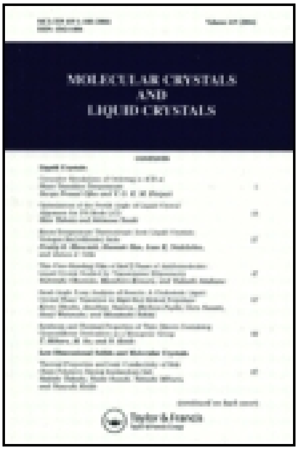

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Photochemistry of Bis-Methacrylic Polymers and Alignment of Liquid Crystals

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Photochemistry of Bis-Methacrylic Polymers and Alignment of Liquid Crystals

V. Kyrychenko[1], **G. Smolyakov**[2], **V. Zagniy**[2], **L. Vretik**[2], **L. Paskal**[2], **V. Syromyatnikov**[2], **and O. Yaroshchuk**[1]
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Photochemical processes leading to the photoinduced anisotropy and the excellent photoaligning properties of bis-methacrylic polymers are discussed. Comparing the data for bis-methacrylic polymers and a series of model compounds, we conclude that Fries rearrangements and crosslinking reactions taking place in bis-methacrylic polymers cause the photoinduced ordering in films of these polymers via the mechanism of photoselection. Thus, all of these photochemical processes contribute to the liquid crystal photoalignment. The induced alignment is thermally stable due to the crosslinking of methacryloyl groups which fix the induced anisotropy in aligning polymer films.

Keywords: liquid crystal alignment; methacrylate; photoalignment; photoinduced anisotropy

1. INTRODUCTION

The basic element of modern liquid crystal displays (LCD) is a properly aligned liquid crystal (LC) layer. The LC alignment is usually achieved by confining LC between two substrates unidirectionally rubbed. However, the rubbing alignment technique has a number of intrinsic drawbacks such as the formation of scratches resulting in a reduced contrast ratio and the creation of a large static charge causing the surface dusting, cross-track shorts, or failure of thin film transistors [1].

The intrinsic problems of the rubbing alignment technique stimulate the development of alternative alignment methods useful for

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industrial applications. Among them, the photoalignment technique shows a good promise. Eliminating the direct mechanical contact with a substrate, it removes the major above-mentioned problems of rubbing. This technique allows continuously changing the parameters of anchoring and can be used in the already completed cells. Moreover, photoalignment suggests an easy patterning procedure. Nevertheless, this approach is still not used in the LCD industry because of many unsolved problems such as a low stability, low pretilt angle, and relatively week anchoring energy.

The shortcomings of the photoalignment are caused by the nature of this alignment effect. The photoalignment results from the orientational order formed in films of some photosensitive materials under illumination with the polarized actinic light. This order arises due to the dichroic absorption of photosensitive groups resulting in angularly selective photochemical transformations. The photoaligning materials are thus classified according to the prevailing photochemistry. Particularly, one can select materials with photosensitive species undergoing the *trans-cis* photoisomerization (azopolymers and azodyes) [2–5], photodestruction (polyimides, polysilanes) [6,7], photo-crosslinking (cinnamate-, chalcone-, and coumarine-containing polymers) [8–11].

The insufficient stability of LC photoalignment is determined by the reversible photochemistry and the orientational relaxation due to molecular motions in the aligning films, as well as by the chemical processes in the LC-aligning layer interface. As we believe, these destructive processes can be eliminated by a proper selection of alignment materials bearing photosensitive groups with a basically new photochemistry.

Recently, we have discovered the excellent photoalignment ability of new polymers with free methacryloyl groups [12,13]. The example of these materials is polymer **P1** presented in Figure 1. These materials provide the excellent LC alignment with high thermal and photostability and a rather high anchoring energy. To understand the reasons for these improvements, the mechanisms of LC alignment on the new photoaligning polymers should be clarified. This means, first of all, that photochemical transformations in the new polymers should be comprehensively studied, and their contribution to the orientational ordering in polymer films and the LC alignment should be elucidated. This series of questions is considered in the present paper.

Materials like **P1** have quite complicated photochemistry. Theoretically, polymer **P1** can undergo the photocrosslinking reaction in combination with two Fries rearrangements shown in Figure 2. To select the reactions contributing to the orientational ordering and

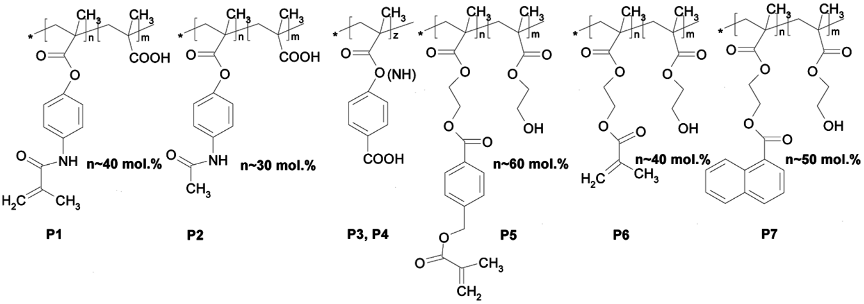

FIGURE 1 Chemical formulas of studied polymers.

LC alignment by **P1**, we synthesized a number of model compounds, in which some or all photochemical reactions presented in **P1** were excluded. The photoinduced ordering and LC alignment by these polymers were subsequently studied.

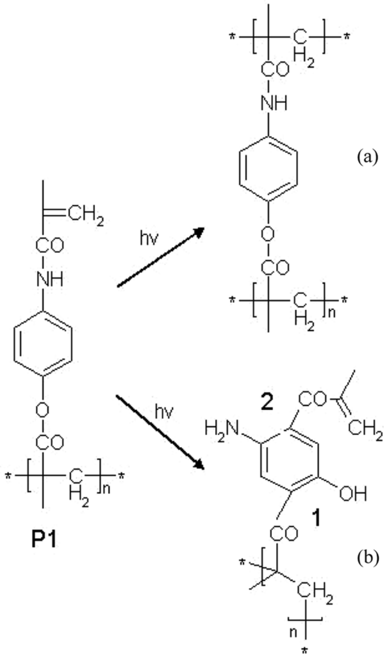

FIGURE 2 Scheme of photochemical reactions in polymer **P1**: photocross-linking (a) and two Fries rearrangements (b).

2. EXPERIMENTAL SECTION

2.1. Alignment Materials

2.1.1. Selection of Materials

A series of studied polymers is presented in Figure 1. As stated above, polymer **P1** represents a new class of photoaligning polymers having photoreactive side chain consisting of the aromatic core and a free methacryloyl group. The other polymers are model ones. In these polymers, some or all types of phototransformations peculiar to **P1** are eliminated. In polymer **P2**, a methacryloyl group is excluded so that only two Fries rearrangements are possible. **P3** and **P4** undergo only one Fries rearrangement due to ester Ph-O-CO (**P3**) or amide Ph-NH-CO group (**P4**). Polymers **P5** and **P6** undergo only the photocrosslinking reaction. The difference between **P5** and **P6** consists in that **P5** contains the aromatic core, while, in **P6**, this core is excluded. Finally, compound **P7** is not able to undergo any sort of transformations peculiar to those of material **P1**.

2.1.2. Synthesis of Materials

In order to obtain the polymers under study, some intermediate substances were synthesized. Intermediate poly(methacrylic acid), poly(2-hydroxyethyl methacrylate), (4-methacryloylamino)phenol, (4-acetylamino)phenol, 4-methacryloylaminobenzoic acid, 4-methacryloyloxybenzoic acid, and 4-(methacryloyloxymethyl)benzoic acid were prepared in accordance with the standard procedure by acylation of the starting compounds with methacryloyl chloride, methacrylic anhydride, or acetic anhydride, respectively. The chemical structure and purity of the obtained intermediates were proved by ^{1}H NMR spectra and thin-layer chromatography.

The starting polymers *poly(methacrylic acid)* and *poly(2-hydroxyethyl methacrylate)* were prepared by the radical polymerization in tetrachloromethane and toluene, respectively. Such solvents were employed to obtain polymer products with relatively low molecular weights to have a possibility for the further dissolving of these polymers in DMF.

Synthesis of poly(methacrylic acid). 5 g (0.058 mole) of methacrylic acid were dissolved in 50 ml of CCl_4, 0.5 g of AIBN were added, and the obtained solution was heated to 80°C and kept at this temperature during 20 min. Precipitated polymethacrylic acid was filtered off, washed with CCl_4, and dried in vacuum. The molecular weight of the obtained polymer was measured by SEC and gave $M_n = 43\ 400$, $M_w = 75\ 600$, $PD = 1.74$

Polymerization of poly(2-hydroxyethyl methacrylate). 5 g (0.038 mole) of ethyleneglycole monomethacrylate were dissolved in 50 ml of toluene, 0.3 g of AIBN were added, and the obtained solution was kept at 80° C during 45 min. Precipitated poly(2-hydroxyethyl methacrylate) was filtered off, washed with toluene, and dried in vacuum. The molecular weight for the obtained polymer was measured by SEC and gave $M_n = 36\ 600$, $M_w = 69\ 900$, $\mathrm{PD} = 1.91$.

Polymers **P1**, **P2**, **P5**, **P6**, and **P7** were obtained by a polymer-analogous method, while homologs **P3** and **P4** were prepared by homopolymerization of the corresponding monomers.

Preparation of **P1**. 1 g of the obtained poly(methacrylic acid) (0.012 mole) was dissolved in 5 ml of dry DMF during 24 h. To the obtained solution 2.12 g (0.012 mole) of 4-methacryloylamino phenol, 2.47 g (0.012 mole) DCC and 0.49 g of DMAP were added. The reaction mixture was stirred at 20° C during 5 days, filtered off, and precipitated into isopropanol. The obtained polymer **P1** was dried in vacuum. The relative molar ratio $n{:}m = 40{:}60$ (Fig. 1) was evaluated using ^{1}H NMR spectroscopy.

Preparation of **P2**. 1 g (0.012 mole) of poly(methacrylic acid) was dissolved in 5 ml of dry DMF and was stirred during 24 h. Into this solution, 1.81 g (0.012 mole) of (4-acetylamino)phenol, 2.47 g (0.012 mol) DCC, and 0.49 g (20 wt.% from DCC) of DMAP were added. The reaction mixture was stirred at 20° C during 5 days, filtered off, and precipitated in water. The obtained polymer **P2** was dried in vacuum. The relative molar ratio $n{:}m = 30{:}70$ (Fig. 1) was evaluated using ^{1}H NMR spectroscopy.

Preparation of **P3** and **P4**. Polymers **P3** and **P4** were prepared by usual homopolymerization of, respectively, (4-methacryloylamino)-benzoic and (4-methacryloyloxy)benzoic acids in DMF solution in presence of AIBN at 80° C.

Preparation of **P5**. 1.04 g (0.008 mole) of poly(2-hydroxyethyl methacrylate) was dissolved in 5 ml of dry DMF and stirred off during 24 h. To this solution, 1.63 g (0.008 mole) of 4-(methacryloyloxymethyl) benzoic, 1.65 g (0.008 mole) of DCC, and 0.33 g (20 wt.% from DCC) of DMAP were added. The reaction mixture was stirred at 20° C during 5 days, filtered off, and precipitated in water. The obtained polymer **P5** was dried in vacuum. The relative molar ratio $n{:}m = 60{:}40$ (Fig. 1) was evaluated using ^{1}H NMR spectroscopy.

Preparation of **P6**. Polymer **P6** was synthesised by acylation of 5 g (0.038 mole) of poly(2-hydroxyethyl methacrylate) by methacryloyl chloride in the presence of triethylamine in 5 ml of dry DMF. After acylation, the obtained polymer **P6** was precipitated in water, filtered off, and dried in vacuum. The relative molar ratio $n{:}m = 40{:}60$ (Fig. 1) was evaluated using ^{1}H NMR spectroscopy.

Preparation of **P7**. 0.40 g (0.00308 mole) of poly(2-hydroxyethyl methacrylate) was dissolved in 4 ml of dry DMF and tetrahydrofurane mixture (1:1) during 24 h. To this solution, 0.53 g (0.0031 mole) of naphthoic acid, 0.63 g (0.0031 mole) of DCC, and 0.13 g (20 wt % from DCC) of DMAP were added. The reaction mixture was stirred at 20°C during 5 days. The obtained polymer **P7** was precipitated in water, filtered off, and dried in vacuum. The relative molar ratio $n{:}m = 50{:}50$ (Fig. 1) was evaluated using ^{1}H NMR spectroscopy.

2.2. Alignment Films and LC Cells

The polymers were dissolved in dimethylformamide at a concentration of 2 wt. % and filtered to 0.2 μm by syringe filters. The polymer films were obtained by the spin coating of polymer solutions on quartz or glass slides. Subsequently, the films were backed at 180°C over 1 h for the solvent evaporation completion. Except the films of pure polymers, we studied films of **P1** and **P5** polymers doped by a photoinitiator Irgacure 907 (3 wt. %). The photoinitiator was used to intensify the crosslinking of methacryloyl groups.

For the illumination of polymer films, we used the full emission spectrum of a high-pressure mercury lamp DRS-500 (Russia) directed normally to the films. To study the photochemical changes in polymers, the films of these polymers were illuminated by a non-polarized light with an integral intensity of 105 mW/cm^2. For the anisotropy induction, the polymer films were illuminated with light linearly polarized by a Glan–Thompson prism. The polarized light intensity was 45 mW/cm^2.

In order to verify the LC alignment quality, we produced antiparallel LC cells. In these cells, the LC layer was sandwiched between a pair of substrates with antiparallel optical axes. The cell thickness was adjusted by spacers with a diameter of 20 μm. The cells were filled with nematic mixture ZLI2293 from Merck at room temperature.

2.3. Experimental Methods

Thin layer chromatography and ^{1}H NMR spectroscopy were employed to determine the purity and the chemical structure of the obtained materials. Thin layer chromatography was performed on Merck Kieselgel plates 60-F254. ^{1}H NMR spectra were recorded by a Varian 400 NMR spectrometer with the use of tetramethylsilane in a DMSO-d$_6$ solvent as an internal standard.

The photochemistry of polymers **P1–P7** was studied by UV/Visible spectroscopy. The UV/Vis absorption spectra were measured by using an S2000 diode array spectrometer from the Ocean Optics Co. In this setup, the samples were set normally to the testing light from a low-intensity deuterium lamp. By the same setup, the polarized UV/Vis absorption spectra were measured and used in the characterization of a photoinduced order. In this case, a Glan–Thomson prism was used to polarize the probe beam. Spectra were measured before and after different doses of irradiation.

The second method used to characterize the induced orientational order was the transmission null ellipsometry (TNE) [14–16]. The optical scheme of the method is the follows. The probe beam (628 nm) is linearly polarized at 45° with respect to the in-plane main axes of the sample x and y. The elliptically polarized transmitted beam is converted into a linearly polarized beam by a quarter wave plate (the axis is parallel to that of a polarizer). The angle φ of the output polarization determined by the rotation of a linear analyzer gives the in-plane retardation $(n_y\text{-}n_x)$d. Then the sample is rotated around the x axis vertically aligned, and the polarization angle φ is measured as a function of the incidence angle θ. The out-of-plane retardation $(n_z\text{-}n_x)$d is determined by fitting a theoretical expression of $\varphi(\theta)$. The TNE was used to study the parameters of orientation in all polymers before irradiation and after successive irradiation steps.

The quality of LC alignment was estimated by the observation of LC cells' transmittance in crossed polarizers with a naked eye and in a polarizing microscope. The alignment quality was estimated by using the scale with five grades: excellent; good (single alignment defects); satisfactory (minor alignment defects); bad (big number of alignment defects in the form of inversion walls, flowing patterns, etc.), and no alignment.

For the estimation of thermal stability, cells were maintained at a temperature of 150°C during 30 min. After the cooling of cells to room temperature, the changes in the LC alignment quality were estimated.

3. RESULTS AND DISCUSSION

3.1. UV Spectra

First, we consider UV/Vis absorption spectra giving information about the photochemistry underlying the orientation ordering in the polymers. The initial spectra and the spectra after different exposure steps for polymers **P1**, **P3**, and **P5** are presented in Figures 3, 4, and 5, respectively. It is evident that the spectra of these polymers contain only one intensive band with the maximum at 240–265 nm. This band is caused by a π-conjugated side chain containing various double

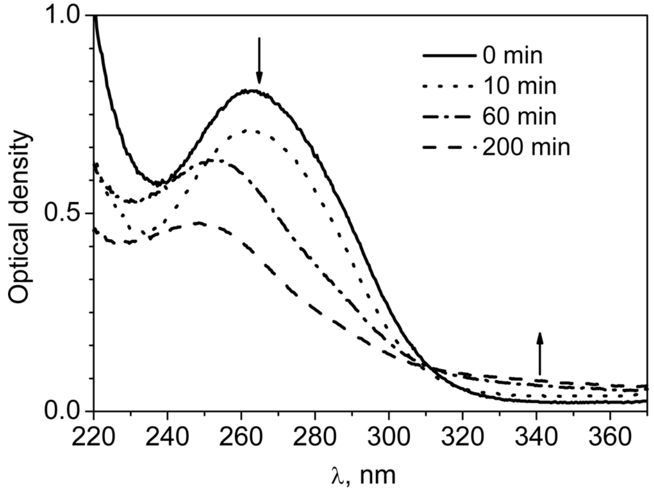

FIGURE 3 UV/Vis spectra of a **P1** film before irradiation and after several irradiation doses. $I = 105\,\mathrm{mW/cm^2}$.

bonds, such as C = C (aromatic rings and terminal methacryloyl groups) and C = O (carbonyl groups). In polymer **P1**, containing all of these groups, the absorption band is maximally shifted to long wavelengths. The exclusion of one or several groups with double bonds

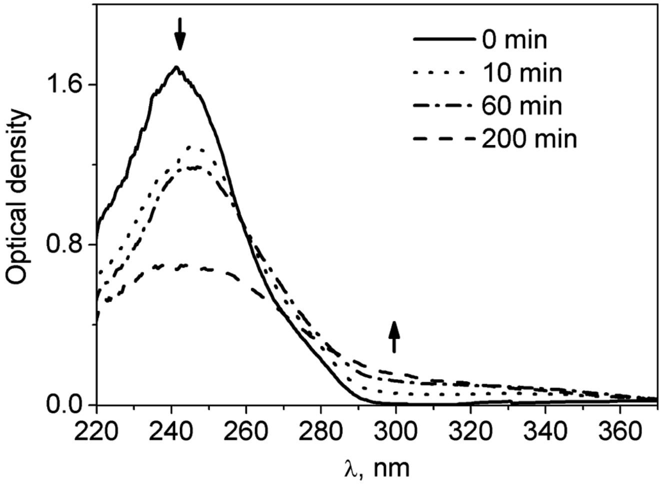

FIGURE 4 UV/Vis spectra of a **P3** film before irradiation and after several irradiation doses. $I = 105\,\mathrm{mW/cm^2}$.

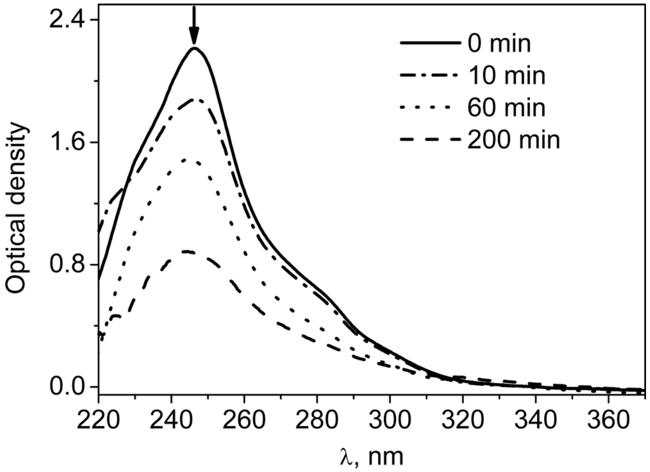

FIGURE 5 UV/Vis spectra of a **P5** film before irradiation and after several irradiation doses. $I = 105\,\mathrm{mW/cm^2}$.

leads to a "blue" shift of the absorption spectra. This rule is true for all polymers under study.

The absorption band with the maximum at 240–265 nm overlaps with a "blue" edge of the irradiation spectrum of a mercury lamp characterized by a broad complex emission band with low intensity. Thus, only this part of emission spectrum influences photochemical changes. Comparing the absorption spectra of our polymers with the emission spectrum of a lamp, one can draw the following conclusions:

1. Because of the broad absorption and emission bands and a small dispersion in the absorption maximum position, one can expect similar coefficients of the integral absorption in different polymers.
2. Because of a low intensity of the emission in the "blue" spectral range, one can predict that high exposure doses are needed to produce photochemical changes and photoanisotropy.

According to Figures 3–5, UV irradiation leads to the gradual decay of the main absorption band. Simultaneously, in polymers **P1-P4**, a broad band in the long-wave region (300–360 nm) appears and becomes more intense. The growth of the long-wave absorption is the evidence of Fries rearrangements occurring in **P1-P4** under illumination. In this case, in homologs **P1** and **P2** capable to undergo two Fries rearrangements (Fig. 2), it is impossible to distinguish the bands caused by

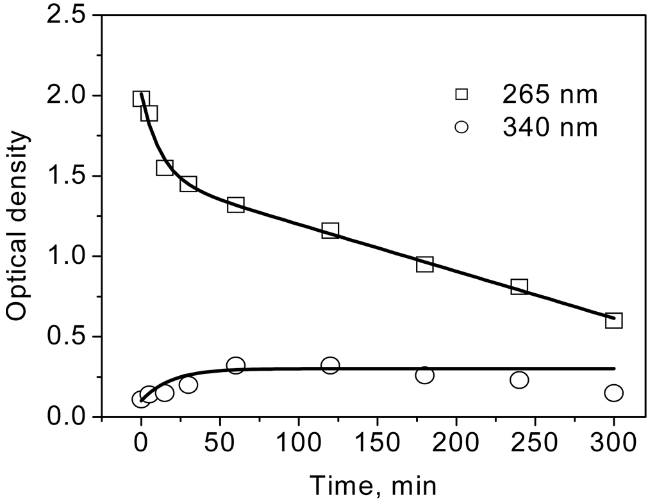

FIGURE 6 Dependences of the optical density in two characteristic bands (~265 and ~340 nm) on the exposure time for polymer **P1**.

different Fries transformations. The long-wave absorption growth was not observed in polymers **P5-P7**, in which Fries rearrangements are theoretically not allowed. The decay of the main absorption band observed in all polymers seems to be caused by a number of factors. This is confirmed by the dependence of the optical density on the exposure dose measured at different wavelengths. These curves for **P1** are shown in Figure 6. The decay of the main absorption band (265 nm) is fitted with two exponents having distinctly different characteristic times (tens of minutes and tens of thousands of minutes). The corresponding curve for the long-wave absorption is satisfactorily fitted with only one exponent with characteristic time equal to the short time of the biexponential short-wave decay. The two-exponential decay of the main absorption is observed for all polymers, except **P7**, for which only the slow decay component was detected. This gives us a reason to believe that: (1) the fast decay corresponds to the polymerization of methacryloyl groups, Fries rearrangements, or their combinations; (2) the slow decay component is caused by photodegradation. These conclusions hold true for pristine polymers, as well as polymers doped by a photoinitiator (in addition to pristine **P1** and **P5**, the photoinitiator-doped counterparts were studied).

Thus, UV spectroscopy does not allow one to distinguish the polymerization and Fries transformations in **P1**. However, in model compounds, all three photochemical processes predicted for **P1** were detected. This indirectly confirms the appearance of all these processes in **P1**. Recently, this conclusion was fully confirmed by IR studies. The corresponding results will be separately published in the forthcoming publication.

3.2. Photoorientation Ordering

The peculiarities of the photoorientational ordering will be considered by the example of polymer **P1** doped by a photoinitiator. First, let us analyze polarized spectra. Figure 7 shows the optical density D of a **P1** film at $\lambda = 265\,\text{nm}$ as a function of the angle α between the polarizations of actinic and testing light. The D(α) curves are presented for different exposure doses. It is evident that D decreases in all direction under UV irradiation. However, the initially isotropic distribution of the optical density becomes anisotropic. Since the optical absorption at $\lambda = 265\,\text{nm}$ is caused by photosensitive chains, this implies their anisotropic distribution (orientational ordering) under irradiation by polarized light. The side chains in the irradiated films are preferably oriented perpendicularly to the polarization direction of actinic light. The optical density components $D_{\|}$ and $D_{\perp}$ for $\alpha = 0°$ and $\alpha = 90°$, respectively, as well as the optical dichroism $\Delta D = D_{\|} - D_{\perp}$,

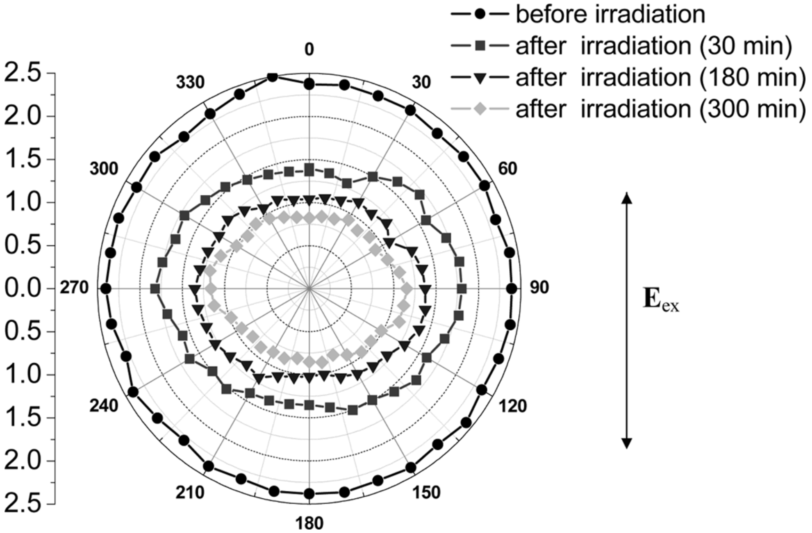

FIGURE 7 Angular dependences of the absorbance of a **P1** film at 265 nm measured after different doses of polarized UV irradiation ($I = 45\,\text{mW/cm}^2$). $\boldsymbol{E}_{\text{ex}}$ is the polarization direction of UV light exciting the orientational ordering.

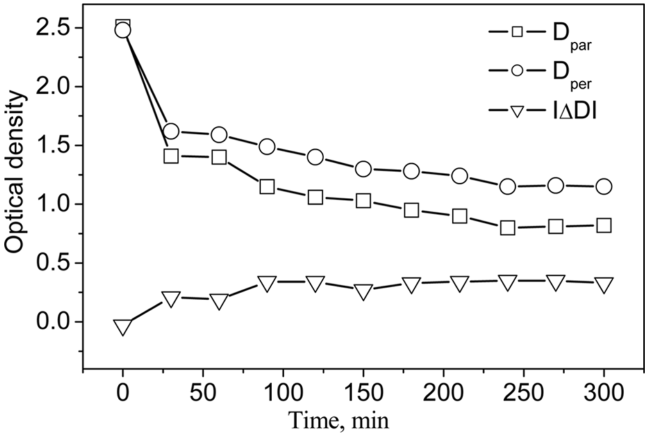

FIGURE 8 Dependences of the optical density coefficients $D_{\|}$ and $D_{\perp}$ (265 nm) of a **P1** film on the polarized light irradiation duration ($I = 45\,\mathrm{mW/cm^2}$).

as functions of the exposure dose are shown in Figure 8. It is evident that $D_{\|},_{\perp}(t)$ curves show the monotonic decay, while the dichroism ΔD gradually grows with a tendency to the saturation.

The curves presented in Figures 7 and 8 correspond to angular photoselection mechanism of photoordering [4]. This mechanism assumes angularly selective conversion of anisotropic photosensitive chains (mono- and polymolecular ones) to more isotropic conformations. These photochemical processes shall not be accompanied by sufficient angular redistribution of photosensitive chains survived irradiation.

Assuming uniaxial ordering of photosensitive chains, based on the known formula [1]

$$S = \frac{D_{\perp} - D_{\|}}{D_{\perp} + 2D_{\|}} \tag{1}$$

one can estimate the order parameter of the side polymer chains. Before irradiation $S \approx 0$, while S reaches 0.11 in the state of saturation.

Figure 9 demonstrates in-plane and out-of-plane retardations (correspondingly, $(n_y\text{-}n_x)d$ and $(n_z\text{-}n_x)d$) as the functions of exposure dose. In agreement with $\Delta D(t)$ curve, the in-plane retardation $(n_y\text{-}n_x)d$ grows with exposure time approaching saturation level. The out-of-plane retardation $(n_z\text{-}n_x)d$ grows and saturates too. Note that in saturation state $n_z \neq n_y \neq n_x$ so that the film is biaxial. On account of this result, the order parameter value earlier obtained should be only

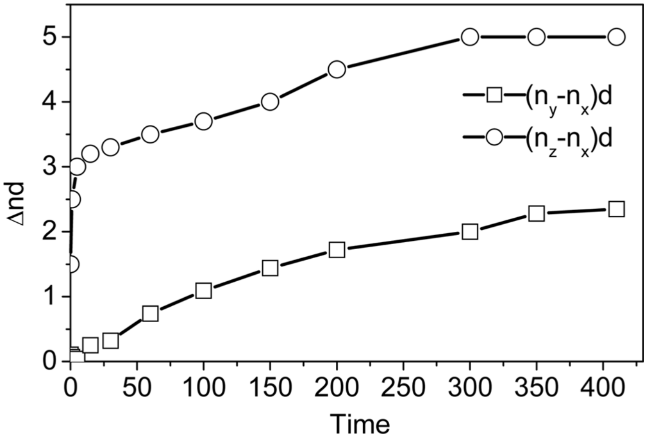

FIGURE 9 The in-plane $(n_y\text{-}n_x)d$ and out-of-plane $(n_z\text{-}n_x)d$ phase retardations of a **P1** film for successive exposure doses of polarized light ($I = 45\,\mathrm{mW/cm^2}$).

considered as a rough estimate of this parameter. Before irradiation, $n_z > n_y \approx n_x$ that means that polymeric side chains are preferentially aligned in the direction of film normal.

The ordering peculiarities are cleared to be similar for all polymers studied, except **P6** and **P7**. The lack of anisotropy in **P7** can be explained by photochemical stability of this material, which is free of photochemical processes peculiar to other polymers. The lack of anisotropy in **P6** is more surprising, since, same as **P5**, it contains polymerizable methacryloyl groups. However, in contrast to **P5**, the side chain of **P6** does not contain aromatic group. This reduces rigidity and anisotropy of side polymeric chain. As result, the photoinduced order is very poor.

Finally, we consider which photochemical reactions lead to orientational ordering. Reducing the kinetic curves of the optical density (Fig. 6) and the parameters of optical anisotropy (Figs. 8 and 9) to one intensity, one can conclude that the characteristic time of orientational ordering is comparable with that of the fast component of the absorption decay. This suggests that the induced anisotropy in the studied polymers is mainly caused by the processes of polymerization and Fries rearrangement or their combinations.

3.3. LC Alignment

Figure 10 shows the photographs of LC cells based on alignment layers made of the polymers under study. The photographs show the

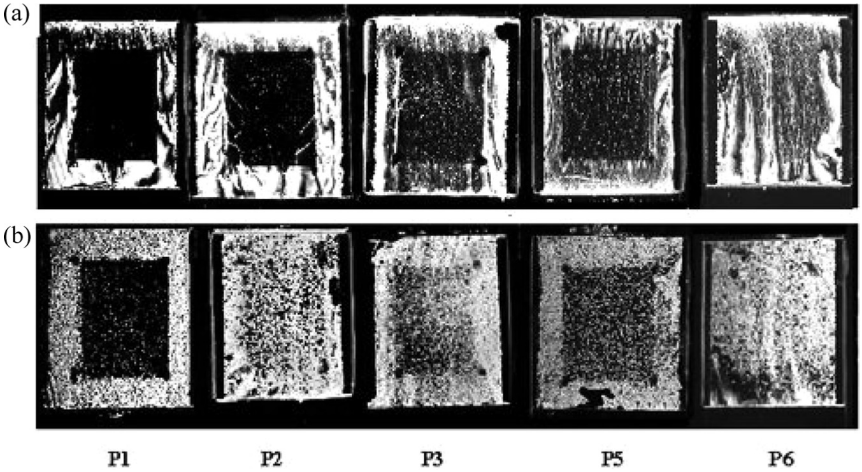

FIGURE 10 The photographs of LC cells viewed between a pair of crossed polarizers: (a) before annealing, (b) after annealing at 150°C during 0.5 h.

state of LC alignment in the cells before and after their annealing at 150° C for 30 min. The corresponding grades of the alignment quality are summarized in Table 1. Analyzing these data, one can conclude that the LC photoalignment is provided by all polymers, except **P6** and **P7**. This agrees well with a lack of photoinduced anisotropy in these polymers. This also suggests that both photochemical liability and anisotropy of photosensitive groups are obligatory conditions of the photoalignment effect. The best quality of LC alignment is revealed by polymers **P1** and **P2** undergoing two Fries rearrangements. The polymers capable to only one Fries reaction or photocrosslinking give

TABLE 1 Photochemistry and Grades of LC Alignment of the Films of Polymers **P1-P7**

		LC alignment	
Polymer	Possible reactions	Before annealing	After annealing to 150°C
P1	Two Fries rearrangements and crosslinking	Excellent	Good
P2	Two Fries rearrangements	Good	No alignment
P3	One Fries rearrangement	Satisfactory	Bad
P4	One Fries rearrangement	Satisfactory	Bad
P5	Crosslinking	Satisfactory	Satisfactory
P6	Crosslinking	No alignment	No alignment
P7	–	No alignment	No alignment

the alignment of a lower quality. On the other hand, the induced alignment is thermally resistant only on the polymers containing methacryloyl groups capable to the crosslinking. This implies that the crosslinking under the polarized light irradiation generates the anisotropy and fixes this anisotropy as well. Thus, all three photochemical processes in **P1** are important for the LC photoalignment. At the same time, they have different functions: the Fries rearrangements yield a high quality of LC alignment, while the photocrosslinking mainly serves to fix the induced orientational order.

4. CONCLUSIONS

It is shown that the high LC photoalignment ability of bis-methacryllic polymers of the **P1** type is caused by the angularly selective depletion of photosensitive side chains due to Fries rearrangements and the photocrosslinking. The presence of the groups capable to these transformations, as well as the aromatic core in the photosensitive chain, is the obligatory condition for the high alignment quality and the high thermal stability of LC alignment.

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