Molecular design and preparation of polyimides as the liquid crystal vertical alignment

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Abstract

The chemical structure of polyimide (PI) is essential for the liquid crystal (LC) vertical alignment. Introductions of various side groups or side chains enable PIs to induce alignment of LCs with different pretilt angles. Also, the change of structure has great influence on the thermal stability, solubility, rubbing resistance etc.The common principles of designing LC vertical alignment, effects of side chain structures on the properties of PIs and factors for the stability of LC vertical alignment are described.

Keywords: polyimide; liquid crystal; vertical alignment.

1. Introduction

Among various liquid crystal display (LCD) technologies,the multi-domain vertical alignment LCDs(MVA-LCDs)have attracted much attention from both academican dindustrial institutions due to the short response time, high contrast ratio and wide viewing angle.[1]This vertical mode requiresthe liquid crystal (LC) molecules to be aligned vertically without an applied external electric field, which means the pretilt angle (the tilt angle between the average orientation of LC molecules and the substrate)must be above 89° to realize good electrical and optical performance of the LCD productions.[2]Thus, many experts have been committed todeveloping high performance materials toinduce vertical alignment of LCs and satisfy requirements of LCDs.

Because of its excellent mechanical and thermal stability, the aromatic polyimide (PI) has become the bestcandidate for LC alignment layer in LCD devices.[3]It has been reported that PIs with hydrocarbon side chains showed good capability to induce LC molecules generate high pretilt angles.[4] Since then, many efforts have been made to explore effective side-chain-type PI that can be used as LC vertical alignment. By means of flexible molecular designof the side chains,our research group synthesized a variety of new functional diaminesand made use of them to prepare a series PIs used as LC vertical alignment.All of the PIswere able to align LCs vertically and some of them can maintain the high pretilt angle above 89°even after a rubbing process. Meanwhile, by introducing different chemical groups, the thermal stability and solubility of PI has been improved.

2. PIs used as LC vertical alignments

2.1 Common principles of designing the LC vertical alignment

The side-chain-type PI as LC vertical alignment layerhas been widely adopted in MVA-LCDs, although a few main-chain-type PIs containing short side groups can obtain high pretilt angles, the pretilt angles hardly reach 89°. Normally, for side-chain-type PIs, their side chains are bulky and consist of rigid units and long alkyl chains.

Guo et al. investigated various PIs whose side chains composed of only rigid alicyclic units, only flexible alkylunits,as well as both alicyclicunits andalkyl units, respectively (Fig. 1A).[5] The results proved that only PI having both rigid unitsandflexible units at the chain end induced vertical alignment of LCs after rubbing. *Liu et al*. compared PIs' side chains containing alkoxy end group of different numbers of carbon atoms (Fig. 1B).[6] And they concluded that only when the number of carbon atoms is greater than or equal to six can the vertical alignment be realized. *Wang et al*. designed a series of PIs whose side chains possess both the biphenyl and the alkoxybut the position of biphenyls changed: some located in the end of side chains, some located in the middle and some located in the starter (Fig. C).[7]Their experiments confirmed that side chains ended up with the alkoxy can induce LC align vertically.

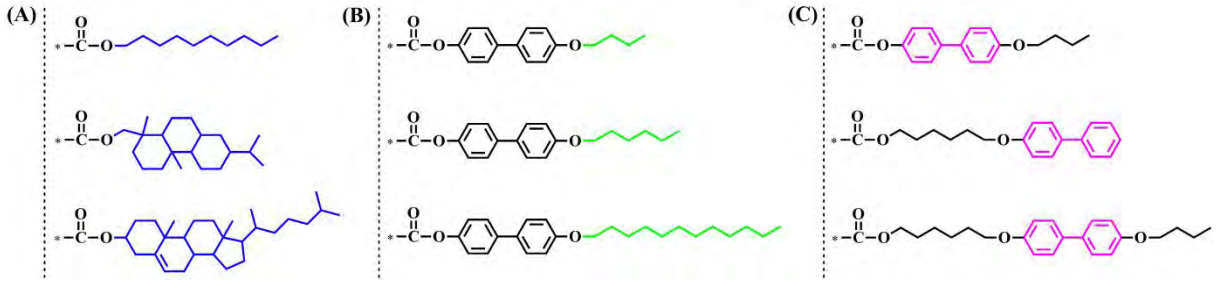

Fig. 1 The side-chain structure of PIs: (A) side chains composed of alicyclic units or alkyl units; (B) side chains containing different numbers of carbon atoms; (C) side chains with different biphenyls positions.

*The main-chain structures of PIs were omitted.

Based on previous researches, it is fair to summarize that the common principles of designing the LC vertical alignment are (1) the side chain need containing rigid units and flexible units, (2) the side chain should end with alkyl chain, (3) the number of carbon atoms would better greater than or equal to six.

2.2 Effect of sidechain structures on the properties of PIs

The materials used as LC alignment layers should be thermally resistant to ensure the alignment stability in the long-term use. Also, the solubility of PI plays a critical role in manufacture procedure. Thus, the thermal stability and solubilityof PI should be taken seriously.

*Yi et al.*increased the number of benzene rings in side chains to improve thermal stability of PIs that the highest Td of dates is 350 °C.[8]*Xia et al*. introduced a naphthalene unit into the side chain which

effectively increased the T_d of PI above 370 ^oC while enhanced itssolubility.[9]Moreover, they designed phthalimide side chains with alkyl chains to further promote the thermal stability, the corresponding PIs exhibited high T_d above 380 ^oC.[10] In addition, *Gong et al*. synthesized soluble PIs containing triphenylamine (TPA)which also showed excellent thermal stability and solubility.[11]All PIs mentioned above can be dissolved in aproticpolar solvents and even in common organic solvents such as tetrahydrofuran and chloroform.

Therefore, it was concluded that rigid groups, such as phenyl, biphenyl,naphthyl etc.,make strong contribution to the thermal stability of PIs. On the other hand the solubility of PIs can be improved by introducing polar groups like CF_3, flexible groups like -O-, twisted three dimensional structures like TPA.

2.3 Factors for the stability of vertical LC alignment

For the alignment technology of LCs, rubbing has been the most widely adopted method due to its simplicity, lowcost, and controllability. If the high pretilt angle could not be maintained after rubbing, the LCD would lose its high performance. So the rubbing resistance plays a crucial role in successful LC vertical alignment layers.

Wang et al. studied the transition of LC alignment from homeotropic to planar on a PI layer with a rubbing treatment.[12]*Che et al*. found that side chains directly linked to PI's backbones without any spacer have better rubbing resistance, while the side chains will be more easily to fall over after rubbing process ifthere is a flexible ether bond exist between the side chain and the backbones.[13] Furthermore, they claimed that the PI possessing rigid backbone had the ability to tolerant higher strength rubbing than that possessing flexible backbone.[14] In other words, the pretilt angle induced by PI whose backbone is rigid is more stable.

In conclusion, for the sake of the stability of vertical LC alignment, choosing PIs whose side chains are directly linked to rigid backbones is the best way.

2.4 A new method to prepare the vertical alignment

As is stated before, only PI having both rigid units and flexible units at the chain end induced vertical alignment of LCs after rubbing. This makes the structures of side chains so complex that more steps of chemical reactions are needed to synthesize ideal functional diamines which are quiet time consuming.

Recently, we have mixed two relative simple functional diamines (as shown in the Fig. 2: one just owns rigid biphenyl while the other just owns flexible alkyl chain) to prepare LC alignment layers. The results are amazing: when the two functional diamines were used separately, vertical alignment of LCs couldn't be obtained after rubbing.[15] However, when they was mixed together to prepare PI, one diamine offered the rigid biphenyl side chain while the other offered the flexible alkyl side chain, the PI thus can align LCs vertically very well.Even after the rubbing process, the pretiltangles of LCswere

still above 89°. This method is expected to simplify the manufacture procedure and reducing the cost.

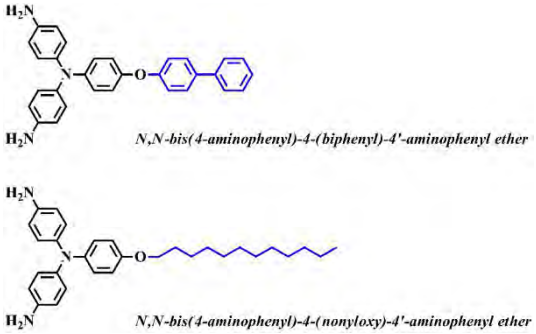

Fig. 2 The structure of two relative simple functional diamines

3. Prospect

As is described in onearticle, the development of new materials will play an important role in the continued technical evolution of LCDs. [1] PI film as one of the most important parts of LCD devices needs further improvements to keep pace with the new requirements of displays. Concerning the advances mentioned above, we believe that these developments of PIs in LC vertical alignment will beneficial to improving display performance and reducing the cost of production.

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