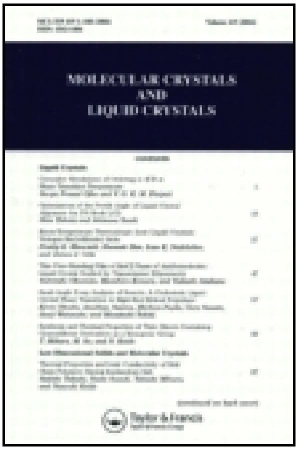

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: V. G. Syromyatnikov, L. O. Vretik, O. V. Yaroshchuk, Y. A. Zakrevskyy, T. M. Kim, J. H. Jo, J. Y. Kim & S. H. Kim (2001): Naphthalene Containing Polymers as New Photoaligning Materials for LCs, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 368:1, 543-549

To link to this article: http://dx.doi.org/10.1080/10587250108029986

Mol. Cryst. and Liq. Cryst., 2001, Vol. 368, pp. 543-549
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Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Naphthalene Containing Polymers as New Photoaligning Materials for LCs

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Polynaphtylmethacrylates (PNMA) are considered as a new class of liquid crystal (LC) photoaligning polymers. The films of PNMA irradiated with polarized UV light provide high quality LC alignment with the easy axis oriented perpendicularly to polarization direction of the exciting light. A maximal value of the azimuthal anchoring energy was estimated as 5×10^{-6} J/m^2. It is close to the best photoaligning materials. Fries rearrangement is considered as a main photochemical reaction leading to anisotropy of PNMA layers.

Keywords: polynaphtylmethacrylate; photoalignment; Fries rearrangement

Although the rubbing of polyimide layers still remains the current method of mass production of liquid crystal displays (LCD), the interest to alternative viable technologies increases. It is caused mainly by principle drawbacks of the rubbing technology such as electrostatic charging and mechanical damage. One of the most attractive alternative to rubbing is photoalignment method proposed about ten years ago [1, 2]. Indisputable advantage of this method is non-contact "soft" treatment of the aligning surface. It provides smooth control of anchoring energy, position of LC easy axis in both azimuthal and polar plane and associated patterning LC cells. In spite of it, photoalignment technique is still not used for the mass production of LCD because of several technological problems. Some of them are low thermostability of the desirable LC alignment, image sticking effect [3] and not sufficiently good reproducibility. The current problems of photoalignment based LCDs will be solved by application of new driving schemes, optimization of the irradiation conditions and synthesis of new photoaligning materials.

Several classes of photosensitive polymers were investigated as photoaligning substrates. First photoalignment was realized using azobenzene compounds [1]. Later on, photoaligning properties of cinnamates [2,4], coumarins [5] and some photosensitive polyimides [6] were investigated. Recently, photoaligning properties of polysilanes were studied [7]. These materials differ in treatment conditions, LC aligning characteristics as well as in a base photochemistry. In spite of the discovering big variety of the materials capable for photoalignment, the principle problems of photoalignment technique mentioned above are not solved yet. So, search of new classes of photoaligning materials is of a great actuality for the practical use of the photoalignment technology.

We report on a new class of photoaligning polymers containing naphthalene derivatives. Possible photochemical processes leading to the surface anisotropy are discussed. LC aligning parameters like anchoring energy and pretilt angle, as well as orientation of the induced easy axis are determined. A comparison with characteristic photoaligning materials is done.

EXPERIMENTAL

Samples

The polynaphthylmethacrylate (PNMA) was chosen for the systematic studies.

Synthesis of PNMA was carried out in the following way. 1-naphthylmethacrylate was synthesized by the reaction of 1-naphthol in acetone solution with methacrylchloride in the presence of triethylamine and crystallised from toluene and hexane. The corresponding polymer PNMA (vitrification temperature Tg=135°C) was synthesized by thermopolymerization in DMFA solution with AIBN as initiator.

The layers of PNMA were obtained by spin coating of the polymer solution in dichloroethane on the quartz or ITO covered glass plates. The prepared films were baked during 1 h at 150°C. After that the PNMA films were exposed to the UV irradiation of a mercury lamp normally to the film plane. For polarization of the irradiation a Glann-Tompson prism was used.

Two types of LC cells were fabricated:

1) symmetrical cells (both substrates are covered by PNMA and irradiated by UV light);
2) combined cells (one substrate is covered by the UV light irradiated PNMA film, whereas second one by rubbed polyimide (PI)).

In both cases the substrates were combined so to obtain both parallel and twisted LC configuration. A cell gap of 20 μm was maintained by glass spacer. We used nematic LC mixtures ZLI4801-000 and MLC6012 by Merck. LCs were filled into cells at room temperature.

Methods

Direction of the induced easy axis was determined observing LC structure in the combined cells assuming alignment on the rubbed PI substrate in the rubbing direction. The LC pretilt angle was measured in combined cells by crystal rotation method as it is described in [8].

The azimuthal anchoring energy W_a was estimated by measuring a twist angle φ in the combined cell. The values of φ and W_a are connected by the formula

$$\xi \sin 2(\alpha - \varphi) = 2\varphi, \qquad (1)$$

derived in [9]. In (1) α is the angle between direction of orientation induced by rubbed substrate and the polarization of the exciting light, $\boldsymbol{E}_{exc}$, $\xi = \frac{Wd}{K}$ is the anchoring parameter (*d* and *K* are the cell gap and LC orientational elastic constant, respectively).

To study dependence of the anchoring energy on the exposure time, combined multi-domain cells were fabricated. A difference in the domains was only irradiation time of a PNMA substrate. Direction of the UV light polarization was fixed; the angle between polarization direction (photo-cured substrate) and rubbing direction (rubbed substrate) was 45°. Twist angle φ in the domains was measured using polarizing microscope.

The UV spectra of the PNMA films were measured by PC conjugated spectrometer KSVU (LOMO, Russia).

RESULTS AND DISCUSSION

Quality of LC alignment was good in both types of the produced cells (Photo 1). The easy axis of LC alignment was induced perpendicularly

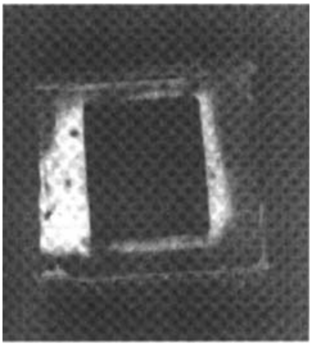


Photo 1. Snapshot of LC cell based on PNMA substrates.

to the direction of light polarization $\boldsymbol{E}_{exc}$. Pretilt angle on PNMA substrates was close to zero for both LCs used in our studies.

A measured dependence of the twist angle φ in the combined cell on the exposure time τ_{exp} is presented in Fig.1. In the same Figure it is shown dependence $W_a(\tau_{exp})$ calculated using formula (1). In these calculations we used α=45°, d=20 μm and K= 10^{-12} N. The curve $W_a(\tau_{exp})$, similarly to other photoorientants, monotonously grows with the increase of τ_{exp} and has a tendency of saturation. In the saturated state $W_a \approx 5\ 10^{-6}$ J/m^2. This value is close to the best photoaligning materials [10].

To elucidate the nature of photoinduced anisotropy in the aligning substrates the UV spectra of PNMA in the films as well as in the toluene solution were measured before and after subsequent periods of irradiation. The data for the PNMA film are presented in Fig.2a. The complex band in the range 260-300 nm corresponds to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions

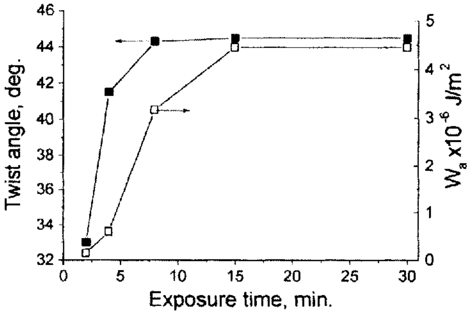


FIGURE 1. Experimental dependence $\theta(\tau_{exp})$ and calculated curve $W_a(\tau_{exp})$.

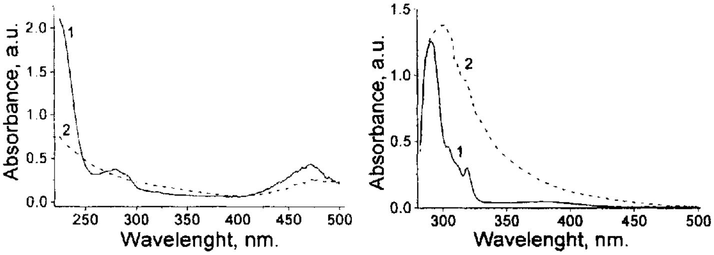
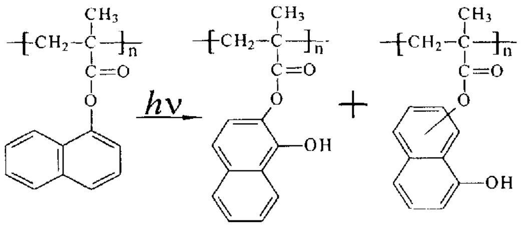


FIGURE 2. UV/Vis spectra of PNMA in film (a) and toluene solution (b). 1-before irradiation; 2-after irradiation (6 mW, 15 min).

in the naphthylmethacrylate links. The maximum at 470 nm presumably appears due to aggregation of naphthyl containing groups. In good agreement with this assumption, the band at 470 nm does not arise in the absorption spectra of PNMA in toluene solution (Fig.2b). Absorption decrease in this area after irradiation can be caused by destruction of the naphthyl aggregates by light.

Changes in absorption spectra of PNMA in toluene solution under UV irradiation are similar to other compounds from the same series and correspond to reaction of Fries photorearrangement [11,12]. The scheme of this reaction in case of PNMA is presented bellow:



Besides, photooxidation process should be taken into account. However, efficiency of the photooxidation is much more lower then of the Fries reaction.

In case of the irradiation with polarized UV light due to the Fries re-arrangement a photoselection process [13] may arise leading to induction of an orientational order in the PNMA film. This anisotropy, as it is commonly accepted [10], is a reason of LC alignment.

CONCLUSIONS

Thus, polynaphthylmethacrylates form new class of polymers capable for LC alignment. A quality of LC alignment and anchoring parameters are comparable with that for the best photoaligning materials. Our studies extend the field of known photochemical reactions leading to induction of an orientational order in the photoaligning substrates. In addition to *trans-cis* isomerisation (azopolymers), dimerisation (cinnamates and coumarins), decomposition (polyimides and polysilanes) the Fries rearrangement causes efficient anisotropy in aligning layers and, as result, high-grade LC alignment.

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