Novel Homeotropic Alignment Materials with Alkylcyclohexylbenzene as Side Chain in Polyimides

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Abstract

VA-LCDs is widely used for recent LCD productions owing to wide viewing angle characteristics with an unusually high contrast ratio. To apply for VA-LCDs, the novel homeotropic alignment materials were synthesized, which have the liquid crystal molecule as a side chain at aromatic diamine in a polyimide structure. These polyimides generated a high pretilt angle 90°. In this paper, the synthesis and alignment properties of new homeotropic alignment materials will be discussed..

1. Objective and Background

Twisted nematic liquid crystal displays (TN-LCDs) have been mainly used for notebook computers in spite of their narrow viewing angle and contrast characteristics. To solve these problems of TN-LCDs, new concepts of LCDs employing the in-plane switching(IPS) mode[1] and vertical alignment(VA) mode[2,3] have been suggested. It is well known that the VA-LCDs have a good black state and thus it has a high contrast ratio.[4] For the VA-LCDs, homeotropic polyimides are used as the liquid crystal alignment materials, which align liquid crystal vertically on substrate at the field–off state.

For LC alignment materials on various LCDs, pretilt angle is one of the most important properties. It is well known that to generate the high pretilt angle in the VA-LCDs, it is necessary to introduce long alkyl chain at aromatic diamine in a polyimide structure [5].

We have synthesized novel homeotropic polyimides derived from novel aromatic diamine with alkylcyclohexylbenzene as a side chain and BTDA, PMDA and CPDA. In this paper, we will discuss the synthesis and 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 (TGA7 from Perkinelmer. Co) The imidization ratio was measured with IR spectroscopy (MB-100 FT-IR from Bomen Co.). Voltage holding ratio (VHR) was measured with 6254 Instruments (TOYO Inc. Co.). The solubility of synthesized polyimides was measured titration method.

Polyimide films were prepared by spin coating on ITO glass, and were rubbed by rubbing machine. Pretilt angles were measured by using the crystal rotational method [6]. Figure 1 indicates the transmittance of laser (He-Ne) light against the sample rotation angle about the axis perpendicular to the laser beam. The solid curve in the Figure 1 shows the theoretical fit, leading to a pretilt angle of 90°. The alignment state of LC was observed by the polarized microscope (Olympus Co. BX-2).

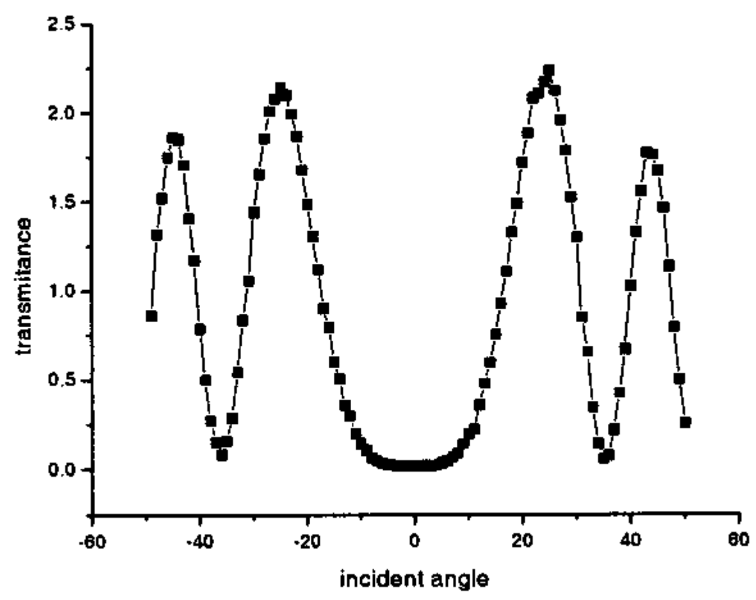
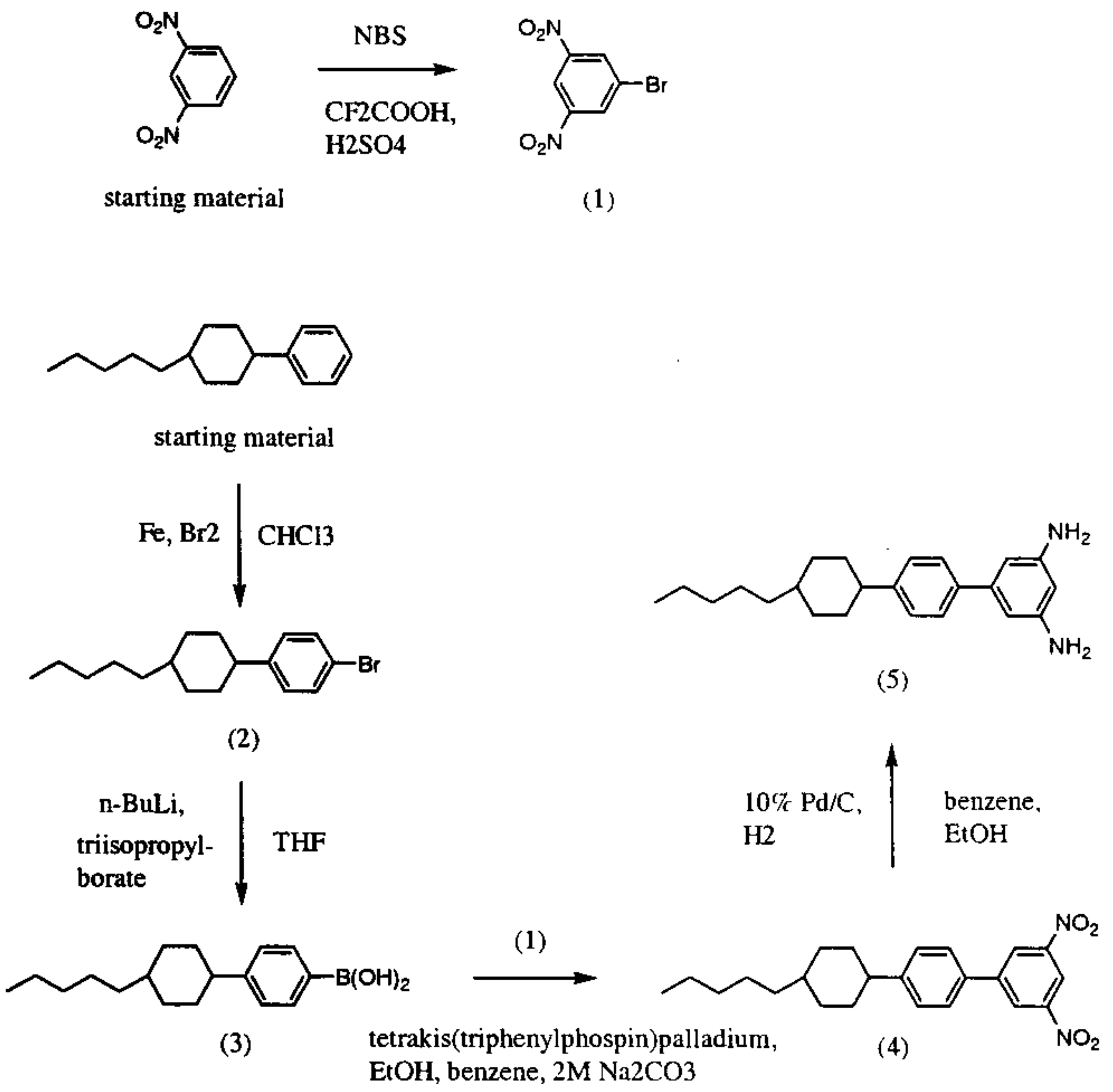


Figure 1. The transmittance versus incident angle for the polyimides (cell thickness of 48um)

3.1. Synthesis of diamine

We synthesized diamine having side chain of 4'-(4-

Pentylcyclohexyl) biphenyl-3, 5-diamine. The synthetic route was shown in Schem 1. 1-Bromo-3, 5-dinitrobenzene was synthesized by bromination of 1, 3-dinitrobenzene [7] and reacted with 4-(pentylcyclohexyl) benzyl boric acid through Suzuki reaction [8]. Diamine which 4'-(4-Pentylcyclohexyl) biphenyl-3, 5-diamine (R5CPP) was prepared by reduction of their coupling compound.



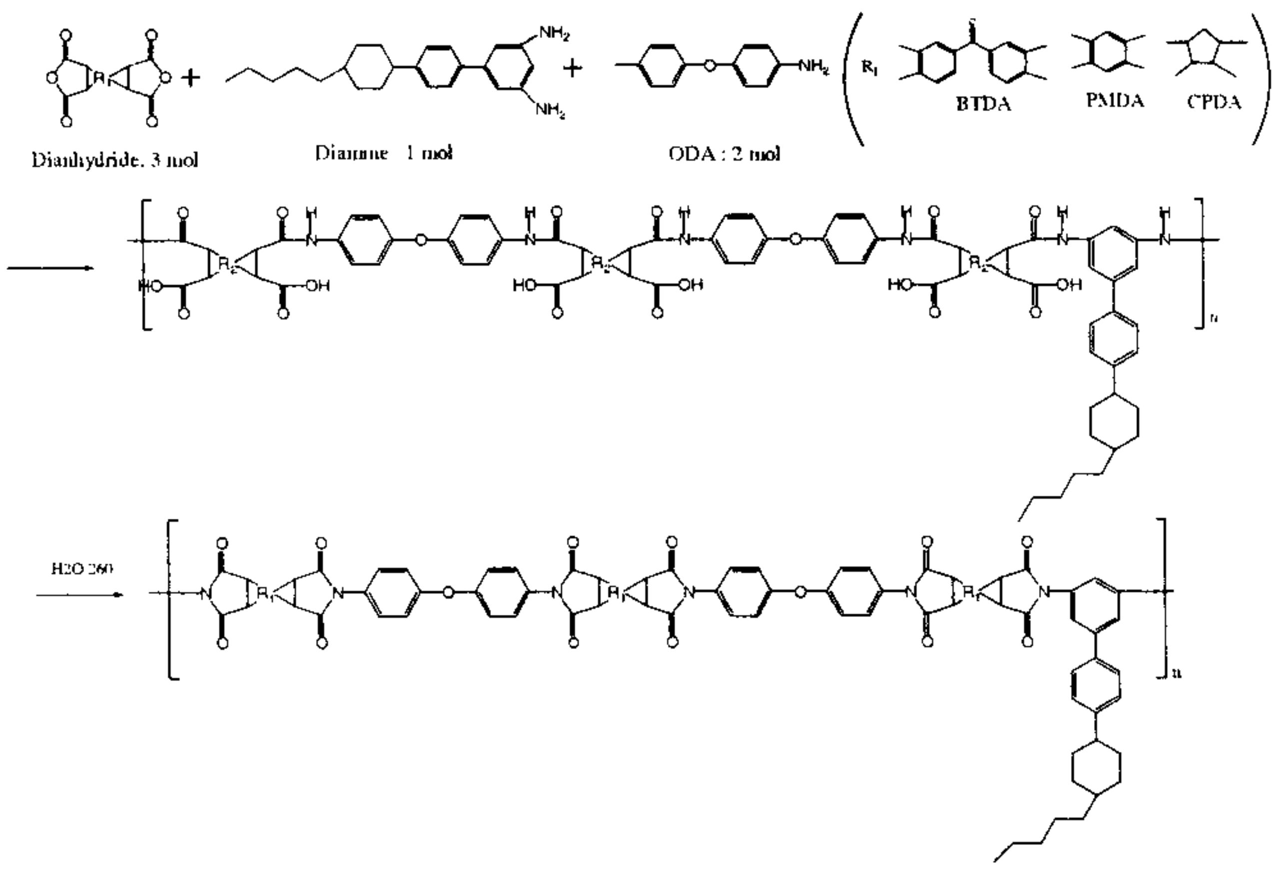
Scheme 1. Synthetic route of diamine with side chains (4'-(4-Pentylcyclohexyl) biphenyl-3, 5-diamine).

3.2. Synthesis of polyimide

Polyamic acid precursors were prepared by copolymerization from mixing dianhydride /diamine / ODA (4, 4'-oxydianiline) monomer (mole ratio of 3:2:1) are dissolved in 1-methyl-2-pyrrolidinone (NMP) to 12 wt% in a nitrogen atmosphere as shown in scheme 2. The three dianhydride monomers, BTDA (3, 3', 4, 4'-benzo-phenone tetracarboxylic dianhydride), PMDA (1, 2, 3, 4-benzene tetracarboxylic dianhydride), CPDA (*cis*-1, 2, 3, 4-cyclopentane tetracarboxylic dianhydride) and ODA were obtained from Aldrich Chemical Co., and diamine was synthesized Scheme1.

The prepared polyamic acid was diluted to 4% in solutions which N-methyl-2-pyrrolidone (NMP) versus butoxyethanol volume ratio is 3:1. Polyamic acid resulting from copolymerization is converted to polyimide by proper thermal curing. Polyamic acid 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.

The imidization ratio was measured by FT-IR.



Scheme 2. The synthetic route of polyimide

4. Result and Discussion

One of the important parameters of liquid crystal alignment is the pretilt angle (θ) which influences the viewing angle and electro-optic properties of the LCDs. [9]

The polyimides were called B-R5CPP (BTDA type PI), P-R5CPP (PMDA type PI), C-R5CPP (CPDA type PI) in this paper.

High pretilt angles were generated by the synthesis alignment materials as shown in Table 1.

Table 1. Pretilt angle of polyimide, respectively

	alignment materials	Pretilt angle
Before rubbing	B-R5CPP	89.9
	P- R5CPP	89.7
	C- R5CPP	89.9
After rubbing	B-R5CPP	89.8
	P- R5CPP	89.7
	C- R5CPP	89.9

The alignment textures were exhibited in Figure 2. The polyimide films were rubbed by a rubbing machine under the following conditions: the translation speed of the sample was 13.3mms^{-1}; the rotation speed of the roller was 500rpm; the pile impression depth P_{rub} was 0.3mm. We used the nematic liquid crystal having negative dielectric anisotropy.

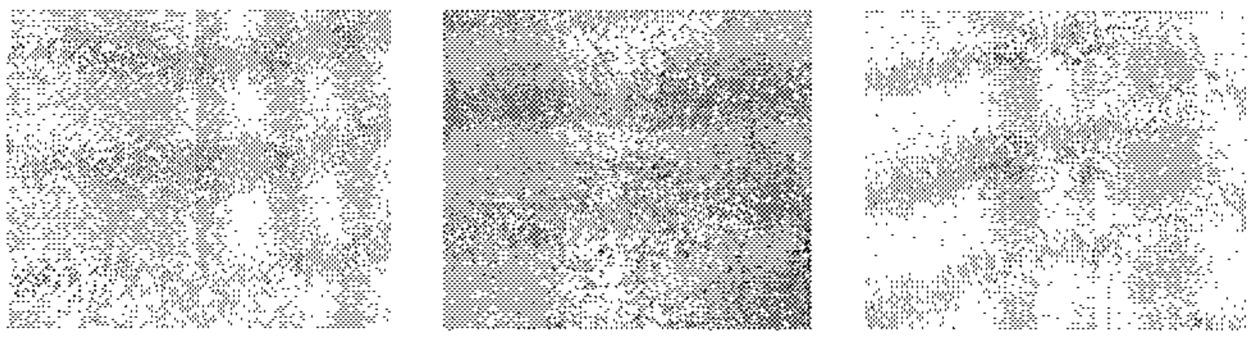
In off state, no defect was observed for cells coated the synthesized polyimides as shown in Figure 2.

(a) (b) (c)

Off state

Figure2. The microscopic textures of off state of the cells coated the synthesized polyimides; (×40) using Mixture LC (a) B- R5CPP, (b) P- R5CPP (c) C- R5CPP

The microscopic textures in on state for each cell represented as shown in Figure 3. At that time, we applied a square-wave AC voltage of 5V. They represented white state without defect at the field–on state. A homoerotic alignment of liquid crystal (LC) molecules obtains over wide areas on the polyimide.



(a) (b) (c)

On state

Figure3. The microscopic textures of on state of the cells for the synthesized polyimides electrode width of 1cm×1cm; (a) B- R5CPP, (b) P- R5CPP (c) C- R5CPP

The solubility in a solvent is especially important property as a basic property of polyimide. There are some difficulties for improvement of the printability in polyimide. [10] The solubility of the polyamic acid about 2-butoxyethanol was measured by titration method. 2-Butoxyethanol in glass-stopcock buret was dropped in polyamic acid precursor which dissolved in 1-methyl-2-pyrrolidinone (NMP) to 4 wt%. After 2-butoxyethanol was dropped the reactants were stirred until precipitates were formed.

Table2 show the maximum dilution weight ratio of 2-butoxyethanol about polyamic acid precursor in NMP. 2-

Table2. The solubility of the polyimids about 2-butoxyethanol

alignment materials	Maximum dilution weight ratio NMP : 2-butoxyethanol
B-R5CPP-PA	1: 2.63
P- R5CPP-PA	1: 3.27
C- R5CPP-PA	1 : 1.82

2-Butoxyethanol has a larger printability in polyimide than NMP. P- R5CPP-PA (PMDA type PI) was showed higher solubility about 2-butoxyethanol than others, so it can offer good printability.

Thermal stability of the polyimide was estimated by the thermogravimetry analysis (TGA) in a nitrogen atmosphere. The polyimide materials were stripped off from the substrates which polyimide coated on ITO glass. The samples were heated from 30°C to 750°C with heating rate 5°C/min in N_2 flow.

Standard of thermal stability was regarded by temperature of weight loss starting point (T_d) and weight loss 10 wt% point (T_{10}). Table3 shows thermal stability of the polyimides. No noticeable weight loss was observed below 270°C for all polyimides. Therefore, all polyimide have high thermal stability until about 500°C

Table 3. Thermal stability of the polyimides

alignment materials	T_d(°C)	T_{10}(°C)
B-R5CPP	286	521
P- R5CPP	278	496
C- R5CPP	292	527

Transmittance is one of the characteristic parameters decides active voltage of module. We measured V-T characteristics using electro-optic system after rubbing. Applied voltage was from 0V to 10V. Table 4 shows the threshold voltage and Figure 4 shows the transmittance versus applied voltage for the polyimides. P-R5CPP was showed high threshold and saturation voltage. The threshold voltage (V_{th}) usually has some connection with frequency, dielectric dispersion of LC materials, alignment [11]. We used same LC materials under the same frequency. So the reason due to the interaction between P-R5CPP polyimide films and LC molecules increases than others.

Table 4. Threshold voltage for the polyimides

alignment materials	V_{10}	V_{90}
B-R5CPP	2.1	3.8
P- R5CPP	2.7	6.7
C- R5CPP	2.4	4.4

It is important that the voltage across the LC cell dose not significantly decrease before it is refreshed during the next addressing cycle. The voltage holding ratio (VHR) is the proportion of the applied voltage and the voltage drop across the LC cell in the frame time. [12] VHR of the polyimides was measured using 6254 Instruments at 60Hz with 5V DC-voltage. The VHR values of polyimides were listed in Table 5.

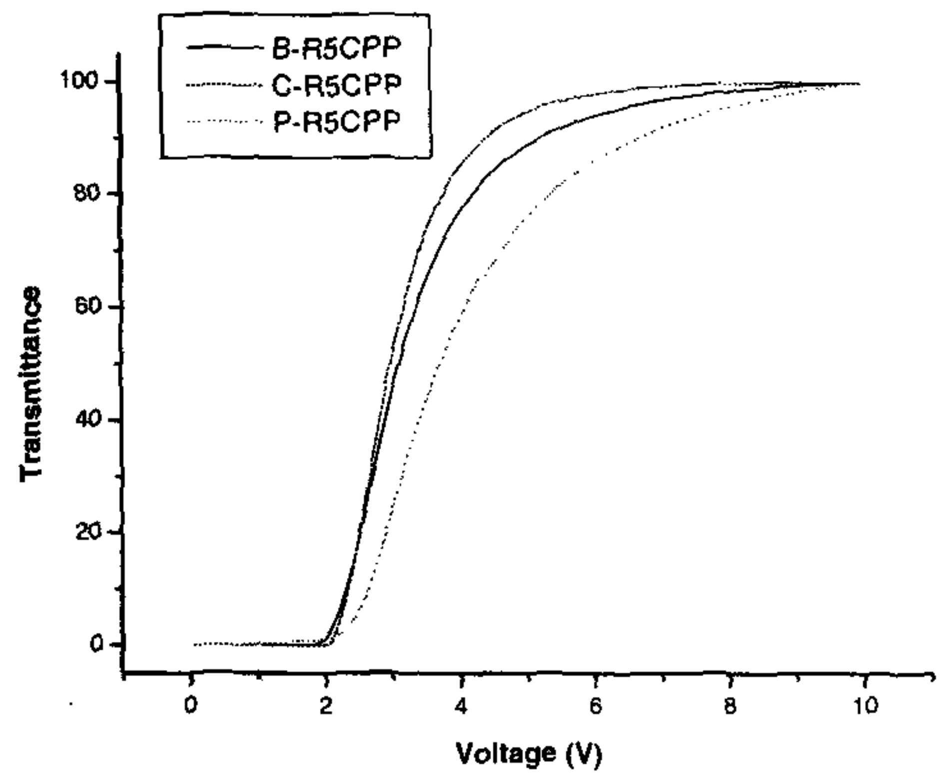


Figure 4. V-T curves of polyimides

VHR of polyimides shows decrease after rubbing. This dermises was induced by contamination within rubbing process. [13]

Table5. VHR of polyimides (at 25°C)

alignment materials	VHR (%) Before rubbing	VHR (%) After rubbing
B-R5CPP	99.39	98.92
P- R5CPP	98.56	95.14
C- R5CPP	99.21	97.06

5. Conclusion

We have synthesized novel homeotropic alignment materials generating high pretilt angle 90°. We could observe the NLC aligned vertically through the polarized microscope. Therefore, the polyimides represented good homeotropic alignment properties. And they also have good solubility and thermal stability.

Consequently, we can find that novel homeotropic alignment materials can be used for practical VA-LCDs.

6. Acknowledgements

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7. References

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