

This article was downloaded by: [National Chiao Tung University 國立交通大學]

On: 27 April 2014, At: 21:28

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/tlct20>

Synthesis of alkyl-branched main chain copolyimides and their effect on the pretilt angles of liquid crystal alignment

Wen-Chin Lee , Jiun-Tai Chen , Chain-Shu Hsu & Shin-Tson Wu
Published online: 11 Nov 2010.

To cite this article: Wen-Chin Lee , Jiun-Tai Chen , Chain-Shu Hsu & Shin-Tson Wu (2002) Synthesis of alkyl-branched main chain copolyimides and their effect on the pretilt angles of liquid crystal alignment, *Liquid Crystals*, 29:7, 907-913, DOI: [10.1080/02678290110116880](https://doi.org/10.1080/02678290110116880)

To link to this article: <http://dx.doi.org/10.1080/02678290110116880>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Synthesis of alkyl-branched main chain copolyimides and their effect on the pretilt angles of liquid crystal alignment

WEN-CHIN LEE, JIUN-TAI CHEN, CHAIN-SHU HSU*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu,
Taiwan 30050, ROC

and SHIN-TSON WU

School of Optics/CREOL, University of Central Florida, Orlando, FL 32816, USA

(Received 16 May 2001; in final form 20 October 2001; accepted 23 October 2001)

Three series of copolyimides containing long alkyl branches were synthesized using the two-step method via poly(amic acid) precursors and chemical imidization. Most of the copolyimides prepared are soluble in polar organic solvents. Good liquid crystal alignment was achieved by buffing the copolyimide films spin-coated onto indium tin oxide glass substrates. The measured liquid crystal pretilt angles range from 0.16° to 15.54° . The Titan simulation program was used to calculate the dipole of each dianhydride structure and correlate with the observed pretilt angles. Main chain copolyimides with a long alkyl side chain, small dipole, and linear, symmetric and rigid core structures are favourable for generating large pretilt angles.

1. Introduction

Uniform molecular alignment plays a crucial role in the electro-optic performance and panel fabrication of a liquid crystal display (LCD) device [1]. Rubbed polyimide (PI) films are commonly used as the alignment layers for large LCD panels because of their outstanding thermal stability, low dielectric constant, excellent chemical resistance and high productivity. In addition, the rubbing process provides a stable pretilt angle on the PI film, preventing reverse tilt disclination of LC molecules with applied voltage. In order to satisfy specific pretilt angle requirements for various LCD modes, several approaches have been developed for controlling the pretilt angle on rubbed PI films [2–11].

Polyimides with long alkyl [3–8] and fluorinated alkyl [9–11] side groups were found to exhibit high LC pretilt angles; these may originate from the low surface energy on the alkyl-branched PI films [4, 9]. Steric interaction between LC molecules and branched long alkyl side chains is another possible cause for high pretilt angles. However, detailed mechanisms governing how the long alkyl side chains affect the LC pretilt angle have not been fully understood. Recently, new studies on pretilt angles for PIs having various side group lengths have been reported [6–8], but, little is known about the effect of main chain structure on the LC pretilt angle.

In this paper, we report systematic studies on LC pretilt angles using different main chain structures while keeping the same alkyl side branch. We have prepared several soluble copolyimides (coPIs) based on 4-(octadecyloxy)-1,3-benzenediamine (18OBD) which has a long linear alkyl group with 18 carbon atoms. Three dianhydrides (BCDA, 6FDA, BPDA) and four diamines (ODA, MDA, PPD, DDS) were used to modify the main chain structures of the coPIs. The coPI films were obtained from their solutions by evaporating the solvents at low temperature. Their application as LCD alignment layers was evaluated, and the correlation between coPI backbone structures and LC pretilt angles is discussed.

2. Experimental

2.1. Materials

In our experiments, 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) was purchased from Aldrich. 4,4'-Biphenyl dianhydride (BPDA), bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA), bis(4-aminophenyl)sulfone (DDS) and 1-chloro-2,4-dinitrobenzene were obtained from TCI. 4,4'-Methylene dianiline (MDA) and *p*-phenylene diamine (PPD) were purchased from Janssen. 4,4'-Diaminodiphenyl ether (ODA) was obtained from Chriskev; 1-octadecanol was obtained from Showa. The nematic LC, 4'-pentyl-4-cyanobiphenyl (5CB) was supplied by Merck.

* Author for correspondence

ODA, MDA, PPD and DDS were recrystallized from ethanol and BCDA from acetonitrile. *N*-methyl-2-pyrrolidone (NMP) was dried via the benzene azeotrope. Anhydrous tetrahydrofuran and pyridine were dried by heating at reflux with sodium under nitrogen, followed by vacuum distillation, and stored with molecular sieves. All other reagents and solvents were used as received.

2.2. Synthesis

As shown in figure 1, the linear alkyl group-containing diamine, 4-(octadecyloxy)-1,3-benzenediamine (18OBD), was synthesized by reduction of 1-(octadecyloxy)-2,4-dinitrobenzene, which had been obtained by etherification of 1-chloro-2,4-dinitrobenzene with 1-octadecanol. The 12 copolyimides were synthesized using the two-step method via poly(amic acid) precursors and chemical imidization. Figure 2 shows the structure of the three dianhydrides and four diamines employed. The poly(amic acid) precursor was prepared by mixing one dianhydride and one diamine with 18OBD in the molar ratio 5:4:1, respectively.

2.2.1. 1-(Octadecyloxy)-2,4-dinitrobenzene

1-Octadecanol (16.9 g, 0.0625 mol), potassium iodide (0.1 g, 0.0006 mol), potassium hydroxide (3.5 g, 0.0625 mol) and 200 ml of tetrahydrofuran were mixed and heated at reflux for 3 h with stirring. 1-Chloro-2,4-dinitrobenzene (5.0 g, 0.0247 mol) was added to the mixture

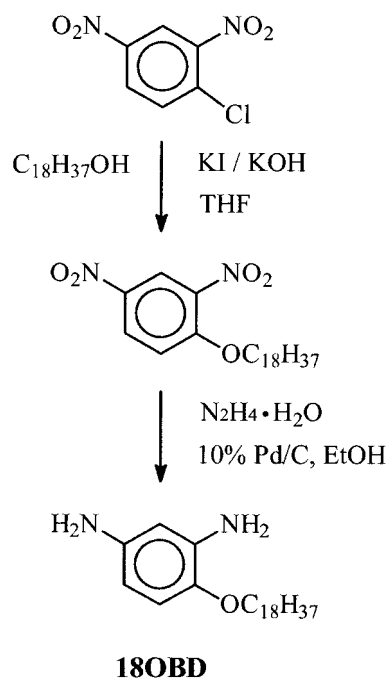


Figure 1. Synthesis scheme for the long alkyl-containing diamine 18OBD.

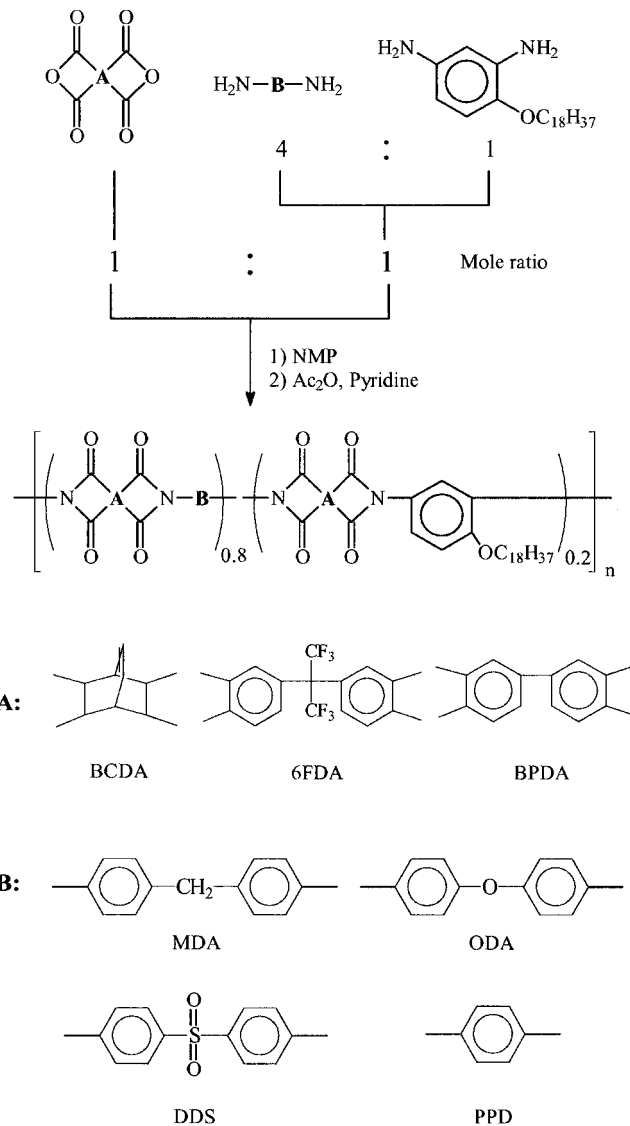


Figure 2. Synthesis scheme for three series of copolyimides based on 18OBD.

which was heated under reflux for a further 21 h. After cooling to room temperature, the solvent was evaporated, and the solid obtained was dissolved in ethyl acetate and washed with distilled water until pH = 7. The organic layer was dried with anhydrous MgSO_4 , the solvent removed in a rotary evaporator, and the crude product recrystallized twice from *n*-hexane to yield 9.23 g (86%) of slightly yellowish crystals; m.p. 64.5°C. ^1H NMR (CDCl_3 , TMS, ppm), δ : 0.88 (t, 3H, $-\text{CH}_3$); 1.26 (m, 28H, $-\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$); 1.49 (m, 2H, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$); 1.90 (m, 2H, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$); 4.23 (t, 2H, $-\text{O}-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$); 7.18 (dd, 1H, ArH of position 6 of 2,4-dinitrobenzene); 8.40 (dd, 1H, ArH of position 5 of 2,4-dinitrobenzene); 8.74 (d, 1H, ArH of position 3 of 2,4-dinitrobenzene).

2.2.2. 4-(Octadecyloxy)-1,3-benzenediamine (18OBD)

1-(Octadecyloxy)-2,4-dinitrobenzene (4 g, 0.0092 mol) was added to 300 ml ethyl alcohol solution containing 0.4 g (10 wt %) of Pd/C (10% Pd on charcoal); the solution was stirred and heated to reflux. After adding 4 ml of hydrazine monohydrate slowly, the mixture was heated at reflux for 24 h. The hot solution was then filtered over celite to remove the catalyst and the solvent removed in a rotary evaporator. The white crystalline product was filtered off and purified by recrystallization twice from ethyl alcohol to yield 2.9 g (84%) of crystals; m.p. 76.5°C. $^1\text{H NMR}$ (CDCl_3 , TMS, ppm), δ : 0.88 (t, 3H, $-\text{CH}_3$); 1.26 (m, 28H, $-\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$); 1.46 (m, 2H, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$); 1.75 (m, 2H, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$); 3.5 (s, broad, 4H, $-\text{NH}_2$); 3.89 (t, 2H, $-\text{O}-\text{CH}_2(\text{CH}_2)_{16}\text{CH}_3$); 6.04 (dd, 1H, ArH of position 6 of 1,3-benzenediamine); 6.15 (d, 1H, ArH of position 2 of 1,3-benzenediamine); 6.6 (dd, 1H, ArH of position 5 of 1,3-benzenediamine). IR (KBr, cm^{-1}): 3416, 3450 (NH_2), 2850, 2920 (CH), 1223 ($-\text{O}-$).

2.2.3. Synthesis of copolyimides

All the copolyimides were synthesized using the conventional two-step method as illustrated in figure 2. In a typical example, ODA (0.3227 g, 0.0016 mol) and 18OBD (0.1515 g, 0.0004 mol) were placed in a 50 ml 2-neck round bottom flask fitted with a magnetic stirrer. The system was purged with nitrogen, and 4 ml of NMP added. After stirring for 10 min, BCDA (0.505 g, 0.002 mol) was added carefully. The neck was rinsed with NMP and the monomer concentration kept at 15 wt %. The mixture was stirred at room temperature under nitrogen until it attained high viscosity. To this solution acetic anhydride (0.76 ml, 0.008 mol) and pyridine (0.65 ml, 0.008 mol) were added and the mixture was stirred at 65°C for 24 h. The hot solution was then poured into vigorously stirred methanol; after filtering and washing with 50 ml methanol, the copolyimide obtained was further purified twice by reprecipitation with methanol from THF solution. The collected product was dried at 100°C under reduced pressure for 24 h to yield 0.65 g (67%) of white solid.

2.3. Characterization and processing

$^1\text{H NMR}$ spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. FTIR spectra were measured on a Nicolet 360 FTIR spectrometer. Gel permeation chromatography was run using an Applied Biosystem 400LC instrument equipped with a 410 differential refractometer, and samples were prepared as 1 mg ml^{-1} in THF solution. The inherent viscosities of soluble coPIs were measured using Ubbelohde viscometers at a concentration of 0.5 g dl^{-1} at 25°C. Thermal transitions

were determined with a Seiko SSC/5200 differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were $10^\circ\text{C min}^{-1}$. The glass transition temperatures (T_g) reported here were observed during the second heating scans at the inflection points. Thermal stability was tested using a Seiko TG/DTA 200 thermal gravimetric analyser under nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$.

2.3.1. Preparation of coPI alignment layers

The synthesized soluble coPIs were used as LC alignment materials. They were dissolved in selective solvents to form 5 wt % solutions. The coPI solutions were spin-coated onto indium tin oxide (ITO) glass substrates at 3000 rpm, and the casts were baked at 100°C for 1 h. The thickness of the coPI layers was measured by a α -stepper to be in the 50–100 nm range. The coPI-coated substrate was buffed 4 times (single direction) by a rubbing machine (Sigma Koki RM-50) with a 48 nm diameter roller covered with a cotton velvet cloth. The fibre length was 2 mm. To summarize the rubbing conditions: roller speed = 200 rpm, speed of substrate state = 7 mm s^{-1} , and pile impression = 0.3 mm.

2.3.2. Fabrication of homogeneous LC cells

An empty cell was constructed by assembling two glass substrates, each covered with a buffed thin coPI layer. The two rubbing directions were anti-parallel. The cell gap was controlled at $\sim 30\text{ }\mu\text{m}$ by dispersed spacer balls. The cell was then filled with the nematic liquid crystal, 5CB, at room temperature and sealed with epoxy resin adhesive. Finally, the 5CB cell was annealed at 50°C (isotropic state) for 10 min to remove flow marks. An optical polarizing microscope (Zeiss Axiophot) was used to observe the evolving LC alignment *in situ*. The pretilt angle of the 5CB cell was measured with an Autronic DMS 101 TBA instrument.

3. Results and discussion

3.1. Synthesis of copolyimides with a long alkyl side group

Three series of coPIs based on the dianhydrides BCDA, 6FDA and BPDA were synthesized using the two-step method illustrated in figure 2. The copolyimides were obtained from poly(amic acid) precursors by chemical imidization. The poly(amic acid)s were prepared by reacting each dianhydride with an equimolar amount of diamine mixture containing 18OBD and another diamine in a particular mole ratio. For comparison purposes, we chose the mole ratio (18OBD: other diamine = 1:4) to be the same as that reported in ref. [4]. Because most of the coPIs are soluble in

polar organic solvents, the mole ratio in the coPIs could be checked by NMR measurements. Figure 3 shows the ^1H NMR spectrum of 6FDA-ODA-18OBD; the peaks of aromatic protons (δ : 7.55, 7.15 ppm and the other aromatic proton) of 18OBD are relatively low and covered by other peaks. The peak of the methylene proton (δ : 4.05 ppm) in 18OBD adjacent to the oxygen atom was chosen to integrate and was compared with the signal (δ : 7.4 ppm) of the aromatic proton of the other diamine, ODA. The compared integration ratio is 1:3.6, which is close to the intended 1:4 mole ratio. The ^1H NMR spectra of the coPIs can also give information on the imidization ratio of the copolyimides. In figure 3, the signal of the NH proton (δ : 9.3–9.6 ppm) has vanished, indicating that the imidization ratio is close to 100%.

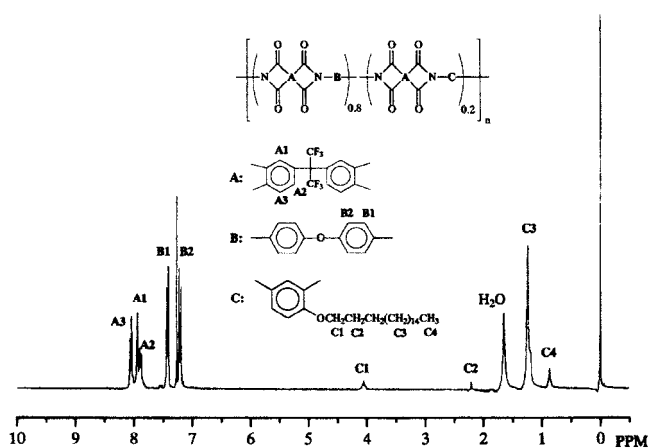


Figure 3. ^1H NMR spectrum (CDCl_3 , TMS) for 6FDA-ODA-18OBD.

3.2. Solubility, molecular weight and thermal characterization of the soluble coPIs

The solubility of the synthesized copolyimides was determined in 10 common solvents; the results are listed in table 1. The three series of coPIs containing the same amount of 18OBD show a drastic solubility difference in various organic solvents. The 6FDA series of coPIs exhibits a better solubility than the other two. In the BPDA series, only BPDA-DDS-18OBD dissolves in polar solvents, such as NMP, DMAc and DMF. According to ref. [12], the incorporation of a large pendant group would enhance the solubility of polyimides. Table 1 shows that incorporation of the long alkyl side chains does increase the solubility of coPIs, but the solubility is still greatly influenced by the structure of the dianhydride employed. Because BPDA has a symmetric structure and has the potential to yield the crystalline polyimide [12], the solubility of the BPDA series is poor in spite of the large alkyl group. In the BCDA series, the four coPIs exhibit the same solubility in test solvents except for a higher solubility of BCDA-DDS-18OBD in MeOH. This could result from the bridging-group, sulfonyl in DDS, as it is known that a large or bulky bridging group enhances solubility [12]. The same phenomenon is observed in the 6FDA-DDS-18OBD and BPDA-DDS-18OBD series. However, the 6FDA series have different solubilities in 2-PTO, DMF, DMSO and CHCl_3 . The effect of diamine structures on solubility are especially manifest in the 6FDA series.

The molecular weight of these soluble coPIs was measured using inherent viscosity (η_{inh}) detection and gel permeation chromatography (GPC). Table 2 summarizes the inherent viscosity data for nine soluble coPIs

Table 1. Solubility^a behaviour of copolyimides based on 18OBD.

Copolyimide	Solvent ^b									
	NMP	DMA _c	γ -BL	2-PTO	THF	DMF	DMSO	CHCl_3	Acetone	MeOH
BCDA-MDA-18OBD	+	+	+	–	Δ	+	+	–	–	–
BCDA-ODA-18OBD	+	+	+	–	Δ	+	+	–	–	–
BCDA-PPD-18OBD	+	+	+	–	Δ	+	+	–	–	–
BCDA-DDS-18OBD	+	+	+	–	Δ	+	+	–	–	Δ
6FDA-MDA-18OBD	+	+	+	+	+	Δ	–	+	+	–
6FDA-ODA-18OBD	+	+	+	Δ	+	+	Δ	+	+	–
6FDA-PPD-18OBD	+	+	+	Δ	+	+	Δ	Δ	+	–
6FDA-DDS-18OBD	+	+	+	+	+	+	+	–	+	–
BPDA-DDS-18OBD	+	+	–	–	–	+	–	–	–	–
BPDA-MDA-18OBD	–	–	–	–	–	–	–	–	–	–
BPDA-ODA-18OBD	–	–	–	–	–	–	–	–	–	–
BPDA-PPD-18OBD	–	–	–	–	–	–	–	–	–	–

^a +, soluble; Δ , partially soluble; –, insoluble at room temperature.

^b NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethyl acetamide; γ -BL, γ -butyrolactone; 2-PTO, 2-pentanone; THF, tetrahydrofuran; DMF, *N,N*-dimethyl formamide; DMSO, dimethyl sulfoxide.

Table 2. Inherent viscosity, molecular weight and thermal analysis results of copolyimides based on 18OBD.

Copolyimides	$\eta_{inh}^a / \text{dl g}^{-1}$	Solubility in THF	GPC M_w	DSC $T_g^b / ^\circ\text{C}$	TGA ^d		
					5% weight loss temperature/ $^\circ\text{C}$	10% weight loss temperature/ $^\circ\text{C}$	Residue wt % at 850 $^\circ\text{C}$
BCDA-MDA-18OBD	0.14	Insoluble	—	216.3	384.1	409.6	0.0
BCDA-ODA-18OBD	0.14	Insoluble	—	223.8	379.6	410.0	0.0
BCDA-PPD-18OBD	0.27	Insoluble	—	— ^c	332.6	372.9	0.0
BCDA-DDS-18OBD	0.24	Insoluble	—	251.8	348.3	375.1	0.0
6FDA-MDA-18OBD	0.47	Soluble	107310	247.4	433.3	480.2	3.4
6FDA-ODA-18OBD	0.38	Soluble	71049	239.2	426.5	466.8	0.0
6FDA-PPD-18OBD	0.21	Soluble	49121	245.3	399.7	443.2	0.0
6FDA-DDS-18OBD	0.10	Soluble	28444	258.2	408.7	462.4	0.0
BPDA-DDS-18OBD	0.20	Insoluble	—	— ^c	401.9	444.4	0.8

^a Measured at a concentration of 0.5 g dl⁻¹ in the coating solvent at 30 $^\circ\text{C}$.

^b Collected during the second heating scans at a heating rate of 10 $^\circ\text{C min}^{-1}$ in nitrogen.

^c No T_g was obtained.

^d Measured at a heating rate of 10 $^\circ\text{C min}^{-1}$.

and GPC data for THF-soluble coPIs. The measured inherent viscosity of coPI solutions is in the range of 0.1–0.47 dl g⁻¹, which is relatively low in comparison with the inherent viscosity of non-branched polyimides. The incorporation of alkyl side chains thus appears to reduce the viscosity of PI solutions; the same phenomenon was reported in previous publications [6, 13, 14]. Since the 6FDA series of coPIs have good solubility in THF, their molecular weights can also be determined by GPC. The molecular weights of 6FDA-MDA-18OBD, 6FDA-ODA-18OBD, 6FDA-PPD-18OBD and 6FDA-DDS-18OBD are 107 310, 71 049, 49 121 and 28 444, respectively. It seems that the molecular weight of a coPI increases as the basicity of the diamine increases. This suggests that the acylation rate constant of a diamine is correlated with its structure (basicity) [15]. In a bridged diamine, the acylation rate constant decreases as the electron-withdrawing ability of the bridge group increases. In the case of ODA and DDS, the electron-withdrawing ability of sulfonyl group in DDS is higher than that of the oxygen atom in ODA. Thus, the molecular weight (acylation rate constant) of 6FDA-ODA-18OBD is higher than that of 6FDA-DDS-18OBD. However, this phenomenon was not found in the BCDA series. It seems that there are factors other than diamine basicity, for example, impurity in BCDA dianhydride (purity >95%, from TCI) which predominantly influence the reactivity between BCDA and diamines.

Thermal analysis results for the soluble coPIs are also summarized in table 2. The T_g of most coPIs is in the 210 to 260 $^\circ\text{C}$ range. In the BCDA and 6FDA series, the coPI based on DDS diamine exhibits a higher T_g because DDS has a highly dipolar bridging group. No T_g was obtained for BCDA-PPD-18OBD or BPDA-

DDS-18OBD during the second heating scans from 35 $^\circ\text{C}$ to 300 $^\circ\text{C}$. Their T_g is probably higher than 300 $^\circ\text{C}$ [16].

The thermal stability of soluble coPIs was evaluated from the 5% weight loss temperature in TGA measurement. The 5% weight loss temperature of these coPIs ranges from 330 to 435 $^\circ\text{C}$ under nitrogen. The incorporation of long alkyl side groups reduces the thermal stability of polyimides in comparison with linear polyimides without side groups. In the BCDA and 6FDA series, the coPIs based on PPD diamine possess a relatively lower thermal stability than other coPIs. It is supposed that the symmetric structure of PPD without a bridging group gives the coPIs based on PPD a more rigid and linear backbone. Thus, there is less space for alkyl side groups to weave through the packed main chains. We suggest that the packed main chains help to stabilize the interweaved alkyl side groups and retard their thermal degradation. Finally, almost all of the coPIs leave no residues after heating to 850 $^\circ\text{C}$.

3.3. LC alignment and pretilt angle

The LC alignment layers were prepared by spin-coating the coPI solutions onto ITO glass substrates. To optimize the solubility of the coPIs, various solvents such as NMP, DMAc, γ -butyrolactone, 2-pentanone, THF, DMF and CHCl₃ were tested. After considering the film property and solvent evaporation rate, we selected a suitable solvent for each coPI series. Homogeneous cells were prepared with rubbed coPI layers and filled with 5CB nematic liquid crystal at room temperature. All the rubbed coPI films aligned 5CB well before annealing. Good uniformity of LC alignment was observed

using an polarizing optical microscopy. The LC cells were then annealed at 50°C for 10 min to eliminate flow marks. Unexpectedly, the LC alignment of the cells prepared with 6FDA-MDA-18OBD and 6FDA-ODA-18OBD deteriorated after annealing.

To understand the alignment degradation, we observed the LC alignment evolution by microscope during the annealing process. We found that domains were formed locally at the beginning and gradually expanded until the whole LC alignment was disordered. In a parallel experiment, another LC cell was prepared with coPI layers baked at 50°C for 1 h after rubbing. These 5CB LC cells showed uniform alignment. This implies that the alignment deterioration results from molecular interactions between coPI layers and 5CB. Judging from the good solubility of the 6FDA series of coPIs, we believe that 5CB molecules in the isotropic state ($T_c \sim 35.3^\circ\text{C}$) can act as a solvent to swell the surface of coPI layers. The 5CB alignment was thus degraded by the swelling.

The pretilt angle of each 5CB cell was measured using the crystal rotation method [17]. An Autronic DMS 101 TBA instrument was used for these measurements; results are summarized in table 3. For each cell, the pretilt angle is reduced somewhat after annealing. But after eliminating the flow marks, the pretilt angle remains stable. For those cells employing BCDA coPI alignment layers, the pretilt angle varies from 2.56° to 14.32°. On the other hand, most of 6FDA and BPDA cells produce less than 1° pretilt angle, except for 6FDA-PPD-18OBD. Its pretilt angle is the highest (15.54°) among all the coPIs studied.

Table 3 demonstrates the main chain structural effect on the pretilt angle. These coPIs have the same amount

of alkyl side groups; however, their pretilt angles vary from 0.16° to 15.54°. Therefore, different main chain structures should make important contributions to the observed pretilt angle variations. In ref. [18], the authors proposed that semi-crystalline polyimides would lead to a higher pretilt angle than amorphous ones. Similar results were found in our experiments. As listed in table 3, the two coPIs based on a linear and symmetric structure (PPD) exhibit large pretilt angles. Other coPIs based on bent structures (ODA and MDA) result in a small pretilt angle. The coPIs based on DDS show mixed results, i.e. high pretilt angle in the BCDA series (4th row in table 3) but low pretilt angle in the 6FDA and BPDA series (the last two rows in table 3).

The large pretilt angle of BCDA-DDS-18OBD could result from the more rigid bridge group in DDS than in ODA and MDA. However, the other two DDS-based coPIs (6FDA and BPDA) are exceptional: their pretilt angle is rather small. Thus, BCDA must have a different effect from the other two dianhydrides (6FDA and BPDA) on pretilt angles. To investigate this, we used molecular modelling to simulate the structures of these three dianhydrides. We chose the ‘Equilibrium Geometry with Semi-Empirical’ method to calculate the dipole of each structure. From the Titan simulation program, we found that the BCDA dipole is clearly different from that of 6FDA and BPDA. The calculated dipole of 6FDA, BPDA and BCDA dipoles are 5.634, 5.596, and 3.818 D, respectively.

Based on previous studies, [4, 5] increasing the electronic attraction between LC and alignment layer molecules tends to decrease the LC pretilt angle. In our studies, the stronger dipoles of 6FDA and BPDA should experience higher electronic interactions than BCDA under the same rubbing conditions. Therefore, the coPIs based on 6FDA and BPDA, in conjunction with DDS (7.725 D), exhibit small pretilt angles as listed in table 3.

On the other hand, the large pretilt angle obtained from a long alkyl-branched PI film could result from the steric interaction between LCs and long alkyl side groups [4, 5]. Our studies indicate that the PI main chain structure greatly influences the LC pretilt angle on the alkyl-branched coPI films. An asymmetric and flexible main chain structure would lead to a small pretilt angle while a symmetric and rigid main chain structure would generate a high LC pretilt angle. The steric interaction of long alkyl side groups seems to be stronger when a linear and rigid PI main chain is employed. Another factor influencing the LC pretilt angle on alkyl-branched coPI films is the dipole interaction of the main chain structure. A strong main chain dipole may enhance the electrical interaction between LC molecules and coPI films and thus reduce the pretilt angle.

Table 3. Measured LC pretilt angles on rubbed copolyimide films.

Copolyimides	Coating solvent ^a	Pretilt angle/degree	
		Before annealing	After annealing ^b
BCDA-MDA-18OBD	DMAc	4.54	2.56
BCDA-ODA-18OBD	DMAc	5.49	5.11
BCDA-PPD-18OBD	DMAc	15.26	14.32
BCDA-DDS-18OBD	DMAc	14.79	13.68
6FDA-MDA-18OBD	γ -BL	0.04	— ^c
6FDA-ODA-18OBD	γ -BL	0.47	— ^c
6FDA-PPD-18OBD	γ -BL	20.88	15.54
6FDA-DDS-18OBD	γ -BL	0.36	0.16
BPDA-DDS-18OBD	DMAc	0.83	0.53

^a DMAc, *N,N*-dimethyl acetamide; γ -BL, γ -butyrolactone.

^b Annealing at 50°C for 10 min.

^c LC alignment deteriorated after annealing.

Thus, by using different main chain structures, we have achieved a relatively broad range of LC pretilt angles. Low LC pretilt angle is particularly attractive for In-Plane-Switching or twisted-nematic LCD modes while high pretilt angle is necessary for the super twisted nematic [19] or surface-stabilized ferroelectric LCDs [20]. The synthesized coPIs are soluble in organic solvents and their processing temperature is quite low. Such features are particularly important for low temperature poly-silicon TFT-LCD processes.

4. Conclusion

We have synthesized and characterized three series of copolyimides based on 4-(octadecyloxy)-1,3-benzene-diamine (18OBD) which has a long linear alkyl group with 18 carbon atoms. Most of these copolyimides show excellent solubility in selected polar solvents. Homogeneous 5CB cells were prepared for examination of the LC alignment performance of soluble copolyimide layers. The LC alignment was generally good except for a swelling phenomenon due to the excellent solubility of 6FDA-based copolyimides. The LC pretilt angles vary wildly from 0.16° to 15.54° , even though the copolyimides are branched with the same amount of alkyl group. It was found that both main chain structures and dipole interactions play key roles in determining the pretilt angle. The main chain copolyimides with long alkyl side group, small dipole, linear, symmetric and rigid core structures are favourable for the generation of large LC pretilt angles.

The UCF group is indebted to AFOSR for financial support under contract number F49620-01-1-0377.

References

- [1] COGNARD, J., 1982, *Mol. Cryst. liq. Cryst.*, **S1**, 1.
- [2] XU, M., YANG, D. K., and BOS, P. J., 1998, *SID Dig.*, 139.
- [3] FUKURO, H., and KOBAYASHI, S., 1988, *Mol. Cryst. liq. Cryst.*, **163**, 157.
- [4] LEE, K. W., PAEK, S. H., LIEN, A., DURNING, C., and FUKURO, H., 1996, *Macromolecules*, **29**, 8894.
- [5] LEE, K. W., LIEN, A., STATHIS, J. H., and PAEK, S. H., 1997, *Jpn. J. appl. Phys.*, **36**, 3591.
- [6] JUNG, J. T., YI, M. H., KWON, S. K., and CHOI, K. Y., 1999, *Mol. Cryst. liq. Cryst.*, **333**, 1.
- [7] LEE, S. W., KIM, S. I., PARK, Y. H., REE, M., RIM, Y. N., YOON, H. J., KIM, H. C., and KIM, Y. B., 2000, *Mol. Cryst. liq. Cryst.*, **349**, 279.
- [8] BAN, B. S., RIM, Y. N., and KIM, Y. B., 2000, *Liq. Cryst.*, **27**, 125.
- [9] SEO, D. S., KOBAYASHI, S., and NISHIKAWA, M., 1992, *Appl. Phys. Lett.*, **61**, 2392.
- [10] SEO, D. S., NISHIKAWA, M., and KOBAYASHI, S., 1997, *Liq. Cryst.*, **22**, 515.
- [11] NISHIKAWA, M., 2000, *Polym. Adv. Technol.*, **11**, 404.
- [12] CLAIR, T. L. ST., 1990, *Polyimides*, edited by D. Wilson, H. D. Stenzenberger and P. M. Hergenrother (New York: Chapman and Hall), pp. 58–78.
- [13] TSUDA, Y., KAWAUCHI, T., HIYOSHI, N., and MATAKA, S., 2000, *Polym. J.*, **32**, 594.
- [14] TSUDA, Y., KANEGAE, K., and YASUKOUCHI, S., 2000, *Polym. J.*, **32**, 941.
- [15] HARRIS, F. W., 1990, *Polyimides*, edited by D. Wilson, H. D., Stenzenberger and P. M. Hergenrother (New York: Chapman and Hall), pp. 1–37.
- [16] CHUN, B. W., 1994, *Polymer*, **35**, 4203.
- [17] WITTER, V., BAUR, G., and BERREMAN, D. W., 1976, *Phys. Lett.*, **56A**, 142.
- [18] YOKOKURA, H., MYRVOLD, B., KONDO, K., and OH-HARA, S., 1994, *J. mater. Chem.*, **4**, 1667.
- [19] SCHEFFER, T. J., and NEHRING, J., 1984, *Appl. Phys. Lett.*, **45**, 1021.
- [20] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.