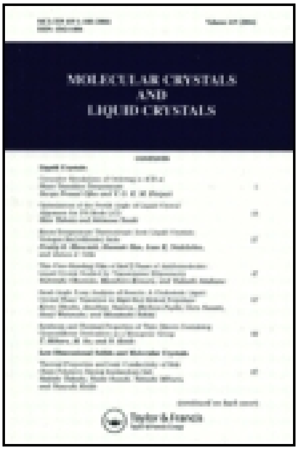


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis of New Vulcan-Shape Aromatic Polyimides for IPS-Mode and Their Alignment Properties

Kyung-Chul Son [a], Dong-Ju Park [a], Yong-Bae Kim [a] & Jae-Cheol Park [b]

[a] Liquid Crystal Research Center, Department of Chemistry, Division of Natural Sciences, Konkuk University, Seoul, Korea

[b] DONGJIN SEMICHEM CO., LTD., Electronic Materials Division, Gyeonggi-do, Korea

Version of record first published: 22 Sep 2010

To cite this article: Kyung-Chul Son, Dong-Ju Park, Yong-Bae Kim & Jae-Cheol Park (2007): Synthesis of New Vulcan-Shape Aromatic Polyimides for IPS-Mode and Their Alignment Properties, Molecular Crystals and Liquid Crystals, 479:1, 81/[1119]-93/[1131]

To link to this article: http://dx.doi.org/10.1080/15421400701675275

Mol. Cryst. Liq. Cryst., Vol. 479, pp. 81/[1119]–93/[1131], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701675275

Synthesis of New Vulcan-Shape Aromatic Polyimides for IPS-Mode and Their Alignment Properties

Kyung-Chul Son
Dong-Ju Park
Yong-Bae Kim
Liquid Crystal Research Center, Department of Chemistry, Division of Natural Sciences, Konkuk University, Seoul, Korea

Jae-Cheol Park
DONGJIN SEMICHEM CO., LTD., Electronic Materials Division, Gyeonggi-do, Korea

In plane switching (IPS)-mode liquid crystal display (LCD) is one of the most useful technologies for a wide range of viewing angles. For IPS-mode application, we synthesized novel diamine containing a methyl group as a bridge and homogeneous alignment materials. A 1∼2 low pretilt angle manifested by changing dianhydrides (BTDA and BPDA) and bridged diamines (ODA and PACM). We measured their pretilt angles using the crystal rotation method with positive liquid crystal (LC). The electro-optical properties of LC cells using these polyimides as alignment films were also investigated. Results show all polyimides manifest a low pretilt angle of below 2 degrees.

Keywords: diamine; IPS mode; polyimide; pretilt angle

INTRODUCTION

TFT-LCD applications were limited to mobile phones and smaller-than-20-inch computer monitors in the early 1990s. Since 2000, however, TFT-LCDs grew in size and have become so popular that they have started to replace conventional CRT devices. Their advantages reside on the fact that they are more compact in size and lighter in weight than CRT. Despite these advantages, several problems such

Address correspondence to Yong-Bae Kim, Liquid Crystal Research Center, Department of Chemistry, Division of Natural Sciences, 1, Hway angdong, Kwangjinku, Seoul 143-701, Korea. E-mail: yongbae@konkuk.ac.kr

as viewing angle, brightness, response time, and contrast ratio still need to be resolved before TFT-LCD technology can be applied to TVs [1].

The patterned vertical alignment (PVA) and IPS modes, which are being commercialized now, were developed as alternatives to the traditional twisted nematic (TN) and super-twisted nematic (STN) modes. At present, the image quality of TFT-LCD is the same as that of CRT, and many requirements have been met owing to various technical developments. Typically, the IPS mode is one of the most valuable technologies for a wider viewing angle. In the case of the existing TN and STN modes, the displayed images differ according to the direction of the eyesight. This is because the LC molecules between two glasses are twisted. On the other hand, in the IPS mode, the LC molecules are parallel; i.e., the LC is switched on the glass plane. Consequently, the transmitted light penetrating the glass from all directions can help with the optical contribution of the LC molecules, thereby facilitating a wider viewing angle [2].

In this article, 1,1-Bis-(4-amino-phenyl)-2-phenyl ethane was synthesized as a novel diamine for IPS-mode application. Novel diamine contains a methyl group that functions as a bridge between the phenyl group and phenyl group with amine group. Because this portion bends to 111 degrees, the LC molecule is also inclined owing to the interaction and exhibits 1∼2 low pretilt angle and good alignment property. To achieve a suitable pretilt angle, the surface energy and the steric effect are considered and the polyimide is synthesized by changing the bridged chain diamine and dianhydride [3,4].

The homogeneous alignment material, which shows 1∼2 degree low pretilt angle, is assessed for suitability in terms of its thermal characteristics, pretilt angle, surface energy, and alignment condition. Moreover, test cells were created and their electro-optical properties were measured.

EXPERIMENTAL

Materials

3,3,4,4-benzophenonetetracarboxylic dianhydride (BTDA), 3,3,4,4-biphenyltetracarboxyic dianhydride (BPDA), and 4,4′-oxydianiline (ODA) were purchased from Aldrich Corporation. 1,4′-Methylenebiscyclohexylamine (PACM) was purchased from the TCI Corporation. The reagents were recrystallized and sublimed before use. Benzyl bromide, 4,4-dichlorobenzopenone, lithium bis(trimethylsilyl) amide, bis(dibenzylidene acetone) palladium, and tricyclohexyl phosphine were likewise purchased from Aldrich Corporation and were used in their purchased form. Solvents were distilled in the presence of a dehydrating agent and stored over molecular sieves. Other reagents were commercial-grade and were used in their purchased form.

Synthesis of Side-Chain Monomers

The side-chain diamine of 1,1-Bis-(4-amino-phenyl)-2-phenyl ethane-diamine was synthesized. The synthetic route is shown in Figure 1. The chemical structure of the product was identified using ^{1}H NMR spectroscopy (with a Bruker Avance 400-MHz spectroscope) and EI mass spectroscopy (with a 70-eV Hewlett Packard 5972 MSD).

1,1-Bis-(4-chloro-phenyl)-2-phenyl-ethanol (1)

Added to magnesium turnings (3.5 g, 0.1433 mol) and an iodine crystal was a solution of benzyl bromide (20.4 g, 0.1194 mol) in ether (100 ml). After being heated under reflux for 2 hours, the Grignard

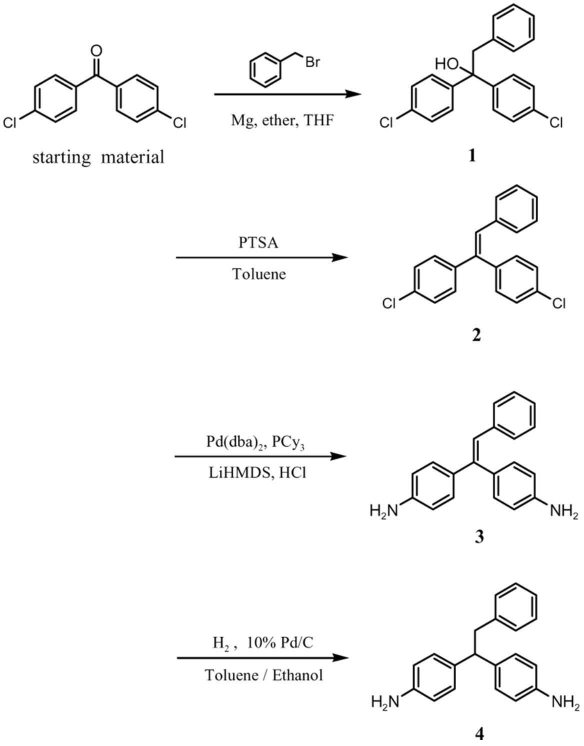


FIGURE 1 Synthetic route of vulcan-shape diamine (VP).

reagent was cooled, and a solution of 4,4′-dichlorobenzophenone (20 g, 0.0796 mol) in tetrahydrofuran (150 ml) was added in a rapid dropwise fashion. Reheating was then initiated with a reflux period of 1 hour, which was required for the consumption of 4,4′-dichlorobenzophenone as indicated in the TLC analysis. The reaction mixture was cooled and quenched with saturated NH4Cl (10 ml). The suspension was stirred for 30 minutes and filtered through celite, and the filtrate was concentrated in vacuo [5]. The product was extracted using chloroform and an NaCl solution. The organic layer was dried over MgSO4 and removed in vacuo to yield a crude yellow product (90% yield).

Mass: 324 (M+), 288, 253, 212, 176 and 126

^{1}H NMR (CDCl$_3$): δ7.21 (d, 2H), 7.20 (d, 4H), 7.13 (d, 4H), 7.12 (d, 2H), 7.08 (t, 1H), 3.32 (d, 2H) and 2.00 (s, 1H)

1,1-Bis-(4-chloro-phenyl)-2-phenyl Ethylene (2)

In a 500-ml three-necked, round-bottom flask equipped with a reflux condenser, 1,1-Bis-(4-chloro-phenyl)-2-phenyl-ethanol (35 g, 0.1020 mol) was dissolved in toluene. P-toluenesulfonic acid 1-ydrate (2.7 g, 0.014 mol) was added. The mixture was refluxed at 130°C for 12 hours. The reaction mixture was added to the NaCl solution, extracted with ether, and dried with anhydrous MgSO$_4$. The evaporation of the solvent yielded a crude brown product (95% yield).

Mass: 324 (M+), 288, 254, 212, 176, 151, 126, 75 and 51

^{1}H NMR (CDCl$_3$): δ 7.42 (d, 2H), 7.36 (d, 4H), 7.27 (d, 4H), 7.26 (d, 2H), 7.11 (t, 1H), 6.92 (s, 1H)

1,1-Bis-(4-amino-phenyl)-2-phenyl Ethylene (3)

In a 500-ml three-necked, round-bottom flask equipped with a reflux condenser, 1,1-Bis-(4-chloro-phenyl)-2-phenyl-ethylene (20 g, 0.06149 mol), lithium bis(trimethylsilyl)amide (43.2 g, 0.2583 mol), tricyclohexylphosphine (2.6 g, 0.0092 mol) and bis(dibenzylidene acetone) palladium (5.3 g, 0.0092 mol)were dissolved in toluene. The mixture was refluxed at 90°C for 12 hours. The reaction progress was monitored using GC/MS. The crude reaction mixture was diluted with ether and the silylamide was de-protected by adding one drop of aqueous 1 N HCl. The mixture was transferred to a separatory funnel and washed with aqueous 1 N NaOH [6]. The organic layer was dried over MgSO4, filtered, and concentrated at reduced pressure. The product was recrystallized with ethanol and ethylene acetate to yield a yellowish product (50% yield).

Mass: 286 (M+), 267, 193, 180 and 165

^{1}H NMR (CDCl$_3$): δ 7.42 (t, 2H), 7.26 (d, 2H), 7.17 (d, 4H), 7.11 (d, 1H), 6.92 (s, 1H), 6.46 (d, 4H) and 3.74 (s, broad, 4H)

1,1-Bis-(4-amino-phenyl)-2-phenyl Ethane (4)

Placed in a high-pressure autoclave was 1,1-Bis-(4-amino-phenyl)-2-phenyl ethylene (10 g, 0.349 mol)dissolved in toluene and ethanol, to which was added 10-wt% palladium on activated carbon (0.1 g). The mixture was maintained for 5 hours under 4 kg/cm^2 H_2 pressure. The Pd/C was filtered and the residue was evaporated in vacuo. The product was recrystallized with ethanol and ethylene acetate to yield a whitish product (40% yield).

Mass: 288 (M+), 197, 180, 168, 91 and 95.

^{1}H NMR ($CDCl_3$): δ 7.25 (t, 2H), 7.13 (d, 2H), 7.07 (d, 1H), 7.00 (d, 4H), 6.58 (d, 4H), 4.06 (t, 1H), 3.74 (s, broad, 4H) and 3.30 (d, 2H).

Synthesis of Polymers

Preparation of Polyamic Acids

All the polyamic acids were synthesized using conventional polycondensation, as illustrated in Figure 2. In a typical example, placed in a flame-dried 50-ml flask equipped with a mechanical stirrer and a nitrogen inlet were 0.00208 mol of 1,1-Bis-(4-amino-phenyl)-2-phenyl

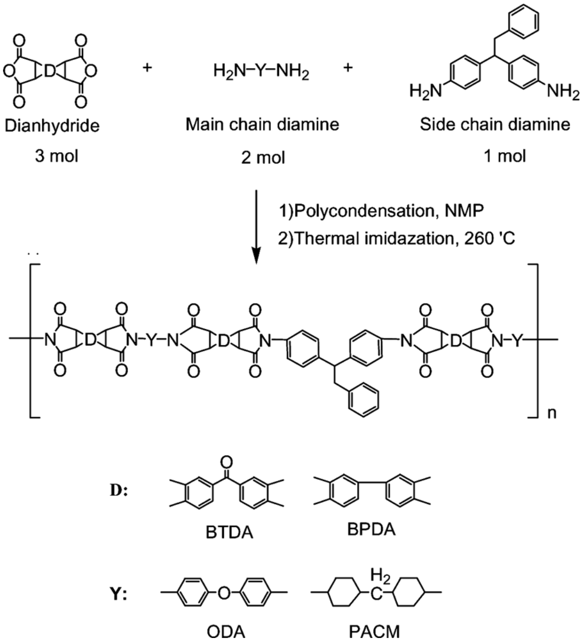


FIGURE 2 Synthetic route of polyimides.

ethane, 0.00416 mol of 4,4′-oxydianiline(ODA), and 12.2 g of purified NMP. The mixture was stirred under a slow stream of nitrogen gas until the diamines were entirely dissolved. 0.00624 mol of BTDA and an additional 13.2 g of NMP were added to one portion. The solution was stirred mechanically for 1 hour at 0°C until it became clear, after which it was again stirred at room temperature for 12 hours under nitrogen. The clear and viscous polyamic acid solution was poured into deionized water to yield a yellowish solid. The solid was washed with additional deionized water and purified methanol. The polyamic acid solid was filtered and dried overnight under vacuum at 50°C, then at 90°C for 12 hours.

Preparation of the PI Alignment Layer

The synthesized polyamic acid solution was used as the LC alignment material. It was dissolved in NMP/2-butoxyethanol (3:1 ratio) to form 4-wt% solutions. The solutions were spin-coated onto indium tin oxide (ITO) glass substrates at 2,600 rpm. The solvent was evaporated at 80°C for 5 minutes, and main curing was carried out at 210°C for 1 hour and 30 minutes. The approximate thickness of the resulting polyimide films was about 600 ± 50 Å.

Fabrication of the LC Cell

The LC cell of the pretilt angle was fabricated from two pieces of rubbed polyimide films assembled in an anti-parallel rubbing direction with a 50-μm-thick microfilm. To determine its electro-optical properties, the LC cell was fabricated from two pieces of rubbed polyimide films assembled in a parallel rubbing direction with glass substrates and inter-digital electrode substrates with a 5-μm electrode width and a 10-μm electrode distance. The cell gap was maintained using 4-μm polymer beads. The LC cell was filled with positive LC (MJ991735: Merck Co.) and sealed using epoxy adhesive.

Characterization and Processing

Gel permeation chromatography was carried out using the Jasco GPC system equipped with an RI detector and a phenogel column in the solution (LiBr/DMAC = 1 g/1 L) at 60°C. The average molecular weight of the polyamic acids was calculated using standard materials (PM-1: Easical, Polymer Lab) and Jasco software. The thermal properties of the polyamic acids were examined with TGA (Perkin Elmer TGA7) in an N2 atmosphere. The pretilt angle of the positive LC (MJ991735: Merck Co.) was measured with an optical instrument set using the crystal rotation method [7]. The contact angles were measured using the sessile drop method with a contact anglemeter (KRÜSS DSA100) and highly pure distilled water and methylene iodide. The surface free energy was calculated using Owens' formula [8]. The voltage holding ratio (VHR) was measured with 6254 Instruments from TOYO Co., Inc. The V-T characteristics were measured using a self-installed electro-optic system setup at room temperature. A voltage of 0–10 V was applied.

RESULTS AND DISCUSSION

Polymer Properties

Molecular Weight and Thermal Characterization

The weight-average molecular weight (Mw) of the VP was examined using gel permeation chromatography (GPC) and summarized in Table 1 with the results of the thermal analysis of the VP. Figure 3 shows the pyrogram of the polyimide and polyamic acid. VP thermal stability was analyzed using a thermogravimetric analyzer (TGA) in the range of 30 ∼ 800°C within a 10°C min^{-1} heating rate. The thermal stability standard was estimated at a 5% weight loss temperature using a TGA measurement [9]. The 5% weight loss temperature of the VP was determined in the range of 380 ∼ 440°C. Since the 5% weight loss temperature of polyimide occurred at over 400°C, it is believed that the polyimide can be thermally stable up to 400°C. The polyimide of the ODA series had a higher decomposition temperature than that of the PACM series. This is because the polyimide of the PACM series, which is characterized by an alicycic structure rather than the aromatic structure of the ODA, consists of single bonds, which are weaker than double bonds. Moreover, the pyrogram shows that the curves of the ODA and PACM series have distinct features.

TABLE 1 Molecular Weight and Thermal Properties of Polyimides based on VP

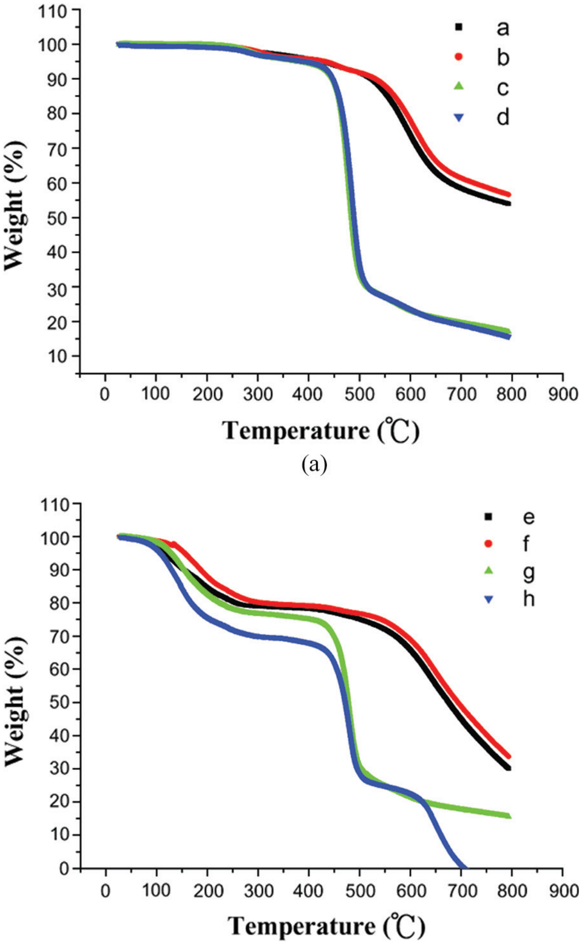
Polyimides	GPC M_w	$T_5{}^b$(°C)	TGA^a $T_{10}{}^c$ (°C)	$T_d{}^d$ (°C)
VP-ODA-BTDA	133500	427	522	569
VP-ODA-BPDA	95200	435	533	575
VP-PACM-BTDA	56300	380	448	456
VP-PACM-BPDA	283200	400	447	457

[a] Measured at a heating rate of 10°C min^{-1} in N^2.

[b] Temperature at 5% weight loss.

[c] Temperature at 10% weight loss.

[d] Temperature at decomposition.



(a)

(b)

FIGURE 3 Thermogravimetric diagrams of polymers: a) VP-ODA-BTDA-PI; b) VP-ODA-BPDA-PI; c) VP-PACM-BTDA-PI; d) VP-PACM-BPDA-PI; e) VP-ODA-BTDA-PAA; f) VP-ODA-BPDA-PAA; g) VP-PACM-BTDA-PAA; h) VP-PACM-BPDA-PAA.

This reflects the structural difference between the aromatic and alicycic structures discussed above. Since the polyimide decomposition temperature of the PACM series exhibits more sharp weight loss than that of ODA series, the thermal decomposition temperature of the polyimide is influenced by dianhydride of the main chain rather than the main diamine.

LC Alignment, Pretilt Angle, and Surface Properties

The alignment characteristic of the IPS cell was observed using a BX60 microscope equipped with a cross-polarizer. Figure 4 shows the microscopic textures of off-state and on-state polyimides. In the off-state polyimides represented by the black areas in Figure 4, no defect was observed in the cells that coated the synthesized polyimide.

The pretilt angle is an important factor that has an impact on the viewing angle and the electro-optical properties. The typical pretilt angle of the alignment material used in the IPS-mode is 1 ~ 2 degrees. To induce a low pretilt angle, the structure of the polyamic acid chain was kept similar to the structure of the main-chain type rather than the side-chain type which shows almost a 90 degree pretilt angle. It is known that showing a low pretilt angle of 1–2 degrees is more difficult than synthesizing polyimide displaying a high pretilt angle. Accordingly, it is important to synthesize novel diamine to obtain a low pretilt angle of 1–2 degrees. The steric effect of the polyimide and the electric effect alignment model should be considered. A low pretilt angle occurs when the side chain is shorter than the LCs' major axis. Reportedly, an alignment layer with a surface energy similar to the surface tension of LC molecules is likely to manifest a medium pretilt angle. However, an alignment layer with a surface energy larger than the surface tension of LC molecules is likely to have a low pretilt angle [10,11,12].

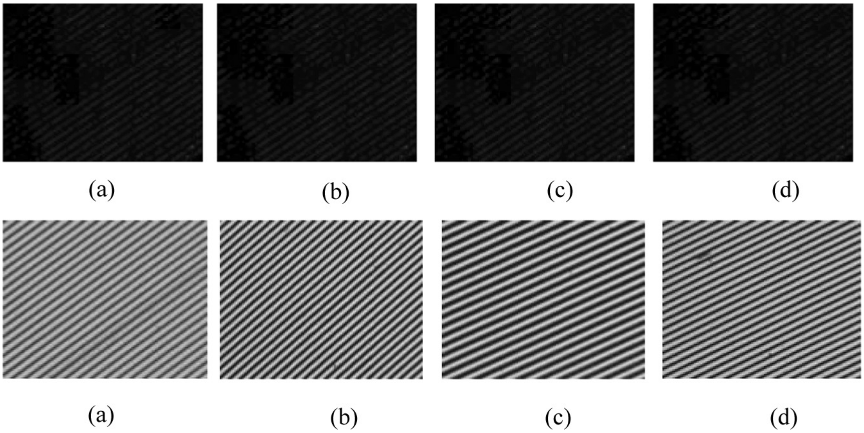


FIGURE 4 The microscopic textures of off-state and on-state of the cells coated the synthesized polyimides: a) VP-ODA-BTDA; b) VP-ODA-BPDA; c) VP-PACM-BTDA; d) VP-PACM-BPDA.

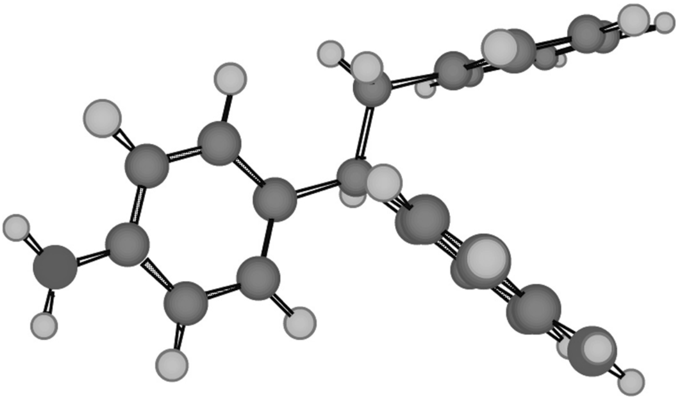


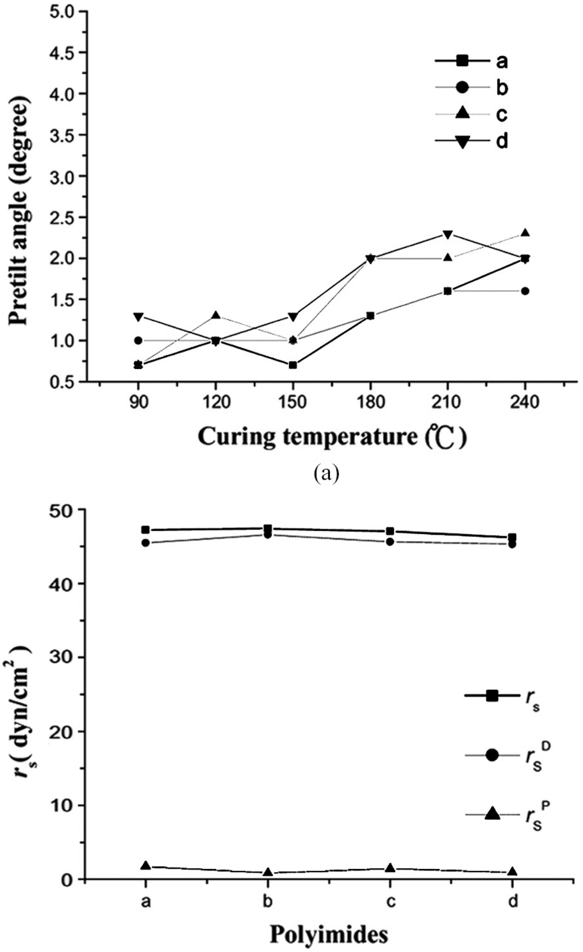
FIGURE 5 The three dimensional model of the novel diamine by Chem office 3D (CS MM2/MOPAC2000).

With the novel diamine we synthesized, the side chain maintained 111 degrees rather than 180 degrees by using methyl group as the bridge between phenyl groups, so that LC equally aligned. Since the LC molecule is inclined together by the inclined phenyl group, a low pretilt angle could be maintained. Figure 5 shows a three-dimensional model of the novel diamine confirmed by Chem office 3D.

The synthesized polyimide was designed considering the steric effect and the electric effect alignment model. Measuring the surface energy of polyimide to certify that and in order to investigate the effect of the methyl group on the pretilt angle, the change in pretilt angle was measured with the curing temperature. Figure 6 shows the changes in pretilt angle. In this measurement, the total surface energies of the PACM and ODA series were approximately 46 dyn/cm^2 and 47 dyn/cm^2, respectively. All polyimides exhibited high surface energy above 45 dyn/cm^2. Moreover, all polyimides manifested a low pretilt angle below 2 degrees at other curing temperatures [13,14,15].

Electro-Optical Properties of PI

The test cell was subjected to five volts for 60 μs at intervals of 16.67 ms using Toyo Company's LCD measurement system 6254, and the VHR was measured at 16.67 ms after voltage removal. Table 2 shows the VHR of each polyimide. If the polarization of the alignment layer is high, the ionic carriers are polarized by the applied voltage and adhere to the alignment layer [16]. Hence, the polyimides of the PACM series have a higher VHR than those of the ODA series. Consequently, the ODA series has a more aromatic structure than the



(a)

(b)

FIGURE 6 The pretilt angle dependent on curing temperature and surface tension of polyimides: a) VP-ODA-BTDA; b) VP-ODA-BPDA; c) VP-PACM-BTDA; d) VP-PACM-BPDA; γ_s (total surface free energy), γ_s^p (polar force), γ_s^d (dispersion force).

polyimides of the PACM series, so that more ionic carriers adhere to the alignment layer, reducing the VHR.

To get the transmittance values, a self-developed optical equipment was used in which a polarizer and an analyzer were crossed at a right angle, a photodiode detected the intensity of radiation after a 632.8-nm laser passed through the test cell, and an analyzer and a digital

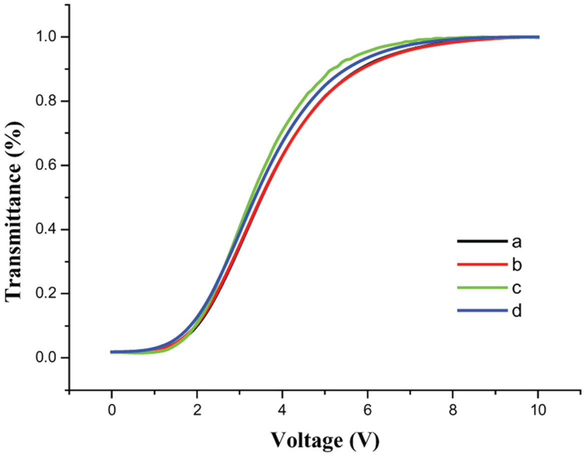


FIGURE 7 The V-T curve of the test cell with various alignment films: a) VP-ODA-BTDA; b) VP-ODA-BPDA; c) VP-PACM-BTDA; d) VP-PACM-BPDA.

multimeter received the signal. Assuming that the transmittance is 100% when the driving voltage is off and 0% when the driving voltage is on, a 10% transmittance (V_{10}) is defined as the optical threshold voltage, and a 90% transmittance (V_{90}) is defined as the optical saturation voltage. The voltage was applied to the test cell with a 1-KHz frequency at a 0.1-V/s rate from 0 to 10 V, and subsequently, a test cell was made after rubbing at 45 degree. V_{th} and V_{sat} in accordance with polyimide alignment layer are shown in Figure 7 and Table 2.

CONCLUSION

This article is mainly about the synthesis and property of homogenous alignment materials, which has a low pretilt angle of 1–2 degrees for IPS-mode application.

TABLE 2 V-T Diagram of Polyimides Based on VP

		45 degree	
Polyimides	VHR (%)	$V_{th}(V_{10})$	$V_{sat}(V_{90})$
VP-ODA-BTDA	93.02	2.0	5.9
VP-ODA-BPDA	98.11	2.0	5.9
VP-PACM-BTDA	98.05	2.0	5.2
VP-PACM-BTDA	99.54	1.9	5.5

In the novel diamine we synthesized, the side chain maintains 111 degrees rather than 180 degrees using a methyl group as the bridge between phenyl groups, so that LC is equally aligned. Since the LC molecule is inclined together by inclined phenyl group, a low pretilt angle could be maintained.

Based on the surface energy measurements, all polyimides exhibit high surface energy above 45 dyn/cm^2. The high surface energy also contributes to the low pretilt angle. The ODA series showed a higher surface energy than the PACM series. This is because the ODA series contained the benzene ring that constitutes π-conjugation, so that mutual interactions between the liquid crystal and the alignment increased and the surface energies became larger. After measuring the pretilt angles based on the curing temperatures, the ODA and PACM series proved suitable for IPS-mode alignment.

Finally, the main-chain structure of polyimides is very important for an alignment to have ideal electro-optical properties. The ODA series contained more benzene rings at its side chain than the PACM series, so its polarity increased and its VHR was lower than that of the PACM series. Typically, when polarity increases, a polarization field is generated and the VHR tends to decrease.

The polyimides we synthesized with novel diamine manifested a low pretilt angle of 1–2 degrees as well as good electro-optical properties, making them potentially useful for IPS-mode application.

REFERENCES

[1] Kim, S. J., Lee, S. Y., Park, J. S., Ko, J. H., Lee, I. S., Hong, Y. T., Soh, H. S., & Kim, W. Y. (2005). *Mol. Cryst. Liq. Cryst.*, *433*, 43.

[2] Tahata, S. & Yuuki, A. (2004). *Mol. Cryst. Liq. Cryst.*, *419*, 13.

[3] Ban, B. S., Rim, Y. N., & Kim, Y. B. (2000). *Liq. Cryst.*, *27*, 125.

[4] Lee, J. B., Lee, H. K., Park, J. C., & Kim, Y. B. (2005). *Mol. Cryst. Liq. Cryst.*, *439*, 161.

[5] Ruenitz, P. C., Bagley, J. R., & Nanavati, N. T. (1988). *J. Med. Chem.*, *31*, 1471.

[6] Lee, S., Jorgensen, M., & Hartwig, J. F. (2001). *Organic letters*, *3*(17), 2729.

[7] Cuminal, M. & Brunet, M. (1997). *Liq. Cryst.*, *22*(2), 185.

[8] Owens, D. K. & Wendt, R. C. (1969). *J. Appl. Polym. Sci.*, *13*, 1741.

[9] Lee, W. C., Chen, J. T., & Hsu, C. S. (2002). *Liq. Cryst.*, *29*(7), 907.

[10] Ban, B. S. & Kim, Y. B. (1999). *J. Phys. Chem.*, *103*, 3869.

[11] Ban, B. S. & Kim, Y. B. (1999). *J. Appl. Polym. Sci.*, *74*(2), 267.

[12] Seo, D. S. (1999). *J. Appl. Phys.*, *87*(7), 3594.

[13] Lee, C. J. (2004). *Mol. Cryst. Liq. Cryst.*, *425*, 189.

[14] Zuo, M., Takeichi, T., Matsumoto, A., & Tsutsumi, K. (1998). *Colloid. Polym. Sci.*, *276*, 555.

[15] Adamson, A. W. (1990). *Physical Chemistry of Surfaces*, 5th Ed. Chap. 13, Wiley: New York, 495.

[16] Koike, Y. & Okamoto, K. (1999). *Fusitsu Sci. Tech. J.*, *35*(2), 221.