Crown-Ether and Azobenzene-Containing Liquid Crystalline Polymers: An Influence of Macromolecular Architecture on Optical Properties and Photo-Orientation Processes

ALEXANDER RYABCHUN, ALEXEY BOBROVSKY, ALEXEY MEDVEDEV, VALERY SHIBAEV

Faculty of Chemistry, Moscow State University, Lenin Hills, Moscow 119991 Russia

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ABSTRACT: A series of novel crown ether-containing photochromic comb-shaped liquid crystalline polyacrylates with different macromolecular structure of side groups were synthesized and investigated. Phase behavior, optical and photo-optical properties of thin spin-coated films of these polymers were studied. A special attention was paid to a comparative study of the photo-orientation phenomena occurring in the polymer films under a polarized light action. It was shown that complex formation with the potassium ions results in the decrease in degree of the photoinduced order that can be used for the creation of new materials for sensor devices. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 625–633, 2011

KEYWORDS: azo polymers; azobenzene groups; complexation; crown ether; liquid-crystalline polymers (LCP); metal-polymer complexes; photochemistry; photochromism; photo-orientation

INTRODUCTION Starting from the discovery of crown ethers in 1960s and until now an active development of materials having features of these compounds takes place. Today crown ethers have found applications for metal ion concentrations, separation and purification, for isotope separations, as catalysts in reactions with participation of anions, for ion-selective sensors and membrane creation.[1–3] Sensor systems' construction of crown ether compounds conjugated with chromophores[4] and fluorophores[5] were described recently. For such substances, changes in absorbance or fluorescence spectra are observed under complexation. Up to now a large number of low molar mass crown ether-containing substances capable of liquid crystalline (LC) phase formation have been synthesized. Formation of complexes may lead to the appearance or disruption of supramolecular structures, such as columnar phases.[6,7] Nevertheless, only a few examples of LC polymers containing crown ether fragments are described in the literature. Mainly these are polymers having mesogens and crown ether groups incorporated in polymer backbone,[8,9] and side-chain homopolymers of acrylic or siloxane types.[10,11] Such polymers combining mesomorphic properties with metal complexation can be considered as "smart" materials. There are even fewer examples of photochromic LC systems based on crown ethers, although properties of amorphous photochromic derivatives, such as spiropyrans, triphenylmethanes, diarylethenes, and azobenzene having crown ether moieties are described quite well.[4,12–14] For example, a series of photochromic azobenzene–crown-containing compounds forming crystalline and nematic phases were presented.[14] It was found that UV-irradiation of these compound's films leads to an increase of ionic conductivity, but irradiation with the visible light has restored the initial level of conductivity. Recently, we have elaborated and described synthetic approaches for the synthesis of wide range of photochromic crown ether-containing LC homopolymers and copolymers based on azobenzenes.[15,16] It was shown that complexation of these compounds with metal ions results in a decrease of clearing temperature, and in some cases, formation of complexes leads to a transition into the amorphous state. In these papers, the kinetic features of photoisomerization of azobenzene moieties were studied in detail.

In this article, we have continued our work launched before[15,16] and have performed synthesis of a series of novel photochromic crown ether-containing polymers with different macromolecular structures. One of the main goals of this work is an investigation of a relation between molecular architecture of the synthesized polymers and photo-optical properties and phase behavior of these polymer materials.

We have synthesized three types of polymers with completely different position of the crown ether fragment with

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Additional Supporting Information may be found in the online version of this article. Correspondence to: A. Bobrovsky (E-mail: bbrvsky@yahoo.com)

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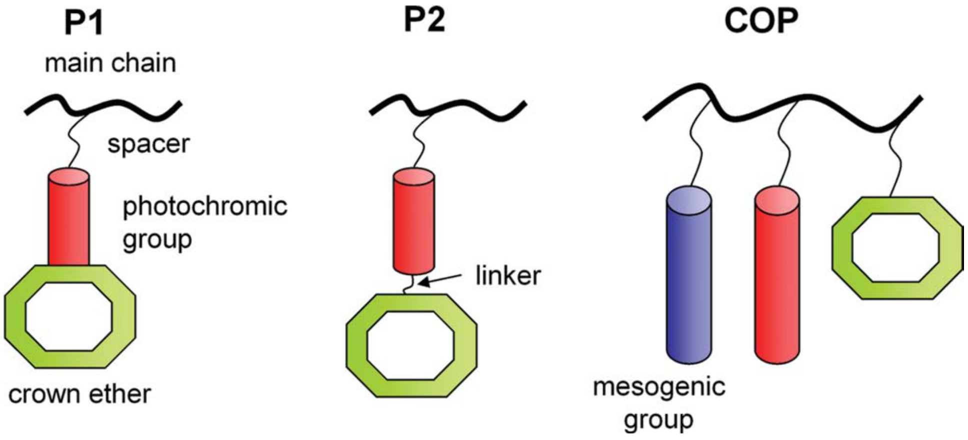
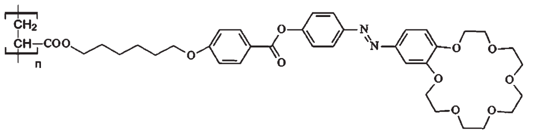


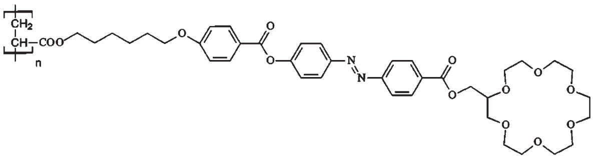
FIGURE 1 Schematic representation of photochromic crown ether-containing LC polymers.

respect to the azobenzene photochromic groups (Fig. 1). All synthesized polymers combine an ability of mesogenic groups to self-assemble (i.e., LC phase formation), an ability of photochromic groups to undergo an isomerization under the light irradiation changing their optical properties, and an ability of crown ether groups for complex formation.

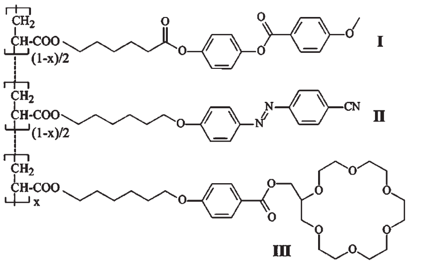
Chemical structures of synthesized polymers are presented below:



P1



P2



Cop5, Cop15
(x = 5, 15 mol%)

Homopolymer **P1** contains the crown ether fragment, which is directly connected with the photochromic group, whereas in homopolymer **P2**, the crown ether moieties and photochromes are linked through the short oxymethylene spacers. Copolymers **Cop5** and **Cop15** are ternary copolymers containing 5 and 15 mol % of nonphotochromic crown ether-containing side groups, respectively; photochromic and mesogenic side groups in copolymers were taken in equal proportions.

Azobenzene moieties were used as photochromic fragments in all synthesized polymers. It is well known that introduction of azobenzene groups in side-chain LC polymers allows one to obtain light-controllable polymer films and coatings, which can be used for optical data recording due to the photoinduced E–Z isomerization followed by co-operative photoorientation of all mesogenic side groups under the polarized light action.[17]

The crown ether fragment was selected as an ionophoric group because of several reasons. First of all, the crown ether-containing side group has a capability to form co-ordination bonds with metal ions that opens the interesting possibilities for obtaining metal-containing LC polymers. Secondly, a complexation can influence the photo-optical properties of multifunctional materials. A combination of these three functions in one and the same macromolecule allows one to obtain a novel type of photoswitchable material sensitive to the nonpolarized or polarized light and capable of complexation with metal ions that present a certain interest for a possible application of such systems as sensor materials.

Thus, the synthesized samples under investigation consisted of two groups of polymers including homopolymers **P1** and **P2** as well as ternary copolymers **Cop5** and **Cop15** consisting of the individual monomer units containing mesogenic nonphotochromic phenylmethoxybenzoate (**I**), photochromic azobenzene (**II**), and ionophoric crown ether groups (**III**).

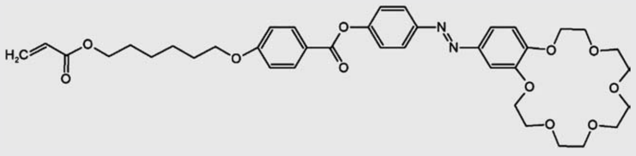
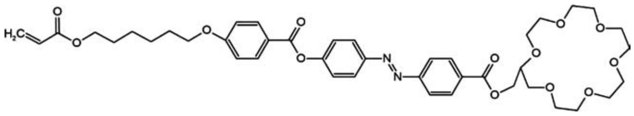
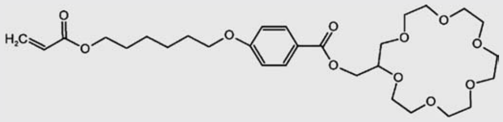
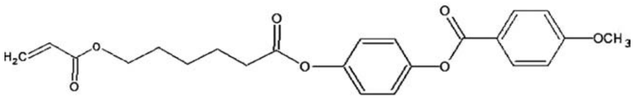
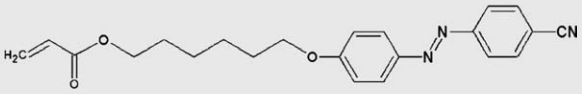
Elucidation of the correlation between the molecular architecture of these polymers and their mesomorphic, optical and photo-optical properties is the main goal of this work.

EXPERIMENTAL

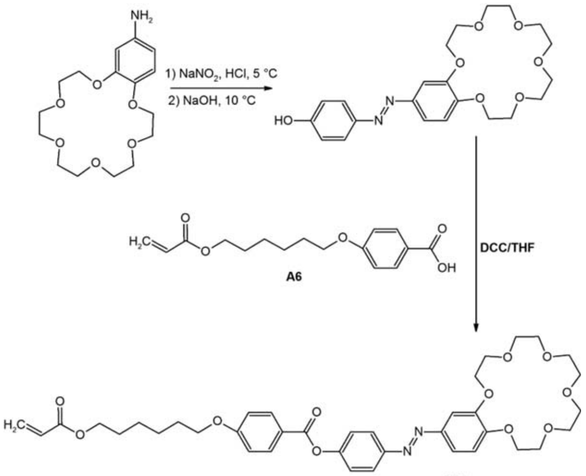
Monomers' Synthesis

Monomer **M1** was synthesized for the first time in this work. Monomers **M2–M5** were synthesized using methods described before (Supporting Information).[15,18,19] Table 1 shows the chemical structures of all synthesized monomers and their melting temperatures.

TABLE 1 Chemical Structures and Melting Temperatures of Crown Ether-Containing, Nematogenic and Photochromic Monomers

Chemical Structure	T_m (°C)	Reference
M1 	55	This paper
M2 	58	13
M3 	52	13
M4 	82	16
M5 	88	17

Synthesis of Monomer M1



M1

Monomer **M1** was synthesized using a two-step synthetic route. In the first step, an azobenzene dye was synthesized using standard azo-coupling with phenol in alkaline media (more detailed procedure is presented in Supporting Information).[20] In the second step, 0.35 g (1.2 mmol) of previously obtained 4-{[6-(acryloyloxy)hexyl]oxy}benzoic acid (A6) synthesized according to ref. 21 was mixed with 0.63 g (1.5 mmol) of azobenzene dye in nonaqueous Tetrahydrofuran (THF) in the presence of 0.03 g (0.25 mmol) of 4-dimethylaminopyridine. To the solution, 0.35 g (1.7 mmol) of *N,N′*-dicyclohexylcarbodiimide cooled by ice with water was added during 1.5 h. The reaction was completed after mixing at room temperature for 24 h. The precipitate of bicyclohexylurea was filtered, and THF was evaporated. The product was purified using column chromatography (silica gel, eluent—chlorophorm/methanol, 15:1). The yield was 0.46 g (55% from theory). The obtained monomer was a dark-orange powder with m.p. 55 °C.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, δ): 1.26–1.87 (m, 8H, CH_2), 3.55–3.85 (m, 12H, CH_2O), 3.97 (m, 4H, CH_2CH_2O), 4.25 (m, 4H, CH_2CH_2O), 4.05 (t, 2H, CH_2O), 4.17 (t, 2H, CH_2O), 5.81 (dd, 1H, $CH_2{=}CH$-*trans*), 6.4 (dd, 1H, $CH_2{=}CH$-*cis*), 6.12 (dd, 1H, $CH_2{=}CH$—), 6.98 (d, 3H, Ar), 7.33 (d, 2H, Ar), 7.6 (d, 2H, Ar, *ortho* to —OOC—), 7.97 (d, 2H, Ar), 8.15 (d, 2H, Ar, *ortho* to —COO—). ^{13}C NMR and MS are presented in Supporting Information.

Polymers' Synthesis

Homopolymers and copolymers were synthesized by radical polymerization of the corresponding monomers in dry benzene. The reaction was performed in the sealed ampoules in argon atmosphere during 100 h at 60 °C in the presence of AIBN (1–2% to monomers mass). For the purification from the low-molar mass admixture, the polymers were washed with boiling methanol for a long time. Polymers were dried in vacuum at 100 °C. Molecular masses of the synthesized polymers were determined by GPC using a "Knauer"

TABLE 2 Yields, Molecular Mass Characteristics, and Phase Transition Temperatures of the Synthesized Polymers

Polymer	Yield (%)	M_w (kDa)	M_w/M_n	Phase Transitions
P1	28	10.3	1.7	g 24 N 103 I
P2	58	5.6	1.5	g 11 N 74 I
Cop0[a]	65	7.9	1.5	g 24 N 120 I
Cop5	53	9.8	1.7	g 21 N 111 I
Cop15	51	8.4	1.6	g 17 N 63 I

[a] Double copolymer without crown ether side groups.

chromatograph (UV-detector; columns "LC-100" with the sorbent 1000 Å; solvent—THF (1 mL/min, 25 °C, PS-standard).

Molecular masses of homopolymers and copolymers (M_w) were between ~6000 and ~10,000. Such low values of molecular masses can be explained by the chain transfer reaction to N=N bond, as was shown in a number of papers[19,22,23] for the diverse polymers based on azobenzene-containing monomers.

^{1}H NMR spectra were measured on "Bruker Avance-400" with frequency of 400 MHz; ^{13}C NMR spectra were measured on "Bruker AC200" with frequency of 200 MHz; chemical shifts were determined using TMS as standard. MS were measured on "Finnigan LCQ" with electrospray ionization of MeOH solution.

Textural observations and phase transition temperature determinations were performed using "Polam-R112" polarizing optical microscope equipped with "Mettler FP-86" hot stage. Temperatures and enthalpies of phase transitions were measured using a "Mettler TA-4000" differential scanning calorimeter with heating (cooling) rates of 10 K/min; sample weights were 5–10 mg.

Polymers films for photo-optical investigations were prepared by spin coating method from chlorophorm solutions. This method allows one to obtain thin homogeneous amorphous polymer films.

Complexes of polymers with potassium perchlorate were prepared as follows. Solutions of polymers in dry THF were added to solution of potassium perchlorate in dry acetonitrile. After slow evaporation of the solvents, the obtained complexes were dried in vacuum at 100 °C. In all cases, the amount of potassium salt was equimolar to the crown ether groups' content.

Electronic absorbance spectra of the spin-coated polymer films and dilute solutions were recorded on a UNICAM UV-500 spectrometer. Photo-optical investigations were performed using a specially designed setup including a diode laser KLM-473/h-150 with wavelength 473 nm. Light intensity as measured using a "LaserMate-Q" (coherent) intensity meter is ~2.0 W/cm^2. Degree of chromophore orientation was measured by a J&M (Tidas) spectrometer. For this purpose, polarized absorbance was measured with an angle step of 10° using Polarizer Control Unit (Owis).

Dichroism values D were calculated by the following Equation (1):

$$D = (A_{\parallel} - A_{\perp})/(A_{\parallel} + A_{\perp})$$

in which $A_{\parallel}$ and $A_{\perp}$ are absorbances along and perpendicular of chromophore orientations, respectively.

RESULTS AND DISCUSSION

Synthesis and Phase Behavior of Polymers

All synthesized polymers display a nematic LC phase that is confirmed by the formation of schlieren and marbled textures and low enthalpies of isotropization (0.7–1.1 J/g).

Polymers' yields, their molecular mass characteristics, and phase transition temperatures are presented in Table 2.

As was shown before, the copolymer containing only azobenzene and phenylbenzoate groups (1:1) obtained by copolymerization of monomers **M4** and **M5** is characterized by a nematic phase with clearing temperature of about 120 °C.[24] Introduction of crown ether groups as side chains causes a decrease in clearing temperatures due to their low anisometry.

Spectral Properties of Polymer Films and Influence of Complexation on Absorbance Spectra

Fig. 2 shows the absorbance spectra of thin films of homopolymers and copolymers. As is seen from the figure, homopolymer **P1** and both copolymers are characterized by an absorbance peak with maximum around 360–370 nm corresponding to a π–π* electronic transition, whereas this peak for homopolymer **P2** is shifted to the short wavelength spectral region with respect to the other polymers due to the presence of the electron-withdrawing carboxylic group. Absorbance peaks of copolymers are practically coinciding because they have an identical photochromic fragment. Polymer **P1** absorbs light at longer wavelength due to the strong

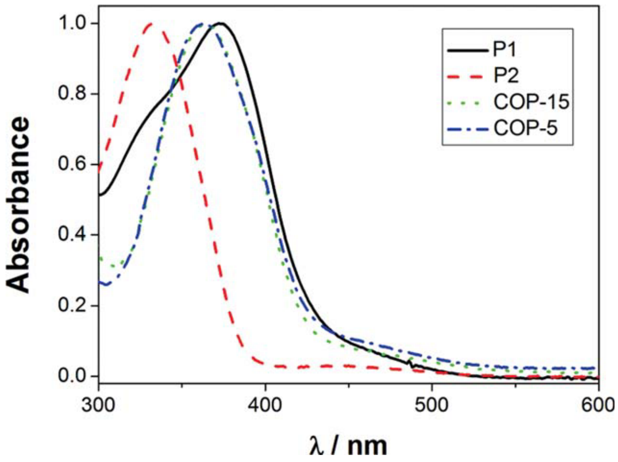


FIGURE 2 Normalized absorbance spectra of photochromic crown ether-containing homopolymers and copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

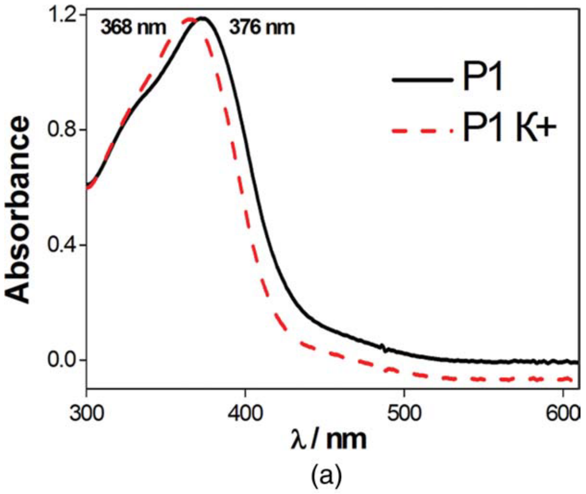


FIGURE 3 Absorbance spectra of the homopolymers **P1** (a), and **P2** films (b) before and after complexation with $KClO_4$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

influence of electron donor oxymethylene groups of the crown ether fragment directly connected with the chromophore. It is well known that the position of the absorbance maximum of azobenzene derivatives depends on types of substituents connected with chromophores.[25]

It is noteworthy that spectra of polymers (for fresh and annealed films) and spectra of dilute polymer solutions are very similar. On the other hand, it is well known that the films of azobenzene with low molar mass and polymer substances are characterized by the formation of J- and H-aggregates, which usually appear after annealing.[26,27] Aggregation processes are always accompanied by significant spectral changes. However, for crown ether-containing homopolymers synthesized in this work, we did not find any spectral changes after annealing at temperatures above their glass transitions. This probably can be explained by the absence of any aggregation processes due to the presence of the bulky crown ether fragments sterically preventing an interaction of the chromophoric moieties in the homopolymers.

Now let us consider how complexation with metal ions influences the spectral features of thin polymers films (Fig. 3). For all polymers, except **P1**, coordination with potassium ions has no effect on either peak position or value of absorbance. Complexation of **P1** films with potassium perchlorate results in a hypsochromic shift of about 8 nm [Fig. 3(a)]. The spectral shift is related to electron density displacement in conjugated electron systems, including azobenzene chromophores and oxygen atoms of crown ether ring, after coordination with positively charged ions.

Introduction of a potassium cation in crown ether “cavity” draws off electron density from the oxygen atoms and, thus, shifts the absorbance peak to the short-wavelength spectral range. A similar effect was demonstrated for the low molar mass crown ether-containing dyes.[13,28]

Photo-orientation Process in Thin Films of the Homopolymers

Irradiation of thin polymer films by blue polarized laser light (473 nm) causes the photoinduced orientation of the side groups in a direction perpendicular to the polarization direction. This process is accompanied by the growth of linear dichroism (eq 1 and Fig. 4). Light action on the previously annealed film induces lower values of dichroism. It can be explained by the formation of a multidomain LC structure. Each separated domain has a definite orientation of side groups, but domains are randomly oriented and the film has no preferred optical axis (dichroism value before irradiation is equal to zero). On the other hand, the ordered LC structure prohibits photo-orientation of the side groups. It should be noted that independently of the thermal prehistory, the dichroism values and orientation degree remain unchanged under a prolonged annealing at temperatures higher than the glass transition temperature.

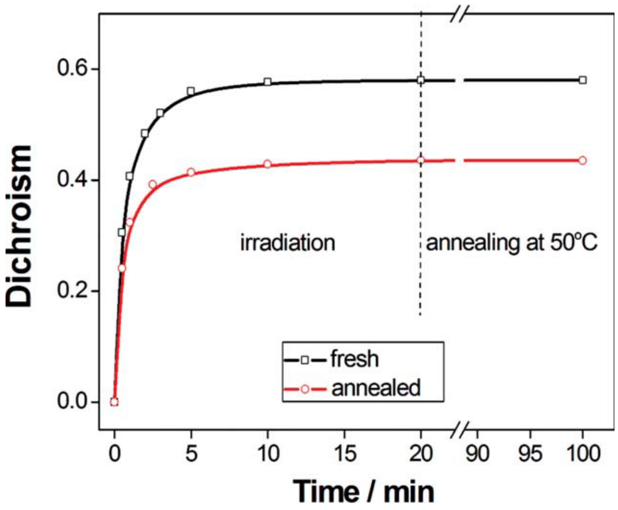


FIGURE 4 Dichroism growth kinetics during the polarized light irradiation of fresh and annealed films of the homopolymer **P1**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

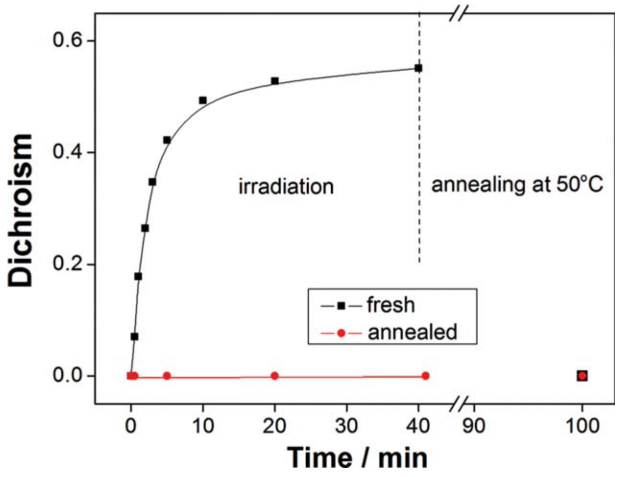
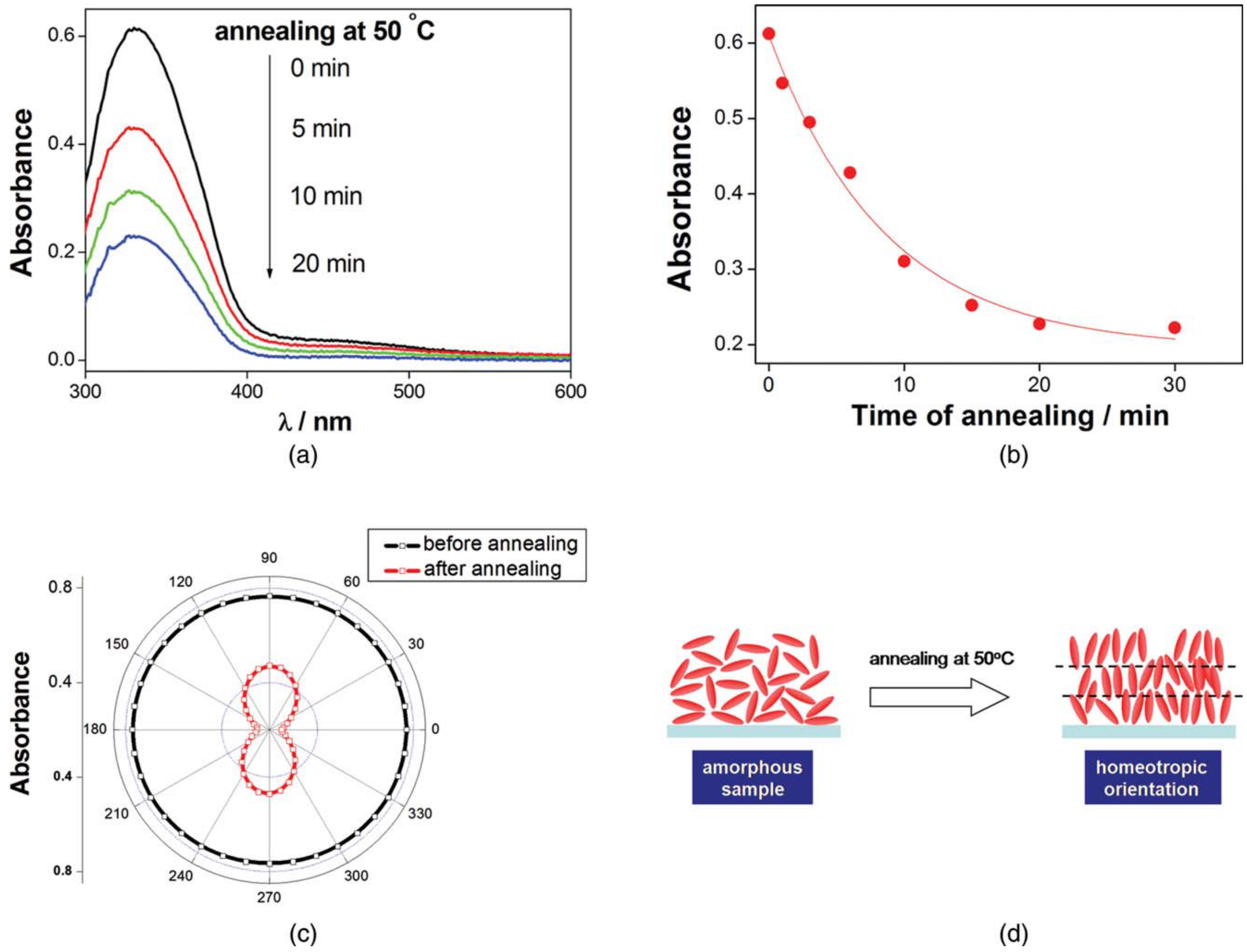


FIGURE 5 Dichroism growth kinetics during polarized light irradiation of the fresh and annealed films of homopolymer **P2**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polarized light irradiation of **P2** films also results in the photo-orientation phenomenon (Fig. 5). Maximum values of dichroism for both homopolymers, **P1** and **P2**, are almost the same. But for the polymer **P2** films, the rate of the dichroism growth is about five times lower than for **P1**. The calculated rate constants, assuming first-order kinetics, are $6.9 \times 10^{-2}\,s^{-1}$ (**P1**) and $1.3 \times 10^{-2}\,s^{-1}$ (**P2**). A difference in the rates of dichroism growth is explained by the different absorbance at 473 nm for homopolymers (Fig. 2).

In contrast to **P1**, annealing of irradiated **P2** films completely disrupts the side groups' orientation (Fig. 5). Moreover, no photo-orientation phenomenon was found in the previously annealed films. During the annealing, a significant decrease in absorbance was found [Fig. 6(a,b)], which can be associated with thermally induced homeotropic alignment of the chromophores. A similar effect was already observed for smectogenic azobenzene-containing copolymers.[29] To experimentally confirm this assumption, we have performed polarized light absorbance measurements of the samples placed



(a) (b)

(c) (d)

FIGURE 6 (a) Spectral changes of **P2** film under annealing; (b) kinetics of absorbance value changes at wavelength corresponding to π–π^* electron transition of azobenzene groups (333 nm) in **P2** film; (c) polar diagrams of polarized light absorbance measured with angle of 45° between film normal and detecting light; (d) schematic representation of homeotropic orientation formation in **P2** films under annealing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

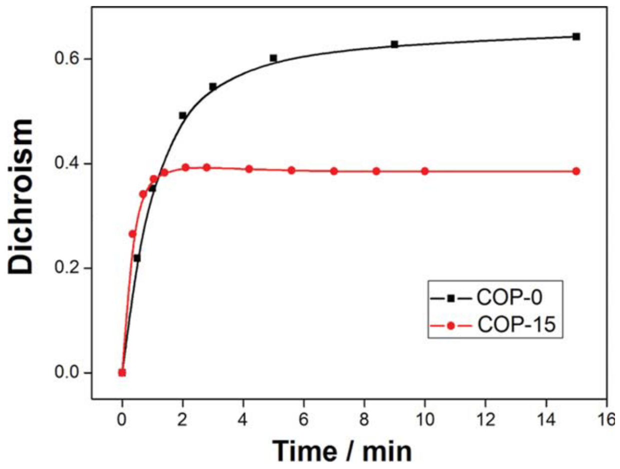


FIGURE 7 Dichroism growth kinetics during the polarized light irradiation in the amorphous films of copolymer **Cop15** and "model" copolymer **Cop0** without crown ether groups and having the same nematogenic and azobenzene side groups.[22] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 45° with respect to light axis. Such geometry allows one to estimate the degree of chromophore orientation in the direction along the normal to the film. Figure 6c shows the polar diagram of the **P2** film before and after annealing at 50 °C during 30 min. In the fresh films no anisotropy of absorbance was found, whereas annealing induces a noticeable value of dichroism, indicating out-of-plane orientation of the chromophores as schematically drawn in Figure 6d.

As was shown previously,[29] a homeotropic alignment in polyacrylates having similar chromophores is provoked by smectic phase formation. Our preliminary X-ray investigations reveal the presence of small-angle reflections corresponing to a distance of about 47 Å, that confirms formation of smectic order fluctuations in homopolymer **P2**. More detailed structural studies are currently in progress to distinguish the formation of a low-temperature smectic phase and the presence of cybotactic smectic fluctuations. Careful polarizing optical microscopy observations did not show any changes of the marble nematic texture to focal-conic or fan-shaped textures typical of the smectic phase.

Photo-orientation Processes in Thin Films of Ternary Copolymers

Let us consider photo-orientation processes in the films of the ternary copolymers. It is interesting to note that the rate of photo-orientation in the copolymer **Cop15** films is higher than that in double copolymer **Cop0** without crown ether groups and having the same nematogenic and azobenzene side groups.[26] This difference can be explained by the lower glass transition temperature of the copolymer having crown ether moieties (Fig. 7). However, it is noteworthy that the maximum achievable value of dichroism for **Cop15** is much lower. Such a difference is associated with the presence of the bulky crown ether fragments reducing the anisometry of the side groups and, consequently, the degree of uniaxial order.

An Influence of Complex Formation on Orientation Degree of Irradiated Films of Polymers

We have supposed that all synthesized polymers can be used as materials for the creation of sensor devices sensitive to the metal ions. To verify this assumption, a thin amorphous film of the homopolymer **P1** was irradiated by the polarized light (473 nm) during 10 min [steady state; maximum dichroism $D_1 = 0.6$, curve 1 in Fig. 8(a)]. Then, the irradiated

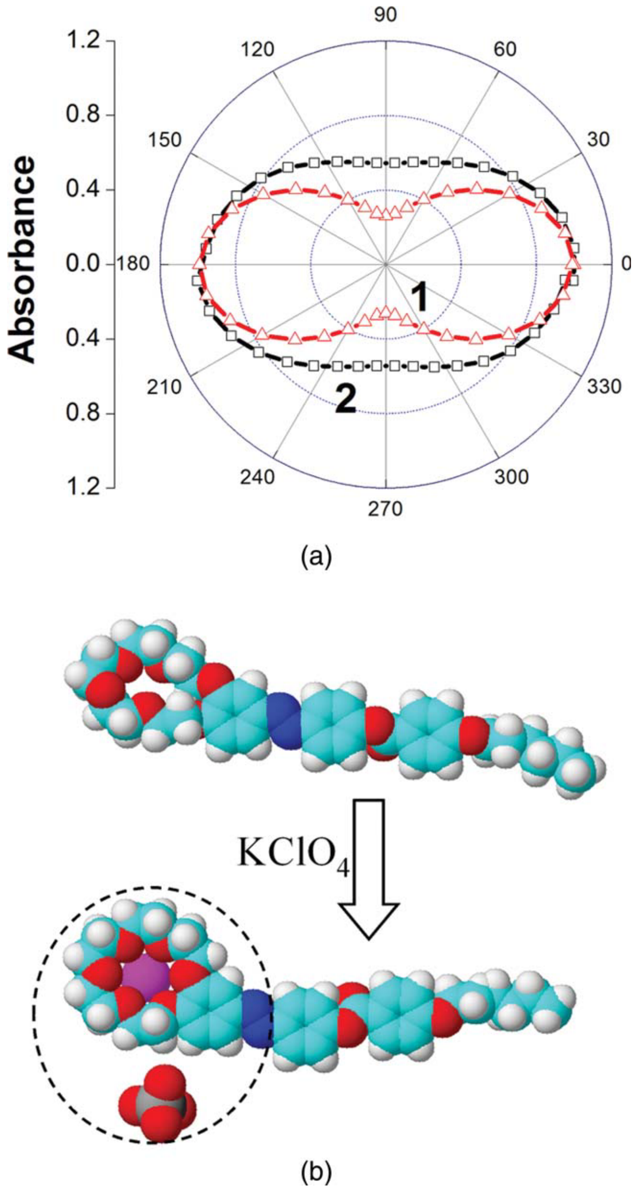


FIGURE 8 (a) Polar diagrams of the polarized light absorbace of **P1** film just after photo-orientation by light action (curve 1), and after complexation with potassium perchlorate in water (curve 2); (b) changes of crown ether-containing group anisometry under complex formation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

film was immersed for 1 h in $\sim 10^{-3}$ M aqueous potassium perchlorate. After this procedure, the dichroism value decreased by half ($D_2 = 0.3$, curve 2 in Fig. 8a). It should be stressed that the absorbance spectrum was also changed namely, the peak position has been shifted to the short-wavelenth spectral region that is associated with complex formation, as discussed above. As for low-molar mass crown ether-containing liquid crystals,[30] complexation reduces the conformational mobility of the crown ether fragment, that is, the latter becomes more rigid (Fig. 8b). Besides, the bulky perchlorate counter ion coordinates with positively charged potassium cation embedded in crown ether ring due to electrostatic attraction. Both factors significantly decrease the anisometry of the side group as a whole and reduce uniaxial photoinduced order and the value of dichroism (Fig. 8b).

CONCLUSIONS

A number of novel crown ether-containing photochromic LC polymers having different macromolecular architecture was synthesized. It was shown that the location of crown ether fragments with respect to the photochromic fragments influences not only the phase behavior and spectral properties but also the kinetics of photo-orientation processes in thin polymer films. Introduction of crown ether fragments as separated nonphotochromic side groups decreases the degree of the photoinduced orientational order. For the first time, the possibility of using photo-optically oriented films of crown ether-containing polymers as sensors for metal ions was demonstrated. It was also shown that complexation of polymers by immersion in water solution of salts results in noticeable decrease in dichroism values of the films. This effect is promising for the creation of polymer-based sensor films and coatings.

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