
Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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# Newly Synthesized Polyimide for Aligning Nematic Liquid Crystals Accompanying High Pretilt Angles

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# Newly Synthesized Polyimide for Aligning Nematic Liquid Crystals Accompanying High Pretilt Angles

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A series of special polyimides was synthesized to use them for aligning nematic liquid crystals accompanying a pretilt angle from a few degrees up to 30 degrees by using a rubbing technique. The chemically synthesized polyimide is comprised of two parts: one is an ordinary long-chain polymer and the other is an extra chemically attached hydrocarbon branch with a finite length. The former part is considered to play a role in aligning liquid crystals in a single direction due to the rubbing and the latter is responsible for producing a high pretilt angle if appropriate rubbing is done. This newly synthesized polyimide was successfully used to make a supertwisted nematic liquid crystal display with 270 degrees twist and 12 degrees pretilt.

*Keywords: liquid crystal, high pretilt angle, polyimide, rubbing technique, supertwisted nematic LCD*

## 1. INTRODUCTION

It was discovered that a high multiplexability and a wide viewing angle could be achieved with twisted nematic devices having twist angles of greater than 90 degrees; it is generally called the supertwisted type LCD(STN-LCD).[1,2] An STN-LCD can be fabricated by giving a twist angle of from 180 degrees to 270 degrees accompanying the necessary pretilt angle, which is an angle between the director of the LC and the substrate, of from 5 degrees to 30 degrees, respectively.

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Recently, a black and white type STN-LCD with very high legibility was developed by introducing a compensating layer for removing color appearing in the conventional STN-LCDs with a yellow or blue mode.[3] These developed types have been utilized in the displays of word processors or computers. Further, a full color LCD has been demonstrated by combing this neutral color dot matrix STN-LCD with an RGB color filter.[4]

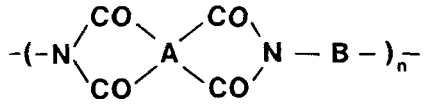
An STD-LCD with a fairly large display area will be better fabricated by using a rubbing technique rather than oblique evaporation of SiO since the latter is not suitable for volume production. For this reason there exists a strong demand for a special polyimide that is capable of producing a stable high pretilt angle by rubbing. We synthesized a special polyimide satisfying this need and we have succeeded in demonstrating an STN-LCD fabricated by the rubbing process.[5] There have been several papers published concerning the production of a high pretilt angle by rubbing: Moseley *et al.*[6] reported that it is possible to obtain a high pretilt by applying a strong rubbing on a selected polyimide, Filas and Patel[7] discussed the mixture of polyimide and silanes, and further Matsumoto *et al.*[8] reported the mixture of polyimide and chromium salt both for aligning nematic liquid crystals (NLCs) accompanying pretilt angles of from several degrees to 90 degrees. However, detailed descriptions about the reliability of the aligning films in this literature are lacking.

This paper describes a chemical synthesis of a special polyimide that is useful for a practical LCD application which needs a stable high pretilt angle, and also the demonstration of the generation of a high pretilt angle depending on both molecular structure and rubbing condition.

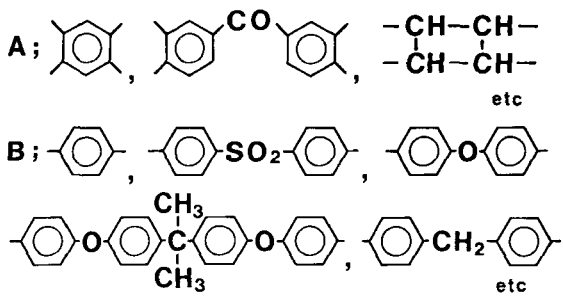
## 2. SYNTHESIS OF THE POLYIMIDE

A wide variety of the polyimides have been widely utilized for producing a planar conformation of NLCs in order to fabricate, e.g., TN-LCDs. Amphiphilic molecules (e.g. silane coupling agent) with an appropriate length of hydrocarbon chain have also been widely used for aligning liquid crystal molecules in a homeotropic conformation. We have explored several hundred possible combinations of the polyimides and branching molecules which are put together by chemical synthesis.

The basic molecular structure of the polyimide is expressed as follows:



where



The chemical synthesizing process, adopted by the present authors, to produce alkyl-branched polyimide, which is capable of generating a stable pretilt angle by rubbing, is shown in Figure 1.

## 3. GENERATION OF HIGH PRETILT ANGLES FOR NEMATIC LIQUID CRYSTALS

The obtained values of the pretilt angles produced by rubbing for NLCs such as cyanobiphenyl 5CB (from Merck or Chisso) or type ZLI-2293 (from Merck) were found to depend systematically on the length of the branched hydrocarbon chains and the strength of the rubbing. Typical examples of the obtained pretilt angles (by applying weak rubbing) are summarized in Table I. The produced pretilt angle was found to increase monotonically with the number of carbons in the molecule in the range of the examination done.

As described in a previous paper we adopted a weak rubbing which gives rise to an induced optical retardation of about 0.1 degree in polyimide films.[5,9]

It was cleared through this series of research work that first, before rubbing, the film was capable of giving a pretilt angle but the directors of LC distribute at random; secondly, an appropriate rubbing with a weak strength is effective to give a good alignment accompanying a

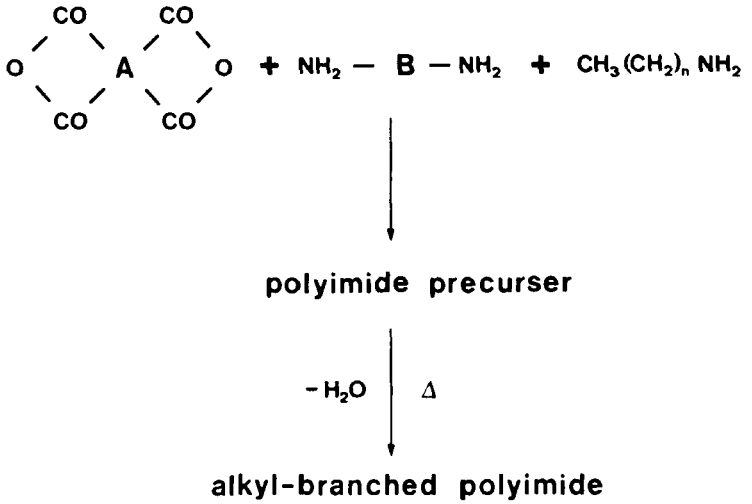



FIGURE 1 Chemical synthesis process to produce alkyl-branched polyimide.

high pretilt; finally, too strong rubbing does not give a high pretilt. The latter seemed to destroy a good form of the branching molecules. The occurrence of the pretilt may be considered to be attributed to the steric interaction between LC molecules and neatly aligned branching chains.

The aligned phase of nematic liquid crystals was found to be stable after an acceleration test done by heating the sample at 80°C for

TABLE I

Obtained pretilt angles using alkylamine branched polyimide (used LC is ZLI-2293, Merck)

| Reacted alkylamine | Alkylamine content in polymer (wt%) | Pretilt angle (deg.) |
|---|---|---|
| $CH_3(CH_2)_{11}NH_2$ | 10 | 10 |
| $CH_3(CH_2)_{15}NH_2$ | 10 | 19 |

TABLE II

Obtained pretilt angles using alkylamine mixed polyimide (LC: ZLI-2293, Merick)

| Mixed alkylamine | Alkylamine content in polyimide(wt%) | Pretilt angle (deg.) |
|---|---|---|
| $CH_3(CH_2)_7NH_2$ | 10 | 6 |
| $CH_3(CH_2)_{15}NH_2$ | 10 | 12 |

several hours and cooling it down again to room temperature; this process was repeated three times.

For a comparison we also conducted an experiment of the generation of a high pretilt by mixing polyimide and alkylamine molecules. It was found that the mixture is also capable of producing a high pretilt angle as summarized in Table II.

Filas and Patel[7] reported that the mixture of polyimide and silanes lost its power to generate a pretilt angle by heating the sample up to 80°C. However the mixture prepared by the authors was found to show a stable pretilted state even though an accelerated heating test was performed.

## 4. CONCLUSION

Polyimide molecules having a branched hydrocarbon chain with an appropriate length were synthesized. They showed a good capability to align nematic liquid crystals accompanying a high pretilt from several degrees to 19 degrees and even up to 30 degrees depending on the length of the branched part and the rubbing strength. It was shown that the aligned phase is durable for the cyclic temperature test (80°C for several hours) and that the developed polyimide is useful, for example, to fabricate a supertwisted nematic LCD.

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