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Polymethacryloylaminoarylmethacrylates: New Concept of Photoalignment Materials for Liquid Crystals

L. Vretik^a, V. Syromyatnikov^a, V. Zagniy^a,
L. Paskal^a, O. Yaroshchuk^b, L. Dolgov^b, V.
Kyrychenko^b & C.-D. Lee^c

^a Macromolecular Chemistry Department, Kyiv National Taras Shevchenko University, Kyiv, Ukraine

^b Institute of Physics, NASU, Kyiv, Ukraine

^c Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan, R.O.C.

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L. Vretik

V. Syromyatnikov

V. Zagniy

L. Paskal

Macromolecular Chemistry Department, Kyiv National Taras Shevchenko University, Kyiv, Ukraine

O. Yaroshchuk

L. Dolgov

V. Kyrychenko

Institute of Physics, NASU, Kyiv, Ukraine

C.-D. Lee

Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan, R.O.C.

New class of highly efficient polymers for liquid crystal (LC) photoalignment is proposed. These polymers are based on methacryloylaminoarylmethacrylates having two methacryloyl groups of different reactivity. The more active O-methacryloyl group is subjected to polymerization, while the less active NH-methacryloyl group undergoes photocrosslinking reaction in combination with Fries rearrangement. The latter process is anisotropic in case of polarized light irradiation that results in LC photoalignment with readily controlled pretilt angle and anchoring energy. The induced alignment shows high thermal and photo-stability.

Keywords: liquid crystal photoalignment; photocrosslinking; polymethacrylate

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Address correspondence to L. Vretik, Macromolecular Chemistry Department, Kyiv National Taras Shevchenko University, Volodymyrs'ka Str. 60, 01033 Kyiv, Ukraine.
E-mail: vretik@list.ru

1. INTRODUCTION

The ability of the films of some photosensitive materials to align liquid crystals after exposing to polarized actinic light is known over fifteen years [1–4]. This alignment method, called as photoalignment, is one of the most attractive alternative to rubbing process. It yields highly uniform LC alignment with controllable easy axis and anchoring energy. The photoalignment is free of many drawbacks of rubbing, such as deterioration of alignment layers and their electric charging.

Besides, photoalignment suggests easy patterning procedure. The photoalignment effect is caused by the orientational order formed in the alignment film under illumination with a polarized actinic light [5–8]. This process is usually accompanied by alteration of film's topology, which also is a factor of LC alignment [9]. The molecular orientational ordering in the photoalignment films occurs due to the angularly selective photochemical reactions, which are distinctly different for the photosensitive species of different type. Based on the prevailing photochemistry the classification of photoalignment materials can be given. The first group form materials with photosensitive species undergoing *trans-cis* photoisomerization. First of all, this group includes azocompounds: chemically [1] and physically [10] adsorbed azodyes, azodye blends and azopolymers [5–8]. The second group is formed with materials having photosensitive fragments predisposed to photodestruction, such as photooxidation, chain scission, etc. The examples of these materials are photosensitive polyimides [11] and polysilanes [12]. The third and the mostly studied group includes materials undergoing photo-crosslinking of cycloaddition type. The materials containing cinnamate [2,3], coumarin [13] and chalconyl [14] chromophore undergo $[2 + 2]$ cycloaddition. The $[4 + 4]$ cycloaddition reaction is typical for anthracenyl chromophore [15].

Each class of materials has own advantages and disadvantages. The azo compounds usually give excellent LC alignment at low exposure dose (less than 0.5 J), which is, however, not sufficiently stable against heat and light, because of reversible photochemistry. The photodesstructive materials commonly require high exposure dose (more than 10 J/cm²) and demonstrate enhanced image sticking. Compared with them, materials undergoing photo-crosslinking demonstrate the best promise. They combine good photosensitivity and high resistance of LC alignment to heat and light, because of irreversible photo-crosslinking products.

In spite of big progress in development of photoalignment materials they are not used yet in commercial LCD. The problems still unsolved are low anchoring strength, image sticking and insufficient alignment

stability. For industrial implication the materials with radically improved alignment characteristics are required. As an attempt in this direction we propose new polymers capable of photo-crosslinking. The crosslinking in these polymers may arise due to radical polymerization of double bonds in addition to cycloaddition crosslinking earlier considered. More particularly, we deal with 4-(N-methacryloylamino)aryl methacrylates containing two methacryloyl fragments. One group is thermally polymerized in the process of polymer synthesis, while the other one crosslinks polymer chains under photoalignment treatment. This provides polymer films with thermally stable and reproducible LC alignment. Systematic variation of methacryloylaminoarylmethacrylate molecule structure is made for better understanding of "structure-photoaligning properties" correlation. The attempts are also paid to reduce exposure dose for LC alignment.

2. EXPERIMENTAL SECTION

Materials

As photoalignment materials we used polymers **poly-M2-poly-M6** obtained by polymerization of monomers **M2-M6** depicted in Figure 1. The different structures were considered to clarify the influence of flexible alkyl spacer on the reactivity of O-methacryloyl and

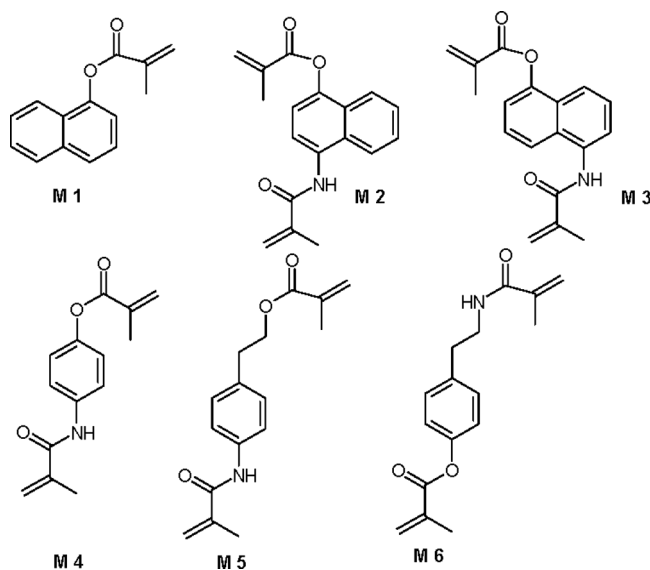


FIGURE 1 Chemical formulas of studied monomers.

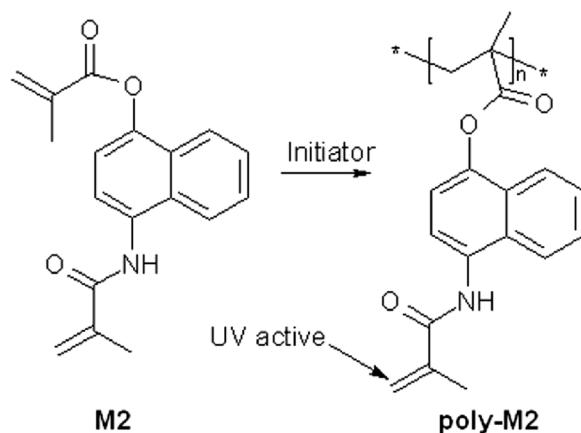


FIGURE 2 Schematic representation of photo-active polymer formation via selective polymerization.

NH-methacryloyl groups in conditions of radical polymerization of monomer as well as the influence of aromatic core structure (naphthalene or phenylene) and presence of the spacer groups on LC photoalignment properties of corresponding polymers. Polymer material **poly-M1** obtained from monomer **M1** earlier developed and tested [16] is used just for comparison purpose.

Because of different reactivity of O- and NH- methacryloyl groups in monomers **M2–M6**, at low degree of monomer conversion one can realize selective polymerization of O-methacryloyl groups with formation of linear soluble polymer products bearing photo- and thermoactive double bonds of NH-methacryloyl groups (Fig. 2). As we believed, these active bonds may react under photoalignment treatment causing surface ordering and LC alignment effect.

The detailed description of monomer synthesis and the root of polymerization are given in the next section.

Synthesis Procedure

The monomer syntheses was carried out via one step acylation of starting materials with double excess of methacrylic anhydride/methacryloyl chloride (syntheses of **M3–M5**) or by two step acylation with isolation in a pure state of intermediate methacrylamide product (syntheses of **M2, M6**). The effectiveness of this synthesis root was preliminarily checked [17]. More precisely, monomers were obtained and polymerized as follow.

Synthesis of 4-(methacrylamido)naphthol methacrylate (M2). 1.7 g (0.02 mol) of Na acetate and 3.1 g (0.02 mol) of methacrylic anhydride were added in the solution of 4.0 g (0.02 mol) of 1,4-aminonaphthol hydrochloride in 30 ml of acetic acid. The reaction mixture was boiled during 2 hours. After cooling to room temperature a residue was formed. The obtained white powder was filtered off and washed with hexane. 2.3 g (51%) of 4-(methacrylamido)naphthol were formed. M.p. = 225–227°C (dec.). R_f = 0.29 (acetone:hexane:benzene = 4:5:7). ^1H NMR identification (400 MHz, DMSO- d_6), ppm: 9.98 (s, 1H, NH), 8.17 (d, 1H, Ar), 7.77 (d, 1H, Ar), 7.45 (p, 2H, Ar), 7.20 (d, 1H, Ar), 7.20 (d, 1H, =CH₂), 6.84 (d, 1H, =CH₂), 2.04 (s, 3H, CH₃).

In the solution of 2.3 g (0.01 mol) of 4-(methacrylamido)naphthol in 10 ml of DMF was added 1.7 g (0.015 mol) of triethylamine. Then 1.9 g (0.015 mol) of methacryloyl chloride was added dropwise with stirring and permanent cooling to 5–10°C. The reaction mixture was kept 5 hours at room temperature and the insoluble TEA·HCl was removed by filtration. Filtration was poured into 200 ml of distilled water and oily residue was formed. The residue was washed with distilled water till neutral reaction in litmus. The obtained product was separated from water phase by filtration. After drying 1.6 g of 4-methacrylamido-naphthyl methacrylate (**M2**) was obtained (54%) M.p.: 122°C. R_f value (acetone:hexane:benzene = 4:5:7) = 0.50.

^1H NMR (400 MHz, DMSO- d_6), ppm: 9.85 (s, 1H, NH), 7.98 (d, 1H, Ar), 7.82 (d, 1H, Ar), 7.57 (d, 2H, Ar), 6.49 (m, 2H, Ar and 1H, =CH₂), 6.02 (d, 1H, =CH₂), 5.97 (s, 1H, =CH₂), 5.55 (s, 1H, =CH₂), 2.15 (s, 3H, CH₃), 2.07 (s, 3H, CH₃).

Synthesis of 5-(Methacrylamido)naphthyl methacrylate (M3). The solution of 4.78 g (0.03 mol) of 5-amino-1-naphthol and 10 ml (0.094 mol) of methacrylic anhydride was heated under the stirring at 90°C during 4 hours at the presence of 0.05 g of H₂SO₄ as catalyst and phenothiazine as inhibitor of polymerization. Then a reaction mixture was poured into 500 ml of distilled water. The precipitated black residue formed in water was filtered off and washed with water till neutral reaction in litmus. The dry black residue was boiled in toluene: hexane mixture (2:5) during 5 minutes and slightly yellowish solution was decanted from the black oily residue. Yellowish precipitate was formed after filtrate cooling. This residue was filtered off and dissolved in 5 ml of acetone. The acetone solution was poured into 100 ml of water containing 5 wt.% of NaOH. The formed white precipitate was filtered off and purified by two time recrystallization with toluene:hexane mixture. 1 g of 5-(methacrylamido)naphthyl methacrylate (**M3**) was obtained. Yield 11%, m.p. = 134–135°C, R_f = 0.89 (eluent acetone:hexane:benzene = 4:5:7).

^1H NMR identification (400 MHz, DMSO- d_6), ppm: 9.87 (s, 1H, NH), 7.87 (d, 1H, Ar), 7.79 (d, 1H, Ar), 7.56 (d, 1H, Ar), 7.53 (t, 2H, Ar), 7.29 (d, 1H, Ar), 6.47 (s, 1H, =CH₂), 6.00 (s, 1H, =CH₂), 5.96 (m, 1H, =CH₂), 5.53 (s, 1H, =CH₂), 2.14 (s, 3H, CH₃), 2.05 (s, 3H, CH₃).

Synthesis of 4-(N-methacryloylamido)phenyl methacrylate (M4). To the solution of 54.5 g (0.5 mol) of 4-aminophenol in 250 ml of dry tetrahydrofuran was added 50.5 g (1 mol) of triethylamine. Then 104.5 g (1.1 mol) of methacryloyl chloride was added dropwise to the solution at the room temperature with stirring and permanent cooling. The reaction mixture was kept 3 days at room temperature and then poured into 1 l of distilled water. The obtained residue was filtered off and washed with water till neutral reaction in litmus. Recrystallization in toluene mixture with silica gel gave 70.3 g of 4-(N-methacryloylamido)phenyl methacrylate (57%). M.p.: 103–105°C. R_f -value (acetone:hexane:benzene = 4:5:7) = 0.93.

^1H NMR (400 MHz, DMSO- d_6), ppm: 9.71 (s, 1H, NH), 7.72 (d, 2H, Ar), 7.01 (d, 2H, Ar), 6.27 (s, 1H, =CH₂), 5.81 (m, 2H, =CH₂), 5.45 (s, 1H, =CH₂), 2.02 (s, 3H, CH₃), 1.97 (s, 3H, CH₃).

Synthesis of 4-(methacrylamido)phenethyl methacrylate (M5). 3.95 g (0.088 mol) of triethylamine was added to the solution of 4 g (0.029 mol) of 4-aminophenethyl alcohol in 50 ml of dry acetone. Then a solution of 9.2 g (0.088 mol) of methacrylchloride in 5 ml of dry acetone was added dropwise with stirring and permanent cooling to 5–10°C. The reaction mixture was kept 3 hours at room temperature. After this the insoluble TEA · HCl was removed by filtration. A clean solution was then poured into 500 ml of distilled water and oily residue was formed. Fresh distilled water was added three times till neutral reaction in litmus. The obtained product was then separated from a water phase by dissolving in benzene. The benzene solution was dried with Na₂SO₄ and the solvent was removed by distillation. 5 g of 4-(methacrylamido)phenethyl methacrylate was obtained. Yield 63%, m.p. = 36°–37°C, R_f = 0.85 (eluent acetone:hexane:benzene = 5:1:1).

^1H NMR identification (400 MHz, DMSO- d_6), ppm: 9.58 (s, 1H, NH), 7.58 (d, 2H, Ar), 7.13 (d, 2H, Ar), 5.99 (s, 1H, =CH₂), 5.77 (s, 1H, =CH₂), 5.77 (s, 1H, =CH₂), 5.58 (m, 1H, =CH₂), 4.25 (t, CH₂-O), 2.89 (t, Ar-CH₂), 1.95 (s, 3H, CH₃), 1.87 (s, 3H, CH₃).

Synthesis of 4-(2-methacrylamidoethyl)phenyl methacrylate (M6). M6 was prepared in two steps. 4.4 g (0.044 mol) of triethylamine was added to the solution of 4 g (0.029 mol) of 4-(2-aminoethyl)phenol in 10 ml of dry acetone and 2 ml of DMF. Then 4.6 g (0.044 mol) of methacrylchloride was added dropwise with stirring and permanent cooling to

5–10°C. The reaction mixture was kept 3 hours at room temperature and the insoluble TEA · HCl was removed by filtration. The filtered solution was then poured into 500 ml of distilled water that resulted in precipitation of solid residue. The obtained product was separated from a water phase by filtration. 4 g of 4-(2-methacrylamidoethyl)phenol was obtained with a yield of 67%. After recrystallization from toluene, m.p. = 133°C, R_f = 0.53 (eluent acetone:hexane:benzene = 3:2:10).

^1H NMR identification (400 MHz, DMSO- d_6), ppm: 8.93 (s, 1H, OH), 7.76 (s, 1H, NH), 6.94 (d, 2H, Ar), 6.62 (d, 2H, Ar), 5.59 (s, 1H, =CH₂), 5.23 (s, 1H, =CH₂), 3.25 (t, CH₂-O), 2.62 (t, Ar-CH₂), 1.85 (s, 3H, CH₃).

1.48 g (0.0147 mol) of triethylamine was added to the solution of 2 g (0.0098 mol) of 4-(2-aminoethyl)phenol in DMF. Then 1.54 g (0.0147 mol) of methacrylchloride was added dropwise with stirring and permanent cooling to 5–10°C. The reaction mixture was kept 3 hours at room temperature. After that the insoluble TEA · HCl was removed by filtration. A filtered solution was poured into 200 ml of distilled water that resulted in formation of solid residue. The obtained product was separated from a water phase by filtration. 2 g of 4-(2-methacrylamidoethyl)phenyl methacrylate was obtained with a yield of 75%. After recrystallization from the acetone:water mixture, m.p. = 93°C, R_f = 0.65 (eluent acetone:hexane:benzene = 3:2:10).

^1H NMR identification (400 MHz, DMSO- d_6), ppm: 7.86 (m, 1H, NH), 7.23 (d, 2H, Ar), 7.00 (d, 2H, Ar), 6.23 (d, 1H, =CH₂), 5.81 (d, 1H, =CH₂), 5.60 (d, 1H, =CH₂), 5.24 (d, 1H, =CH₂), 3.36 (m, 2H, CH₂-NH), 2.78 (m, 2H, CH₂-Ar), 2.01 (s, 3H, CH₃), 1.85 (s, 3H, CH₃).

Polymerization procedure. The polymerization root given below for monomer **M2** was employed as a general procedure for synthesis of homopolymers of **M2–M6** (polymers **poly-M2–poly-M6**) with variation of polymerization time (see section “Results and discussion”).

For the polymerization 0.5 g of 4-(methacrylamido)naphthyl methacrylate (**M2**) and 0.005 g of azobisisobutyronitrile (AIBN) were dissolved in 5 ml of dimethylformamide. The reaction vessel with the solution was subsequently closed air-tight. The solution was heated to 80°C for 90 minutes. Thereafter, the reaction vessel was opened and the solution was added dropwise to 100 ml of ethanol while stirring at room temperature. The separated polymer was filtered off, dried and dissolved in 3 ml of dimethylformamide. Subsequently, this solution was added dropwise to 50 ml of ethanol. Filtration and drying at 40°C in a vacuum gave 0.085 g (17%) of poly(4-(methacrylamido)-naphthyl methacrylate) (**poly-M2**). IR identification (KBr), cm⁻¹: broad 3460, 3340 (NH), 1750 (–O–CO–), 1680 (amide I), 1660,

1500, 1250, 947, 661 (aryl), other signals 2930, 1621, 1530, 1390, 1340, 1320, 1220, 1130, 814, 760, 594.

Material Characterization

Thin layer chromatography was performed with Merck Kieselgel plates 60F254. NMR spectra were recorded with a Bruker AM400 FT-NMR-spectrometer (400 MHz) with TMS as internal standard. IR spectra were run on a Nicolet 5SXB FTIR-spectrophotometer. The UV/Vis spectra of polymers were measured by Ocean Optics spectrometer in the spectral range 220–600 nm. GPC-measurements were performed using PSS-SDV columns and DMF eluent containing LiBr at a flow rate of 1.0 mL/min. The calibration curves for GPC analysis were obtained using PSS polystyrene standards (1000–400000 D). Differential scanning calorimetry was carried out with a Perkin-Elmer DSC 7.

LC Cells and Photoalignment Tests

The **poly-M2-poly-M6** polymers were dissolved in DMF at concentration 1 wt% and filtered to 0.2 μm by syringe filter. The polymer films were obtained by spin coating of the polymer solutions on the quartz or ITO covered glass plates and subsequent backing at 150°C over 1 h. The photoalignment action was provided by a broad band irradiation from a high pressure mercury lamp DRS-500 linearly polarized by a Glann-Tompson prism. To impart unambiguous direction of LC pretilt the substrates were irradiated in two steps: first with polarized UV light (14 mW/cm², 10 min) and then with non-polarized UV light (78 mW/cm², 1 min) by sample rotation of 90° around its normal. Both irradiations were carried out obliquely at the incidence angle of 45°.

Two types of LC cells were constructed. In the most common case LC cell was made by sandwiching the LC between a pair of glass/ITO substrates coated with photoalignemnt layer and irradiated as described above. To obtain a uniform director orientation across the cells, they were assembled in an antiparallel fashion. This means that direction of irradiation with non-polarized light were antiparallel to each other. Cell thickness was adjusted by spacers with a diameter of 20 μm . These cells, termed symmetrical cells, were used to determine the type of LC alignment (homeotropic, planar or tilted), and also to measure pretilt angle of LC.

To define the alignment direction in the cell plane and the value of azimuthal anchoring energy we also constructed cells consisting of one rubbed polyimide substrate and a photoaligned substrate (asymmetrical cells). The easy axis of the photoalignment substrate was turned

90° with respect to the rubbing direction of the polyimide substrate. The rubbed substrate was used as a reference one with predetermined alignment direction and strong azimuthal anchoring. The thickness of these cells was reduced to 6 μm to increase upper limit of anchoring energy measurement.

The cells were filled at room temperature with nematic mixture ZLI2293 from Merck. We judged the alignment quality by cell observation in a light box and polarizing microscope using evaluation scale with five grades: (1) excellent; (2) good (single alignment faults); (3) satisfactory (minor alignment faults); (4) bad (big number of alignment faults in a form of inversion walls, flowing patterns, etc.) and (5) no alignment. The pretilt angle was measured by crystal rotation method, while azimuthal anchoring coefficient was estimated by spectroscopic method described in Ref. [10].

3. RESULTS AND DISCUSSION

Monomer Structure and Polymerization Rate

According to synthetic procedure described above, linear soluble in organic solvents polymer materials were obtained with satisfactory yields. The maximum polymerization yield, when linear soluble product still could be obtained, is strongly dependent on the chemical nature of aromatic core (naphthalene or phenylene) and presence of alkyl tail in monomer molecule.

Naphthalene-containing monomers **M2** and **M3** could be radically polymerized into soluble in DMF linear polymer products up to 70 wt.% monomer conversion. Free $\text{C}=\text{CH}_2$ potentially photoactive double bonds were registered in IR spectra of corresponding polymers **poly-M2** and **poly-M3** at 1621 and 1630 cm^{-1} respectively.

The maximum yield of soluble polymer for phenylene-containing monomers **M4–M6** falls down to 30 wt% of monomer conversion. Free $\text{C}=\text{CH}_2$ double bonds were registered in IR spectra of polymers **poly-M4**, **poly-M5** and **poly-M6** at 1621, 1622 and 1623 cm^{-1} respectively. The total polymerization rate of O-methacryloyl group for monomer **M5** is 20 times higher comparing with other studied monomers. This means that selective polymerization process is hardly controlled.

Due to broad overlapped signals in IR and ^1H NMR spectra of **poly-M2–poly-M6** it is not possible to make correct calculations for the ratio of non-reacted and reacted NH-methacryloyl and O-methacryloyl fragments.

We will show later that polymer yield could be considered as an indirect determinant of the efficiency of LC photoalignment with

TABLE 1 Polymerization Yield, GPC Data and LC Alignment Results for **poly-M4**

Polymer yield, wt. %	M _w	M _n	M _w /M _n	Low molecular weight fraction, wt. %	Alignment quality
12	29 400	12 600	2.3	12	excellent
23	50 500	28 600	1.8	36	good
35	60 000	33 600	1.9	22	excellent/good

poly-M2-poly-M6 films. To clear this correlation, several samples with different polymer yield were prepared for each of **M2–M6** monomers changing time of polymerization.

The GPC results presented in Table 1 for **poly-M4** show quasilinear grow of polymer weight with the yield of polymerization. Interestingly, in addition to relatively high maximum corresponding to fraction with high molecular weight for which masses presented in Table 1 are calculated, GPC curve contains additional maximum in a low molecular weight region. The relative content of this fraction clearly correlates with LC alignment as discussed below.

The UV/Vis spectra (Fig. 3) show that polymers are transparent in visible and near UV spectral range that predetermines good

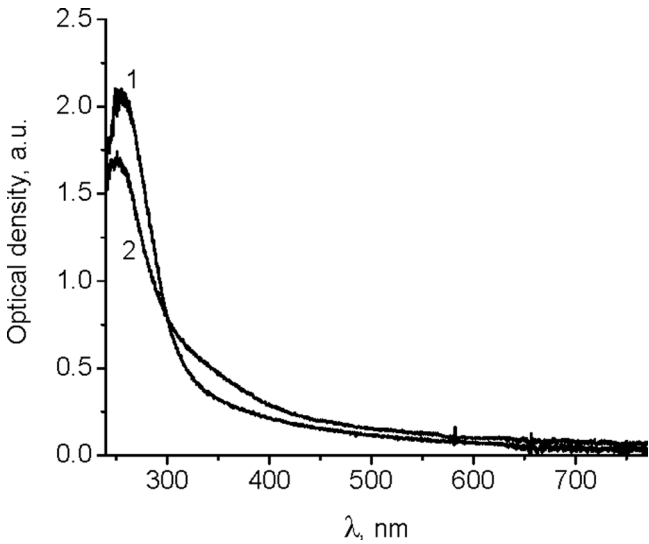


FIGURE 3 UV/Visible spectra of **poly-M4** film before (1) and after (2) irradiation with non-polarized UV light (70 mW/cm², 15 min).

photostability of these compounds and, predictably, their orientational structures.

Photoalignment Peculiarities

The properties of **poly-M2-poly-M6** are strongly dependant on polymerization yield. At high polymerization yield (usually higher than 70 wt.%) the polymer products are highly crosslinked and so insoluble in organic solvents used for film coating purpose. At lower yield (typically, 70–40 wt.%) material can be dissolved, but quality of LC alignment is rather poor. Finally, if the yield is lower than some critical value, acceptable LC alignment is detected. The quality of LC alignment is excellent or good in both parallel and 90° twist configuration (Fig. 4). For all polymers the easy axis of LC alignment was induced perpendicularly to the direction of light polarization \mathbf{E}_{exc} .

The critical values of polymerization yield for **poly-M2-poly-M6** are presented in Table 2. Analyzing these data the following conclusions can be drawn:

- (1) The highest critical yield (50 wt.%) is obtained for naphthalene containing polymer **poly-M3**.

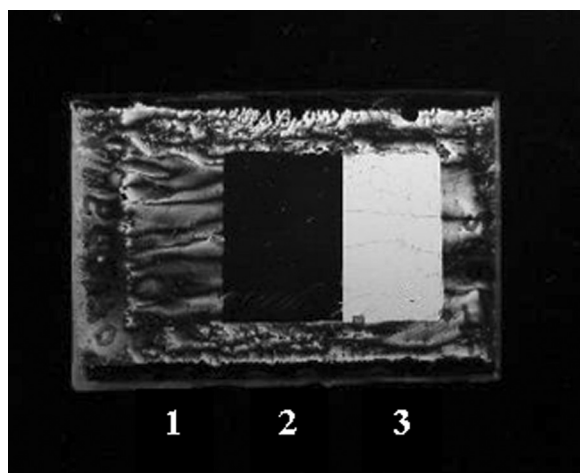


FIGURE 4 Photo of asymmetric cell containing rubbed PI and photoaligned **poly-M4** layer viewed between a pair of crossed polarizers. The photoalignment substrate contains 3 domains: (1) non exposed area; (2) easy axis is induced parallel to rubbing direction; (3) easy axis is induced perpendicular to rubbing direction.

TABLE 2 Polymerization Yield, Solubility and Characteristics of LC Alignment for **poly-M4-poly-M6**

Monomer	Yield, wt. %	Solubility	Alignment quality	LC pretilt angle
M2	48	DMF	good/excellent	0.3°–0.8°
M3	50	DMF	good	0°–0.6°
M4	35	DMF	excellent	0.4°–1.2°
M5	29	DMF	excellent	0°–0.5°
M6	30	DMF	excellent/good	1.0°–2.2°

- (2) The incorporation of phenyl core instead of naphthalene core (**poly-M4-poly-M6**) leads to improvement of LC alignment quality.
- (3) The incorporation of alkyl tail between O or NH methacryloyl group and aromatic core (**M5**, **M6**) reduces the yield of soluble polymer (**poly-M5**, **poly-M6**) giving some enhancement of LC pretilt angle.

Taking into account these results we were further focused on polymer **poly-M4** giving the best promise. Table 1 comprises GPC data and a grade of LC alignment for **poly-M4** samples obtained

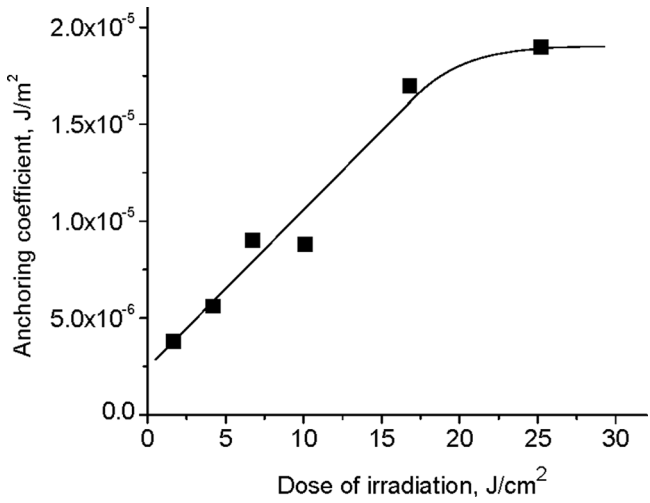


FIGURE 5 Azimuthal anchoring coefficient as a function of exposure dose for **poly-M4** alignment film.

with different polymerization yield. For all polymer samples the molecular weight distribution is bimodal consisting of a higher molecular weight fraction (for which M_w , M_n and M_w/M_n values are derived) and a broad lower molecular weight fraction. One can see that LC alignment improves when the lower molecular weight fraction decreases. This fraction, in turn, grows with polymerization yield.

The azimuthal anchoring strength on **poly-M4** alignment films monotonically grows with an exposure dose reaching saturation level at about 20 J/cm^2 (Fig. 5). The maximal value $W_a = 2 \cdot 10^{-5} \text{ J/m}^2$ approaches maximal values obtained for photoalignment materials with photocrosslinking fragments [18]. The minimal dose needed for good alignment was about 2 J. To reduce the exposure dose, **poly-M4** was doped with Michler's ketone (MK) earlier used as photosensitizer for cinnamate polymer [19]. By adding 25wt.% of MK we obtained double decrease of exposure dose. This shows effective way for the further material improvement.

The **poly-M2-poly-M6** alignment layers demonstrate good alignment stability. The LC cells based on them endure aging at 120°C over 2 h without any noticeable alignment deterioration. This strongly contrasts with poor thermal stability of **poly-M1** layers having no crosslinking fragments in the molecule [16]. Consequently, one can conclude important role of the crosslinking in the maintenance of photooriented state of polymer film and LC alignment.

Let us finally discuss possible photoalignment mechanisms determined by the processes of photochemical transformation. By analogy with cinnamates [20] one can believe that film's anisotropy and LC alignment are mainly determined by the non-reacted anisotropic fragments orientationally ordered in the direction perpendicular to UV light polarization due to the angularly selective transformations. The studied polymers are potentially able to undergo Freies rearrangement and photocrosslinking via $[2 + 2]$ -cycloaddition and/or or photopolymerization of NH-methacryloyl fragments. Excellent LC alignment on the films of **poly-M1** capable to only Freies rearrangement suggests important role of this photochemical process in generation of LC alignment. To provide good LC alignment [16], Fries rearrangement should be highly polarization sensitive process. The photocrosslinking appearing in **poly-M2-poly-M6** radically enhances stability of the induced order. But it is unclear now whether crosslinking fragments are anisotropically distributed in the irradiated film and so participate in the alignment process. A detailed study of the mechanisms underlying LC alignment on **poly-M2-poly-M6** films is currently being pursued in our laboratory.

4. CONCLUSIONS

Principally new concept for the design of LC photoalignment polymers is proposed and experimentally proven by the use of methacryloylaminomethacrylates having two methacryloyl groups of different reactivity. The more active O-methacryloyl group is subjected to polymerization, while the less active NH-methacryloyl group undergoes crosslinking reaction under photoirradiation. These materials provide excellent LC alignment with low pretilt angle and widely varied azimuthal anchoring excelling conventional materials by high thermal stability. The materials have flexible design allowing further optimization. Among the most important tasks is a search of new synthesis roots giving increased yield of polymerization.

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