Synthesis and Properties of Novel Homeotropic Alignment Materials with Long Side Chain

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Abstract

VA-LCDs is widely used for recent LCD productions owing to good viewing angle and high contrast. To apply for VA-LCDs, we have synthesized novel homeotropic alignment materials, which all generated high pretilt angles (90°). The thermal stabilities of them were observed by thermogravimetric analysis (TGA). Transmittances of the NLC cell used the new alignment material were not changed before and after thermal annealing at 120°C for 24hrs. In this work, the synthesis and alignment properties of new homeotropic alignment materials will be reported.

1. Objective and Background

Twisted nematic liquid crystal displays (TN-LCDs) have made great progress in quality, and are widely used in flat panel displays. However, poor viewing angle and contrast characteristics remain the major problems. To solve these problems of TN-LCDs, vertical alignment liquid crystal displays (VA-LCDs) have been proposed [1]. It is well known that the VA-LCDs have a good black state and thus it has a high contrast ratio. In the VA-LCDs, homeotropic alignment materials vertically align liquid crystal molecules on substrate at the field–off state. To generate high pretilt angle, it should be introduce the long alkyl chain as the side chain in a polyimide structure.

Therefore, we have synthesized novel homeotropic alignment materials derived from octadecylphenyl diamine and BTDA, PMDA and CPDA. In this paper, we will discusses about alignment properties of new homeotropic alignment materials

2. Experimental

The chemical structures of products were confirmed by ^{1}H NMR spectroscopy (Bruker Avance 400 Spectroscope) and EI mass spectroscopy (70eV) Hewlett Packard 5972 MSD). And the thermal stabilities of polyimides were observed by thermogravimetric analysis (TGA). The imidization ratio was measured with IR spectroscopy (MB-100 FT-IR from Bomen Co.). Voltage holding ratio (VHR) was measured with 6254 Instruments from TOYO Inc.Co.

Pretilt angles measured by using the crystal rotation method [3] with the system self-set up. Figure 1 indicates the diagram of the measuring system of pretilt angle. From the angle, Φ, where the extremum occurs on the curve of transmission-vs-rotation angle, we can extract the pretilt angle, θ measured from substrate normal, of the liquid crystal cell. For homeotropic alignment, the extremum occurs at an angle where the incident light is parallel to the LC director within the LC cell. The magnitude of δ, measured from cell normal, can be approximately expressed as $\sin(90-\theta) = \frac{\sin\psi_x}{n_o}$ for homeotropic alignment, where n_o is ordinary index of refraction of liquid crystal.

The alignment state of LC was observed by the polarized microscope of Olympus Co. BX-2

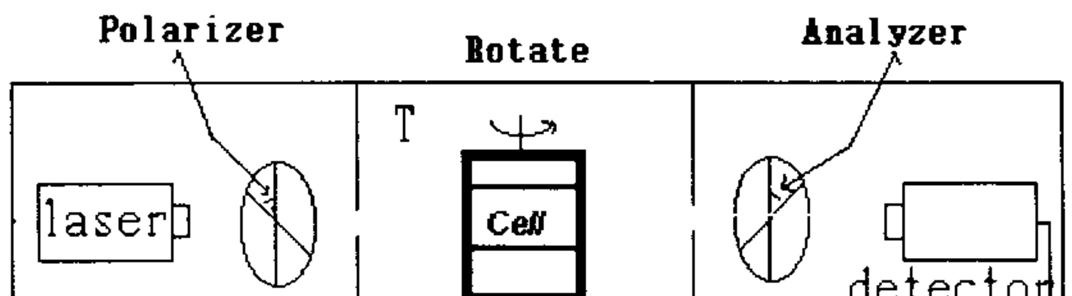
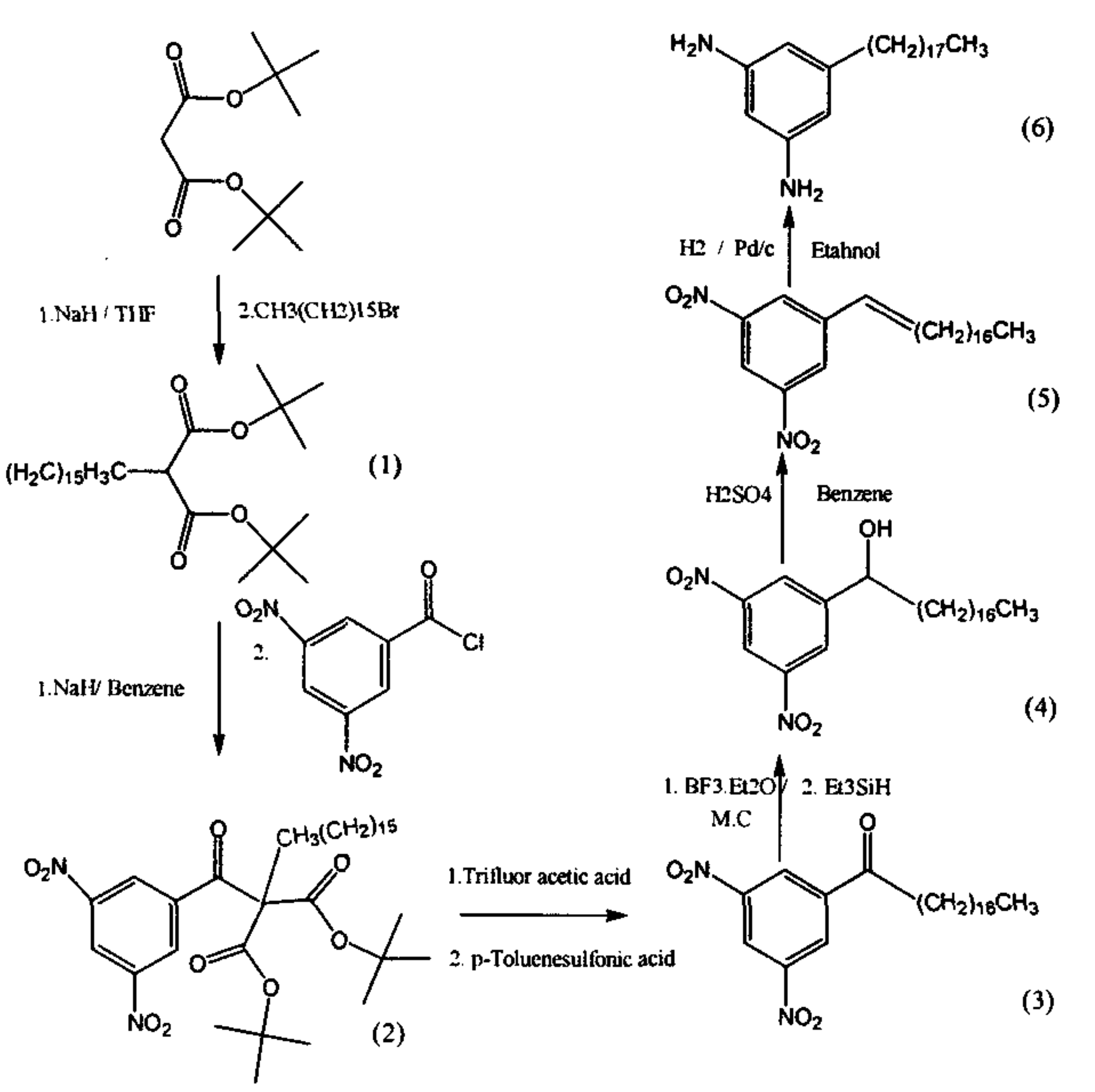


Figure 1. The diagram of measuring system of pretilt angle

3.1 Synthesis of 5-Octadecyl 1,3-diaminobenzene

For the synthesis of alignment materials, polyamic acid precursors [4] were prepared by copolymerization from mixing dianhydride/diamine (with side chain)/ODA(4,4'-oxydianiline) monomer. The three dianhydride monomers, BTDA (3,3', 4,4'-benzophenone tetracarboxylic dianhydride), PMDA (1,2,3,4-benzene tetracarboxylic dianhydride), CPDA (*cis*-1,2,3,4-cyclopentane tetracarboxylic dianhydri-de) were obtained from Aldrich Chemical Co., and diamine having long alkyl chains was synthesized.

To generate higher pretilt angles, it should be introduced long alkyl groups in a polyimide structure.[5] Therefore, we synthesized 5-Octadecyl 1,3-diaminobenzene by the synthetic route was shown in Scheme 1.



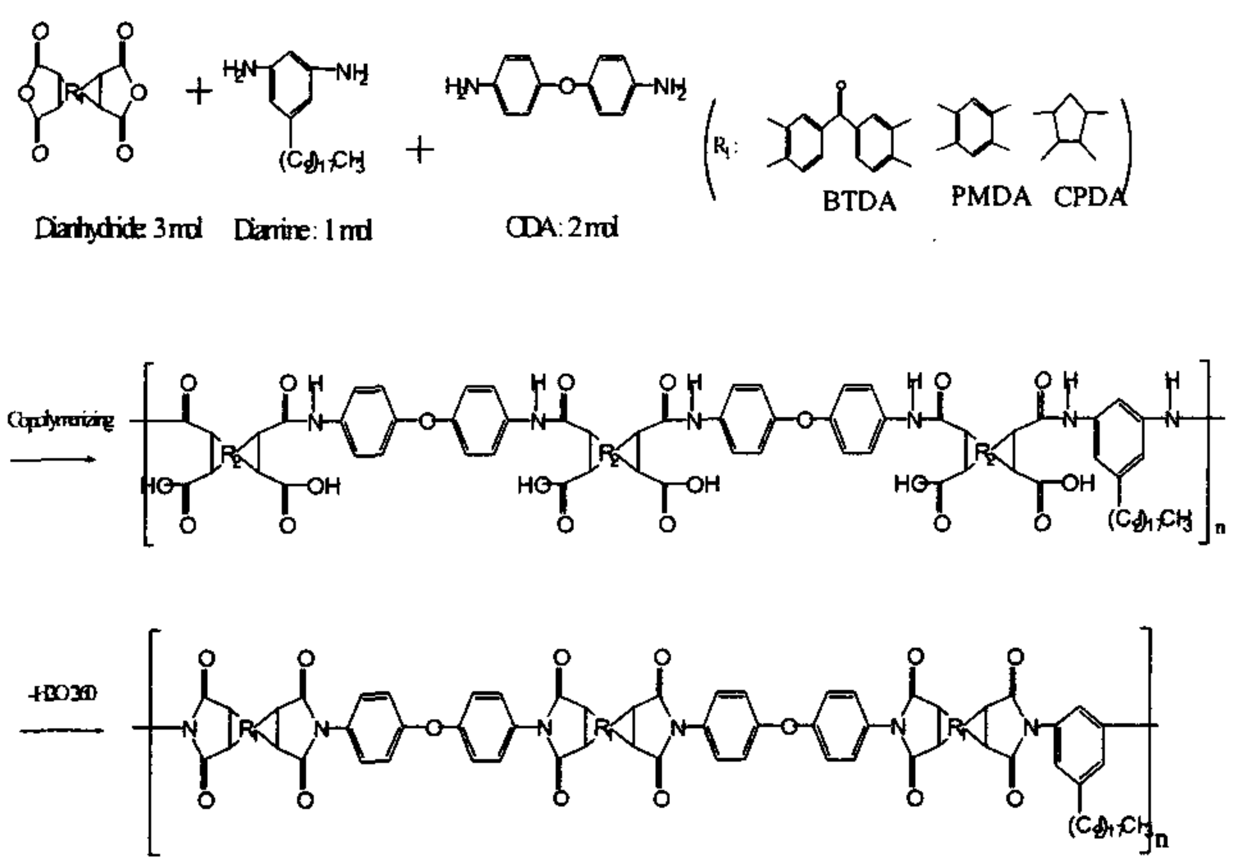
Scheme1. Synthetic route of 5-Octadecyl 1,3-diamino benzene.

3.2. Synthesis of polyamic acid

Generally, cross-linked polyamic acid resulting from co-polymerization is then converted to polyimide by proper thermal curing.

Dianhydride of three types, ODA and the diamine (mole ratio of 3:2:1) are dissolved in 1-methyl-2-pyrrolidinone (NMP) to 12 wt.% in a dry 250ml round-bottom three-necked flask equipped with a mechanical stirrer in a nitrogen atmosphere. The reactants were stirred for 4hrs at 0~5°C.

The prepared co-polyamic acid was diluted to 4% in N-methyl-2-pyrrolidone (NMP). These solutions were coated using spin coater on ITO glass substrates and pre-cured at 80° for 5min, and then main-cured at 260° for 1 hour. In this condition, the polyimides occurred the imidization. The imidization ratio was measured by FT-IR.



Scheme2. The synthetic route of polyimide

4. Results and Discussion

One of the important parameters of liquid crystal alignment is the pretilt angle (θ) which influences the viewing angle characteristics and electro-optic properties of the LCDs. To measure their pretilt angles, we used crystal rotation method.

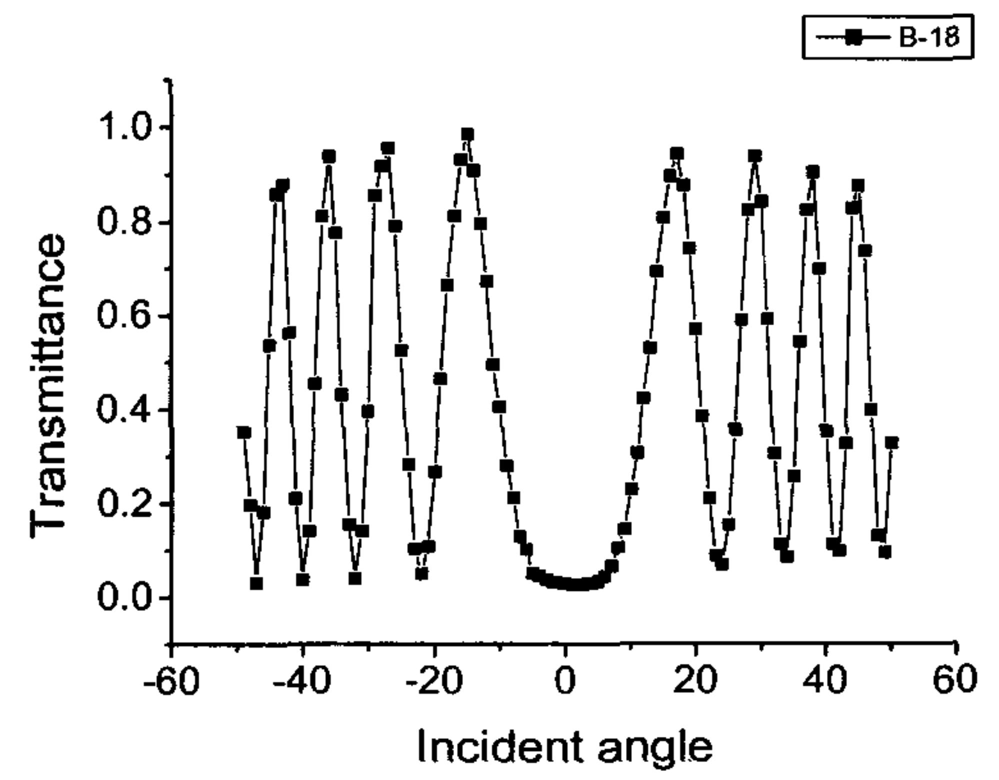


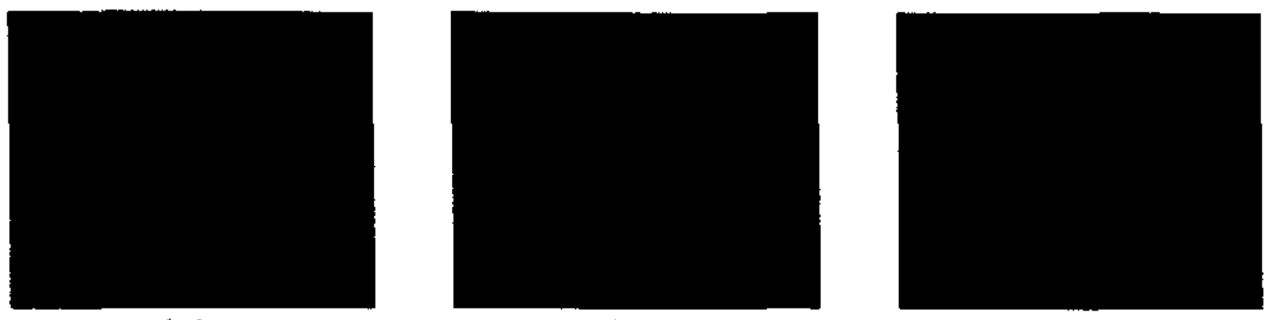
Figure 2 The transmittance versus incident angle for the polyimides

As shown in Figure 2, the transmittance versus incident angle were measured, we could obtain pretilt angles as listed in Table 2.

Table 2. Pretilt angles of the synthesis polyimides.

Name	Symmetry angle	Pretilt angle
B-18	0.2	89.9
P-18	0.5	89.7
C-18	0.3	89.8

Figure 3 shows the microscopic texture for the off-state of NLC cell homeotropically aligned to coated the synthesis polyimides. No defect was observed for all cells.



(a) (b) (c)

Figure 3. The microscopic textures of off state of the cells coated the synthesized polyimides; (a) B-18, (b) P-18 (c) C-18

We also observed the alignment state in the fringe-field using patterned electrodes.[6] The top glass substrate has electrode fully, and the bottom glass substrate has inter-digital electrodes with a distance of 20μm and an electrode width of 200μm×600μm. The structure of patterned electrodes is as shown in Figure 4.

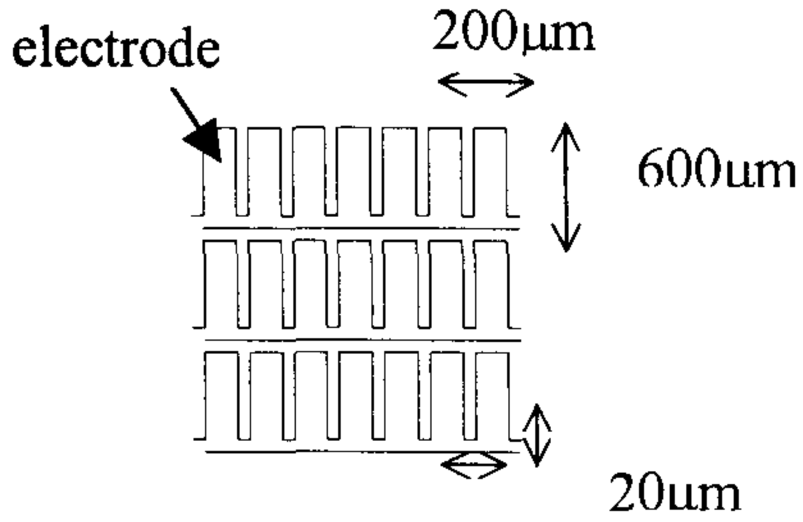
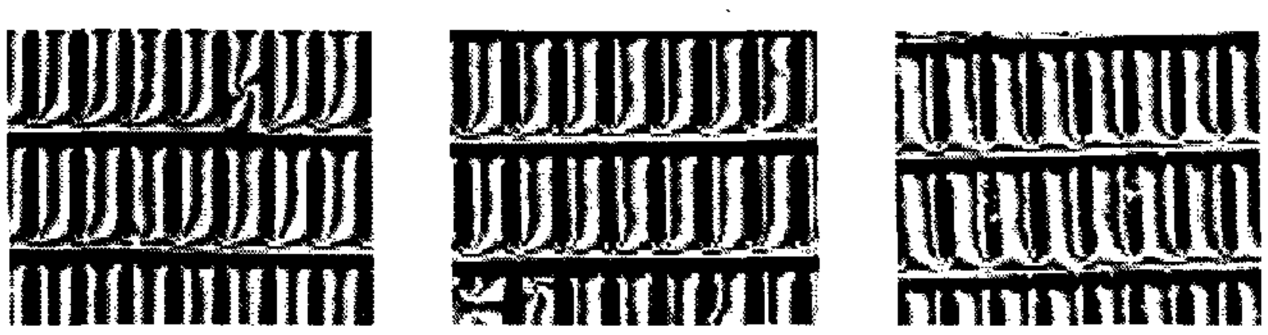


Figure 4. The structure of electrodes

The microscopic textures in the fringe-field for each cell represented as shown in Figure 5. We applied a square-wave AC voltage of 5V.



(a) (b) (c)

Figure 5. The microscopic textures of alignment states for the synthesized polyimides in the fringe-field; (a)B-18, (b)P-18, (c)C-18 (×40) using Mixture LC

In on state, we can observed that the synthesized polyimide showed multi-domains in each electrode. The disiclination lines were generated along the disclination of LC alignment direction into the domain. The almost same trends for LC alignment in one fringed electrode were observed. They are not different for 3 kinds of polyimide

Thermal stability of the polyimide was estimated by the thermogravimetry analysis (TGA) in a nitrogen atmosphere

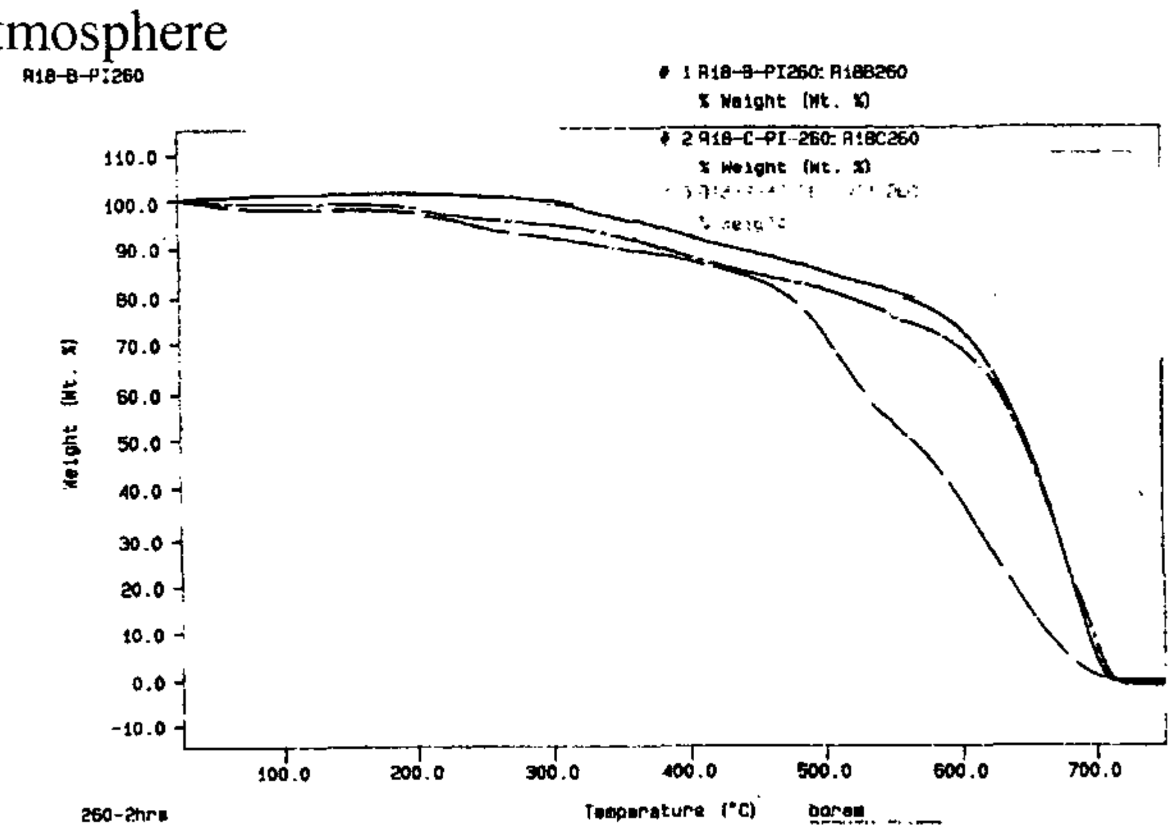


Figure 6. The curves of TGA

The samples were heated from 30°C to 750°C with heating rate 5°C/min in N_2 flow. Figure 6 shows TGA curves of the polyimide. No noticeable weight loss was observed below 300°C for all polyimide. Therefore, all polyimide have high thermal stability until 300°C.

To examine LC alignment stability on the new polyimide films, we prepared VA-cells filled with a nematic LC having a negative dielectric anisotropy. And we measured V-T characteristics of the test cell before and after annealing at 120°C for 24hrs as shown in Figure 7.

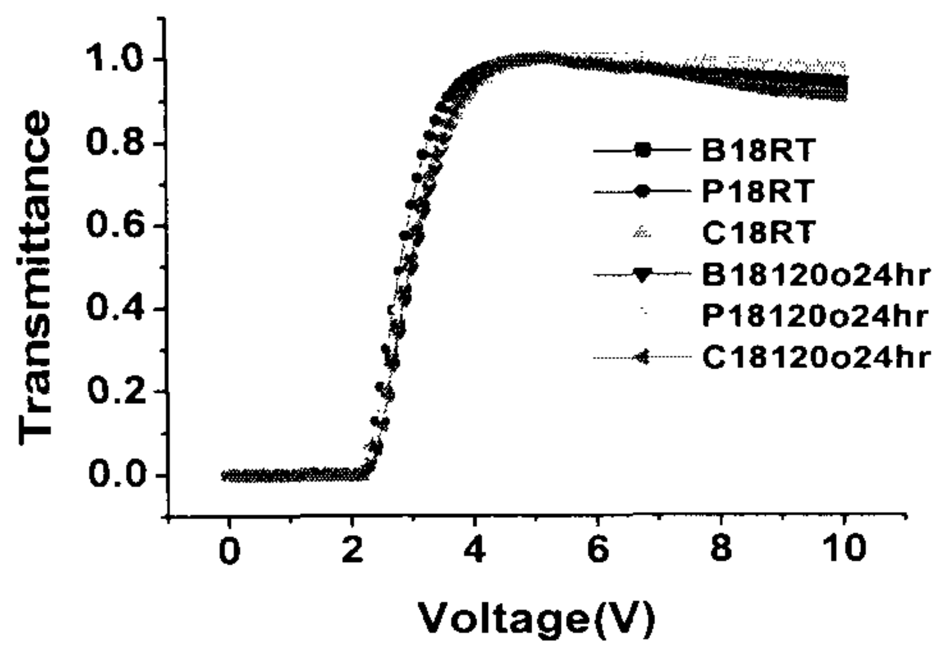


Figure 7. V-T curves of polyimides

No noticeable curve change was observed between before annealed and after it. This means that the alignment state of LC molecules did not damage by annealing at 120°C for 24hr. In the result of measurements, we may say that these new polyimide were thermally stable. Consequently, we can use these for practical LCD application.

To drive TFT-LCD application, the voltage holding ratio (VHR) is one of the important factor to define the ability of LC pixel to keep the state activated by electric field during the frame time.[7] The VHR values of the polyimide were measured using 6254 Instruments at 60Hz with 5V DC-voltage, and were listed in Table 3.

Table3. VHR of polyimides (at 25°C)

PI	VHR(%)
B-18	93.08
P-18	96.05
C-18	98.91

5.Conclusion

For application in VA-LCDs, we have synthesized novel homeotropic alignment materials generating high pretilt angle 90°. We could observe that the NLC on the synthesized polyimide films aligned vertically. And also, these alignment materials exhibited good homeotropic alignment properties, and a good thermal stabilities until 300 °C.

Consequently, these homeotropic alignment materials could be used for practical VA-LCDs.

6. Acknowledgements

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7. References

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