A Novel Generation of Photoactive Comb-Shaped Polyamides for the Photoalignment of Liquid Crystals

Alexander Ryabchun,¹ Alexey Bobrovsky,¹ Sung-Ho Chun,² Valery Shibaev¹

¹Chemistry Department of Moscow State University, Moscow 119991, Russia ²LG Chem, Ltd 104-1, Moonji-dong, Yuseong-gu, Daejeon 305-380, Korea Correspondence to: A. Ryabchun (E-mail: ryabchunmsu@gmail.com)

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ABSTRACT: A new approach to the synthesis of photoactive comb-shaped homo- and copolyamides containing azobenzene, cinnamate, and coumarin side groups for photoalignment of liquid crystals was elaborated. Photooptical properties and photoorientational ability of these polymers with respect to liquid crystals were studied. It was shown that polarized UV irradiation of all spin-coated polyamides leads to orientation of liquid crystalline molecules deposited on the polyamide thin films. The synthesized polymers containing cinnamate and coumarin side groups as well as azobenzene-containing cyanoand nitro-substituted polymers demonstrated good orientation ability in relation to liquid crystals displaying photoinduced planar orientation with high dichroism values within the range

INTRODUCTION The creation of orientational (alignment) materials for liquid crystalline (LC) displays remains one of the more important problems of the current LC display technology. Today, there are many ways of orienting of liquid crystal molecules, such as rubbed polyimide coating, obliquely deposited metal coatings, surfactants, surface gratings, etc.¹⁻³ To obtain a planar uniaxial orientation of liquid crystals in displays, the rubbed polyimide layers are usually used; however, they have a number of drawbacks are usually used. These disadvantages include electrostatic charges generation, fine dust particles formation, etc.⁴ Because of the rapid development of the LC display manufacturing, the polyimide coatings (rubbing technology) no longer satisfy the needs of the industry. Hence, a large number of research groups and laboratories have focused their attention on the study and development of some new materials and methods for LC alignment.^{5,6} One of the most promising areas in this field involves developing of new photoalignment layers (or photocontrollable "command surfaces"). Usually, these layers represent low-molar-mass molecules adsorbed on the surface or chemically connected to it.⁷⁻¹⁰ In addition, some polymers of different structures (linear, comb-shaped, grafted on the of 0.68–0.72. Contrary to the above-mentioned polyamides, azobenzene-containing fluorosubstituted polymers induced a homeotropic orientation of liquid crystals. It was shown that the synthesized photoactive polyamides can be considered as promising photoalignment materials for application in display technology, photonics, and other "smart" optical devices. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4031–4041

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surface) containing photosensitive groups, such as azobenzene, cinnamate, or coumarin, $^{6,11-13}$ are also very often used for the same aims. The operating principle of these materials is based on the noncontact (as opposed to mechanical rubbing of polyimide coatings) activation of the aligning layers by irradiation with polarized UV light. Irradiation induces angular-selective photochemical reactions and a small anisotropy of surface free energy at the surface of photoalignment layer, which causes orientation of the LC molecules in a certain direction.

There are a number of photoreactions and photoprocesses that can be used for the LC-photoalignment: (1) photoorientation and photoselection (caused, for example, by E/Z-isomerization), which is typical for azobenzene^{14–17} and cinnamate¹⁸ derivatives; (2) angular selective [2+2]-photocycloaddition (dimerization) (stilbene,¹⁹ cinnamate,²⁰ and coumarin²¹ derivatives, benzylidenephtalimidine, and benzylideneacetophenone²²); (3) photodegradation,^{23,24} allowing to create orientation by means of degradation products.

A distinctive feature of photoalignment layers is the ability to control some orientation parameters: the anchoring

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FIGURE 1 Schemes of orientation of side photoactive groups under the UV irradiation and alignment of liquid crystals on the photoalignment layer: (a) initial unoriented layer of polymer; (b) oriented layer of polymer; and (c) alignment of low-molar-mass liquid crystal deposited on the polymer layer.

energy, pretilt angle, and alignment direction. In the case of reversible photoreactions (i.e., E-Z isomerization of azobenzenes), the aligning direction can be changed repeatedly by irradiation with UV light via variation of polarization plane direction.^{4,9,25}

Figure 1 schematically illustrates the principle of liquid crystals alignment by means of photochromic azobenzenecontaining polymer. Polarized light induces uniaxial orientation of photochromic side groups, which are aligned in the direction perpendicular to the polarization plane of the light as is shown in Figure 1(a,b). Such irradiated layer can work as "command surface" and orient nematic LC-director (**n**) of low-molar-mass liquid crystal in the same direction [Fig. 1(c)].

Over the past few decades, new photoalignment materials and methods have been actively developed. Many laboratories engaged in LC science have begun to apply the photoalignment layers for orientation of LC molecules; there is even a commercial example of such uses by Sharp, Corp.²⁶

The commonly used polymers as photoalignment materials are the comb-shaped polymers with photochromic side groups: polyacrylates, polymethacrylates, polyvinyl esters, etc. These polymers are not the best as photoaligning materials, as far as they are partially soluble in liquid crystals, they have low glass transition temperatures, and as a result, they do not keep the LC orientation.⁹ A growing interest in new LC-photoalignment substances with advanced properties motivated us to develop a novel type of such materials with high thermostability. In this respect, one of such types of polymers close to polyimides (normally used for LC-alignment by rubbing) is polyamides because of ability to form intra- and intermolecular hydrogen bonds stabilizing the material.

This study is the first attempt to synthesize photosensitive polyamides (polyaspartic acid amides). The proposed method is based on the polymer-analogous ring-opening reaction of poly(succinimide) (PSI) with aliphatic amines (Fig. 2). A similar approach was described in Refs. ²⁷ and ²⁸. For the synthesis of comb-shaped polyamides with side aliphatic chains, the authors of these articles modified PSI by various aliphatic amines to produce amphiphilic biodegradable derivatives of polyaspartic acid for medical applications. We have changed the chemistry of the reactants by using instead of



FIGURE 2 The main idea of the synthesis of the side chain photoactive polyamides by polymer analogous reaction of PSI with photoactive amines.

usual aliphatic amines the amines with photoactive groups chemically attached to the opposite tails of them. The basic idea of this method is shown in Figure 2. Thus, as a result of the described reaction, photoactive comb-shaped polyamides were obtained. It is noteworthy that this reaction occurs with ring opening in α position and in β one (see Fig. 2). Typically, the product of β -opening predominates than the α opening²⁹; for clarity sake, Figure 2 shows only the monomer unit for β -opening reaction.

As photoactive side groups, azobenzene, cinnamate, and coumarin derivatives were used. The chemical structures of terminal substituents (see "-R" in Fig. 2) of the synthesized side-chain polyamides are listed in Table 1. Among them several azobenzene-containing polyamides with different substituents in benzene ring (-CN, -NO₂, and -F), two coumarin derivatives differ by the position of a linkage to an aliphatic spacer, and a number of cinnamate derivatives with various substituents in benzene ring (-H, -F, and -OCH₃) were obtained. It should be stressed that, on the basis of the proposed synthetic approach, a successful attempt to get copolyamide was also realized. Thus, this study can be roughly subdivided into two parts devoted to the (i) synthesis and (ii) study of LC photoalignment properties of polyamides. The synthetic section contains the description of photochromic amines synthesis, obtaining of PSI, and its chemical modification by photoactive amines.

EXPERIMENTAL

Synthesis of Low-Molar-Mass Compounds

Amines containing azobenzene and coumarin terminal fragments were synthesized according to scheme given in Figure 3.

Synthesis of tert-Butyl-N-(3-brompropyl)-carbamate (1)

To a cooled (ice bath) and stirred suspension of (3-bromopropyl)amine (2.50 mol), di-*tert*-butyl dicarbonate (Boc₂O) (2.50 mol), and dichloromethane (1.25 L), triethylamine (3.00 mol) was added dropwise over 3 h. After stirring for 1 day, dichloromethane was added and the solution was washed with 1*M* KHSO₄, water, and brine, and the mixture was dried over anhydrous Na₂SO₄ and concentrated in vacuum. Compound (**1**) was isolated as clear light-yellow oil, with the yield ~94%.

TABLE 1 Structural Formulas of the Photoactive Side Groups of the Synthesized Polyamides and Copolyamide

Abbreviated Name of Polyamide	Spacer Length, n	Structural Formulas of Photoactive Side Groups
P6Cin	6	
P6CinF	6	
P6CinOMe	6	
P3Coum-6	3	
P3Coum-7	3	
P3AzoCN	3	
P3AzoNO ₂	3	$-0-\sqrt{\bigcirc}-N=N-\sqrt{\bigcirc}-NO_2$
P3AzoCN2	3	
P3AzoF	3	-0- $N=N F$
P3AzoF2	3	-0-
Copolyamide	6	-o-()-N=N-()-CN; ~30 mol %
	6	NH−C; ~70 mol %





FIGURE 3 Scheme of synthesis of the aliphatic amines with terminal azobenzene and coumarin fragments.

General Procedure of (3-i) Synthesis

4.2 mmol *tert*-buthyl-*N*-(3-brompropyl)-carbamate (1), 3.8 mmol (2-i) (the azobenzene derivatives was synthesized according to standard approach of azo-coupling reactions, see Supporting Information) and 6 mmol of anhydrous potassium carbonate were placed into the round-bottom flask. Then, 20–30 mL of the anhydrous acetone was added, and the mixture was refluxed during 24 h. Reaction was controlled by thin layer chromatography (eluent: mixture of chlorophorm/methanol, 10/1). After completion of the reaction, the precipitate was filtered off and washed three times with acetone. Solvent was evaporated and residue dried in vacuum. The obtained powder of (3-i) was recrystallized from ethanol and dried on air, with the yield ~91%.

General Procedure of (4-i) Synthesis

Substance (3-i) was suspended in small amount of ethylacetate, and then 2 mL of concentrated hydrochloric acid was slowly added dropwise during 1 h under intensive stirring. After 2 h, the precipitate was filtered off, washed several times by 5% aqueous solution of potassium carbonate, evaporated, and dried in vacuum at room temperature. As a result, the powder (**4-i**) was obtained, with the yield \sim 87%.

General Procedure of (7-j) Synthesis

The synthesis of amine (**7-j**) was carried out in two stages (Fig. 4). At the first stage, compound (**6-j**) was obtained according to standard method of ester preparation as follow: dicyclohexylcarbodiimide (1.4 mmol) was added to a solution of pentafluorophenol (1 mmol), cinnamic acid derivative (**5-j**) (1.2 mmol), and 4-dimethylaminopyridine (0.1 mmol) in anhydrous tetrahydrofuran (THF) (30 mL) cooled with ice water for 1.5 h. After adding all dicyclohexylcarbodiimide, the reaction mixture was kept at room temperature for 24 h. The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, the precipitate of dicyclohexylurea



FIGURE 4 Scheme of synthesis of the aliphatic amines with cinnamate terminal groups.



SCHEME 1 Synthesis of poly(succinimide).

was filtered off, and THF was evaporated. The product (**6**-**j**) was purified by column chromatography (eluent: mixture of chloroform /methanol, 10/1).

At the second stage, 10% THF solution of (**6-j**) was slowly added to 10-fold excess of hexamethylendiamine in THF. After 1 h, the reaction mixture was poured in chloroform, and the formed precipitate was filtered out. The residue was washed five times with water for complete removal of hexamethylendiamine traces. Then, combined organic layer was dried over Na₂SO₄ and evaporated. The yield of the last stage was ~80%.

Polymer Synthesis

Synthesis of PSI

The thin layer of paste consisting of $_{D,L}$ -aspartic acid and 85% phosphoric acid (50 wt %) was heated for 2–3 h at 190 °C in a vacuum (Scheme 1). The resulting foamed glassy mass was dissolved in a minimum amount of dimethylforma-mide (DMF) and precipitated to the water. The resulting precipitate was filtered and washed with water (then with methanol) to remove the trace of phosphoric acid. After this, the precipitate was dried in vacuum at 100 °C for 8 h. The yield of the final product was 90%.

Synthesis of Polyamide P3AzoCN

The solution of 2.5 mmol of **PSI** in 5 mL of dry DMF was placed into the glass ampoule, and then the solution of 2.6 mmol of amine (**4-1**) in 5 mL of dry DMF under stirring during 10 min was added (Scheme 2). Then, argon was purged through the reaction mixture during 30 min. After that, the ampoule was sealed and placed in oil bath at 50 °C. After 24 h, ampoule was opened, and DMF was removed using rotor evaporator. The residue was dissolved in chloroform with the addition of 5 vol % of methanol to obtain solution with the concentration of ~10%; after that, hexane was added until the finishing of precipitate formation. Reprecipitation

was carried out three times. The obtained precipitate containing polymer **P3AzoCN** was filtered and dried in vacuum at 90 °C. Yield, 0.65 g (70%).

Polyamides **P6Cin**, **P6CinF**, **P6CinOMe**, **P3Coum-6**, **P3Coum-7**, **P3AzoNO₂**, **P3AzoCN2**, **P3AzoF**, **P3AzoF₂**, and **Copolyamide** were obtained by the same procedure as **P3AzoCN**. ¹H NMR spectra of synthesized polyamides are presented in Supporting Information (Fig. S1). In the case of **Copolyamide**, mixture of corresponding amines (30 mol % azo- and 70 mol % cinnamate-containing amine) was applied for PSI modification. According to NMR data, composition of **Copolyamide** corresponds to the initial mixture of amines.

Samples Preparation

To characterize the LC-alignment properties of polyamides, the sandwich-like glass cells with a gap of 10 μ m predetermined by Teflon spacers were prepared. Before assembling of cells, the glass substrates were spin coated (2000 rpm, 1 min) by DMF solution of tested polyamide (~ 0.2 wt %) with following prebacking at 80 °C for 10 min. The thickness of coatings was about 10 nm. The obtained cells were irradiated using a linear polarized polychromatic light of ultrahigh pressure mercury lamp during 10 min. At the last stage after illumination, the cells were filled with the LC mixture containing nematic MLC6816 from Merck. To estimate the degree of LC-orientation, 0.1 wt % of dichroic dye ASh253 (dichroic dye ASh253 was provided to us by Dr. A. Shimkin and Dr. V. Shirinyan, to whom we express our thanks) was added (absorbance maxima is 614 nm in MLC6816 host).

Structure of ASh-253



For optical investigations, the thin films of tested polyamides were prepared on quartz substrates by spin coating of DMF solution (\sim 0.1 g/mL) with following prebacking at 80 °C.

Physicochemical and Photooptical Investigations

The phase transitions of the polymers were studied by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min).



SCHEME 2 Synthesis of azobenzene-containing homopolyamide P3AzoCN.



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

Chemical structure of obtained substances was verified by NMR spectroscopy; TMS was used as standard and DMSO-d6 and deuterochlorophorm were used as the solvent. ¹H NMR was registered using «Bruker Avance-400» spectrometer with the frequency 400 MHz..

The photochemical properties were studied using a special instrument equipped with a DRSh-350 ultrahigh pressure mercury lamp (polychromatic light) and MBL-N-457 diode laser (457 nm, CNI Laser). To prevent heating of the samples due to IR irradiation of the lamp, water filter was used. To obtain plane-parallel light beam, quartz lens was used. The intensity of light was equal to ~15 mW/cm² for lamp and ~2 W/cm² for laser as measured by LaserMate-Q (Coherent) intensity meter. Spectral measurements were performed using Unicam UV-500 spectrophotometer.

The study of photoorientation process and quality of LCphotoalignment verification were performed using polarized UV/visible spectroscopy. For this purpose, the angular dependence (with a step-width of 10°) of the polarized light absorbance was measured using a photodiode array UV/visible spectrometer TIDAS (J&M) equipped with rotating polarizer (Glan–Taylor prism controlled by computer program).

The dichroism values were calculated from the spectra using:

$$D = (A_{||} - A_{\perp}) / (A_{||} + A_{\perp}), \tag{1}$$

where A_{\parallel} and A_{\perp} are polarized absorbance parallel and perpendicular to the orientation of dye molecules, respectively.

RESULTS AND DISCUSSION

Synthesis

The idea behind the proposed method of photochromic polyamides synthesis consists in chemical modification of **PSI** by low-molar-mass amines containing photochromic fragments. This method opens a great possibility to synthesize a variety of side chain homo- and copolyamides by applying amines with varied structure. Furthermore, not only the photoactive amines but also any functionalized ones can be used.

To obtain amines with azobenzene and coumarin terminal fragments, we used the three-step synthetic scheme shown in Figure 3. At the first stage, the protection of amino-group of 3-brompropylamine by the action of di-*tert*-butyl dicarbonate (Boc_2O) was carried out. After that, the substrate (**2**-**i**) (azo dye or coumarin) containing phenol fragment was linked to the substance (**1**) to form ether (**3**-**i**) (Williamson ether synthesis). At the final stage, the removal of the *Boc* protecting group led to pure, uncharged amine (**4**-**i**).

The proposed method for azobenzene- and coumarincontaining amines is not suitable for the synthesis of amines with cinnamate terminal fragments, since cinnamic acid derivatives do not have active phenol fragments, which are necessary for Williamson reaction. Therefore, an alternative two-step reaction for their synthesis was developed by us (Fig. 4). At the first stage, the esterification reaction of pentafluorophenol and a cinnamic acid derivative (**5-j**) was carried out. Pentafluorophenol was chosen as a good "leaving" group in nucleophilic reaction. The resulting compound (**6-j**) was reacted with a 10-fold excess of hexamethylenediamine to obtain monosubstituted diamine (**7-j**). All amines, (**4-i**) and (**7-j**), were obtained according to the general procedures given in Experimental section; their ¹H NMR spectra are presented in Supporting Information.

Let us briefly discuss PSI synthesis. PSI is commonly used for obtaining of poly(aspartic acid), which is expected to be one of the promising water-soluble and biodegradable polymers in medicine. There are many different routes for PSI preparation.^{29,30} The bulk acid-catalyzed polycondensation of D,L-aspartic acid was chosen for PSI producing. Reaction scheme (1) and method description were presented above. ¹H NMR spectrum of DMSO-d6 solution of **PSI** is shown in Figure 4. The signals at 2.7, 3.2, and 5.3 ppm assigned to the methylene and methine protons of the main chain of PSI, respectively, were observed. Molecular mass characteristics of prepared PSI were measured by capillary viscosimetry. Degree of polymerization (p) calculated from the equations $\mathbf{p} = 3.52 \times (\eta_{re})^{1.56}$ and $[\eta] = 1.48 \times 10^{-2} \times M^{0.64}$ (for poly(β -benzyl-DL-aspartate).³¹ The degree of polymerization of **PSI** was equal to 280, that is, $M_w \sim 27$ kDa.

It is well known that **PSI** is very reactive compound in respect to organic and inorganic bases including aliphatic amines.²⁹ To obtain the comb-shaped polyamides, the polymer-analogous nucleophilic ring-opening reaction of **PSI** under the action of aliphatic amines with terminal photoactive groups was developed.

As far as all polyamides were prepared by the same procedure, let us consider a concrete example of cyanoazobenzenecontaining polyamide **P3AzoCN** synthesis (see Reaction 2). ¹H NMR spectrum of **P3AzoCN** is characterized by the new signals at 1.9 and 3.9 ppm (Fig. 5). In addition, the ring opening of succinimide units resulted in the appearance of a new signals at 4.4–4.9 ppm assigned to the methine proton of the backbone units. The disappearance of signal at 5.3 ppm confirms that the modification of **PSI** comprise 100%. ¹H NMR spectra of all others synthesized polyamides are presented in Figure S1 (see Supporting Information).

All the synthesized polyamides represented themselves either white or orange powders readily soluble in DMF, DMSO, NMP, and mixture of chloroform and methanol. As far as the modification degree of **PSI** was around 100%, the molecular weight of the final polymers can be estimated from the degree of polymerization of the original **PSI**. It was found that M_w values of all synthesized polymers laid in the range between 90 and 113 kDa.



FIGURE 5 ¹H NMR spectra of PSI and P3AzoCN (solvent: DMSO-d6, 25 °C).

Phase Behavior of Polyamides

It is noteworthy that all polyamides having the identical chemical structure of the polymer backbone are characterized approximately the same values of glass transition temperatures, which is in the range of 160–170 $^\circ\rm C$ (according to DSC data).

All cinnamoyl- and coumarin-containing polymers (as revealed by polarizing optical microscopy method) are amorphous substances and they do not display any birefringence even after a prolonged annealing.

Owing to the presence of the rod-like mesogenic azobenzene fragments, the polyamides P3AzoCN, $P3AzoNO_2$, P3AzoF, and $P3AzoF_2$ demonstrate LC phase formation. According to the polarized optical microscopy they display a nematic LC



FIGURE 6 Polarized optical microscopy image of polyamide P3AzoCN.

phase with the marble texture (Figs. 6 and S2 in Supporting Information). The nematic phase is stable up to the decomposition of polyamides (250-270 °C). It should be emphasized that polyamide **P3AzoCN**₂ containing additional cyanogroup in comparison with **P3AzoCN** does not form any LC phase, because an existence of additional cyanosubstituent in *ortho*-position decreases aromatic fragment anisometry. **Copolyamide** also does not form mesophase because it contains only 30 mol % of azobenzene fragments, which is not enough to form LC phase.

Optical Properties of Polyamides

The absorbance characteristics of photoalignment materials play a significant role in their perspective of photooptical application. Figure 7 shows the absorption spectra of thin films of the synthesized polyamides prepared on quartz substrates. As can be seen from Figure 7(a), red shift of absorption peak is taking place for azobenzene-containing polyamides in a series of their derivatives with substituents: F, 2F, CN, NO₂, and 2CN.

For polyamides containing derivatives of cinnamic acid [Fig. 7(b)], bathochromic shift of the spectra is observed with its increasing in the following substituent order: F, H, and OCH_3 . The observed spectral changes are associated with an increase in the electron-donor character of the substituents in the considered series of polyamides.

The spectrum of **copolyamide** (Table 1) has two absorption bands corresponding to the side fragments of *p*-methoxycinnamic acid ($\lambda_{max} \sim 294$ nm) and azobenzene ($\lambda_{max} \sim 365$ nm) [Fig. 7(b)]. The variation of the structure in coumarin series results in significant change in the absorption spectrum. So polymer **P3Coum-7** is characterized by one absorption peak, but **P3Coum-6** has two maxima [Fig. 7(c)]. The presence of two peaks can be attributed to keto-enol tautomerism of





FIGURE 7 Absorbance spectra of (a) azobenzene-, (b) cinnamate-, and (c) coumarin-containing polyamide films spin coated on quartz substrate.

7-oxy-substituted coumarin. In the case of 6-oxy-substituted coumarin (polyamide **P3Coum-6**), such tautomerism is not possible, and there exists only one resonance form.³²

The main optical properties relating to absorbance bands of polyamides are summarized in Table 2. It is clearly seen that all tested polymers have a good absorbance properties (extinction coefficient $> 10^4$) in the UV region, which make it possible to use Hg lamps for photoalignment layers activation.

Photoorientation Properties of Azobenzene-Containing Polyamide Films

As discussed in Introduction, LC-photoalignment properties of photochromic polymers are associated with angularly selective photoprocesses, particularly, photoorientation phenomenon in azobenzene-containing polymers. This phenomenon leads to an appearance of photoinduced dichroism and birefringence in polymer films. To investigate photoorientation processes, the thin layers of azobenzene-containing polyamides prepared by spin-coated method were illuminated by polarized laser light (457 nm, ~2 W/cm²). Polarized light induces uniaxial orientation of photochromic side groups, which are aligned in the direction perpendicular to the polarization plane of the light, as is schematically shown in Figure 1.

The polarized absorbance spectra and polar diagrams for **P3AzoNO₂** [Fig. 8(a,b)] demonstrate an orientation of side chain azobenzene fragments before and after irradiation. As is seen in Figure 8(b), the direction of photochromic fragments is perpendicular to electric vector (polarization plane) of the laser beam. The same processes are observed for other azobenzene-containing polyamides.

Figure 9 shows the kinetics of the photoinduced dichroism growth during irradiation. Maximal achievable dichroism values for all azobenzene-containing polyamides are quite small (0.10-0.33) when compared with azobenzene-containing polyacrylates studied earlier.^{33,34} Low dichroism values could be explained by competitive out-of-plane (homeotropic) chromophores alignment during light action.³⁵

Introduction of additional *ortho*-substituents (polyamides **PAzoCN**₂, **PAzoF**₂, and **PAzoNO**₂) results in decrease of dichroism values in comparison with mono-*para*-substituted chromophores (Fig. 9), which is associated with decreasing in chromophore anisometry.

It should be pointed out that occurrence of the photoorientation phenomena in the synthesized polyamide films under polarized light action is warranted for their good LCphotoalignment properties.

LC-Photoalignment Properties of Polyamides

For investigation of LC-photoalignment properties of synthesized polyamides, the LC cells were filled with MLC6816 doped by dichroic dye ASh-253 (see detail in Experimental section). Figure 10(a) shows the absorption spectra of polarized light of the cell filled with LC mixture, which was aligned by polyamide layer of **P6CinOMe**. As can be seen from Figure 9(a), rotation of the sample (inset photographs) relative to the plane of polarization of detecting beam light leads to dramatically change of the absorption spectrum.

TABLE 2 LC-Photoalignment Properties of Polyamides

		Absorbance		
Гуре of Polymers	Abbreviation	Maximum (nm)	Dichroism	Alignment direction ^a
Cinnamic acid-containing polyamides	P6Cin	272	0.72	Perpendicular
	P6CinF	278	0.63	Perpendicular
	P6CinOMe	294	0.72	Perpendicular
Coumarin-containing polyamides	P3Coum-6	278/346	0.62	Parallel
	P3Coum-7	325	0.69	Parallel
Azobenzene-containing polyamides	P3AzoNO ₂	355	0.68	Perpendicular
	P3AzoCN	353	0.69	Perpendicular
	P3AzoCN2	375	0.70	Perpendicular
	P3AzoF	336	0	Homeotropic
	P3AzoF2	345	0	Homeotropic
Cinnamic acid and azobenzene based concluamide	Copolyamida	294/365	0.70	Perpendicular

^a Alignment direction with respect to polarization plane of UV light.



This phenomenon indicates the presence of a uniaxial orientation of liquid crystal molecules that is more clearly demonstrated in Figure 10(b).

Polar diagram shows the direction of the preferred orientation of the LC molecules in the cell. One can see that the orientation of liquid crystals is perpendicular to the plane of polarization of UV light, which was used to activate photoalignment coating before filling a cell with liquid crystal. Moreover, the estimated value of the dichroism (D) corresponding to absorbance of dichroic dye (at 614 nm) was equal to 0.72. It corresponds to a good uniaxial orientation of liquid crystal in the cell. For comparison, the dichroism values of the similar cell aligned by rubbed polyimide coating (which is used in display technology) was 0.69.



FIGURE 8 Polarized absorbance spectra (a) and polar diagrams (b) for polymer **PAzoNO₂** before and after 60 s of laser irradiation (457 nm, I = 2 W/cm²).





FIGURE 10 Polarized absorbance spectra of the cell (insert photograph) prepared using polyamide **P6CinOMe** as photoalignment layer and filled by nematic mixture MLC6816 doped with blue dichroic dye (a). Corresponding polar diagram of absorbance. Before filling, cell was irradiated by polarized UV light for 10 min (b).

LC-photoalignment properties of all synthesized polyamide materials are listed in Table 2. It is clearly seen that all polymers, with the exception of fluorine-containing polyamides **P6CinF, P3AzoF,** and **P3AzoF₂** and **P3Coum-6**, display good alignment ability with respect to liquid crystals (comparable with rubbed polyimide layers). For the latter polymers, dichroism values are slightly lower (\sim 0.62). However, the dichroism values are very stable, and the orientation of liquid crystals as alignment is preserved for prolonged time (several months).

It should also be emphasized that the direction of the orientation of the LC molecules is usually perpendicular to the plane of polarization of the used UV light. The exceptions are the two groups of polyamides. The first one is coumarincontaining polyamides **P3Coum-7** and **P3Coum-6**, which induces an LC orientation in the direction parallel to the polarization plane of UV light. Such behavior is typical for this class of compounds and is determined by cyclobutane adducts formed by the axis-selective photodimerization. However, opposite situation can be realized in some cases.⁴ The second group is fluorine-containing azobenzene polyamides **P3AzoF** and **P3AzoF**₂, which stimulate an orientation in a direction perpendicular to the plane of the LC cell, that is, homeotropic one. Furthermore, these materials induce homeotropic orientation even without exposure by UV light.

As was shown in previous section, the investigation of photoorientation processes under the action of laser irradiation (457 nm) in thin layers of polyamides revealed that their dichroism values (D) corresponding to maxima were small and lay between 0.05 and 0.33 (Fig. 9). It is noteworthy that even such small dichroism values provide a good orientation of the LC molecules deposited on such coatings due to small surface energy anisotropy required for effective LC orientation.³⁶

CONCLUSIONS

A novel series of comb-shaped polyamides with photoactive side groups were synthesized by means of chemical modification of PSI. Their phase behavior, optical, and photooptical properties and LC-photoalignment ability were studied. It was shown that irradiation of polyamides layers with polarized UV light leads to orientation of LC molecules deposited on them. The relatively simple synthetic approaches developed in this work, high thermal stability and good photoalignment properties of the prepared polyamides, give opportunity to consider them as promising materials for application in display technology, optics, photonics, and so on.

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