Photochromic liquid-crystalline copolymers containing crown ether groups

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An approach was developed for the synthesis of new multifunctional photosensitive liquidcrystalline copolymers of the acryl series containing azobenzene, ionophoric, and mesogenic groups in the same macromolecule. The phase behavior of the copolymers was studied. Most of these copolymers were demonstrated to form nematic mesophases. An increase in the concentration of crown-containing groups to 26 mol.% leads to amorphization of the copolymers. The influence of complexation of the crown ether groups of the copolymers with potassium perchlorate on the mesomorphic properties of the systems was investigated. A comparative study of the photooptical properties of the copolymers in solution and thin films was performed.

Key words: azobenzene, crown ether fragments, complexation properties, photochromic properties, multifunctional comb-shaped liquid-crystalline copolymers.

In connection with the huge interest in the design of nanomaterials, our recent attention has been drawn to the problems of the synthesis of multifunctional polymers and polymer composites consisting of different-type nanometer-sized components bearing various functions. These are liquid-crystalline (LC) copolymers containing mesogenic side groups (they serve as models of the molecular structures of low-molecular-weight liquid crystals, which are, in turn, typical nanosized particles), as well as any other substituents on a nanosize scale bearing a particular functionality. These can be fragments of dyes or photochromic compounds, chiral optically active and nonlinear-optical groups, biologically active fragments, luminescent and fluorescent groups, and electrically and magnetically active fragments.^{1,2}

The schematic representation of a hypothetical macromolecule of a comb-shaped LC copolymer containing mesogenic, chiral, photochromic, and reactive functional groups is shown in Fig. 1. Mesogenic groups that are quantitatively dominant in this system and determine the ability of the polymer to undergo self-organization and form an LC phase are the key structural elements of these macromolecules. Any of these molecular groups (taken either individually or together with other groups) impart the desired functional properties, such as photochromic, electrical, optically active, *etc.*, to the final LC polymers at will of researchers.

Since such copolymers are generally synthesized by the copolymerization of monofunctional nanosized monomers, the synthesis of these compounds is based on the commonly used bottom-up method of the design of nanomaterials.^{3–5} A similar principle of the self-assembly is



Fig. 1. Schematic representation of the macromolecule of a multifunctional comb-shaped copolymer containing mesogenic (1), chiral (2), photochromic (3), and functional groups (4) covalently bound to the main chain (5) by aliphatic spacers (6).

observed in the living nature, where complex (multifunctional) protein macromolecules are assembled from 20 simple amino acids. The primary structure of protein molecules determines the further more complex processes giving rise to the secondary and ternary structure.

In the case under consideration, complex structurally organized and functionally integrated multifunctional polymer LC systems are assembled from nanostructures (monomers and functional fragments) with a size of tens of nanometers. The tendency of mesogenic groups to undergo self-organization and form mesophases is the driving force for the formation of such systems. The presence of functional groups having different structures and different physicochemical properties has also a substantial effect on the properties of LC polymers by imparting new properties to these self-organized anisotropic systems. This is finally responsible for their particular performance char-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2332–2242, December, 2007. 1066-5285/07/5612-2414 © 2007 Springer Science+Business Media, Inc. acteristics and fields of application. These functional LC polymers are often referred to the so-called smart materials, which meet the requirements imposed on modern engineering devices. Such materials should consume the minimum amount of energy, have a small size and weight, a high efficiency, and can be able to be easily incorporated into technological lines and systems.^{6,7}

Among a wide range of smart materials, such as conducting and electroluminescent polymers, polymer catalysts, and biomimetic and fluorescent polymer systems, particular attention is given to photochromic materials and polymer sensors.

It is well known that photosensitive systems play a considerable role in the living nature, to be more precise, in the photosynthesis processes. In addition, various photosensitive materials have long been in use as integral parts of various industrial and domestic apparatus and devices.

Photochromic materials light-controlled at the molecular and supramolecular levels have attracted attention of researchers working in various areas, such as synthetic chemists, photochemists, and photophysicists.^{8,9} Due to the progress in the nanoindustry of materials, a new field of investigation, the nanophotonics, has been vigorously developed.

In continuation of our studies on the photooptical properties of photochromic LC polymers, $^{11-13}$ we developed an approach to the synthesis of new multifunctional comb-shaped LC polymers bearing simultaneously three types of functional fragments in the side chains, such as mesogenic groups, photochromic azobenzene-containing groups, and functional crown-containing fragments capable of forming complexes with metal ions (Fig. 2).

It is well known that the introduction of azobenzenecontaining groups into comb-shaped LC polymers allows the design of light-controlled polymer films and coatings, which can be used with advantage for the optical information recording and storage due to the photoinduced E-Z-isomerization reactions of azobenzene groups followed by the cooperative photoorientation of the side groups under polarized light. In the present study, we report a new approach to the synthesis of photochromic LC polymers, which are characterized by the presence of both mesogenic groups providing the formation of a mesophase and the simultaneous presence of photochromic and ionophoric groups in a single monomeric unit capable of exerting a mutual effect on the photochromic and complexation properties of the polymers. Selected possible combinations of mesogenic, photochromic, and ionophoric side groups are presented in Fig. 2. However, we restricted ourselves to the consideration of solely binary copolymers (see Fig. 2, a, b).

The choice of the crown-containing fragment as an ionophoric fragment was determined primarily by its high activity with respect to the formation of coordination bonds with metal ions, as well as by the ability of crown-containing molecules to undergo self-assembly in solution and in the solid phase giving rise to complex supramolecular structures.¹⁰

It should be noted that data on the synthesis and properties of crown-containing comb-shaped LC polymers are available in the literature. For example, the study of combshaped LC copolymers of the acryl series containing 15-crown-5 groups¹⁴ showed that the complexation of macrocyclic fragments of the copolymer with metal ions can be used as an efficient tool for controlling the mesomorphic properties of polymers.

Investigations of low-molecular-weight photosensitive crown-containing systems are of great interest. Photochromic fragments can substantially influence the complexation properties of the crown ether group^{15,16} and, on the contrary, the complexation with metal salts can change the photooptical properties of such systems (the kinetics, the mechanism and the type of photochemical reactions, and the absorption and fluorescence spectra).^{15,17,18} For example, the Z isomer of azobenzene-containing crown ether was demonstrated¹⁵ to form stable complexes with alkali metal ions (Na⁺, K⁺, Rb⁺, and Cs⁺), whereas the E isomer of this compound cannot form such complexes. In addition, a decrease in the rate of the thermal $Z \rightarrow E$



Fig. 2. Schematic representation of the macromolecules of binary (a, b) and ternary (c) copolymers consisting of mesogenic (I), photochhromic (2), and crown-containing fragments (3).



isomerization upon complexation with metals was documented,¹⁵ a change in the isomerization rate being substantially dependent on the type of the metal ion. To further develop procedures for the synthesis of different-type crown-containing systems and improve our knowledge and approaches to the synthesis of multifunctional systems, we synthesized a new type of photochromic ionophoric (crown-containing) LC polymers. The structures of the macromolecules are schematically presented in Fig. 2, a, b. The structural formulas of the resulting copolymers of the acryl series **P-1**-*X*—**P-4**-*X* are shown below.

We studied the phase behavior and the photooptical properties of the new copolymers and investigated the influence of complexation of the copolymers with potassium perchlorate on their mesomorphic and photooptical properties.

Experimental

The TLC analysis was carried out on Merck TLC Silica Gel $60F_{254}$ plates. The column chromatography was performed on Fluka Silica Gel for Column Chromatography, 60.

Synthesis of monomers. The approach to the synthesis of new monomers of the acryl series containing crown ether (monomer M-1) or photosensitive groups (monomers M-2, M-3, and M-4) is illustrated in Schemes 1–4, respectively. The nematogenic monomer 4-[6-(acryloyloxy)hexanoyloxy]phenyl-4-methoxybenzoate (M-5) was synthesized according to the procedure described earlier.¹⁹

Scheme 1



ABA is 4-[6-(acryloyloxy)hexyloxy]benzoic acid, DCC is dicyclohexylcarbodiimide.

Scheme 2



i. 2-(Hydroxymethyl)-18-crown-6.

1,4,7,10,13,16-Hexaoxacyclooctadecan-2-ylmethyl 4-[6-(acryloyloxy)hexyloxy]benzoate (M-1). Dicyclohexylcarbodiimide (0.29 g, 1.4 mmol) was added to a solution of ABA (0.29 g, 1 mmol),²⁰ 2-(hydroxymethyl)-18-crown-6 (Merck) (0.35 g, 0.0012 mol), and 4-dimethylaminopyridine (0.02 g) in anhy-

drous THF (30 mL) cooled with ice water for 1.5 h. The reaction mixture was kept at ~20 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the precipitate of dicyclohexylurea that formed was filtered off, and THF was evaporated. The product was purified by col-



i. 2-(Hydroxymethyl)-18-crown-6.

Scheme 4



umn chromatography (toluene—ethyl acetate, 1 : 1, as the eluent). The yield was 0.34 g (60%). IR, v/cm⁻¹: 2936, 2856 (CH₂); 1720 (C=O); 1632 (CH₂=CH—); 1600, 1512 (C=C, Ar); 1256 (C–O–C, ArOR); 1168 (C–O–C). ¹H NMR (CDCl₃), δ : 1.26–1.87 (m, 8 H, 4 CH₂); 3.38–3.75 (m, 21 H, CH, 10 CH₂O); 4.05–4.52 (m, 8 H, 4 CH₂O); 5.77 and 6.35 (both d, 1 H each, CH₂=CH—, *J* = 10.7 Hz, *J* = 17.3 Hz); 6.14 (dd, 1 H, CH₂=CH—, *J* = 10.4 Hz, *J* = 17.8 Hz); 6.91 (d, 2 H, Ar, *J* = 9.3 Hz); 7.9 (d, 2 H, Ar, *J* = 8.9 Hz).

1,4,7,10,13,16-Hexaoxacyclooctadecan-2-ylmethyl 4-[(E)-4-(2-acryloyloxyethyl)(ethyl)aminophenyldiazenyl]benzoate (M-2). Azo compound 1 was synthesized by the azo-coupling reaction with amine in an acidic medium analogously to the procedure described earlier.²¹ In the second step, triethylamine (2 mL) was added to a solution of azo compound 1 (3.1 g, 0.01 mol) in anhydrous THF (100 mL). Then acryloyl chloride (1.35 g, 0.015 mol) was added dropwise to the reaction solution cooled with ice water for 1 h. The progress of the reaction was monitored by TLC. Within 12 h after the beginning of the reaction, the precipitate of triethylamine hydrochloride that formed was filtered off, and THF was evaporated. The compound was purified by column chromatography (chloroform-methanol, 10:1, as the eluent). The yield of compound 2 was 2 g (55%). Compound M-2 was synthesized by mixing compound 2 (0.37 g, 1 mol), 2-(hydroxymethyl)-18-crown-6 (Merck) (0.35 g, 1.2 mmol), and 4-dimethylaminopyridine (0.02 g) in anhydrous THF (20 mL). Then DCC (0.29 g, 1.4 mmol) was added to the reaction solution cooled with ice water for 1.5 h. The reaction mixture was kept at ~20 °C for 24 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the precipitate of dicyclohexylurea that formed was filtered off, and THF was evaporated. The product was purified by column chromatography (chloroform-methanol, 7:1, as the eluent). The yield was 0.29 g (45%). IR, v/cm^{-1} : 2934, 2853 (CH₂); 1714, 1691 (C=O); 1627 (CH₂=CH-); 1595, 1506 (C=C, Ar); 1378 (C–N); 1130 (C–O–C). ¹H NMR (CDCl₃), δ: 1.15 (t, 3 H, Me, J = 7.2 Hz); 3.32–3.75 (m, 25 H, CH, 12 CH₂O); 4.21-4.60 (m, 6 H, 3 CH₂); 5.78 and 6.37 (both d, 1 H each, $CH_2=CH-$, J = 10.5 Hz, J = 16.6 Hz); 6.12 (dd, 1 H, $CH_2=CH_-$, J = 10.7 Hz, J = 17.5 Hz); 6.93 (d, 2 H, Ar, J = 9.3; 7.75 (d, 4 H, Ar, J = 9.1 Hz); 8.18 (d, 2 H, Ar, J = 8.9 Hz).

4-[4-(1,4,7,10,13,16-Hexaoxacyclooctadecan-2-ylmethoxycarbonyl)phenyldiazenylphenyl 4-(6-acryloyloxyhexyloxy)]**benzoate** (M-3). In the first step, azo dye 3 was synthesized by the azo-coupling reaction of *p*-aminobenzoic acid with phenol in an alkaline medium.²¹ In the second step, the hydroxy group of azo dye 3 was protected with chloroethoxyformate according to a standard procedure.²² The third step involved the formation of acid chloride 5 by the reaction of compound 4 with thionyl chloride.²² In the fourth step, triethylamine (2 mL) was added to a solution of 2-hydroxymethyl-18-crown-6 (0.29 g, 1 mmol) in anhydrous THF (30 mL). Then acid chloride 5 (0.4 g, 1.2 mmol) was added dropwise to the reaction solution cooled with ice water for 1 h. The progress of the reaction was monitored by TLC. Within 12 h after the beginning of the reaction, the precipitate of triethylamine hydrochloride that formed was filtered off, and THF was evaporated. The compound was purified by column chromatography (chloroform as the eluent). The yield of compound 6 was 0.4 g (70%).

In the fifth step, the hydroxy group was deprotected with ammonia to prepare phenol $6.^{22}$

In the last step, monomer M-3 was synthesized. For this purpose, ABA (0.09 g, 0.0003 mol), compound 7 (0.2 g, 0.4 mmol), and 4-dimethylaminopyridine (0.01 g) were dissolved in anhydrous THF (15 mL). Then DCC (0.09 g, 0.42 mmol) was added to the solution cooled with ice water for 1.5 h. The reaction mixture was kept at ~20 °C for 24 h. The progress of the reaction was monitored by TLC. The precipitate of dicyclohexylurea that formed in the course of the reaction was filtered off, and THF was evaporated. The product was purified by column chromatography (toluene-ethyl acetate, 1 : 1, as the eluent). The yield was 0.11 g (65%). IR, v/cm^{-1} : 2926, 2861 (CH₂); 1700 (C=O); 1610 (CH₂=CH-); 1587, 1490 (C=C, Ar); 1263 (C-O-C, ArOR); 1118 (C-O-C). ¹H NMR (CDCl₃), δ: 1.26–1.87 (m, 8 H, 4 CH₂); 3.4–3.75 (m, 21 H, CH, 10 CH₂O); 4.00-4.52 (m, 8 H, 4 CH₂O); 5.78 and 6.37 (both d, 1 H each, $CH_2 = CH_{-}$, J = 11.0 Hz, J = 17.8 Hz); 6.15 (dd, 1 H, $CH_2 = CH_-$, J = 10.0 Hz, J = 17.4 Hz); 7.01 (d, 2 H, Ar, J = 9.6 Hz); 7.48 (d, 2 H, Ar, J = 9.2 Hz); 7.72 (d, 2 H, Ar, J = 8.9 Hz); 8.15 (d, 6 H, Ar, J = 9.0 Hz).

Methyl 4-[4-(2-acryloyloxyethyl)(ethyl)aminophenyldiazenyl]benzoate (M-4). Compound 2 (0.5 g, 1.4 mmol), anhydrous methanol (0.1 mL, 2 mmol), and 4-dimethylaminopyridine (0.03 g) were mixed in anhydrous THF (20 mL). Then DCC (0.4 g, 2 mmol) was added to the solution cooled with ice water for 1.5 h. The reaction mixture was kept at ~20 °C for 24 h. The progress of the reaction was monitored by column chromatography. Then the precipitate of dicyclohexylurea that formed was filtered off and THF was evaporated. The product was purified by column chromatography (chloroform-methanol, 10:1, as the eluent). The yield was 0.29 g (55%). IR, v/cm^{-1} : 2931, 2849 (CH₂); 1718, 1697 (C=O); 1630 (CH₂=CH-); 1598, 1510 (C=C, Ar); 1381 (C-N); 1142 (C-O-C). ¹H NMR (CDCl₃), δ : 1.15 (t, 3 H, Me, J = 7.2 Hz); 3.35 (m, 4 H, 2 CH₂); 3.87 (c, 3 H, OMe); 4.26 (t, 2 H, CH₂, J = 5.9 Hz); 5.78 and 6.37 (both d, 1 H each, CH₂=CH-, J =10.5 Hz, J = 16.6 Hz); 6.12 (dd, 1 H, CH₂=C<u>H</u>-, J = 11.1 Hz, J = 17.5 Hz); 6.93 (d, 2 H, Ar, J = 9.3 Hz); 7.75 (d, 4 H, Ar, J = 9.5); 8.18 (d, 2 H, Ar, J = 9.0 Hz).

Synthesis of polymers (general procedure). All copolymers were prepared by the radical copolymerization of monomers M-1, M-2, M-3, or M-4 with M-5 initiated by azoisobutyric acid dinitrile (2 wt.%). To purify the copolymers from low-molecular-weight compounds and oligomeric products, the samples were refluxed in methanol for 6 h. The compositions of the copolymers were determined by UV spectroscopy. Since the copolymerization was carried out to high degrees of conversion, the difference between the compositions of the final copolymers and the starting monomeric mixtures was at most 4%.

Complexes of copolymers with potassium perchlorate (general procedure). The copolymers were dissolved in anhydrous THF. Then a solution of potassium perchlorate in anhydrous acetonitrile was added to the solution of the copolymer. The resulting solution was concentrated with slight heating. The complexes thus prepared were kept *in vacuo* at 80 °C to remove the residual solvent.

It is known that the stability constant of the complex of 18-crown-6 ether with potassium perchlorate varies in the range of 10^6-10^8 L mol⁻¹ depending on the polarity of the solvent. Hence, the equilibrium in the reversible reaction (Scheme 5) is almost completely shifted to the right. The high stability constant is associated with the good match between the atomic

radius of the potassium ion and the size of the cavity of the 18-membered ring in 18-crown-6 ether (2.66 and 2.6–3.2 Å, respectively²³). Consequently, the complexes of the copolymers with potassium perchlorate are formed in virtually quantitative yields. In all cases, potassium perchlorate was introduced into the polymers in an amount equivalent to the content of the crown ether groups in the polymers.

Scheme 5



Instrumental investigation. The phase behavior of the copolvmers was studied with a LOMO P-112 polarizing microscope equipped with a Mettler TA-400 thermal analyzer. The photochemical properties were studied on the specially designed apparatus equipped with a DRSh-250 high-pressure mercury lamp. The light at a wavelength of 436 nm was obtained with an interference filter. The light intensity was 0.5 mW cm⁻² (determined with the use of a LaserMate-Q laser power meter (Coherent)). The spectroscopic measurements were carried out in the UV-Vis region on a Tidas (J&M) spectrometer. Films of the copolymers for photooptical measurements were prepared by the spin-coating method. The molecular weights of the copolymers were determined by gel permeation chromatography on a Knauer chromatograph equipped with an UV detector and LC-100 columns packed with the sorbent 100, 500, and 1000 Å with the use of THF as the solvent (1 mL min⁻¹) at 25 °C and using the polystyrene standard.

Results and Discussion

Synthesis of crown-containing monomers and polymers. In all cases, photochromic and crown-containing copolymers were synthesized starting from the same acryl monomer M-5. The synthesis of the latter has been described earlier.¹⁹ The homopolymer of this monomer forms two types of nematic mesophases¹³ exhibiting the rather high clearing (isotropization) temperature $T_{\rm I}$ (~100 °C). Hence, we used compound M-5 as the major nematic component of all the copolymers synthesized in the present study.



The newly synthesized crown-containing monomers with different structures (monomers M-1, M-2, and M-3) were used as the second component. The first monomer (M-1) contains solely the crown ether group. More structurally complex monomer M-2 bears the photochromic azobenzene fragment linked to the macrocyclic ionophoric 18-crown-6 group by the ether bond. Monomer M-3 is more extended and contains, along with the photochromic and crown ether fragments, an additional benzene ring, resulting in an additional increase in the anisometry of this monomer. All crown-containing compounds M-1-M-3 were synthesized as described in the Experimental section and were chromatographically purified. The molecular structures of these compounds were established by NMR spectroscopy. The ¹H NMR spectrum of one of the monomers, M-3, is shown in Fig. 3.

Photochromic monomer **M-4** was synthesized as a model compound. This compound is an analog of **M-2** and contains the methoxy group instead of the terminal crown ether fragment.

The copolymers were synthesized by the radical copolymerization of monomers M-1-M-4 with the nematogenic monomer. Their compositions were determined by UV spectroscopy. For copolymers P-1, P-2, P-3, and P-4, the content of the photochromic groups was 14, 26, 28, and 28 mol.%, respectively. For copolymers P-2-14 and P-3-28, the molecular weights estimated by gel permeation chromatography are 6400 and 3000, respectively (based on the polystyrene standard). This corresponds to the degree of polymerization of ~10-15. Such a low degree of polymerization is attributed to the chain-transfer reaction to the N=N double bond of the photochromic monomers.

Phase behavior of copolymers. Let us initially consider the phase behavior of the simplest photochromic copolymer **P-4**-28 containing the nematic methoxyphenylbenzoate group and the photochromic azobenzene fragments in the side chains. The acryl homopolymer of the first of the above-mentioned composites is known to form two types of nematic mesophases, *viz.*, the low-temperature two-dimensionally ordered mesophase (the nematic modification of TDK) and the usual nematic mesophase (N) with the melting point $T \sim 100$ °C. The introduction of 28% azobenzene units into this polymer does not disturb



Fig. 3. ¹H NMR spectrum of monomer M-3.

the character of the nematic packing of the side groups but leads to a lowering of the isotropization temperature to 81 °C. Such a substantial lowering of the isotropization temperature of the copolymer compared to $T_{\rm I}$ of the homopolymer (100 °C) can be attributed to both a decrease in the molecular weight of the copolymer (which is associated with the chain-transfer reaction to the N=N double bond in the synthesis of the copolymer) and the difference in the side-chain length.

The phase behavior of the copolymers is presented below (copolymers P-2-26 and P-2-26 (K⁺) are amorphous due to which the phase transition does not occur); N is the nematic phase and I is the isotropic melt; the phase transition temperatures are given in degrees Centigrade.

Copolymer	Phase behavior
P-1 -10	N 93 I
P-1 -10 (K ⁺)	N 81 I
P-2 -14	N 84—86 I
P-2 -14 (K ⁺)	N 75-77 I
P-3 -28	N 102 I
P-3 -28 (K ⁺)	N 83 I
P-4 -28	N 81 I

The consideration of crown-containing copolymers **P-1**-10, **P-2**-26, and **P-3**-28 revealed the characteristic features of their phase behavior. First, the presence of bulky crown-containing groups in the copolymers leads to a substantial decrease in their thermal stability. The introduction of 10% crown-containing units leads already to a sharp lowering of the isotropization temperature (see data for **P-1**-10). A complication of the structure of the crown-containing side group by including the azobenzene group in the monomeric unit leads to an even more substantial distortion of the LC structure. Thus, in the presence of 14% of crown-containing groups, the isotropication.

pization temperature of copolymer P-2-26 decreases to 84-85 °C; the further increase in the content of these groups to 26% causes the complete amorphization of copolymer P-2-26.

At the same time, an increase in the anisometry and rigidity of the crown-containing mesogenic unit as a result of incorporation of three benzene rings (P-3-28) diminishes the disordering influence of the bulky crown-containing terminal fragment, resulting in the rise of the isotropization temperature to $102 \,^{\circ}$ C.

The investigation of the complexes of the copolymers with potassium perchlorate showed that all samples are characterized by the lowering of the isotropization temperature compared to the corresponding starting samples (see above).

Therefore, in spite of the fact that the complexation of potassium perchlorate with the crown ether fragment leads to the encapsulation of K^+ in the macrocycle, the presence of the ClO_4^- counterion causes a substantial decrease in the anisometry of the crown-containing fragment (Fig. 4), resulting in a decrease in thermal stability of the mesophase.



Fig. 4. Molecular model of the monomeric crown-containing unit of copolymer **P-1**-10 and its complex with potassium perchlorate.

Photooptical properties of copolymers and their complexes. The copolymers contain azobenzene groups, which can undergo the reversible light-induced E-Z isomerization (Scheme 6). The forward reaction $(E\rightarrow Z)$ is induced by light at the wavelength corresponding to the $\pi-\pi^*$ transition of the dye. Due to instability of the Z isomer of the azo compound, the reverse reaction proceeds spontaneously but its rate can be increased under light irradiation at the wavelength corresponding to the $n-\pi^*$ transition or upon heating.

Scheme 6



The changes in the absorption spectrum of **P-2**-26 (a solution in chloroform) under irradiation at $\lambda = 436$ nm for 60 s are shown in Fig. 5.

It can easily be seen that the intensity of the peak at 450 nm rapidly decreases under irradiation. This peak corresponds to absorption of the *E* isomer. In addition, a slight increase in the intensity of the peak shoulder at 360 nm is observed. This is associated with an increase in the content of the *Z* isomer of the azobenzene group.²⁴



Fig. 5. Changes in the absorption of P-2-26 (solution in chloroform, the concentration is ~10⁻⁵ mol L⁻¹) under light irradiation at $\lambda = 436$ nm for 60 s. The changes in the intensity of absorption during light irradiation at $\lambda = 450$ nm are shown in the inset.

Let us consider the characteristic features of the photoisomerization of the photochromic groups of the copolymers in solution. The changes in the intensity of absorption caused by irradiation of copolymer **P-2**-26 (curve 1) in chloroform are presented in Fig. 6. The intensity of the peak corresponding to the E isomer reaches the minimum value within ~10 min after the beginning of irradiation and then remains unchanged. The irradiation of the complex of copolymer P-2-26 with potassium perchlorate, **P-2**-26 (K^+), (curve 2) causes virtually no changes in the absorption of the E isomer. This is evidence that the $E \rightarrow Z$ isomerization does not proceed. The factors responsible for the observed suppression of isomerization are considered below. It should be noted that the spectra of the copolymers remain unchanged upon complexation (Fig. 7); the position of the absorption maximum corresponding to the $\pi - \pi^*$ transition of the azo group remains unchanged.

This phenomenon was observed also in films of the complex of copolymer **P-2**-26 with potassium perchlorate. Figure 8 shows that the changes in the absorption in thin films of copolymer **P-2**-26 (curve 2) and of the com-



Fig. 6. Changes in the intensity of absorption at a wavelength of 450 nm after irradiation of solutions of the copolymers in chloroform at $\lambda = 436$ nm for 10 min: **P-2**-26 (*I*) and complex **P-2**-26 (K⁺) (2).



Fig. 7. Normalized absorption spectra of copolymer P-2-26 (1) in chloroform and of its complex P-2-26 (K^+) (2).



Fig. 8. A decrease in the intensity of absorption at a wavelength of 450 nm under irradiation at $\lambda = 436$ nm in films of copolymers **P-4**-28 (1), **P-2**-26 (2), and **P-2**-26 (K⁺) (3).

plex of **P-2**-26 with potassium perchlorate (curve 3) under light irradiation at a wavelength of 436 nm. It can easily be seen that the absorption of **P-2**-26 (K⁺) corresponding to the *E* isomer of the azo compound remains virtually unchanged.

To explain this phenomenon, it is necessary to consider the E-Z isomerization. The reaction can proceed by two mechanisms, the so-called inversion and rotation mechanisms^{25a} (Scheme 7).

The substantial difference in the mechanisms is that the isomerization by the rotation mechanism proceeds through the bipolar transition state and is accompanied by a rather large change in the volume, whereas the hybridization of the nitrogen atom by the inversion mechanisms does not require a considerable free volume. Electron-releasing and -withdrawing substituents in azobenzene stabilize the bipolar transition state in the rotation mechanism due to which it becomes energetically more favorable.^{25b} Since the photochromic group in copolymer **P-2**-26 contains the electron-releasing and -withdrawing terminal substituents, two equilibrium forms can exist (Scheme 8).

Form II is stabilized by the *push-pull* effect due to the presence of an electron-releasing substituent (D) at one end and an electron-withdrawing substituent (A) at the other end. The character of the N=N double bond becomes less pronounced due to the electron density redistribution. Hence, the $E \rightarrow Z$ and $Z \rightarrow E$ isomerizations can proceed by the rotation mechanism through mesomeric form II as a result of rotation of the substituents about the bond between the nitrogen atoms.

Mesomeric form II is formed both in the case of the E and Z isomers. Apparently, the perchlorate ion additionally stabilizes this transition state by an ionic interaction. Since the Z isomer of the azo compound is energetically less favorable than the E isomer, this stabilization of the transition state leads to a substantial increase in the reaction rate of the $Z \rightarrow E$ isomerization, and, consequently, to the changes in the kinetics of the $E \rightarrow Z$ isomerization under irradiation. Thus, the rate of the reverse thermal transition from the Z to E isomer is so high that the irradiation does not cause changes in the ratio between the concentrations of the Z and E isomers.

To confirm these conclusions, we performed a special experiment. The results of this experiment are presented in Fig. 9. A solution of model copolymer **P-4**-28 in chloroform was irradiated with light at a wavelength of 436 nm for 10 min until the photostationary state was attained. Then a solution of potassium perchlorate, in which the amount of the salt was equivalent to the amount of the photochromic groups in the copolymer, was added dropwise to the sample with continuous irradiation. In this case, the concentration of the *E* isomer of the photochromic





Scheme 8



mic fragment rapidly increased, resulting in an increase in the absorption up to almost the initial value within 12 s. In other words, this indicates that, in the presence of potassium perchlorate, the ratio between the concentrations of two isomeric forms of the azo fragment in copolymer **P-4**-28 is shifted toward the larger percentage of the *E* isomer due to a high rate of the reverse thermal $Z \rightarrow E$ isomerization.

To analyze the influence of the bulky crown ether group on the kinetics of photoisomerization in amorphized films of the copolymers, we compared the kinetics of isomerization of **P-4**-28 containing the terminal methoxy group and its crown ether analog **P-2**-26. We investigated the kinetics of the reverse thermal $Z \rightarrow E$ process. The isomerization of azobenzene derivatives is known to be the first-order reaction. In the general form, the kinetic equation for this reaction can be written as follows: $n/n_0 = \exp(-kt)$, where *n* and n_0 are the running and initial concentrations of the *Z* isomer, respectively, *k* is the rate constant, and *t* is the time. The n/n_0 ratio was deter-



Fig. 9. Photooptical behavior of a solution of copolymer **P-4**-28 in chloroform in the presence of potassium perchlorate under light irradiation at $\lambda = 436$ nm; the instant of addition of KClO₄ is indicated by an arrow.

mined from the spectroscopic data as $(A - A_{\infty})/(A_0 - A_{\infty})$, where A is the absorption measured at the instant t, A_0 and A_{∞} is the absorption at t = 0 and $t \rightarrow \infty$, respectively.²⁶ The rate constant k can be determined from the parameters of the plot in the coordinates $(A - A_{\infty})/(A_0 - A_{\infty})$ and t. The kinetic curves characterizing the $Z \rightarrow E$ isomerization for copolymers **P-2**-26 and **P-4**-28 are shown in Fig. 10. The calculated rate constants have very similar values $(5.6 \cdot 10^{-3}$ and $5.8 \cdot 10^{-3} \text{ s}^{-1}$, respectively). Consequently, the kinetics of the isomerization reaction in films is independent of the volume of the terminal substituent in the photochromic group.

To conclude, we developed procedures for the synthesis of new crown-containing photochromic acryl monomers bearing the azobenzene fragments and synthesized binary multifunctional copolymers containing ionophoric and photochromic groups starting from these monomers. The phase behavior and the photooptical properties of the copolymers were studied. The complexation of potassium perchlorate with the crown ether groups of the copolymers was found to lead to the lowering of the clearing temperature of the LC phase up to the complete amorphization of the samples. This phenomenon is, apparently, associated with a decrease in the anisometry of the side crown-containing groups of the copolymers.

The characteristic features and the kinetics of the photooptical behavior of the newly synthesized copolymers was studied in detail. It was found that the complex of the copolymer with potassium perchlorate **P-2**-26 (K⁺) does not undergo $E \rightarrow Z$ photoisomerization under irradiation in solution and thin films. This can be attributed to a substantial increase in the rate of the reverse $Z \rightarrow E$ isomerization in the presence of potassium perchlorate. The investigation of the kinetics of isomerization in films of the copolymers showed that the reaction rate is independent of the bulkiness of the terminal fragment of azobenzene groups of the copolymers.



Fig. 10. Kinetic curve for the $Z \rightarrow E$ isomerization in the coordinates $(A - A_{\infty})/(A_0 - A_{\infty})$ and the time for films of **P-4**-28 (*I*) and **P-2**-26 (*2*). The rate constants *k* for the reactions calculated from the parameters of the curves are $5.3 \cdot 10^{-3}$ and $5.7 \cdot 10^{-3}$ for **P-4**-28 and **P-2**-26, respectively.

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