

Synthesis and Properties of New Aromatic Polyimides for IPS-mode

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Abstract

In-plane-switching (IPS)-mode LCD is one of the most useful technologies for a broad range of viewing angles. To apply for IPS-LCDs, we synthesized novel homogeneous alignment materials, changing dianhydrides (BTDA and BPDA) and bridged diamines (ODA and PACM). We measured their pre-tilt angles using the crystal rotation method with positive LC and their surface properties.

1. Introduction

In the early 1990s, the applications of TFT-LCD were limited to mobile phones and smaller-than-20-inch computer monitors. Since 2000, however, as the size of TFT-LCD expanded, they have become so popular as to replace conventional CRT devices. The main reason for this is that they are more compact in size and lighter in weight than CRT. Despite these advantages, several hurdles such as viewing angle, brightness, response time, and contrast ratio still remain before the TFT-LCD technology can be applied to TVs [1].

To address such problems, the PVA (patterned vertical alignment) and IPS (in-plane switching) modes were developed as alternatives to the traditional TN (twisted nematic) and STN (super-twisted nematic) modes, and being commercialized. At present, the image quality of TFT-LCD is the same as that of CRT, and many requirements have been met due 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 (liquid crystal) 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 and also help achieve a wider viewing angle [2].

In the present paper, we synthesized new aromatic polyimides for IPS-mode. We examined their thermal property, surface energy. In addition, we investigated its pretilt angle in alignment film by a crystal rotation technique.

2. Experimental

2.1 Materials

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

2.2 Synthesis of side chain monomer

We synthesized side chain diamine of vulcan shape

diamine. We synthesized various polyamic acids with synthesized monomer and the aligning films on the ITO glass were prepared by the thermal imidization.

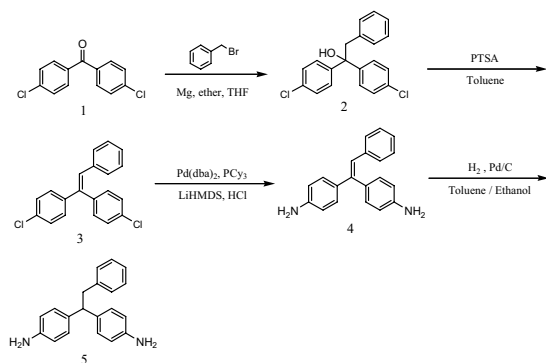


Figure 1. The synthetic route of side chain diamine.

2.3 Synthesis of polyamic acid

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-aminophenyl)-2-phenyl 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.

2.4 Measurement

Gel permeation chromatography was run by 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 imidization was determined from the FT-IR measurement. (bomem FT-IR) The pretilt angle of the positive LC (MJ991735: Merck Co.) was measured with an optical instrument set using the crystal rotation method [3]. 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 [4].

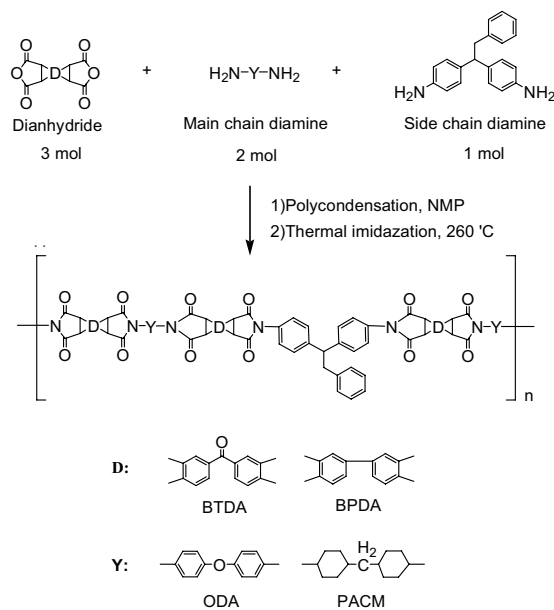


Figure 2. The synthetic route of polyimide.

3. Results and Discussion

3.1 Molecular weight and Thermal characterization

The number-average molecular weight (M_n) 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. The thermal stability of the VP was analyzed using a thermogravimetric analyzer in the range of 30~800 °C within a 10-°C min⁻¹ heating rate. The standard of thermal stability was estimated at a 5% weight loss temperature using a TGA measurement [5].

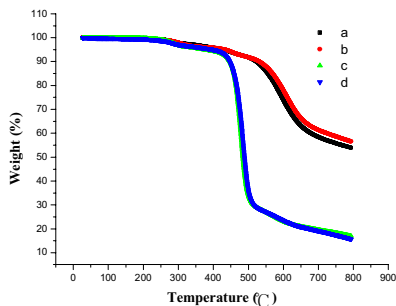


Figure 3. Thermogravimetric diagrams of polymers ; a) VP-ODA-BTDA-PI; b)VP-ODA-BPDA-PI; c) VP-PACM-BTDA-PI; d) VP-PACM-BPDA-PI

The 5% weight loss temperature of the VP was determined in the range of 380~440 °C. Judging from the fact that the 5% weight loss temperature of polyimide occurred at over 400 °C, it is believed that it can be thermally stable up to 400 °C.

Table 1. Molecular weight and thermal properties of polyimides based on VP

Polyimides	GPC	TGA ^a (°C)		
	Mn	T ₅ ^a	T ₁₀ ^b	T _d ^c
VP-ODA-BTDA	74000	427	522	569
VP-ODA-BPDA	61700	435	533	575
VP-PACM-BTDA	16800	380	448	456
VP-PACM-BPDA	21300	400	447	457

^a Temperature at 5% weight loss

^b Temperature at 10% weight loss

^c Temperature at decomposition

The polyimide of the ODA series had a higher decomposition temperature than that of the PACM series, since the polyimide of the PACM series, composed of the alicyclic 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. This is the structural difference of the aromatic and alicyclic structures discussed above.

3.2 Pretilt angle , Imidiazation and Surface properties

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 orientation material used in the TN mode was 4~7 degrees, whereas the IPS mode’s alignment material required a pretilt angle of 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.

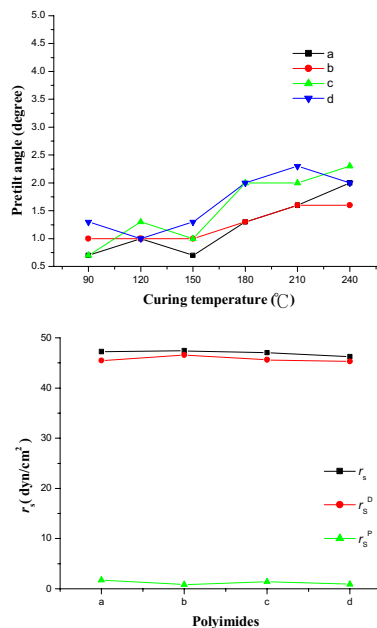


Figure 4. The pretilt angle dependent on curing temperature and surface rension of polyimides; a) VP-ODA-BTDA; b)VP-ODA-BPDA; c) VP-PACM-BTDA; d) VP-PACM-BPDA; γ_s (total surface free energy), γ_s^p (polar force), γ_s^d (dispersion force)

In addition, the steric effect of the polyimide and the electric effect alignment model was considered. A low pretilt angle occurs when the side chain is shorter than the liquid crystals’ major axis. Reportedly, an alignment layer with a surface energy similar to the surface tension of liquid crystal molecules is likely to show a medium pretilt angle. However, an alignment layer with a surface energy larger than the surface

tension of liquid crystal molecules is likely to have a low pretilt angle [6, 7, 8]. The synthesized polyimide was designed considering the steric effect and the electric effect alignment model. Figure 4 shows the changes in the pretilt angle and the surface energy of each polyimide in accordance with its curing temperature. In this measurement, the total surface energies of the PACM and ODA series were around 46 dyn/cm² and 47 dyn/cm², respectively. The PACM series showed a lower surface energy than the ODA series [9, 10, 11]. All polyimides showed a low pretilt angle of below 2 degree.

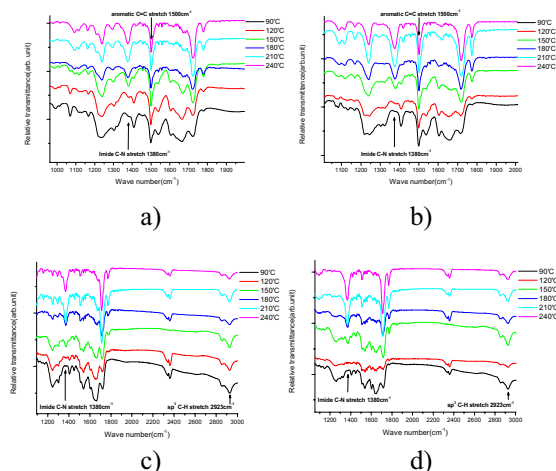


Figure 5. The IR spectrum of the polyamic acid; a) VP-ODA-BTDA; b) VP-ODA-BPDA; c) VP-PACM-BTDA; d) VP-PACM-BPDA

Figure 5 shows the IR spectrum of polyamic acids depending on the curing temperature. All the polyamic acid were completely converted into the polyimides at 240°C for 1h 30min.

4. Conclusion

The goal of this study is the synthesis and property identification of homogenous alignment, which has a 1~2-degree low pretilt angle, for IPS-LCD. In terms of thermal stability, the alignment of the ODA series showed a higher decomposition temperature than that of the PACM series. Moreover, all the alignments showed a high thermal stability applicable to their display. The ODA series showed a higher surface energy than the PACM series. This is because the

ODA series contained the benzene ring constitute π -conjugation, so that mutual interactions between the liquid crystal and the alignment increased and the surface energies became larger. After measuring the pre-tilt angles in accordance with the curing temperatures, ODA and PACM series proved suitable for an alignment of IPS-LCD.

Consequently, the synthesized alignment showed a good pretilt angle and electro-optical properties and is expected to be used for IPS-LCD.

5. Acknowledgements

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