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Synthetic Routes in Its Solving**

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Problem of Photoalignment in the LCD's Development: Synthetic Routes in Its Solving

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Hereinafter we discuss our last five years investigations in the field of new highly efficient polymers for liquid crystal (LC) photoalignment. New polymers finally proposed are based on methacryloylaminoarylmethacrylates with two methacryloyl groups of different reactivity. Fries rearrangement and photocrosslinking/photopolymerization are such photochemical reactions which take place in their films under the action of UV light. In a case of polarized light irradiation rearrangement results in LC photoalignment. The problem of pretilt angle and anchoring energy control as well as thermal stability of the induced alignment are discussed.

Keywords: arylmethacrylate; fries rearrangement; liquid crystal photoalignment

1. INTRODUCTION

Photoalignment has advantages in comparison with rubbing, plasma alignment and some other technologies in LCD's industry. 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.

Generally, three main classes of materials that are used for photoalignment layers can be categorized [1]: azo-containing polymers and monolayers, crosslinkable materials, e.g. cinnamates, coumarines, chalcones and materials undergo photodegradation, e.g. polyimides. Each class of materials has own advantages and disadvantages.

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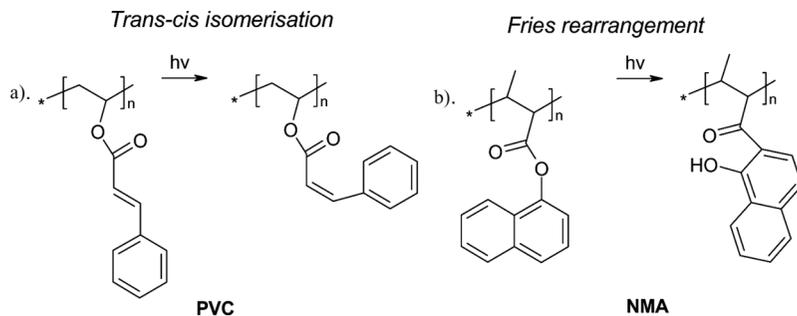


FIGURE 1 Photoisomerization of: (a) poly(vinylcinnamate) and (b) poly(naphthylmethacrylate).

Azo-containing alignment materials are colored and their long-term stability is poor, because of configuration relaxation (*cis-trans*) and sensitivity to visible light. *Trans-cis* isomerization is responsible for the alignment in cinnamate-containing polymers (e.g. polyvinylcinnamate, **PVC**, see Fig. 1(a)). In addition, an anisotropic dimerization process leads to the better thermal stability of the alignment obtained in cinnamate, coumarine, chalcone, diphenylacetylene-containing materials. Successful photoalignment achieved in polyimide materials was attributed to the anisotropic decomposition in such type polymer layers. But polar anchoring energy of the polyimide is reduced because of degradation products presence and they affect to the enlargement of image sticking, too.

Photoalignment materials are not used yet in commercial LCD because of such unsolved problems as low anchoring strength, image sticking, insufficient alignment stability etc.

We have found new series of materials with arylmethacrylates moieties (e.g. 1-naphthylmethacrylate, **NMA**) [2], which would provide LC photoalignment due to another isomerization reaction called Fries rearrangement. This reaction is not reversible and photoproducts are stable in the visible light.

2. EXPERIMENTAL SECTION

Materials

The detailed description of monomer synthesis and the root of 50 polymerization are given in Ref. [2,4,5,8,9,11].

Kinetic Experiments

Kinetic curves were obtained by dilatometry in conditions excepted as standard for all monomers discussed: 5 wt.% of the monomer solutions

in DMF, with presence of 1 wt.% of AIBN as initiator in inert atmosphere (argon) at 60, 70 and 80°C.

LC Cells and Photoalignment Tests

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/cm^2 , 10 min) and then with non-polarized UV light (78 mW/cm^2 , 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 photoalignment 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.

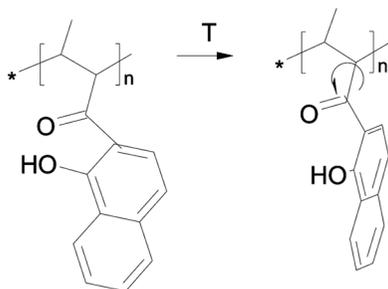
To define the alignment direction in the cell plane and the value of azimuthal anchoring energy we also constructed cells consisting of one rubbed polyimide substrate and a photoaligned substrate (asymmetrical cells). The easy axis of the photoalignment substrate was turned 90° with respect to the rubbing 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. [3].

3. RESULTS AND DISCUSSION

The employed photoreaction as an alternative for *trans-cis* isomerization is Fries photorearrangement (Fig. 1(b)), which is a common reaction for aromatic esters and amides.

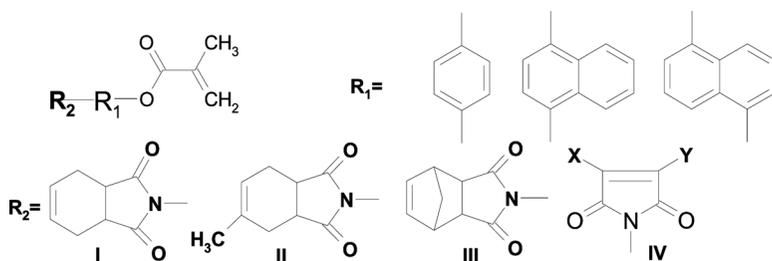
Fries rearrangement is not reversible as *trans-cis* isomerization. However, the obtained photoalignment of LC in **NMA** film was not thermally stable, too [2]. It could be explained due to the rotation around single C–C bond in the obtained photoproducts at the elevated temperatures:



As the next step in this direction we tried to synthesise poly(aryl methacrylates) with free reactive double bond as side group which could be used for further thermo- and photocuring. By this manner we expected to make photoalignment in the polymers more thermally stable.

3.1. Tetrahydrophthalimido- and Maleimidoaryl Methacrylates: Polymer Syntheses and Alignment Quality

Multifunctional monomers with double bonds of different reactivity as tetrahydrophthalimido- ($R_2 = \text{I–III}$) and maleimidoaryl methacrylates ($R_2 = \text{IV}$) were synthesized:



We realized thermoinitiated radical polymerization of these monomers [4,5]. Both tetrahydrophthalimide and maleimide units were found to take part in crosslinking processes during of their thermoinitiated radical polymerization. Nevertheless, on the kinetic curves two stationary parts were observed: A- polymerization with formation of linear polymers and B- insoluble crosslinked products were obtained (see Fig. 2). It means that two consecutive polymerization processes take place: initial polymerization of double bond in O-methacryloyl fragment and following crosslinking due to the maleimide double bond.

At low degree of monomer conversion O-methacryloyl groups were selectively polymerized with formation of linear soluble polymer products bearing free double bonds of imide cycles capable to react in [2 + 2] cycloaddition with high quantum yields [6,7]. The maximum polymerization yield, when linear soluble product still could be obtained, was strongly dependent on the chemical nature of aromatic core (naphthalene or phenylene), substituent presence in the imide cycle and temperature of the process [4,5]. Temperature increasing leads to increasing of crosslinking (see Fig. 2, compare curves for 60°C and 80°C).

Only for maleimidophenyl methacrylate ($R_1 = \text{phenyl}$, $R_2 = \text{IV}$ with $X = Y = \text{H}$) it was not possible to obtain soluble polymer material and LC alignment was not tested.

The kinetic curves (monomer conversion versus polymerization time) obtained for this monomer at different temperatures had no division into two parts as it was observed for all other monomers

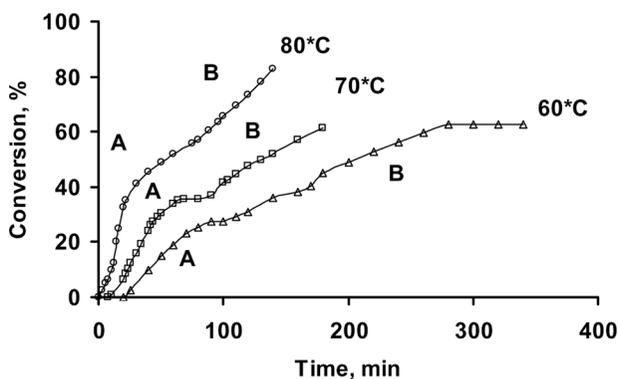


FIGURE 2 The kinetic curves of thermoinitiated radical homopolymerization of tetrahydrophthalimidophenyl methacrylate (in 5 wt.% of the monomer in DMF, 1 wt.% of AIBN, inert atmosphere) at different temperatures.

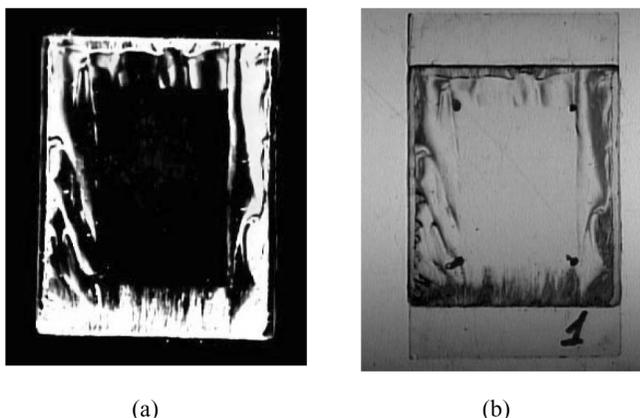


FIGURE 3 Photographs of photoaligned LCDs with polarized UV exposure on the poly(tetrahydrophenyl methacrylate ($R_1 = \mathbf{phenyl}$, $R_2 = \mathbf{I}$)) surfaces (a) normal, (b) parallel location of analyzer.

(see Fig. 2). So, we made a conclusion, that O-methacryloyl and maleimide double bonds copolymerise what results in immediate crosslinking. 145

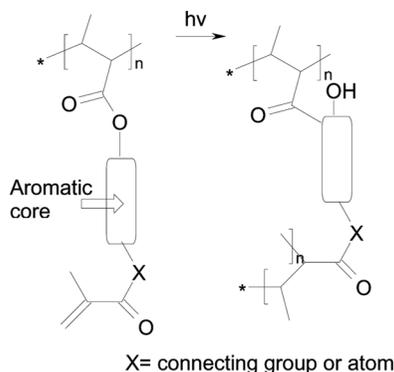
The quality of LC alignment was tested for all other obtained polymers. Unfortunately, only alignment on polymers obtained from tetrahydrophenyl methacrylate ($R_1 = \mathbf{phenyl}$, $R_2 = \mathbf{I}$) was good in both parallel and 90° twist configuration (see Fig. 3). The easy axis of LC alignment was induced perpendicularly to the direction of light polarization \mathbf{E}_{exc} . However, this alignment was not thermally stable. 150

Quality of LC alignment tested for poly(citraconylimidophenyl methacrylate) ($R_1 = \mathbf{phenyl}$, $R_2 = \mathbf{IV}$ with $\mathbf{X} = \mathbf{H}$, $\mathbf{Y} = \mathbf{CH}_3$) was not reproducible, it was different for different samples synthesised with a small deviation in polymer yield and in the changes in syntheses scale. For other materials quality of LC alignment was rather poor. 155

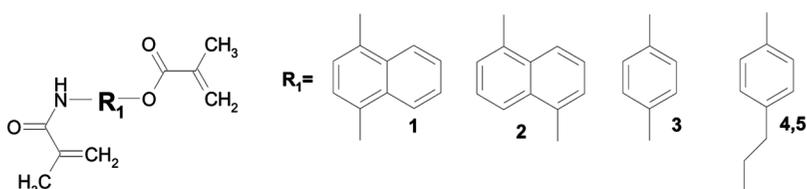
Thus, from these two classes of new monomers, it was possible to select only one perspective monomer structure and this structure could not be flexibly changed. Taking into account that for industrial implication the materials with readily improved alignment characteristics are required, a new class of monomers was designed and tested. 160

3.2. Methacryloylamidoaryl Methacrylates 165

It was expected that crosslinking in new designed polymers with following structure



could arise thermal stability of anisotropy due to radical polymerization of free double bonds. As possible synthetic route for such polymers syntheses we have tried a direct polymerization of corresponding monomers:



We realized selective polymerization of O-methacryloyl groups with formation of linear soluble polymer products bearing photo- and thermoactive double bonds of NH-methacryloyl groups. As we believe, the last-named free double bonds undergo anisotropic crosslinking reaction in case of polarized light irradiation.

The obtained LC photoalignment shows thermal and photo-stability as well as easy control of the pretilt angle and anchoring energy [9]. The LC cells based on them endure aging at 120°C over 2 h without any noticeable alignment deterioration. The maximal value $W_a = 2 \cdot 10^{-5} \text{ J/m}^2$ for polymer based on compound **V** approached maximal values obtained for photoalignment materials with photocrosslinking fragments [10]. The minimal dose needed for good alignment was about 2 J. By adding 25 wt% of Michler's ketone we obtained double decrease of exposure dose.

In order to control pretilt angle we varied hydrophobicity of polymer based on monomer **V** by means of using its fluorinated copolymers. Fluorinated copolymers based on 4-(N-methacryloylamino)phenyl methacrylate were proved as materials for liquid crystal (LC) photoalignment with a wide range variation of pretilt angle [11]. As fluorinated chains 2,2,3,3-tetrafluoropropyl methacrylate and 2,2,3,3,

4,4,5,5-octafluoropenthyl methacrylate were used. It was revealed that both lengthening of fluorine chain and increase of mole concentration of fluorine fragment leads to growth of liquid crystal pretilt angle. Growth of pretilt angle with a concentration of fluorinated chains, more pronounced in a series with longer fluorinated chain, was observed. The pretilt angle of TN LC ZLI 2293 was smoothly varied in the range 0°–20°. Additionally, the uniform high pretilt angle (89°–90°) alignment is realized for VA LC MJ961180. 195 200

All experimental data obtained shows a big potential for the further material improvement. However, properties of polymers based on methacryloylamidoaryl methacrylates are strongly dependent on polymerization yield. If only the yield is higher than some critical value, acceptable LC alignment is not detected [10,11]. For the most perspective monomer 4-(N-methacryloylamino)phenyl methacrylate ($R_1 = 3$) the critical yield is 35 wt.%. 205

The kinetic curves obtained for monomers 1–5 at different temperatures had no legible divisions into two parts as it was observed for tetrahydrophthalimido- and some maleimidoaryl methacrylates (see Section 3.1). In case of O-methacryloyl and NH-methacryloyl double bonds presented in a same molecule it is more difficult to avoid their crosslinking during polymerization. So, an enhancement of soluble reactive polymer yield is a main synthetic problem now. 210 215

4. CONCLUSIONS

New polymer materials based on methacrylamidoaryl methacrylates employed for LC photoalignment gave a big promise due to their flexible design allowing further optimization. Searching of new routes giving increased yield of polymerization or alternative methods, e.g. polymer analogues reactions, are the next synthetic task. 220

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