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Synthesis of Soluble and Thermal Stable Polyimides for Vertical Alignment of Liquid Crystal

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Liquid crystal displays (LCDs) with the multi-domain vertical alignment show advantages as wide viewing angle, high contrast ratio and fast responsive time, so the research of the vertical alignment layer has become a chief topic in the field of the liquid crystal (LC) alignment[1]. Generally, polyimide (PI) films are used as alignment layers in the displays. Due to their rigid chain characteristics, traditional aromatic PIs are normally insoluble. Thus, PI processing is generally carried out with poly(amic acid) (PAA) intermediate and then converted to PI via rigorous thermal treatment (250–300°C)[2], which is fatal to the substrate used in the LCD. Many methods to prepare soluble PI were reported. It was found that factors which can cause increase in solubility usually result in the decrease in the thermal stability of PI. To the best of our knowledge, the research on the preparation of soluble and thermally stable PI for vertical alignment of LC has rarely been reported. In the study, a series of dimines were synthesized, which had different number of benzene ring and different length of alkoxy end group in their side chains. The main purpose of this study is to obtain soluble, thermally stable and transparent PI alignment layers for vertical alignment of LC.

A series of diamines with a side chain containing rigid biphenyl unit and nonpolar alkoxy side end group [4-alkoxy-biphenol-3', 5'-diaminobenzoate] (Cn-PDA, n = 4, 6, 12) were synthesized and their chemical structures were confirmed by fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance spectroscopy (^{1}H-NMR). Then three PAAs were prepared by copolymerization of pyromellitic dianhydride (PMDA), 4, 4'-methylenedianiline (MDA) and Cn-PDA in N-methyl-2-pyrrolidone (NMP) and structural identification of all PAAs was performed by ^{1}H-NMR. PIs was obtained when PAA films spin-coated on glass substrates were pre-baked on hot stage at 100 ℃ for 30 min and then cured in oven at 250 ℃ for 1 h and chemical structures of all PIs were confirmed by FT-IR. LC cells were fabricated using these PIs as the alignment layer for characterization of the alignment properties of LCs. It was found that the planar alignment was obtained when PI with side chain containing alkoxy side end group of 4 carbon atoms was employed and the vertical alignment was observed when alkoxy side end groups of 6 or 12 carbon atoms were included. A uniform vertical alignment was validated by polarizing microscopy. These PIs prepared via thermal imidizaiton mentioned above were insoluble, though they could generate vertical alignment of LCs.

In order to increase the solubility of PI, a series of PIs were copolymerized from 4-dodecyloxy-biphenyl-3', 5'-diaminobenzoate (Cn-PDA, n = 8) shown in Fig 1, 3, 3'-dimethyl-4,4'-methylene-dianiline (DMMDA) and 4, 4'-oxydi(phthalic anhydride) (ODPA) via chemical imidization in m-cresol at 180□. ODPA instead of PMDA was employed because the ether bond it contained could increase the flexibility of polymer backbone. DMMDA instead of MDA was used because the existence of methyl group in its backbone would inhibit close packing, which reduce the chain-chain interaction. The bulky side chain contained by C8-PDA had similar effect to methyl group of DMMDA. The results showed that the PIs possessed excellent solubility in polar aprotic solvents and easily formed thin flexible films by solution casting. It could be suggested that the synergistic effect of the flexible ether bridge segments in the polymer backbone of ODPA, the pendant methyl group of DMMDA and the long alkoxy side groups of C8-PDA resulted in main chain flexible and hindered the packing together of the polymer chains, which made PIs soluble. The resultant PI films exhibited high transparency at wavelengths above 400 nm and induced excellent uniform vertical alignment of LC.

In order to increase the thermal stability, PIs with more benzene rings in side chain is prepared. Two kinds of diamines (C8-BPDA and C4-BPDA) shown in Fig 1 containing three benzene ring in side chain, one benzene ring more than Cn-PDA, were synthesized which had different length of alkoxy end group in their side chains. It was found that PIs derived from C8-BPDA and C4-BPDA exhibited excellent solubility and rubbing resistance in comparison with PI from C8-PDA and the pretilt angle could be controlled over 89° with rubbed alignment layers. This is related to their more rigid side chains, which were less likely to fall down toward the polymer bulk phase during the rubbing process, but are more likely to maintain a high degree of vertical conformation. Hence, they could still induce the vertical alignment of LCs after strong rubbing. The thermal gravimetric analysis results showed that the thermal degradation of all PIs under nitrogen atmosphere occurred over 320℃, and PI derived from C8-BPDA showed the best thermal stability. This result could mainly be attributed to its increased side chain rigidity and the lowest side chain content necessary for the vertical alignment of LC. The wide-angle X-ray diffraction patterns indicated amorphous morphology of PIs. The resultant PI films were light colored and maintained high transparence in visible light region.

In conclusions, by increasing the number of benzene ring in side chain, the soluble PI with the thermal stability could be obtained at the same time.

Cn-PDA, n=4, 6, 8, 12

C8-BPDA

C4-BPDA

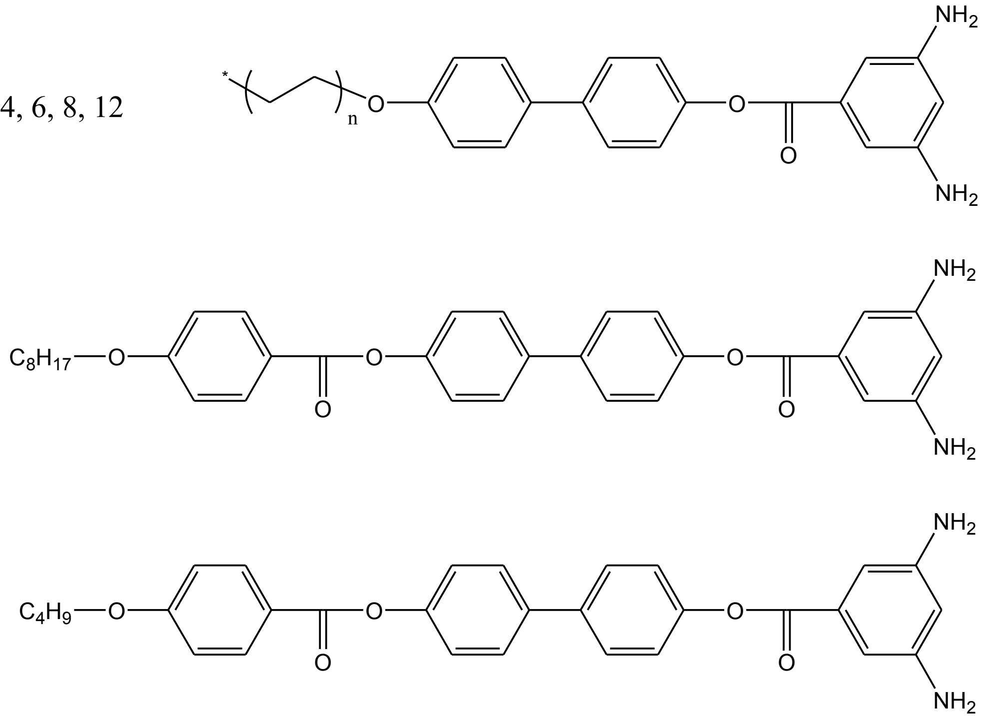

Fig 1. The structures of three functional diamines

Reference

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