

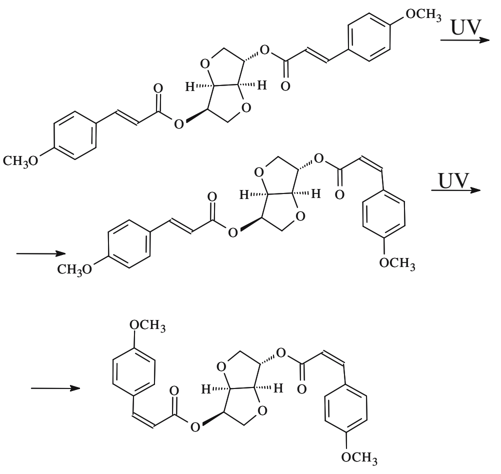
For the first blend, we used a chiral derivative of isosorbide Hexsorb (8.5 wt.%):



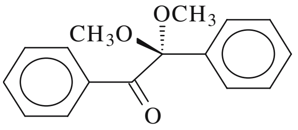
Hexsorb

For the second blend, a derivative of isosorbide and cinnamic acid Cinsorb was chosen (8.5 wt.%). This substance contains double bonds, and under UV irradiation, E–Z isomerization is possible:

Cinsorb

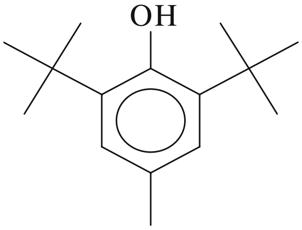


The main difference between Cinsorb and Hexsorb is the presence of the double bonds in Cinsorb. This means that under UV irradiation of the system containing this substance, two processes may take place: photopolymerization of diacrylate monomer and photoisomerization of chiral dopant. In addition, the photoinitiator Irgacure 651 was added into both blends (2.0 wt.%):



Irgacure 651

In order to prevent unwanted uncontrolled thermopolymerization the inhibitor, *4-methyl-2,6-ditert-butylphenol* was introduced (2.0 wt.%):



The absorbance maximum of the photoinitiator is 335 nm (Fig. 2). Therefore, the irradiation with 365 nm leads to formation of the network in both types of blends (Fig. 1). Chiral photochromic dopant Cinsorb absorbs in the short-wave region of the spectrum (313 nm, Fig. 2). UV-irradiation (313 nm) of the blend containing Cinsorb induces E–Z isomerization of the dopant, which results in helix untwisting which can be fixed afterwards by 365 nm irradiation (Fig. 1). Other components of mixtures (DA, Hexsorb and inhibitor) absorb light at shorter wavelengths, below 300 nm and they are not involved directly in photochemical processes described above.

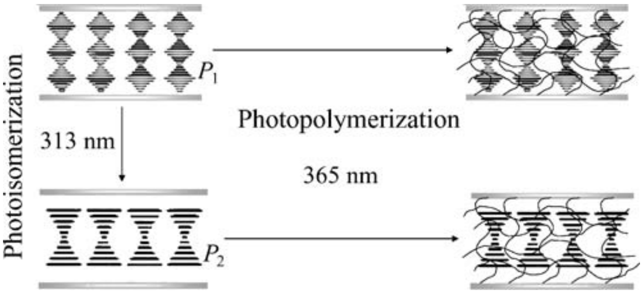


Fig. 1 The scheme of the photoinduced processes in films of cholesteric photopolymerizable blends, *P* helix pitch, $P_2 > P_1$

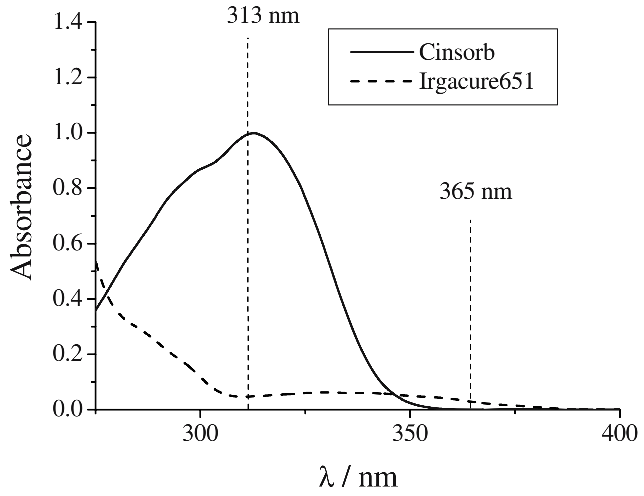


Fig. 2 UV-spectra of photoinitiator Irgacure 651 and chiral-photochromic dopant Cinsorb in dichloroethane solution. The concentration of substances in solution is almost equal to mixture composition

Experimental part

Preparation of blends and films

Blends were prepared by dissolution of the components in chloroform and then were dried on air. Residual solvent was removed by heating in vacuum at a temperature a little bit lower than the isotropization temperature (110–115 °C). Samples of planar-oriented films were prepared between two glasses; the thickness was fixed using glass spacers (11 μm). For samples' preparation, a thermostatic cell "Mettler FP-86" was used. The samples were made at temperatures 10–15 °C below the clearing temperature (T_{cl}). Planar texture of the samples was formed as a result of mechanical shear. Afterwards, the samples were annealed for 15–20 min at the same temperature.

Methods

Polarization microscopy

The phase transition temperatures were determined using polarization microscope "LOMO R-112" equipped with controlled hot-stage "Mettler FP-86." Observations were made using crossed polarizers.

The selective light reflection studies

Selective light reflection was studied by measuring light absorbance using spectrometer J&M TIDAS. For studying temperature dependence of the selective light reflection, a specially constructed cell was used compatible with the thermostatic cell "Mettler FP-80." The accuracy of such measurements was 0.1 °C. The spectra were obtained after annealing of the samples.

Photopolymerization

The samples were photopolymerized at different temperatures in the LC state. The study of the photo-optical properties of the blends was performed using a specially constructed optical set-up including mercury lamp DRSh-250. Light with λ=313 and 365 nm was separated using interference filters. To avoid heating of the sample because of the IR irradiation of the lamp, a water filter was used. To obtain the planar-parallel beam of light, a quartz lens was used. The light intensity was determined by intensity analyzer (gauge) Laser Mate-Q (Coherent).

Results and discussion

Phase behavior

According to the polarization microscopy study, both blends (DA/Cinsorb and DA/Hexsorb) are crystalline at room temperature and, after heating, first become LC and then transform into isotropic state (Table 1).

It is clearly seen from optical microscopy that the phase transition from crystalline to LC state is accompanied by an appearance of "oily strikes," which are typical for the cholesteric phase [19]. Besides, the selective light reflection above the melting point is observed. This also confirms cholesteric structure formation.

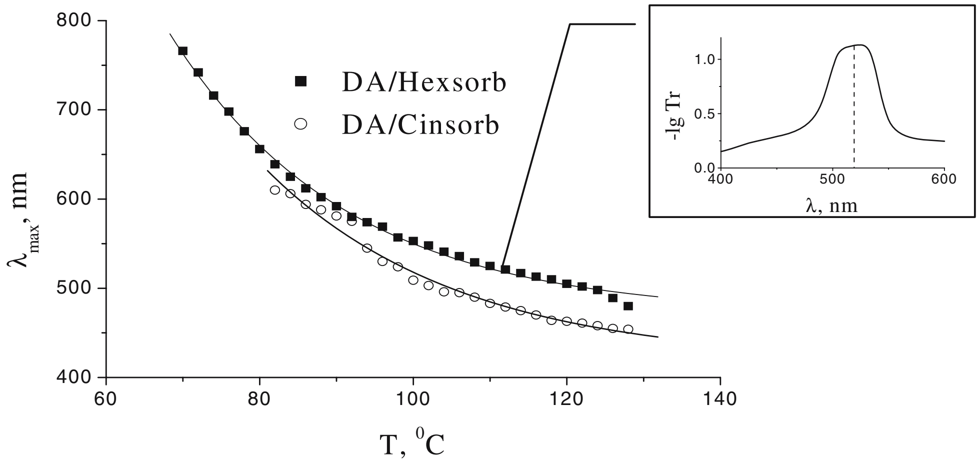
Temperature dependences of the selective light reflection maximum

It is well known that cholesterics reflect the circularly polarized light [20]. The directions of the polarization of the light and of the cholesteric helix are the same. This allows one to study the optical properties of cholesterics by measuring transmittance (Tr) of the thin films using a spectrometer. Thus, the transmittance minimum corresponds to the reflection maximum. In Fig. 3, the dependence of the logarithm of the transmittance of the right-handed circularly polarized light for the planarly oriented film of one of the blends as a function of the wavelength is

Table 1 Phase transition and optical properties of cholesteric blends

Blend	Phase transition temperatures, °C	λ_{max} at T=0.8 T_{cl}, nm
DA/Cinsorb	Cr 104–105 N* 129.3 I	469
DA/Hexsorb	Cr 105–107N* 128.8 I	545

Fig. 3 The temperature dependence of the wavelength maximum for blends DA/Cinsorb and DA/Hexsorb and the dependence of lgTr as a function of the wavelength for DA/Hexsorb (t=112 °C)



presented. This spectrum corresponds to almost complete reflection of the right-handed circularly polarized light.

Using the selective light reflection spectra obtained at different temperatures, the temperature dependences of the wavelength maximum of the selective light reflection were derived for both blends (Fig. 3).

The shift of the wavelength maximum into the long-wavelength region of the spectrum with the temperature decrease is observed. Probably, it is explained by an appearance of the smectic order elements during cooling of the sample. This effect was observed earlier [19] and was explained by increasing of the twisting constant of liquid crystal during the formation of layer structure elements.

Photopolymerization of cholesteric blends

During irradiation of the DA/Hexsorb and DA/Cinsorb samples with λ=365 nm, fast crosslinking is observed. During this process, the selective light reflection peak position is fixed. After irradiation, the films become insoluble in chloroform, while before that the blends were completely soluble in this solvent. Polarization microscopy shows that the texture of the samples doesn't change during irradiation.

During irradiation, the position of the selective light reflection peak changes. The kinetic curves obtained during photopolymerization are presented in Fig. 4. They can be divided into four portions. The first one (I) corresponds to the induction time, which is typical for the radical polymerization. During this time, the value of λ_{max} for the blend DA/Cinsorb doesn't change; however, in the case of the blend DA/Hexsorb, λ_{max} slightly changes during the first few seconds. This means that the helix pitch is almost constant and the structure is rather stable. During the second time period (II), the value of λ_{max} increases; in other words, the helix pitch increases. This probably can be explained by the decreasing in the order parameter because of the oligomer products formation, resulting in appearance of the helix defects and its untwisting. The third region (III) of the curve shows λ_{max} decreasing

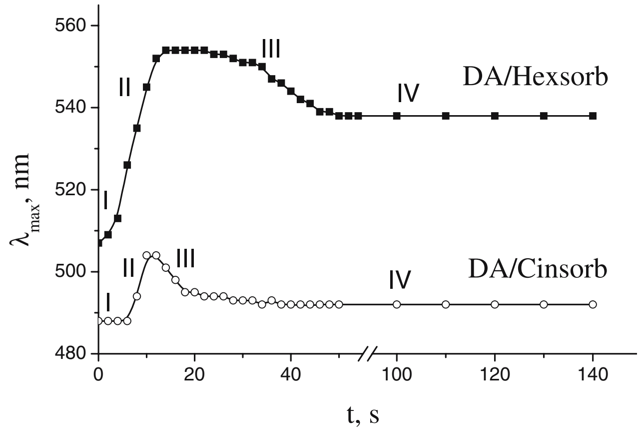


Fig. 4 The time dependence of the wavelength maximum for blends DA/Cinsorb and DA/Hexsorb; λ_{irr}=365 nm, T_{irr}=115 °C

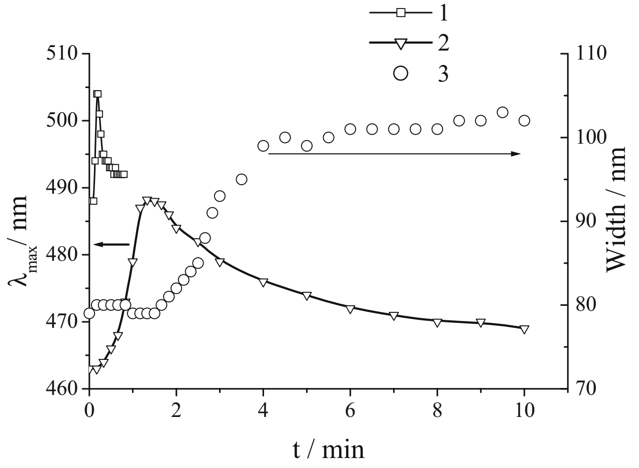


Fig. 5 The dependence of the wavelength maximum on the irradiation time for DA/Cinsorb blend with different photoinitiator concentration (1–2%, 2–0.5%) and the dependence of the selective light reflection peak width on the irradiation time (3–0.5% of photoinitiator); λ_{irr}=365 nm, T_{irr}=115 °C

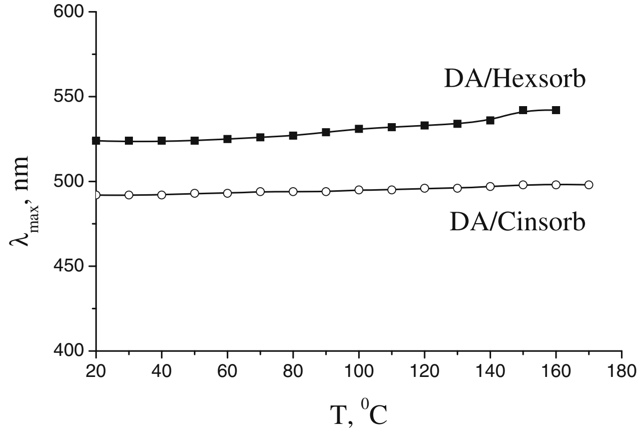


Fig. 6 The temperature dependence of the λ_{max} for blends DA/Cinsorb and DA/Hexsorb after irradiation; λ_{irr}=365 nm, T_{irr}=115 °C

pointing out the pitch decrease because of the network shrinkage [13]. Finally, in the fourth portion (IV) of the curve, the values of λ_{max} become constant again. This means that the helix pitch is fixed in the solid state and the helical supramolecular structure is preserved. Thus, these data confirm the stable network formation. It should be mentioned that the value of λ_{max} after irradiation differs from the initial one. This difference is small for DA/Cinsorb (less then 10 nm), while for DA/Hexsorb, $\Delta\lambda$= 30 nm. The time of helix shrinkage in region III for blend DA/Hexsorb is four times greater than for DA/Cinsorb.

The initiator concentration effect on kinetics of photo-crosslinking is shown in Fig. 5. The four-fold decrease of the initiator concentration results in increasing of the full reaction time from 40 s to 10 min. The increasing of the initiator concentration doesn't influence $\Delta\lambda$.

One of the most important characteristics of cholesterics is the selective light reflection peak width. We studied the change of this parameter during irradiation (Fig. 5). It was shown that the peak width increases, especially in portion III of the kinetic curve. This peak widening can probably be explained by the growth of the amount of the structural defects in the formed network as a result of the distortion of the helical structure of the sample during shrinkage.

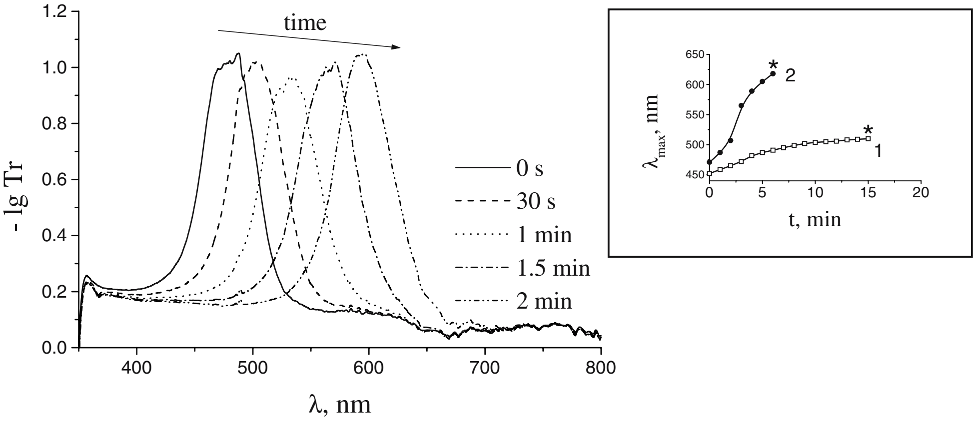
In Fig. 6, temperature dependences of the wavelength maximum of the selective light reflection for the cross-linked samples are presented. It is clearly seen that after irradiation there is almost no temperature dependence of λ_{max}, whereas before irradiation this dependence was obvious (Fig. 3). This means that during irradiation, a polymer network with fixed helix pitch was obtained. Thus, crosslinking leads to stabilization of optical properties up to decomposition temperature of the blend samples.

Helix pitch photoregulation due to photoisomerization of chiral photochromic dopant

During irradiation of the DA/Cinsorb sample with λ=313 nm E–Z isomerization of C=C double bond in dopant Cinsorb is observed, which results in the shift of the selective light reflection peak to the long-wavelength region of the spectrum after 2–3 min of irradiation (Fig. 7). During further irradiation (5 min), the selective light reflection peak degeneration takes place. This is the result of cholesteric helix deterioration, which is clearly seen in the polarizing microscope. Thus, it is impossible to fix the selective light reflection during irradiation with this wavelength. To solve this problem, we divided the experiment into two parts (Fig. 1). Firstly, the samples were irradiated with λ=313 nm for 2 min. This time is enough for Cinsorb E–Z isomerization. Afterwards, the sample was irradiated with λ=365 nm for 10 s. This results in network formation with planar texture and selective light reflection in the "green" region of the spectrum. For this system, the temperature dependence of the wavelength maximum of the selective light reflection was obtained. λ_{max} doesn't change with temperature, as it was shown previously, but before irradiation there was a strong dependence.

The influence of the irradiation light intensity was studied. The samples of DA/Cinsorb were irradiated with λ=313 nm using the different intensity of the UV-light. It is

Fig. 7 The dependence of lg Tr from the wavelength and the dependence of the wavelength maximum as a function of the irradiation time for DA/Cinsorb blend at different light intensities of the irradiation (1–I=0.22 mW/cm^2, 2–I=0.44 mW/cm^2, *asterisks* represent the deterioration of the selective light reflection peak); λ_{irr}=313 nm, T_{irr}=115 °C



seen (Fig. 7) that the two-fold increasing of the intensity leads to the decreasing of the complete peak deterioration time by approximately three times. The increase in the intensity results in the variation of the λ_{max} value, which can be fixed later by the photopolymerization process.

Conclusions

For the first time, the optical properties and cholesteric helix pitch changes during photopolymerization of the blends consisting of bifunctional nematogenic diacrylate monomer and chiral dopant were studied. The photocrosslinking kinetics was investigated in details and several stages of this process were discovered and described.

Optical properties of the blend containing chiral photochromic dopant capable of E–Z photoisomerization under UV irradiation with λ=313 nm were studied. The decreasing of the dopant helical twisting power during photoisomerization is observed. This leads to the helix untwisting and shift of the selective light reflection peak to the long-wavelength region of the spectrum. The possibility of photoregulation of optical properties of such blends with further fixation of structure by means of photocrosslinking during irradiation with λ=365 nm was demonstrated.

Acknowledgments This research was supported by the Russian Foundation of Fundamental Research (05-03-33193) and Federal Scientific Technical Program (contract no. 02.434.11.2025). A.B. gratefully acknowledges the Russian Science Support Foundation, the research fellowships provided by INTAS (reference no. 03-55-956).

References

1. Shibaev V, Freidzon Ya (1989) Cholesteric polymers with side chain mesogenic groups: structure, optical properties and intramolecular mobility. In: McArdle CB (ed) Side chain liquid crystal polymers. Blackie, Glasgow, p 260
2. Shibaev V, Bobrovsky A, Boiko N (2003) Prog Polym Sci 28:729
3. Bobrovsky A, Boiko N, Shibaev V (1998) Polym Sci Ser A 40:232
4. Bobrovsky A, Boiko N, Shibaev V, Springer J (2001) Liq Cryst 28:919
5. Yarmolenko S, Shepeleva L, Kutyulya L, Vashchenko V, Drushlyak T, Ponomarev O (1995) Zh Obshchey Khimii 65:145
6. Broer DJ, Boven J, Mol GN (1989) Makromol Chem 190:2255
7. Broer DJ, Henderickx I (1990) Macromolecules 23:2474
8. Broer DJ, Lub J, Mol GN (1995) Nature 378:467
9. Brehmer M, Lub J, Van de Witte P (1998) Adv Mater 10:1438
10. Stohr A, Strohriegl P (1998) Macromol Chem Phys 199:751
11. Binet C, Mitov M, Mauzac MJ (2001) Appl Phys 90:1730
12. Guillard H, Sixou P, Reboul L, Perichaud A (2001) Polymer 42:9753
13. Maxein G, Keller H, Novak BM, Zentel R (1998) Adv Mater 3:341
14. Ruslim C, Ichimura K (2001) Adv Mater 13:37
15. Vill V, Fischer F, Thiem J (1998) Z Naturforsch 43a:1119
16. Yoshioka T, Ogata T, Nonaka T, Moritsugu M, Kim S-N, Kurihara S (2005) Adv Mater 17:1226
17. Chen SH, Jin RJ, Katsis D, Mastrangelo JC, Papernov S, Schmid AW (2000) Liq Cryst 27:201
18. Lub J, Nijssen WPM, Wegh RT, De Francisco I, Ezquerro MP, Malo B (2005) Liq Cryst 32:1031
19. Chandrasekhar S (1994) Liquid crystals. Cambridge University Press, New York
20. Belyakov VA (1992) Diffraction optics of complex-structured periodic media. Springer, Berlin Heidelberg New York