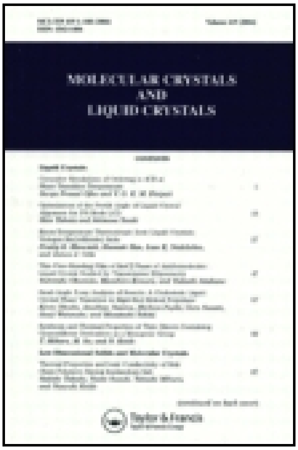

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The Structural Effects on the Pretilt Angle of Alignment Materials with Alkylcyclohexylbenzene as a Side Chain in Polyimides

Jong-Beom Lee [a], Hyun-Kyung Lee [a], Jae-Chul Park [a] & Yong-Bae Kim [a]

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

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Jong-Beom Lee
Hyun-Kyung Lee
Jae-Chul Park
Yong-Bae Kim
Liquid Crystal Research Center, Department of Chemistry, Division of Natural Sciences, Konkuk University, Seoul, Korea

We have investigated the relationship between the surface property of rubbed polyimides and the variation of pretilt angle according to the side chain and main chain structures. We calculated the surface free energy of synthesized polyimide surface by measuring the contact angles of distilled water and methylene iodide on the rubbed polyimide surface. Consequently, we found that pretilt angles on rubbed polyimides changed according to the side chain and main chain structures of the polyimide. Our calculations show that LC pretilt angles of polyimide films with a liquid crystal structure as a side chain were approximately 90° when a linear and rigid polyimide main chain and a side chain of suitable length were employed.

Keywords: alignment materials; liquid crystal; pretilt angle; side chain type polyimide; surface free energy

INTRODUCTION

Liquid crystal displays (LCDs) are widely used in devices such as, video cameras, laptop and desktop computers due to the LCD's portablility, flatness, low voltage requirements, and low power consumption. For optimal electro-optic performance of an LCD, a uniform alignment of the liquid crystal (LC) molecules is essential. Rubbing technology, which easily achieves this uniformity, has been used in LCD production [1,2].

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

Through the rubbing process, LC molecules are aligned parallel with the rubbing direction, and a definite pretilt angle is generated. This spretilt angle influences the performance of LCD devices; in addition the angle should have a specific value applicable to various kinds of LCD modes. For example, in the case of VA-LCDs, nematic LC molecules are vertically aligned on the substrate at the field-off state [3–5].

Various kinds of organic and inorganic materials were examined for LC alignment film. Among them, polyimide is one of the most suitable materials for LC alignment with respect to their heat resistance, chemical stability, and mechanical strength. Rubbed polyimide film can align LC molecules with a constant pretilt angle [6–12]. In other words, when the liquid crystal molecules align in a direction such that the free energy of the system is minimized without external energy, the surface aligning energy becomes zero. In general, this aligning direction is called an easy axis [7]. The chemical structure of polyimide and the entire conformation of polyimide chain are considered responsible for generating this easy axis on polyimide surface. The chemical structure of polyimide and its conformation in the surface region are related to the electronic and steric effect, respectively. Thus, many investigators have reported that the factors affecting pretilt angles are both the electronic interaction and the steric effect [7,8].

In previous work, we investigated the vertical alignment on substrate, introducing various kinds of side chain in polyimide structure. And we proposed the alignment model for the dependence of the LC molecule arrangement on side chain length in side chain structure [9]. On the basis of this model, we synthesized the alignment films with various structures and lengths of side chain [9,10]. From the results, we could confirm that pretilt angle increases with the elongation of alkyl chain. In the present paper, we synthesize polyimides having the liquid crystal structure as a side chain, and its pretilt angle and surface free energy were measured. We show the relationship between the surface free energy and the pretilt angle in alignment film with side chain. From this relationship, we investigate the change of pretilt angles on rubbed polyimides, depending on the side and main chain structures.

EXPERIMENTAL

Materials

3,3,4,4-benzophenonetetracarboxylic dianhydride (BTDA), 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), cis-1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) 1,2,3,4-cyclobutanetracarboxylic dianhydride (CBDA) and 4,4′-oxydianiline (ODA) were purchased from the Aldrich Corporation. 5-(2,5-Dioxo-tetrahydro-furan-3-yl)-3a,4,5,9b-tetrahydro-naphtho[1,2-c]furan-1,3-dione (TDA), 1,4′-Methylenebiscyclohexylamine (PACM) and 4,4′-Methylenebis-2-methylcyclohexylamine (ANCAMINE) were purchased from the TCI Corporation. The reagents were recrystallized and sublimed before use. 4-pentylcyclohexylbenzene and 4-propylcyclohexylbenzene were purchased from the Canto 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.

Synthesis of Side Chain Monomers

We synthesized side chain diamine of 4′-(4-Pentylcyclohexyl) biphenyl-3,5-diamine. The synthetic route is shown in Figure 1. The chemical structure of the product was identified by ^{1}H NMR spectroscopy (Bruker Avance 400 MHz Spectroscope) and EI mass spectroscopy (70 eV Hewlett Packard 5972 MSD).

1-Bromo-3,5-dinitrobenzene(1)[13]

In a 250 ml round-bottomed flask, equipped with overhead stirrer, was placed 50 ml of trifluoroacetic acid, 100 mmol of 1,3-dinitrobenzene, and 20 ml of sulfuric acid (98%). The mixture was stirred vigorously, and 150 mmol of NBS was added in portions over an 8 hours period. The mixture was heated at 48°C for 2 days. The reaction mixture was poured into 200 ml of ice water, the organic layer separated, and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried over $MgSO_4$. After the CH_2Cl_2 was evaporated, recrystallization gave the product. (53% yields) Mass spectrum: 247 (M^+), 246, 200, 155, 75, 63, 51 ^{1}H NMR($CDCl_3$): δ 9.0(s, 1H), 8.7(s, 2H)

1-Bromo-4-(4-pentylcyclohexyl)benzene (2)

In a 500 ml three-necked round bottomed flask equipped with a dropping funnel was placed 150 mmol of 4-pentylcyclohexylbenzene in $CHCl_3$ (300ml) and a little iron powder. 100 mmol of bromine liquid was slowly added and stirred. After 12 h, the reaction mixture was quenched with NaOH and extracted with $CHCl_3$. After the evaporation of $CHCl_3$, Recrystallization with EA and EtOH gave the white powder. (91% yields) Mass spectrum: 308 (M^+), 257, 165, 131, 55 ^{1}H NMR ($CDCl_3$): δ 7.3(d, 2H), 7.0(d, 2H), 2.9(q, 1H), 1.6(t, 4H), 1.3 ~ 0.9(m, 15H)

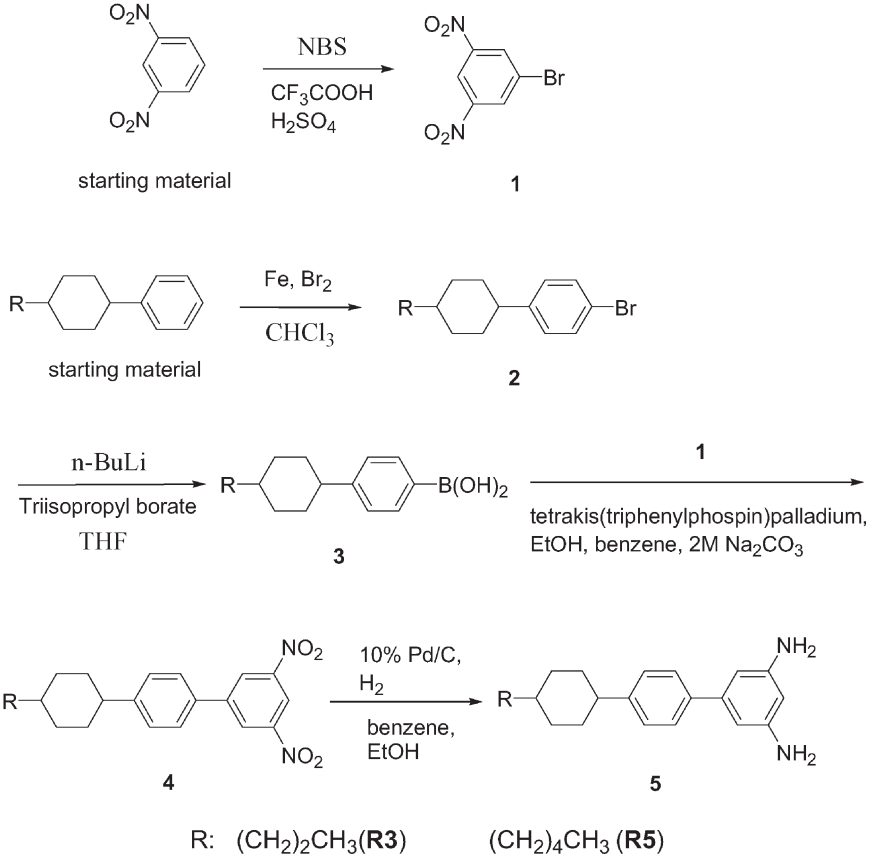


FIGURE 1 Synthetic route of diamine as a side chain.

4-(Pentylcyclohexyl)benzyl Boric Acid (3)

In a 500 ml three-necked round bottomed flask equipped with a nitrogen inlet, 65 mmol of 1-bromo-4-(4-pentylcyclohexyl)benzene in dried THF was cooled to −78°C, and then 77 mmol of 2.5 M BuLi was slowly added. After the mixture was maintained at −78°C for 30 min, 130 mmol of triisopropyl borate was added while maintaining the temperature. The reaction mixture was warmed to room temperature and neutralized with 10% HCl. The product was extracted with diethylether. The organic layer was dried over $MgSO_4$ and removed in vacuo to give a white crude product. The product recrystallized with hexane was given. (71% yields) ^1H NMR ($CDCl_3$): δ 7.2(t, 2H), 7.1(d, 2H), 2.9(q, 1H), 1.6(t, 4H), 1.5(q, 1H), 1.3∼0.9(m, 15H)

3,5-Dinitro-4′-(4-pentylcyclohexyl)biphenyl (4) [14]

In a 500 ml three-necked round bottomed flask equipped with reflux condenser, 20 mmol of 1-bromo-3,5-dinitorbenzene was dissolved in benzene. Tetrakis (triphenylphosphine) palladium (0.2 g) and 2 M sodium carbonate (70 ml) were added. 20 mmol of 4-(pentylcyclohexyl) benzyl boric acid dissolved in ethanol was added. The mixture was refluxed at 95°C for 24 h. The reaction mixture was quenched into the NaCl solution, extracted with ether, and dried with anhydrous $MgSO_4$. The evaporation of the solvent and recrystallization gave the yellowish solid. (68% yields) Mass: 396 (M^+), 270, 257, 165, 131, 55 ^1H NMR ($CDCl_3$): δ 9.1(s, 1H), 8.9(s, 2H), 7.4(d, 2H), 7.2(d, 2H), 2.8(m, 1H), 1.6 ~ 0.9(m, 20H).

4′-(4-Propyl-cyclohexyl)-biphenyl-3,5-diamine(5)

In a high-pressure autoclave was placed 18 mmol of 3,5-dinitro-4′-(4-pentylcyclohexyl)biphenyl dissolved in benzene and ethanol, and palladium 10 wt% on activated carbon (0.5 g) was added. The mixture was maintained for 3 h under 4 kg/cm^2 pressure of H_2. The Pd/C was filtered off and the residue was evaporated in vacuo. The product was recrystallized with ethanol to yield the yellowish solid product. (95% yields) Mass: 336 (M^+), 270, 211, 115, 71, 55 ^1H NMR ($CDCl_3$): δ 7.4(d, 2H), 7.2(d, 2H), 6.0(d, 2H), 5.6(d, 1H), 1.6 ~ 1.5(m, 5H), 1.3 ~ 0.9(m, 15H)

Polymer Synthesis

Preparation of Poly(amic acid)s

In a flame-dried 50 ml flask equipped with a mechanical stirrer and anitrogen inlet were placed 2 mmol of 4′-(4-pentyl-cyclohexyl)-biphenyl-3,5-diamine, 4 mmol of 4,4′-oxydianiline (ODA) and 5 ml of purified NMP. The mixture was stirred under a slow stream of nitrogen gas until the diamines were entirely dissolved. 18 mmol of BTDA and an additional 4 ml of NMP were added in one portion. The solution was stirred mechanically for 1 h at 0°C, becoming clear, then it was stirred at room temperature for 12 h under nitrogen. The clear and viscous poly (amic acid) solution (R5CPP-B-O) was poured into deionized water to yield a white solid. The solid was washed with additional deionized water and purified methanol. The polyamic acid solid was filtered and dried overnight under vacuum at 40°C, then at 90°C for 12 h.

Preparation of Polyimide Layer

The polyamic acid solution with 4% solid content in NMP/2-butoxyethanol (3:1 ratio) was coated on indium-tin oxide glass by spin-coating. The solvent was evaporated at 80°C for 5 min, and curing was carried out at 260°C for 1 h. The approximate thickness of the resulting polyimide films was about $600 \pm 50\,\text{Å}$.

Measurements

Pretilt Angle

The rubbing process was performed as described in the paper. The rubbing strength (RS) was calculated using the empirical expression [9]. The rubbing conditions include the number of the revolution per minute (500 rpm), the moving speed of the roller (16.7 mm/s), the radius of the roller (75 mm), and the depth of rubbing (0.1 mm or 0.3 mm). The test cell was assembled with two pieces of glass substrates, ensuring the rubbing direction antiparallel to each other. We maintained the cell gap by using microfilms with 48 μm thickness. The cell was filled with nematic LC (MJ961213: Merck Co.) and sealed with epoxy adhesive. Pretilt angle was measured with laboratory equipment set by applying the crystal rotation method [15].

Surface Free Energy

The dispersion and polar force of the rubbed PI films was calculated by Owens's formula (Eq. (1)):

$$(1+\cos\theta)\gamma_L = 2(\gamma_S^d \times \gamma_L^d)^{1/2} + 2(\gamma_S^p \times \gamma_L^p)^{1/2} \tag{1}$$

Where the d and p refer to the dispersion force and polar force components [16,17]. The value of γ_S^d and γ_S^p can be determined from the measure contact angle θ, using more than two different liquids whose surface free energy (γ_L^d, γ_L^p) is known. We can get the surface free energy of the rubbed PI films, using the reference data: $\gamma_W = 72.8\,\text{dyn/cm}$; $\gamma_W^d = 21.8\,\text{dyn/cm}$; $\gamma_W^p = 51.0\,\text{dyn/cm}$ for distilled water and $\gamma_{MI} = 50.8\,\text{dyn/cm}$; $\gamma_{MI}^d = 49.5\,\text{dyn/cm}$; $\gamma_{MI}^p = 1.30\,\text{dyn/cm}$ for methylene iodide. Preparation of polyimide films on the ITO glass and rubbing process were carried out as above described. Contact angle was measured by the sessile drop method, using a contact anglemeter (Phoenix 300: Seo Co.). After liquid was dropped on the rubbed PI surface, we left it undisturbed to attain the equilibrium state for 2 min. The measurements were made at room temperature.

RESULTS AND DISCUSSION

Table 2 shows the structure of a side chain synthesized and reported from a previous paper [10,12] and its calculated length. Also the pretilt angle on polyimide films with these side chains is shown in Figure 3.

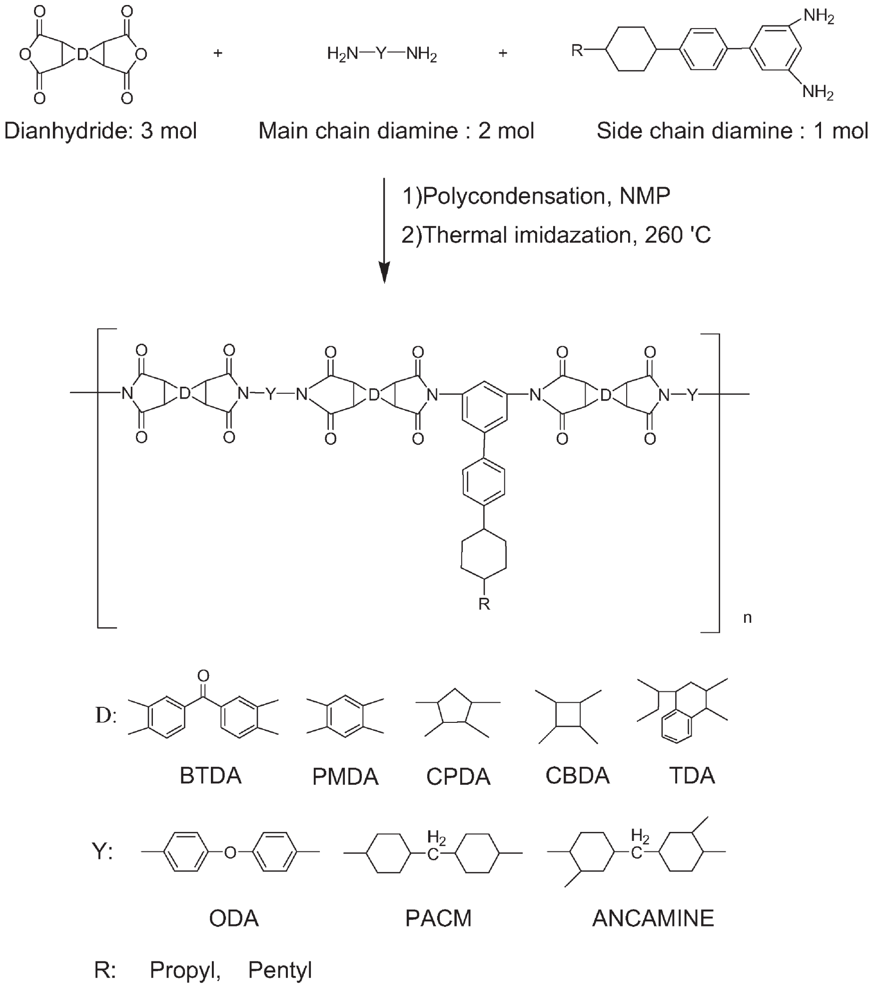


FIGURE 2 The synthetic route of polyimides.

We can see that pretilt angles on polyimide films with an 18-alkyl ester side chain are significantly lower than those of an 18-alkyl side chain. Although the length of an 18-alkyl side chain (21.6 Å) is almost the same as the length of an 18-alkyl ester side chain (24.0 Å), we could confirm that the vertical alignment was hindered by the introduction of the ester group. On the basis of the concept of an increase in pretilt angle being dependant on side chain elongation, we assumed that an 18-alkyl ester side chain is held on the backbone of the polyimide by an ester group. The ester group has

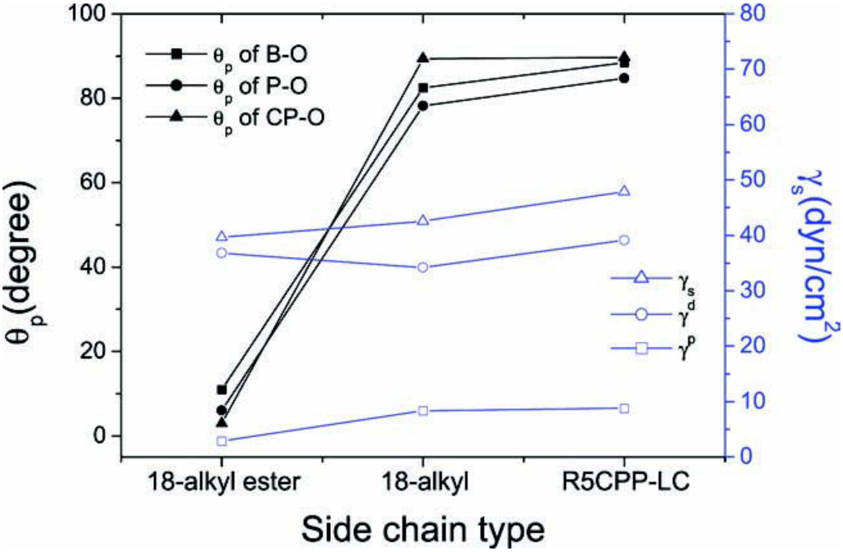


FIGURE 3 LC pretilt angles and surface tension dependence of side chain structures; γ_s (total surface free energy), γ^p (polar force) and γ^d (dispersion force), rubbing depth = 0.3 mm.

a bent structure, which makes it difficult for it to provide upward support for an LC molecule. On the other hand, the pretilt angle on polyimide films with an LC side chain exhibits high pretilt angularity, similar to the 18-alkyl side chain. The reason for this is that the LC side chain has a rodlike structure characteristic of an LC molecule. Although the length of an LC side chain is shorter than the length of an 18-alky side chain, the LC side chain can stand vertically on substrate due to the rigidity of the LC side chain.

The factors affecting the pretilt angle are not only the steric effect, but also the strength of the electronic interaction between LC molecules and their alignment layer surface [6,8,11]. The high pretilt angles of an LC are strongly related to the low surface energy. In order words, the polar surface produces a smaller pretilt angle than the nonpolar surface due to the strong electronic interaction between LC molecules and the polymer surface. In order to identify the electronic effect on pretilt angle depending on a side chain structure, we added surface free energy content to the Y-axis as shown in Figure 3. The LC pretilt angle increases with an increase in total surface free energy. This trend of variation in LC pretilt angles does not correlated with conventional concepts. Hence, we need to reconsider the concept on the generation of pretilt angles on side-chain-type polyimide film.

In the case of the main-chain-type polyimide, the steric effect between the long side chain and LC molecules is not a factor. That is to say that the LC molecule lies on the surface of the polyimide backbone without interacting with the side chain. Thus, the total surface free energy considerably affects pretilt angles due to the interaction between LC molecules and the polyimide backbone. However, the pretilt angle on polyimide with side chain is affected by the steric effect between the LC molecule and the side chain attached to the polyimide backbone. If the LC molecule occupies the space formed by the side chain interval, it was attracted to that position by the attractive force between LC molecules and the polar group in the polyimide backbone. This polar functional group includes imide in repeat unit of polyimide. This can be described as the polar force, which is known to greatly contribute to the pretilt angle rather than the dispersion force. When this attractive force is strong, the LC molecule will be gradually vertical on polyimide backbone. Therefore, in the case of side-chain-type polyimides, the pretilt angle increases with an increase in polar force.

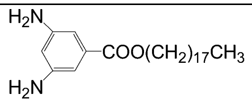
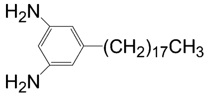
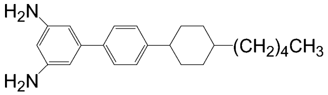
RELATIONSHIP BETWEEN THE PRETILT ANGLE AND MAIN CHAIN STRUCTURES

We conducted studies on variations in the LC pretilt angles by using various 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 structure of the polyimide. Their combinations are presented in Table 1. We can see that the main

TABLE 1 Synthesized Polyimide Series

Side chain diamines	Dianhydrides	Main chain diamines	Combination
R3CPP	BTDA	ODA	R3CPP-B-O
	PMDA	ODA	R3CPP-P-O
	CPDA	ODA	R3CPP-CP-O
	CBDA	ODA	R3CPP-CB-O
	TDA	PACM	R3CPP-TDA-P
	TDA	ANCAMINE	R3CPP-TDA-A
R5CPP	BTDA	ODA	R5CPP-B-O
	PMDA	ODA	R5CPP-P-O
	CPDA	ODA	R5CPP-CP-O
	CBDA	ODA	R5CPP-CB-O
	TDA	PACM	R5CPP-TDA-P
	TDA	ANCAMINE	R5CPP-TDA-A

TABLE 2 Side Chain Type and their Structures

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)

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

chain structure 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 depending on the side chain length. Polyimide films with more linear and rigid main chain structures

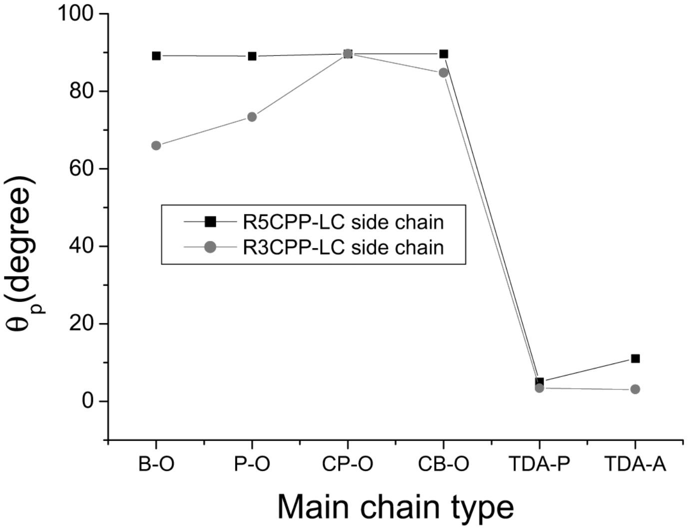


FIGURE 4 LC pretilt angles on polyimide films rubbed by a 0.1 mm rubbing depth.

(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, giving a rigid structure. However, asymmetric and flexible main chain structure (TDA-PACM and TDA-ANCAMINE) leads to a low pretilt angle. (R3CPP: 3.1–3.4°, R5CPP: 5.0–11.1°) Diamines, such as PACM and ANCAMINE, have an alicyclic structure allowing it to bend easily. In this regard, their combinations do not have a linear and rigid structure, and thereby exhibit low pretilt angles. The steric effect of alkyl or LC side chain strongly affects the pretilt angle when linear and rigid main chain structure is employed. The reason is that a linear and rigid main chain structure makes the space for a vertically standing LC molecule. Therefore, the linear and rigid main chain should be introduced in order to produce the vertical alignment of LC.

CONCLUSION

We synthesized polyimides having the liquid crystal molecule as a side chain. We found that polyimide films having a LC side chain can support standing 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 an increase in the polar force resulting from the strength of the interaction between the LC molecule and polyimide backbone. The pretilt angle of polyimides with a LC side chain changes depending on the main chain structures, so a polyimide with linear and rigid main chain exhibits high pretilt angles. On the basis of these findings, we can design other polyimide structures to achieve vertical alignment.

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