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Fluorinated copolymers based on 4-(N-methacryloylamino)phenyl methacrylate are proposed as materials for the liquid crystal (LC) photoalignment with a wide range of variations of a pretilt angle. As fluorinated chains, 2,2,3,3-tetrafluoropropylmethacrylate and 2,2,3,3,4,4,5,5-octafluoropentylmethacrylate are used. The growth of a pretilt angle with the concentration of fluorinated chains, more pronounced in a series with longer fluorinated chain, is observed. The pretilt angle of TN LC ZLI 2293 is smoothly varied in the range 0°–20°. Additionally, the uniform high pretilt angle (89°–90°) alignment is realized for VA LC MJ961180.

Keywords: fluorinated copolymer; liquid crystal photoalignment; methacrylate; pretilt angle

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1. INTRODUCTION

Over the last decade, a big amount of works has been directed towards the photo-induced liquid crystal (LC) alignment [1–4] as an alternative route of the rubbing method. The photoalignment effect is due to the ordering of polymer fragments under the action of polarized ultra-violet (UV) light. The photoalignment method allows one to induce an anisotropy on the alignment layer preventing contact, pollution, electrical charging and mechanical destruction of the surface. It has been reported that the LC alignment occurs with films having the *cis-trans*-isomerization of azo-chromophore or cinnamate chromophore [5–10]; photo-crosslinking of cinnamate, coumarin [11], chalconyl [12] chromophore by the (2 + 2) cycloaddition reaction or photo-crosslinking of anthracenyl chromophore by a (4 + 4) cycloaddition reaction [13] on the illumination with UV light; cationic photopolymerization involving the ring opening of epoxide groups for the alignment fixation [14–16]. But the existing photoaligning materials have a number of drawbacks, such as low anchoring energy, low thermal stability and photostability, and hard control of an LC pretilt angle. So many efforts are directed to the searching for new photoaligning materials with improved characteristics.

In our previous work [17], we proposed bis-methacrylics (particularly 4-(N-methacryloylamino)phenyl methacrylate) as a new class of photoaligning materials. Such materials have two methacrylic groups with different reactivities. One group is thermally polymerized in the process of synthesis of the polymer, while the other one anisotropically crosslinks polymer chains under the photoalignment treatment. These materials demonstrate the improved stability of LC alignment, but, however, impact to an LC small pretilt angle.

In order to control the pretilt angle, we propose to vary the hydrophobic properties of methacrylates by means of using their fluorinated copolymers. 4-(N-methacryloylamino)phenyl methacrylate copolymerized with 2,2,3,3-tetrafluoropropylmethacrylate and 2,2,3,3,4,4,5,5-octafluoropentylmethacrylate are considered. Controlling the type and content of fluorinated chains, we expect to control the LC pretilt angle.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization of Alignment Materials

All solvents of p.a. quality (Aldrich) were stored over molecular sieves of 3 or 4 Å. All chemicals were purchased from Aldrich and used without further purification.

Monomer synthesis was done by the usual acylation of aminophenole (Fig. 1). Particularly, 4-(N-methacryloylamino)phenyl methacrylate was synthesized via acylation of 4-aminophenole (1) in dry tetrahydrofuran with methacryloyl chloride (2) at 15–20°C [17].

Copolymers were synthesized by the following method: 4-(N-methacryloylamino)phenyl methacrylate (MAPhM) and 2,2,3,3-tetrafluoropropylmethacrylate or 2,2,3,3,4,4,5,5-octafluoropentylmethacrylate in a corresponding molar ratio with 1 wt.% of AIBN in dry dimethylformamide were heated to 80°C, and polymer product was isolated by precipitation into diethyl ether.

By this way, two series of copolymers were synthesized with two different fluorinated agents (Fig. 2 a, b). Copolymers inside the series differ from each other by the x:y ratio, i.e. by the mole fraction c_f of fluorinated tails in the main chain. In the series of copolymers based on 2,2,3,3-tetrafluoropropylmethacrylate, homologues with c_f equal to 41.2, 57, and 70 mole % were obtained. In turn, in the series with 2,2,3,3,4,4,5,5-octafluoropentylmethacrylate, the c_f values were 10, 41.2, 50, and 70 mole %.

The characterization of polymers was performed by different methods. Thin layer chromatography was performed with Merck Kieselgel plates 60F254. NMR spectra were recorded with a Bruker NMR-spectrometer (500 MHz) with TMS as internal standard. IR spectra were run on a Nicolet 5SXB FTIR-spectrophotometer. GPC-measurements were performed using PSS-SDV columns and a DMF eluent containing LiBr at a flow rate of 1.0 L/min. The calibration curves for GPC analysis were obtained using PSS polystyrene standards (1000 – 400 000 D). Differential scanning calorimetry was carried out with a Perkin-Elmer DSC 7.

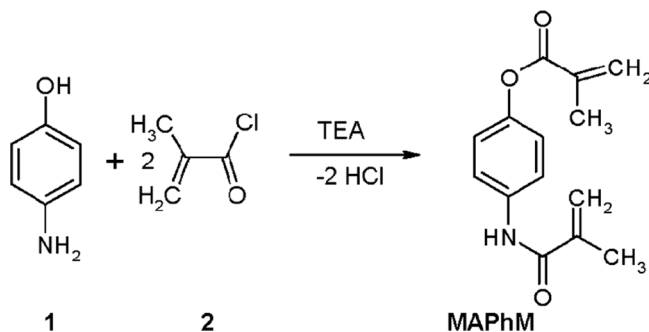


FIGURE 1 Scheme of synthesis of 4-(N-methacryloylamino)phenyl methacrylate.

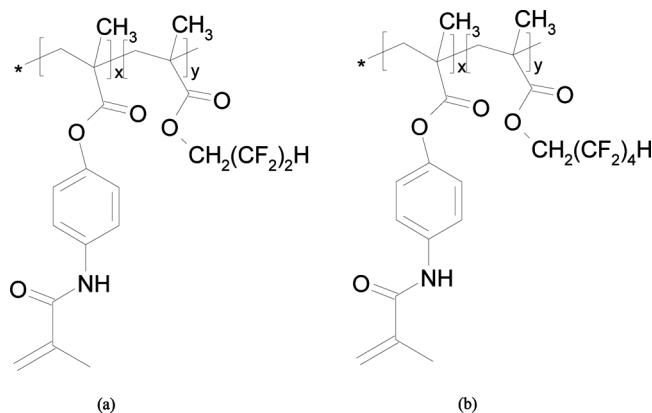


FIGURE 2 Groups of copolymers of MAPHM: (a) with 2,2,3,3-tetrafluoropropylmethacrylate; (b) with 2,2,3,3,4,4,5,5-octafluoropentylmethacrylate.

2.2. Testing of LC Alignment

The quality of LC photoalignment was investigated in the following way. A 2-wt.% solution of the investigated polymer in dimethylformamide was spincoated (3000 rpm, 1 min) on the glass substrate. The obtained film was pre-baked during 10 min at 100°C, then baked at 180°C during 1 h. After that, the polymer film was normally irradiated by polarized UV light ($I = 28 \text{ mW/cm}^2$, $t = 15 \text{ min}$) and then obliquely irradiated by unpolarized UV ($I = 100 \text{ mW/cm}^2$, $t = 1 \text{ min}$). At last, a symmetric optical cell (the cell thickness is 20 μm) with antiparallel LC alignment was made from the irradiated substrates. The cell was filled by liquid crystal ZLI 2293 ($\Delta\epsilon > 0$) or MJ 961180 ($\Delta\epsilon < 0$). The quality of liquid crystal alignment was estimated by the observation of a sample in polarized light (a light box and a polarizing microscope). The pretilt angle of a liquid crystal in the cell was measured by the commonly used crystal rotation method [18].

3. RESULTS AND DISCUSSION

It was revealed that both MAPHM homopolymer and its fluorinated copolymers provide the LC alignment of excellent quality (Fig. 3).

Using copolymers with different fluorinated chains allows us to control the liquid crystal pretilt angle. Figures 4 and 5 demonstrate

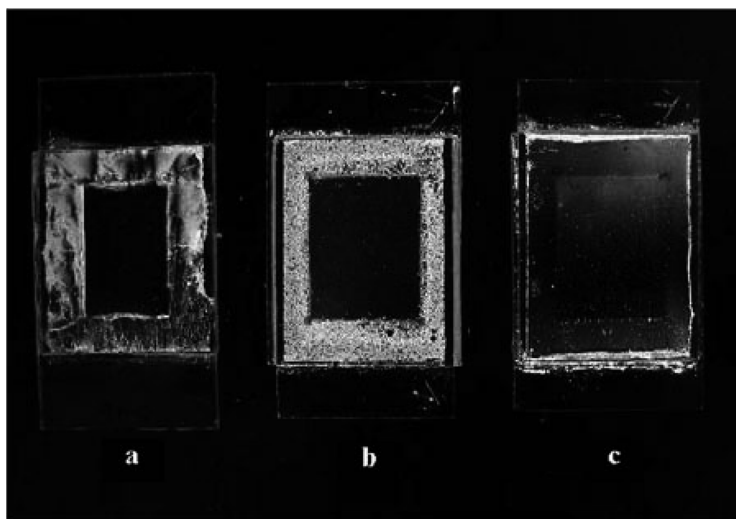


FIGURE 3 Photoalignment of liquid crystal MJ961180 ($\Delta\epsilon < 0$) in the cell based on: (a) poly-MAPhM, planar alignment; (b) MAPhM copolymer with 2,2,3,3-tetrafluoropropylmethacrylate ($c_f = 57$), tilted alignment; (c) MAPhM copolymer with 2,2,3,3,4,4,5,5-octafluoropentylmethacrylate ($c_f = 70$), vertical alignment. Symmetrical cells are in crossed polarizers.

the monotonous increase of the pretilt angle with concentration of fluorinated chains. One can see also that, for TN LC ZLI2293, the longer fluorinated tail promotes a higher value of the pretilt angle than the shorter one at the same mole concentration in the polymer. This difference is less pronounced for VA LC MJ961180 having negative dielectric anisotropy. The pretilt angle of LC ZLI2293 is varied in the range 0° – 20° . In turn, the pretilt angle of MJ961180 runs the whole range of pretilt angles, i.e., it changes from 0° to 90° . The values close to 90° are easily achieved, which makes these materials promising for the VA mode.

Noteworthy, even if the concentration of non-photosensitive fluorinated monomers is 50–70 mole%, the alignment quality is good. Thus, the LC pretilt angle changes with the concentration of fluorinated tails without noticeable changes in the alignment quality. In addition, in contrast to copolymers with cinnamate units [19], LC photoalignment in copolymers with methacrylic reactive groups is much more stable. These results make such method of pretilt angle variation extremely promising for applications.

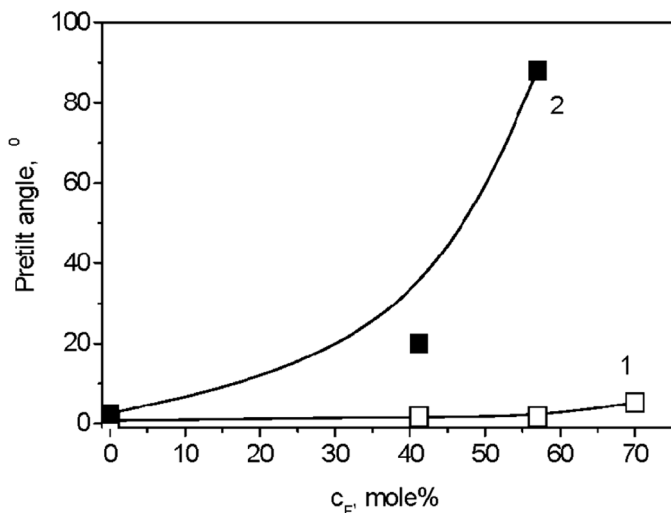


FIGURE 4 Dependence of LC pretilt angle vs. mole concentration c_f of fluorinated fragments in 2,2,3,3-tetrafluoropropylmethacrylate. (1) ZLI2293 ($\Delta\epsilon > 0$); (2) MJ961180 ($\Delta\epsilon < 0$).

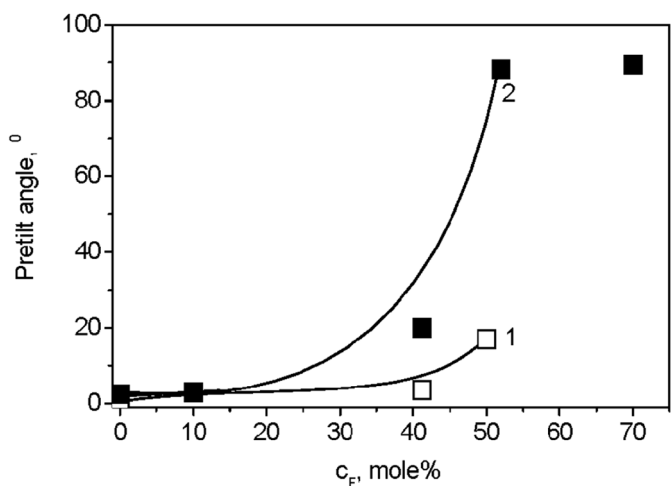


FIGURE 5 Dependence of LC pretilt angle vs. mole concentration c_f of fluorinated fragments in 2,2,3,3,4,4,5,5-octafluoropentylmethacrylate. (1) ZLI2293 ($\Delta\epsilon > 0$); (2) MJ961180 ($\Delta\epsilon < 0$).

CONCLUSIONS

We have proposed an effective method to control the LC pretilt angle on the methacrylate copolymer surface. Copolymerization of methacrylic monomers with fluorinated fragments of different lengths and different concentrations in copolymer is considered. It is revealed that both the lengthening of a fluorine chain and the increase of the mole concentration of a fluorine fragment leads to the growth of the liquid crystal pretilt angle. Fluorinated chains increase the polymer hydrophobic properties and promote a gradual change of the LC alignment from a planar to tilted and then to vertical alignment. The increase of the pretilt angle with the concentration of hydrophobic chains is not accompanied with the worsening of the LC alignment and alignment stability. This fact makes the method extremely promising for industrial applications.

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