

The Structural Effects on The Pretilt Angle of Alignment Materials with Alkylcyclohexylbenzene as a Side Chain in Polyimides

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Abstract

Polyamic acid precursors were prepared by mixing various main chain dianhydrides, main chain diamines and side chain diamines. Copolyimide films with alkylcyclohexylbenzene as a side chain were prepared by thermal imidization of polyamic acid precursors. Pretilt angles on rubbed polyimides changed according to the side chain and main chain structures of the polyimide. Consequently, we found that LC pretilt angles of polyimide films with a liquid crystal structure as a side chain showed to be approximately 90° when a linear and rigid polyimide main chain and a side chain of suitable length were employed.

1. Introduction

Liquid crystal displays (LCDs) are widely used in devices such as, monitors, laptops, etc, due to their portability, flatness, low voltage requirements, and low power consumption. For optimal electro-optic performance of LCD, it is essential to obtain a uniform alignment of the liquid crystal (LC) molecules.

This pretilt angle is known to significantly influence the performance of LCD devices. For the VA-LCDs, polyimides are used as the liquid crystal alignment materials, which align liquid crystal vertically on the substrate at the field-off state.[3,4,5]

A few publications have reported that the factors affecting pretilt angles are not only the electronic interaction between LC molecules and their alignment layer surface, but also the steric interaction between LC molecules and the conformation of

alignment material.[6,7]

In this paper, we synthesized polyimides having the liquid crystal structure as a side chain. Pretilt angles on rubbed polyimides were changed according to the side chain and main chain structures of the polyimides. We calculated the surface tension of synthesized polyimide surface by measuring the contact angles of distilled water and methylene iodide on the rubbed polyimide surface. The relationship between the surface free energy and the pretilt angle was investigated. Also, we investigated the change of pretilt angles on rubbed polyimides depending on the side and main chain structures.

2. Experimental

2.1 Synthesis of side chain monomers

We synthesized a side chain diamine of 4'-(4-Pentylcyclohexyl) biphenyl-3, 5-diamine. The synthetic route was shown in Figure 1. 1-Bromo-3, 5- dinitrobenzene was synthesized by bromination of 1, 3- dinitrobenzene, [8] and then reacted with 4-(pentylcyclohexyl) benzyl boric acid through Suzuki reaction.[9] 4'-(4-pentylcyclohexyl) biphenyl-3, 5-diamine (abbreviation: R5CPP) was prepared by reducing of their coupling compound. 4'-(4-cyclocyclohexyl) biphenyl-3, 5-diamine (abbreviation: R3CPP) was synthesized through the same procedure. The chemical structures of products were identified by ¹H NMR spectroscopy (Bruker Avance 400 Spectroscope) and EI mass spectroscopy (70eV Hewlett Packard 5972 MSD).

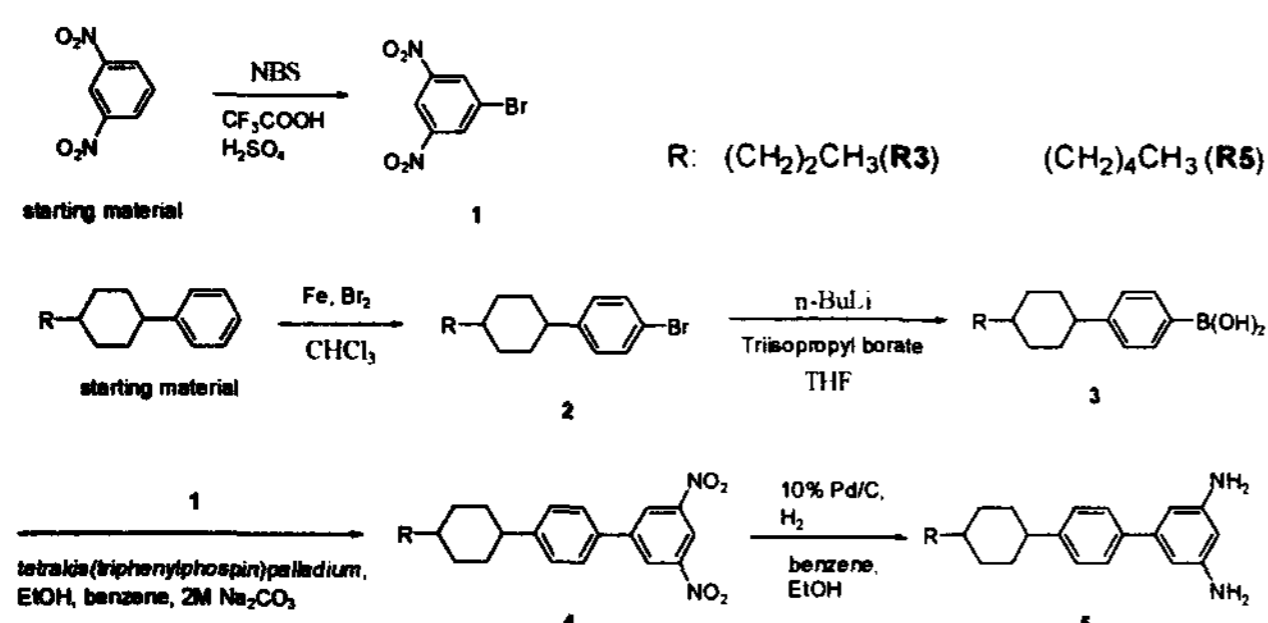


Figure 1. Synthetic route of diamine as a side chain.

2.2 Preparation of alignment films and Measurements

Polyamic acid precursors were prepared by copolymerization after mixing dianhydride, main chain diamine and side chain diamine (mole ratio of 3:2:1) in 12 wt% solid concentration of 1-methyl-2-pyrrolidinone (NMP) in a nitrogen atmosphere as shown in Figure 2. The solution of the resultant polyamic acid was coated using spin coater on ITO glass substrates. Polyamic acid was converted to polyimide by thermal imidization through pre-curing at 80° for 5min and main-curing at 260° for 1 hour. Pretilt angles of nematic LC (MJ961213: Merck Co.) were measured with an optical instrument set by applying the crystal rotation method. [10] ITO glass substrates rubbed with each rubbing depth was combined with 48um microfilm. Contact angles were measured by the sessile drop method using a contact anglemeter (Phoenix 300: Seo Co.) with highly pure distilled water and methylene iodide. The surface free energy was calculated by Owens's formula. [11]

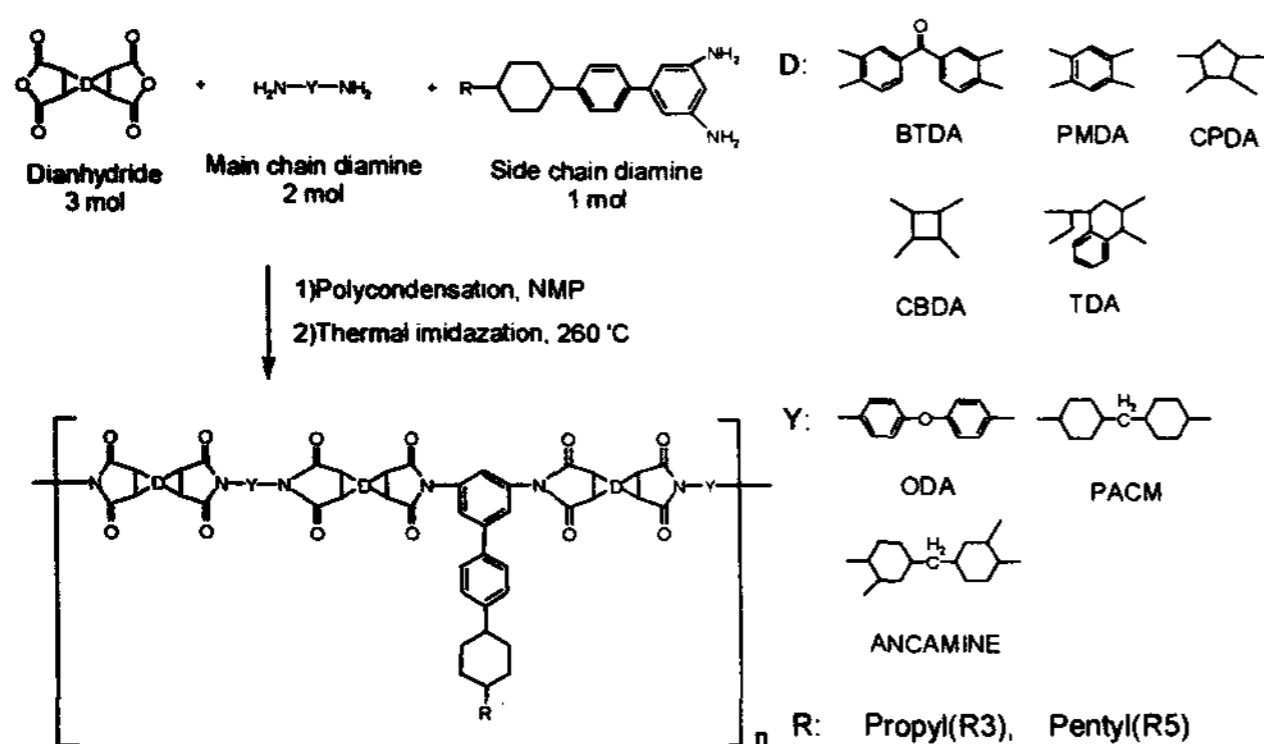


Figure 2. The synthetic route of polyimides

3. Result and Discussion

3.1 Relationship between pretilt angle and side chain structures

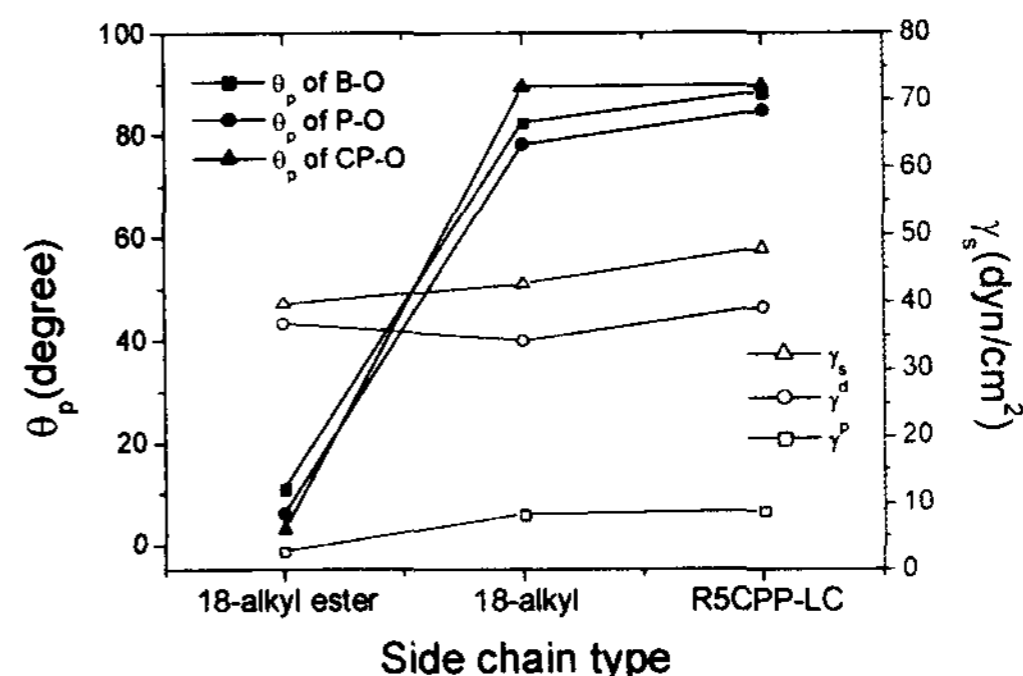


Figure 3. LC pretilt angles and surface tension dependence of side chain structures; γ_s (total surface free energy), γ^p (polar force) and γ^d (dispersion force), rubbing depth=0.3mm.

Side chain type	The structures of side chains	Side chain length(Å) ^a
18-alkyl ester		24.0
18-alkyl		21.6
R5CPP-LC		10.8(R3CPP) 13.1(R5CPP)

Table 2. Side chain type and their structures.

^a After the molecular conformation obtained by using MM2 of Chem 3D ultra 7.0, each length is calculated.

Several publications reported that a side-chain-type polyimide exhibits high pretilt angle of LCs. It is proposed that an alignment model for the dependence of the LC molecule arrangement on side chain length. [12] Polyimides with various side chains have been suggested based on this model. It is reported that LC pretilt angles on polyimide films having 18-alkyl side chain containing ester group (18-alkyl ester) exhibit 3~11°. [12] The introduction of 18-alkyl side chain (18-alkyl) could achieve almost 90° of the pretilt angle [13] In this work, we introduce a LC structure as a side chain with side chain length such as 10.8Å in R3CPP and 13.1 Å

in R5CPP. Consequently, LC pretilt angles on polyimide films according to side chain types are shown in Figure 3 and each side chain and their structures are shown in Table 2. We can see that LC pretilt angles on polyimide films with an 18-alkyl ester side chain are significantly lower than 18-alkyl side chain. Although the length of a 18-alkyl side chain (21.6Å) is almost the same as the length of 18-alkyl side chain (24.0Å), we could confirm that the vertical alignment was hindered by the introduction of an ester group. Based on the concept of the increase of pretilt angles depending on side chain length, it is assumed that an 18-alkyl ester side chain lie down on the backbone of polyimide by an ester functional group. The ester functional group has a bent structure, which makes it difficult to support LC molecules upward. On the other hand, LC pretilt angles on polyimide films with a LC side chain exhibit high pretilt angle, similarly to an 18-alkyl side chain. However, a LC side chain has a rodlike structure due to the characteristics of liquid crystal molecules. Although the length of a LC side chain is shorter than the length of 18-alkyl side chain, polyimides having a LC side chain are enough to stand LC molecules due to the rigidity of the LC side chain.

The factors affecting the pretilt angle (θ_P) are not only steric interaction, but also the strength of electronic interaction between LC molecules and their alignment layer surface.[7, 14, 15] The high pretilt angles of LC are strongly related to the low surface energy. In other words, the polar surface produces a smaller θ_P than the non-polar surface, due to the stronger electronic interaction between LC molecules and polymer surface. In order to identify the electronic effect on the affecting pretilt angles according to side chain structures, we added the surface free energy content to a Y-axis as shown in Figure 3. The LC pretilt angles on polyimide surface were found to increase with the increase of total surface free energy. This trend of variation of LC pretilt angles on polyimide films isn't correlated with conventional concept. Hence, we need to approach the concept on the generation of pretilt angles on side-chain-type polyimides surface. In case of the main-chain-type polyimide, the steric interaction

between long side chain and LC molecules will not be presented here. That is to say that LC lies down on the surface of polyimide backbone without interacting with the side chains. In this case, the total surface free energy (surface polarity) considerably affects pretilt angles due to the interaction between LC molecules and polyimide backbone. However, LC pretilt angles on polyimides with a long side chain are affected with the steric interaction between LC molecules and long side chain on polyimide backbone. If the LC molecule lies in space among the side chain intervals, they become attracted by attractive force between LC molecules and imide group of polyimide backbone. This can be described as the polar force. The polar force induced by mainly hydrogen bonds [11] is known to greatly contribute to the pretilt angle rather than the dispersion force. [16] Hence, this polar force should be connected to the hydrogen bonding between hydrogen of LC and oxygen of imide group. If this attractive force is strong enough, LC molecule will be strongly attracted vertically in the direction of polyimide backbone. Therefore, in case of side-chain-type polyimides, the pretilt angles will increase with the increase of polar force.

3.2 Relationship between the pretilt angle and Main chain structures

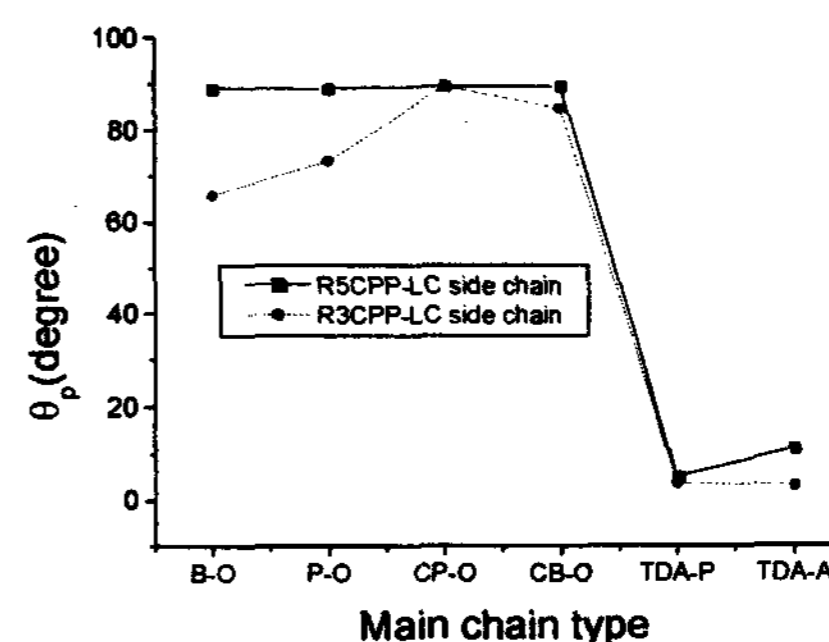


Figure 4. LC pretilt angles on polyimide films rubbed by a 0.1mm rubbing depth

We conducted studies on the variation of the LC pretilt angles by using different main chain structures while keeping the same side chain of liquid crystal molecules. Five dianhydrides (BTDA,

PMDA, CPDA, CBDA and TDA) and three diamines (ODA, PACM and ANCAMINE) were used to modify the main chain structures of the polyimides. Their combinations are presented in Table 1. We can see that different main chain structures would contribute significantly to the pretilt angle variations as shown in Figure 4. As a whole, polyimides of R3CPP-LC side chain exhibit lower pretilt angle than R5CPP-LC side chain. This is due to the steric effect according to the side chain length. Polyimide films based on the more linear and rigid structures (BTDA, PMDA, CPDA and CBDA) exhibit high pretilt angles (R3CPP: 66-89.7°, R5CPP: 89.1-89.7°). They have benzene rings, cyclopentane rings and cyclobutane rings to make a rigid structure. However, an asymmetric and flexible main chain structure (TDA-PACM and TDA-ANCAMINE) lead to a low pretilt angle. (R3CPP: 3.1-3.4°, R5CPP: 5.0-11.1°) Diamines such as PACM and ANCAMINE have a alicyclic structure allowing it to bend easily. Moreover, the structure of TDA is asymmetric to have cyclohexyl ring and single bond carbon allowing it to change and rotate flexibly. In this regard, their combinations do not have a linear and rigid structure, and thereby exhibit low pretilt angles. These findings were reported in a previous literature. [6] The steric interaction of long alkyl or LC side chain seems stronger when a linear and rigid polyimide main chain is employed. The reason is when a linear and rigid polyimide main chain is introduced, the space for attracting vertically in the direction of polyimide backbone becomes available. Consequently, it becomes necessary for a linear and rigid main chain to be introduced to produce the vertical aligning of LC.

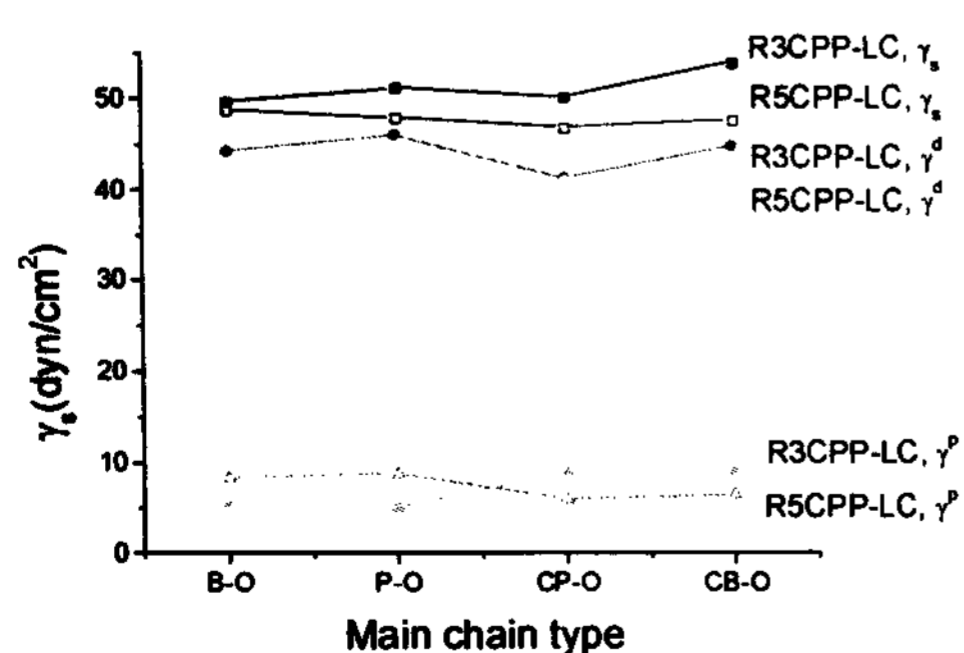


Figure 5. Relationship between the surface tension and main chain structures; γ_s (surface free energy), γ^p (polar force) and γ^d (dispersion force)

The surface free energy (γ_s), polar force (γ^p) and dispersion force (γ^d) of the rubbed polyimide surfaces according to the main chain type are shown in Figure 5. The total surface free energy of polyimide surface having R3CPP-LC side chain is higher than that of R5CPP-LC side chain. The reason is that the longer the alkyl chains of LC side chain structure are, the more the polar groups of polyimide backbone are masked, which in turn causes the total surface free energy to become lower. In case of R3CPP-LC side chain, the pretilt angles increase with the increase of polar forces, whereas in case of R5CPP-LC side chain, the pretilt angles become saturated to almost 90° in spite of the decrease of polar force. Hence, we can conclude that R5CPP-LC side chain has a suitable length to stand LC molecules than R3CPP-LC side chain.

4. Conclusion

We synthesized polyimides having the liquid crystal molecule as a side chain. We found that polyimide films having a LC side chain are enough to stand LC molecules due to the rigidity of the side chain, and thus exhibit high pretilt angles. Also, the pretilt angles of a side-chain-type polyimide increase with the increase of the polar force subscribed the strength of interaction between LC molecule and polyimide backbone. One side, the pretilt angle of polyimides with LC side chain was changed according to main chain structures, polyimides with linear and rigid main chain exhibit high pretilt angles. Based on these findings, we will design other polyimide structures to achieve vertical alignment.

5. Acknowledgements

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6. References

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