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Effect of side chain structure of polyimides on a pretilt angle of liquid crystal cells

Yoon Jung Lee [a], Jung Geun Choi [a], In-kak Song [a], Jae Min Oh [b], Mi Hye Yi [a,*]

[a] *Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yuseong, Daejeon 305-600, South Korea*
[b] *Cheil Industries, Inc., 332-2, Gocheon-dong, Uiwang-si, Gyeonggi-do 437-711, South Korea*

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Abstract

A series of poly(amic acid)s had been synthesized from cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA) and 4,4′-diaminodiphenyl methane (DDM) and functional diamines with various side chain structures. The functional diamines, like 3,5-diamino benzoic acid hexadecane-1-yl ester which had long alkyl or rigid alicyclic side chains with different flexibility had been synthesized. Pretilt angles of liquid crystal cell fabricated with the poly(amic acid)s were measured and investigated factors affecting on the pretilt angles. The pretilt angles of the liquid crystal on the polyimide (**5a**) with rigid side group was 0.6°, on the other hand, the pretilt angle on the polyimide (**5b**) and (**5c**) with flexible side chains were very high above 89.6°. Furthermore, the pretilt angle of liquid crystal on the polyimide (**5c**) film having rigid cylindrical structure with 6-methylheptyl at the chain end was still high above 86.0° even after the rubbing process.

Keywords: Polyimide; Side chain structure; Liquid crystal alignment

1. Introduction

Liquid crystal display device is composed of several materials such as a liquid crystal, a color filter and a liquid crystal alignment layer. The liquid crystal alignment layer has an important role to align liquid crystal molecules uniformly [1–8]. Recently, a vertical alignment method has been used to induce to improved alignment of the liquid crystals (LCs) with negative dielectric anisotropy for a faster response time and a higher contrast ratio compared to a twisted nematic liquid crystal displays [9,10]. In this display, a homeotropic polyimide layer has been used as the liquid crystal alignment layer, which aligns liquid crystals vertically at the field-off state and the pretilt angle has to be controlled above 89° after a rubbing process. It is well known that the generation of the pretilt angles is highly dependent upon the interactions of the polyimides with liquid crystals [11–15]. Paek and his coworkers reported that the pretilt angle of the liquid crystals on the rubbed film surface was determined by several factors of the anchoring energy, steric effect, and electronic interaction, and etc. [16,17]. They showed the polyimides with *n*-octadecaoxy side chain gave relatively large pretilt angles of 13.3° after a rubbing treatment. Wang and Kim et al. [18–20] reported about an effect of long alkyl side group on the pretilt angle, which showed that nonpolar long alkyl side chains increased the pretilt angle to 86°. But the reports showed that the pretilt angles of the liquid crystal cells fabricated with the polyimides containing the alkoxy or the alkanoate substituents were not enough for the liquid crystal alignment layer for the multi-domained vertically aligned mode, which required the pretilt angle above 89° after the rubbing process. Recently, Ree et al. reported on a polyimide with *n*-octyl side chain, which gave large pretilt angle despite relatively short alkyl side end group [21]. They had introduced a rigid rod like aromatic structure into the polyimide backbone to impart large pretilt angle. But the fully aromatic structure of the polyimide could deteriorate some properties required for the liquid crystal alignment layers such as transmittance at visible light region and electro-optic properties. Therefore, we have synthesized the polyimides from alicyclic dianhydride and newly designed three kinds of functional diamines with different side chain flexibility. Energy minimized structures of the functional diamines were calculated by a HyperChem® v 7.5, which was shown in Scheme 1. As shown in Scheme 1, the side chain lengths of the diamines were controlled from 17.2 to 20.2 Å

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* Corresponding author. Tel.: +82 42 860 7291; fax: +82 42 861 4151.
E-mail address: mhyi@krict.re.kr (M.H. Yi)

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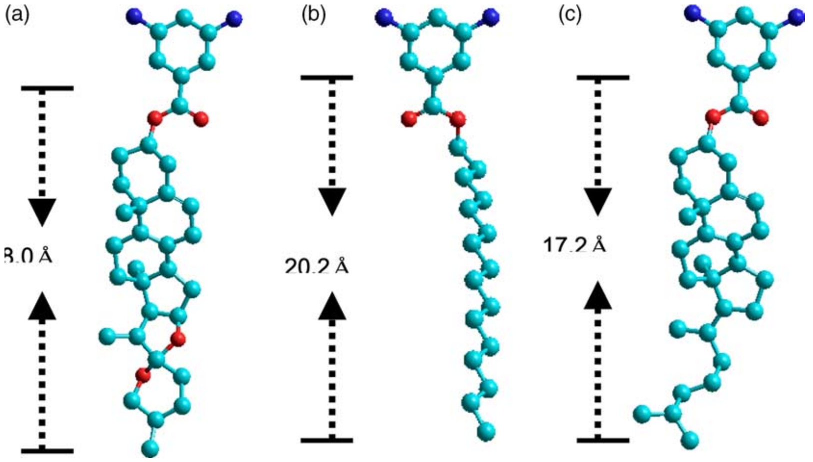


Scheme 1. Energy minimized structures of the functional diamines (calculated by a HyperChem$^{\circledR}$ v 7.5) (a) **4a** (b) **4b** (b) **4c**.

and the flexibility of the side chain were varied by an introduction of chemical structure with different flexibility. In this study, we have synthesized three functional diamines, 3,5-diaminobenzoic acid (3β,5β,25*S*)-spiro-stan-5-en-3-yl ester (**4a**), 3,5-diamino benzoic acid hexadecane-1-yl ester (**4b**) and 3,5-diaminobenzoic acid 10,13-dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl ester (**4c**), which has different side chain structures with similar chain length. That is, a series of the poly(amic acid)s had been synthesized from cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA) and 4,4′-diaminodiphenyl methane (DDM) and the functional diamines with different side chain structures. And an effect of the side chain structure of the functional diamines on the pretilt angles of the liquid crystal cell before and after rubbing process have been investigated.

2. Experimental section

2.1. Materials

4,4-Diaminodiphenylmethane (DDM, >98%, Tokyo Chemical Industry Co., Ltd) was purified by a recrystallization from 2-methyl-propan-1-ol. 3,5-Dinitrobenzoyl chloride and hexadecan-1-ol were purchased from Aldrich. (3β,5β,25*S*)-Spiro-stan-5-en-3-ol (mp 205 °C, >95%) and 10,13-dimethyl-17-(6-methyl heptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (mp 149 °C, >95%) were purchased from Tokyo Chemical Industry Co., Ltd. 1-Methyl-pyrrolidin-2-one (NMP, 99%, bp 202 °C, Kanto Chemical Co., Inc.) was used without a further purification. Positive type liquid crystal (4′-pentyloxy-biphenyl-4-carbonitrile, K15, $\Delta\varepsilon = 0.2120$, $n_e = 1.7420$, $n_o = 1.5300$) was purchased from Merck Ltd.

2.2. Measurement

All NMR spectra were taken on a Bruker AMX 500 with *N*,*N*-dimethylformamide-d_7 (DMF-d_7), *N*,*N*-dimethyl sulfoxide-d_6 (DMSO-d_6) or $CDCl_3$ as solvents. FT-IR spectra were measured on KBr pellet by Bio-Rad Digilab Division FTS-165 spectrometer. Elemental analysis were measured with a FISONS Instruments EA-1108. Inherent viscosities of the poly(amic acid)s were measured with a capillary viscometer at a concentration of 0.5 g/dL in NMP at 30 °C. Surface tension was calculated from a contact angle of water and diiodomethane on the polyimide film cured at 230 °C for 30 min, which was measured by PEONIX 300 contact angle analyzer. Spin-coating process was performed with a PMW32 spinner (Headway Research Co., Ltd). A rubbing machine was purchased from Sin-do Eng. Lab. Ltd and equipped with a nylon velvet cloth. A pretilt angle was measured with Sesim PAMS-100T. The energy minimized structures of the three diamines were calculated using HyperChem$^{\circledR}$ v 7.5 (Hypercube, Inc., 2002). The film thickness was determined with KLA-Tencor Alpha-Step 500 instrument. Contact angles of a deionized water and methylene iodide on the surface of the polyimide films were measured by a Rame-hart telescopic goniometer and Gilmont syringe with a 25-gauge flat-tipped needle. A Young's harmonic-mean equation was applied to predict the surface tensions from the contact angles. The pretilt angle (θ_p) was measured by a crystal rotation method apparatus.

2.3. Monomer synthesis

2.3.1. 3,5-Diaminobenzoic acid (3β,5β,25S) -spiro-stan-5-en-3-yl ester (4a)

Compound **4a** was synthesized by a hydrogenation reaction of 3,5-dinitrobenzoic acid (3β,5β,25*S*)-spiro-stan-5-en-3-yl ester (**3a**), which was synthesized in a 500 mL four-neck round bottomed flask equipped with a mechanical stirrer and a condenser. (3β,5β,25*S*)-Spiro-stan-5-en-3-ol (20.73 g, 0.05 mol) was added into 11.53 g (0.05 mol) of 3,5-dinitrobenzoyl chloride in pyridine. The solution was stirred at 110 °C for 24 h. After cooling, the mixture was precipitated in excess water and filtered. The crude product was recrystallized from methanol to give 20.5 g of DN-SS. The purified **3a** (17.0 g, 0.028 mol) were dissolved in ethanol and 1.5 g of palladium on carbon (Pd/C, 1.5 g) was added as a catalyst. Hydrogenation reaction was conducted for 24 h at 50 °C under hydrogen atmosphere of 30–40 psi. Then, the solution was filtered for removing Pd/C, which was evaporated to remove the solvent. The crude product was recrystallized from methanol to afford 7.06 g of **4a**: yield, 46%; ^{1}H NMR ($CDCl_3$) δ 6.78 (s, 2H, ArH), 6.19–6.17 (t, 1H, ArH), 5.40 (d, 1H, CH=C), 4.80–4.70 (m, 1H, CH), 3.66 (bs, 4H, NH_2), 3.38–3.36 (m, 3H, CH, CH_2), 2.84–2.35 (d, 3H, CH), 2.00–1.00 (m, 21H, CH, CH_2), 1.08, 0.99–0.97 (s, 6H, CH_3), 0.80–0.78 (d, 6H, CH_3) ppm, FT-IR (KBr pellet) 3429, 3350 (primary amine, $\nu_{N–H}$), 2951–2872 (ν_{CH}), 1709 ($\nu_{C=O}$), 1603 (aromatic, $\nu_{C=C}$) cm^{-1}. Elemental Anal. Calcd for $C_{34}H_{48}N_2O_4$: C, 73.49; H, 8.36; N, 5.53; O, 12.63; found C, 74.06; H, 8.92; N, 5.06; O, 11.96; mp 107.4, 186.3, 265.5 °C.

2.3.2. 3,5-Diaminobenzoic acid hexadecane-1-yl ester (4b)

Compound **4b** was prepared by a similar method to that of **4a** with hexadecan-1-ol (12.1 g, 0.05 mol) instead of (3β,5β,25*S*)-spiro-stan-5-en-3-ol. A white crystal product was obtained by a recrystallization from methanol: yield, 75.6%; ^{1}H NMR ($CDCl_3$) δ 6.78 (d, 2H, ArH), 6.18–6.16 (t, 1H, ArH), 4.27–4.23 (q, 2H, CH_2), 3.68 (bs, 4H, NH_2), 1.75–1.70 (m, 2H, CH_2), 1.41–1.26 (m, 26H, CH_2), 0.90–0.86 (t, 3H, CH_3) ppm, FT-IR (KBr pellet) 3414, 3325 (primary amine, $\nu_{N–H}$), 2956–2851 (ν_{CH}), 1711 ($\nu_{C=O}$), 1604 (aromatic, $\nu_{C=C}$) cm^{-1}. Elemental Anal. Calcd for $C_{23}H_{40}N_2O_2$: C, 73.36; H, 10.71; N, 7.44; O, 8.50; found C, 74.58; H, 11.12; N, 7.36; O, 6.94; mp 71.3 °C.

2.3.3. 3,5-Diaminobenzoic acid 10,13-dimethyl-17-(6-methyl-heptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1H-cyclopenta[a]phenanthren-3-yl ester (4c)

Compound **4c** was prepared by the similar method to that of **4a** with 10,13-dimethyl-17-(6-methyl heptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetra-decahydro-1*H*-cyclopenta[*a*]phenanthren-3-ol (19.3 g, 0.05 mol) instead of (3β,5β,25*S*)-spiro-stan-5-en-3-ol. The crude compound was recrystallized from methanol: yield, 54%; ^{1}H NMR ($CDCl_3$) δ 6.78 (d, 2H, ArH), 6.19–6.17 (d, 1H, ArH), 5.4 (d, 1H, CH=C), 4.81–4.77 (m, 1H, CH), 3.67 (bs, 4H, NH_2), 2.44–2.41 (d, 2H, CH), 2.00–0.91 (m, 26H, CH, CH_2), 0.69, 0.85, 0.86, 1.03 (s, 12H, CH_3), 0.87. 0.88 (d, 3H, CH_3) ppm, FT-IR (KBr pellet) 3432, 3367 (primary amine, $\nu_{N–H}$), 2939–2867 (ν_{CH}), 1705 ($\nu_{C=O}$), 1619 (aromatic, $\nu_{C=C}$) cm^{-1}. Elemental Anal. Calcd for $C_{34}H_{52}N_2O_2$: C, 78.41; H, 10.06; N, 5.38; O, 6.14; found C, 77.67; H, 10.24; N, 5.36; O, 6.73; mp 60.6, 181.7 °C.

2.3.4. Synthesis of cyclobutane-1,2,3,4-tetracarboxylic dianhydride (CBDA)

A solution of maleic anhydride (100 g, 1.02 mol, λ_{max}=280 nm) in 150 mL of chloroform was photoirradiated at 300 nm for two weeks at room temperature. The crude CBDA was precipitated from the solution and collected by a filtration, which was purified by a recrystallization from acetic anhydride to give a white solid product. Yield, 40.0%; MS (*m/e*): 196 (M^+). ^{1}H NMR (DMF-d_7) δ 4.01 (s, cyclobutane ring, C*H*, endo form), 4.13 (s, cyclobutane ring, C*H*, exo form) ppm. ^{13}C NMR (DMF-d_7) δ 39.8 (cyclobutane ring, *C*H), 172.1 (*C*=O) ppm. Elemental Anal. Calcd for $C_8H_4O_6$: C, 48.99; H, 2.06; found: C, 48.30; H, 2.07%; mp 112 °C.

2.4. Polymer synthesis

Three kind of the poly(amic acid)s (**5a**–**5c**) were prepared from CBDA, DDM and the functional diamines (**4a**–**4c**). A typical polymerization procedure is as follows. To a 100 ml of a reactor equipped with a mechanical stirrer and a nitrogen-inlet, 3.57 g of DDM (0.018 mol) and 1.10 g (0.002 mol) of DA-SS as the functional diamine were dissolved in 100 ml of NMP and then 3.92 g of CBDA (0.02 mol) was added slowly to the solution. The reaction mixture was stirred at 0 °C for 24 h with a nitrogen flow. Molar ratios of CBDA:DDM: the functional diamine and solid content were fixed to 10:9:1 and 20 wt%, respectively. The synthesized poly(amic acid)s were named **5a**–**5c**. For a comparison, a poly(amic acid) without the side chain was prepared from CBDA and DDM, which was named **5d**.

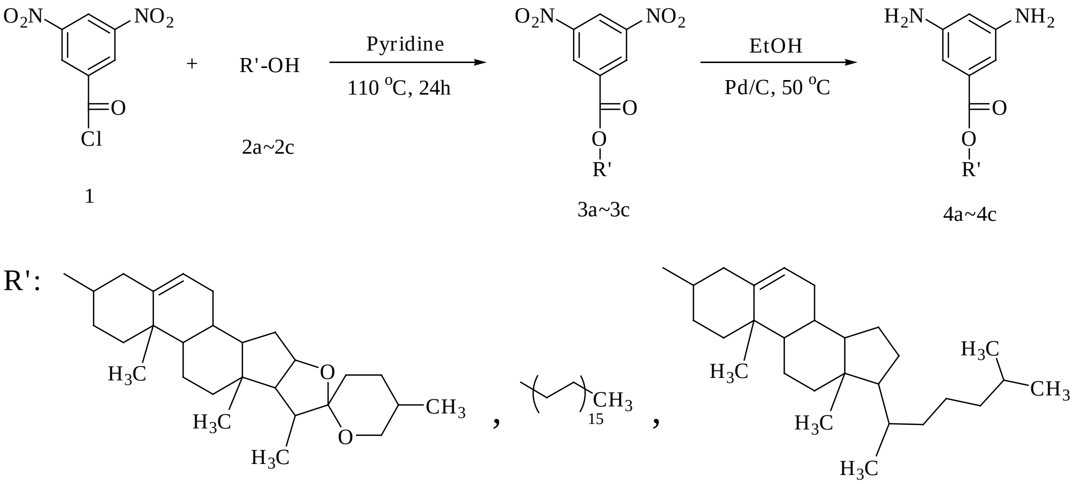
2.5. Preparation of polyimide films (6a–6d)

Five grams of the polyamic acid solution with a solid content of 20 wt% was diluted to a concentration of 5 wt% using solvent mixtures of NMP (3.6 g), γ-butyrolactone (7.6 g) and 2-butoxyethanol (3.8 g) and spin-coated onto a indium tin oxide (ITO) coated glass substrate at 2500 rpm for 60 s. The coated films were pre-baked at 90 °C for 10 min and cured at 230 °C for 30 min, which gave the polyimide films (**6a**–**6d**). A thickness of the polyimide film was in the range of 600–800 Å. The polyimide film on glass substrates were rubbed using a laboratory rubbing machine with a roller covered by a nylon velvet cloth. A rubbing depth was controlled to 0.25 mm and a rotation speed of a roller was fixed to 1000 rpm. A radius of the roller and a speed of substrate stage were 10 cm and 100 mm/s, respectively. Liquid crystal cells for the pretilt angle measurement was assembled using two pieces of the rubbed substrates in a anti-parallel rubbing direction using a 80 μm thick adhesive film spacer. A positive type liquid crystal (K15) was injected between a cell gap by a capillary method at room temperature followed by a sealing the injection hole with a photo-curable epoxy resin (ThreeBond 3052, ThreeBond Co., Ltd).

3. Results and discussion

3.1. Monomer synthesis

CBDA was synthesized from maleic anhydride by a photoirradiation reaction at a wavelength of 300 nm for 2 weeks at room temperature [22]. Structure of CBDA was confirmed by ^{1}H NMR spectroscopy as well as elemental analysis. The functional diamines were easily prepared from 3,5-dinitroaniline as shown in Scheme 2. Structural identification of the functional diamines was confirmed by ^{1}H



Scheme 2. Synthesis of the functional diamines.

NMR and FT-IR spectroscopy as well as elemental analysis. Triplet at 6.17–6.19 (1H) and 6.78 (2H) ppm are the characteristic peaks of the phenyl ring protons of the functional diamines. The peaks at 3.66–3.68 (4H) ppm and multiplets at 1.0–2.0 ppm is due to the protons of diamino group and the methylene/methyne protons, respectively. Singlets at 0.78–1.08 ppm are the characteristic peaks of the methyl protons of at the diamines.

3.2. Polymer synthesis

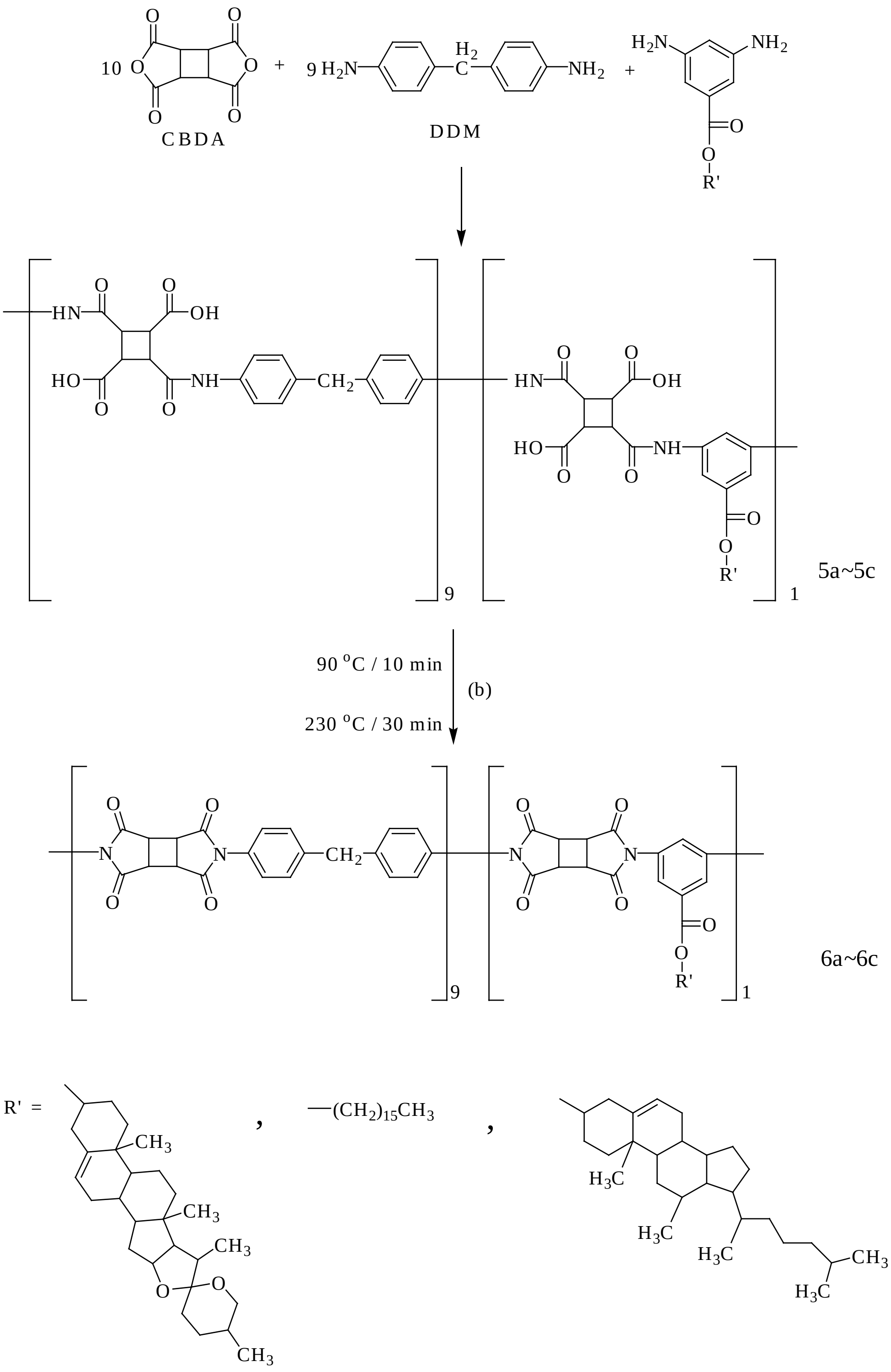
A series of the poly(amic acid)s was synthesized from CBDA and MDA and the functional diamines as shown in Scheme 3. Composition of the functional diamine to total amount of the diamines was fixed to 10 mol% to obtain the poly(amic acid)s with high molecular weights to give good film forming properties. As shown in Table 1, inherent viscosities of the poly(amic acid)s measured using an Ubbelhode-type viscometer in NMP were in the range of 0.50–0.84 dL/g. By an introduction of the functional diamines with bulky side chain, the inherent viscosities were decreased compared to that of **5d** prepared from DDM only. But, they are enough for a formation of thin films with good quality. Structural identification of the poly(amic acid)s was confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR spectrum of **5b** is shown in Fig. 1. The two broad peaks at 10.3–10.5 and 9.9–10.1 ppm are the characteristic peaks of the amide protons of the poly(amic acid) prepared from two different diamines and the doublet of doublet at 7.49–7.11 ppm are the characteristic peaks of the phenyl ring protons of the poly(amic acid). Polyimide films were prepared by a spin-coating followed by a curing reaction at 230 °C for 30 min. Results of the synthesis was summarized in Table 1.

3.3. Characterization of the liquid crystal display cell fabricated with the poly(amic acid)s

Pretilt angle is an important parameter that determines the optical properties of liquid crystal display devices. The pretilt angle has been affected by various factors, such as surface tension, surface morphology, steric effect and electronic interaction of the liquid crystal with the alignment layer, etc. It might be caused by a processing condition like a rubbing process as well as a chemical structure of the polyimide. As well known, the rubbing process has been widely used technique to realize a homogeneous alignment of the liquid crystal molecules onto the polymer surface. Thus, a lot of studies have been carried out in order to understand a physical mechanism responsible for the liquid crystal alignment on the polymer surface. In this study, we have synthesized the poly(amic acid)s which has the different side chain structures and then investigated a relationship between the pretilt angle and surface property of the polyimide film. In this study, we have synthesized the functional diamines containing the side groups with different flexibility. Compound **4b** has the flexible long hexadecan-1-yl side chain, on the other hand, **4a** and **4c** have rigid alicyclic side chain and rigid alicyclic side chain with flexible 6-methylheptan-2-yl group at the end, respectively. An effect of the side chain flexibility on pretilt angles of the liquid crystal display devices fabricated with the polyimides was investigated.

3.3.1. Effect of the side chain structures on the surface tension

It has been well known that the pretilt angle of the liquid crystals on a rubbed film surface was affected by several factors such as anchoring energy, steric effect, and electronic interaction, and surface tension. We had investigated the surface tension of the polyimides to find a relationship between the pretilt angles. As shown in Fig. 2, the surface tension of the polyimide (**6d**) without the side chains prepared from CBDA and DDM showed the biggest value about 46.7 mN/m, which increased to 47.4 mN/m by a rubbing treatment. On the other hand, **6a–6c** with the side chains showed lower surface tensions compared to that of **6d**, which ranged from 38.6 to 43.0 dyn/cm. It might be due to an introduction of non polar side groups into the polyimide backbones. The surface



Scheme 3. Synthesis of the poly(amic acid)s and the polyimides.

tensions of the **5a–5c** films also increased to 41.2–44.4 dyn/cm after the rubbing process.

3.3.2. Effect of side chain structures on the pretilt angles before the rubbing process

Pretilt angles of the liquid crystal cell fabricated using the polyimides was shown in Fig. 3. As shown in the figure, the liquid crystal was not aligned on the surface of the CPI-0 and CPI-1 film without the rubbing treatment. On the other hand, the pretilt angles of the liquid crystal cell fabricated with **6b** and **6c** prepared from **4b** and **4c** with flexible alkyl side chain were very high, which ranged from 89 to 90° before the rubbing process. That is, the pretilt angles were remarkably increased by an introduction of the functional diamines with flexible side

Table 1
Synthesis of the poly(amic acid)s from various functional diamines

Type of the poly(amic acid)	Functional diamine	Mole ratio of monomers[a]	η_{inh} (dL/g)[b]
5a	**4a**	10:9:1	0.50
5b	**4b**	10:9:1	0.75
5c	**4c**	10:9:1	0.84
5d	Not used	10:10	1.56

[a] Composition of monomer is CBDA:DDM:functional diamine.

[b] Inherent viscosity measured at 30 °C in NMP with a concentration of 0.5 g/dL.

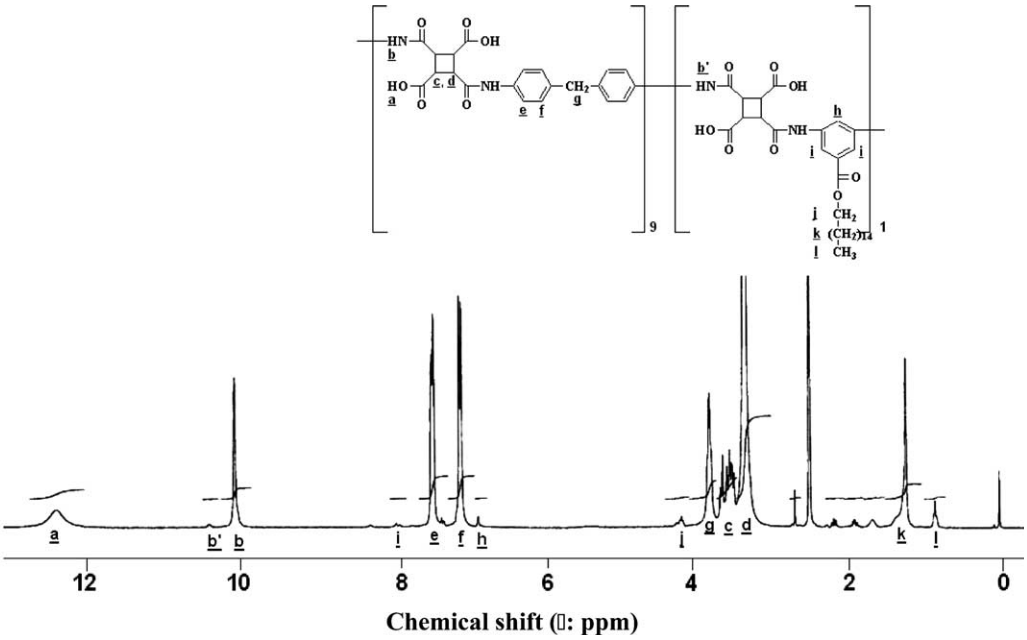


Fig. 1. ^{1}H NMR spectrum of the **5b** (solvent: DMSO-d_6).

chains, which made the liquid crystals align homeotropically. As shown in Figs. 2 and 3, the surface tensions of the polyimide (**6a** and **6b**) were similar, but the pretilt angle of two polyimide films is very different. From this result, it can be seen that the pretilt angles of the liquid crystal cell using the polyimides with side chains were affected by a geometric structure of the polyimide film surfaces not the surface tension. It is a converse result with previous reports, which reported that the pretilt angle was decreased with increase of the surface tensions [18,19].

3.3.3. Effect of the rubbing process on the pretilt angles

As shown in Fig. 3, the liquid crystal was not aligned on the surface of the **6a** and **6d** film without the rubbing treatment. After the rubbing process, the pretilt angle of liquid crystal on **6a** and **6d** film were 0.6 and 3.4°, respectively. The **6a** with rigid alicyclic side chain gave low surface tension about 41.4 dyn/cm, but the pretilt angle was 0.6, which was very low value compared to those of **6b** and **6c**. In case of **6b**, the rubbing process induced the increase of the polarity of the polyimide films by an insertion of the non polar flexible hexadecan-1-yl group into the polymer bulk phase during the rubbing process, which resulted in change of a geometric structure of the polyimide thin films and the increase of a flatness of thin film to make the liquid crystal molecules to lie flater. On the other hand, the pretilt angle of the liquid crystal display cells fabricated with the **6c** containing rigid '10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-

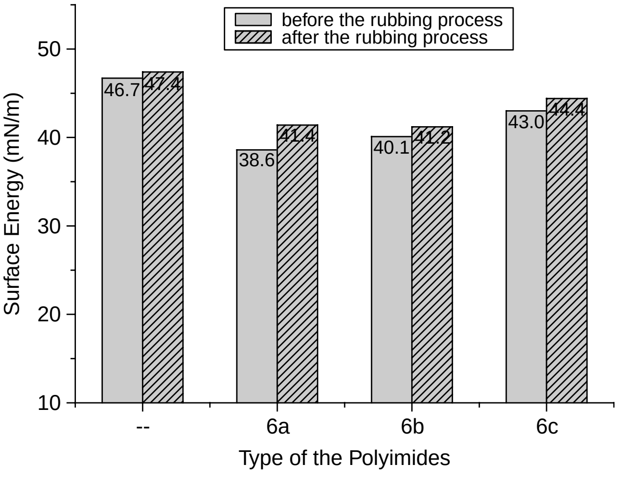


Fig. 2. Surface tensions of the polyimides (a) before and (b) after the rubbing process.

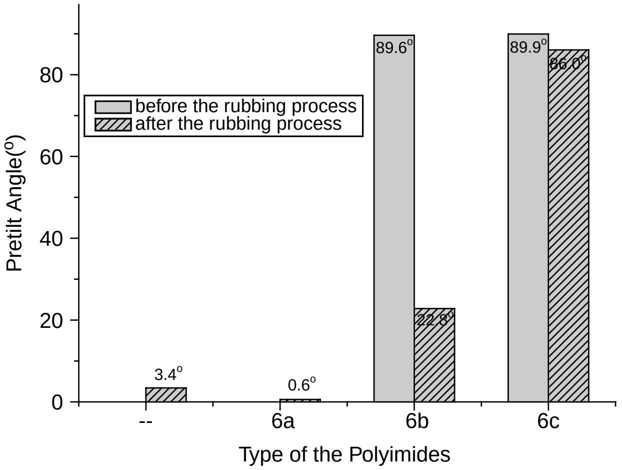
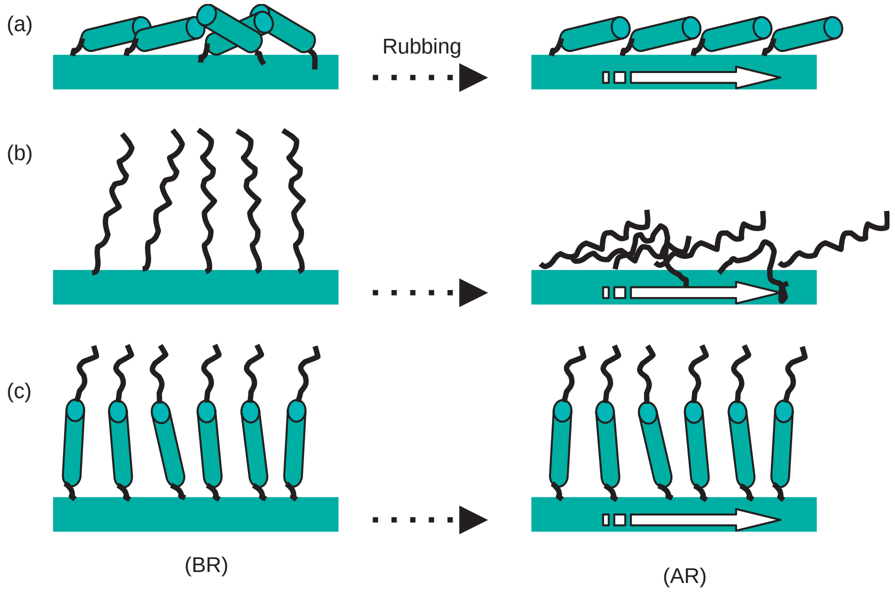


Fig. 3. Pretilt angles of liquid crystal cells fabricated with the polyimides (a) before and (b) after the rubbing process.

cyclopenta[*a*]phenanthren' group with flexible '6-methylheptane-2-yl' group at the end was much higher than that of the liquid crystal display cells fabricated with **6b** with flexible hexadecan-1-yl side chain. That is, the pretilt angles of the liquid crystal display cells fabricated with the polyimide, **6c** containing rigid alicyclic side group were much higher than that of the liquid crystal display cells fabricated using the polyimide, **6b** with flexible hexadecan-1-yl moiety. From the result, it can be seen that the hexadecan-1-yl group of CPI-2 might easily be re-orientied toward the polymer bulk phase compared to that of the CPI-3 connected with more rigid 10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren group. That is, the rigid alicyclic group might restrict a movement of the alkyl chain into the polymer surface, which resulted in an enrichment of non polar alkyl side chain at the outmost layer of the polyimide surface. That is, the polyimide prepared from **4c** with rigid alicyclic connecting group showed higher pretilt angle about 86° even after the rubbing process than that of the **6b** connected with flexible hexadecan-1-yl side group. Therefore, a generation mechanism of the pretilt angles for the polyimides synthesized from the three different diamines can be proposed, which is shown in Scheme 4. As shown in Scheme 4, the hexadecan-1-yl group of the polyimide (b) might be easily re-oriented inward polymer bulk phase compared to that of the polyimide (c) with short alkyl group connected with more rigid cylindrical group. On the other hand, as shown in Scheme 4(a), the polyimide with rigid alicyclic side chain without the flexible alkyl group aligned the liquid crystal homogeneously after the rubbing process.

4. Conclusions

A series of the poly(amic acid)s was synthesized from CBDA, DDM and the functional diamines, which has the side groups with different flexibility. An effect of the side chain flexibility on pretilt angles of the liquid crystal display devices fabricated with the polyimides was investigated. Surface tension of the polyimide (**6d**) without the side chains showed the biggest value about 46.7 dyn/cm. On the other hand, **6a**–**6c** with the side chains showed lower surface tensions compared to that of CPI-0, which ranged from 38.6 to 43.0 dyn/cm. The pretilt angle of liquid crystal on **6a** and **6d** film were 0.6 and 3.4°, respectively, after the rubbing treatment. The polyimide, **6a** with rigid alicyclic side chain without the flexible alkyl group aligned the liquid crystal homogeneously. On the other hand, the pretilt angles of the liquid crystal cell fabricated with **6b** and **6c** prepared from **4b** and or **4c** with flexible alkyl side chain were very high, which ranged from 89 to 90° before the rubbing process. The pretilt angles were remarkably increased by an



Scheme 4. Proposed mechanism of the microscopic molecular reorientation of the polyimide surface induced by the rubbing process (a) the polyimide with rigid side chain (**6a**), (b) the polyimide with flexible side chain (**6b**), (c) the polyimide containing rigid alicyclic side group with flexible 6-methylheptan-2-yl group (**6c**) (BR, before the rubbing process; AR, after the rubbing process).

introduction of the functional diamines with flexible side chains, which made the liquid crystals to align homeotropically. Furthermore, the polyimide prepared from **4c** with rigid cyclindrical connecting group showed the highest pretilt angle above 86° even after the rubbing process. From the result, it can be seen that the pretilt angles of the liquid crystal cell using the polyimides with side chains were affected by a geometric structure of the polyimide film surfaces not the surface tension.

This work has showed the novel liquid crystal alignment layer with large pretilt angle even after a rubbing process, which can be used for advanced liquid crystal device like vertically aligned liquid crystal display.

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