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Kil-Yeong Choi [a], Bum Jin Lee [a], Mi Hie Yi [a] & Hwan Kyu Kim [b]

[a] Advanced Materials Division, Korea Research Institute of Chemical Technology, P. O. Box 107, Yusong, Taejon, 305-600, Korea

[b] Department of Pôlymer Science and Engineering, Hannam University, Taejon, 306-791, Korea

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Synthesis and Characterization of Colorless Polyimides for Liquid Crystal Alignment Layer

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[a]*Advanced Materials Division, Korea Research Institute of Chemical Technology, P. O. Box 107, Yusong, Taejon, 305–600, Korea and* [b]*Department of Polymer Science and Engineering, Hannam University, Taejon, 306–791, Korea*

A series of soluble polyimides has been synthesized by polycondensation reaction of 5-(2,5-dioxotetrahydrofuryl)-3-methyl-cyclohexane-1,2-dicarboxylic anhydride (DOCDA) and the mixture of *p*-phenylenediamine(*p*-PDA) and the newly prepared diamine with pendant hexadecaoxy group(DA-L-16O) via one step polymerization in *m*-cresol at high temperature. The inherent viscosities of the resulting polymers measured in NMP were in the range of 0.27 to 1.42 dL/g, which was decreased with the increase of the content of the diamine with the pendant hexadecaoxy group. The obtained polyimides were highly soluble in common aprotic polar solvents and some of them were even soluble in common organic solvents such as tetrahydrofuran, cyclohexanone, chloroform. The glass transition temperatures of the polyimides were in the range of 186~327°C and most of the polyimides had good transparency in the wavelength of 400~700nm. The pretilt angle of liquid crystals (BL-002, Merck Ltd.) with polyimides having alkoxy side chain was investigated, which revealed that the increase of alkoxy side chain in polyimide resulted in higher pretilt angles.

Keywords: hexadecaoxy side chains; soluble polyimide; pretilt angle; liquid crystals; surface property

INTRODUCTION

Liquid crystal displays have been widely used for simple numeric displays to large information displays because of their low voltage and current, high contrast ratio. As well known, liquid crystal display device is composed of several materials such as liquid crystal, color filter and liquid crystal alignment layer[1]. Especially, liquid crystal alignment layer has an important role to align liquid crystal molecules in uniform. The polymers as a liquid crystal alignment layer should have some properties to be fabricated into liquid crystal devices. The requirement for alignment layer are deeply related to the fabrication process. That is, as the size of liquid crystal display devices is increased, the thin film forming property over a large area is becoming more important. And the low temperature curing or low solvent evaporation temperature are required because of relatively low thermal stability of the color filter. Furthermore, excellent liquid crystal alignment property, mechanical strength, and transparency are also required to obtain the liquid crystal device with good quality. So, polyimides have been currently used as a liquid crystal alignment layer due to their outstanding key properties such as thermal stability, high mechanical strength, excellent electrical properties and so on[2-3] . However, conventional polyamic acid type aromatic polyimides have some problems such as dark color caused by charge transfer complex and high imidization temperature above the temperature of 300 ℃. Therefore, significant synthetic efforts have been conducted to improve the processability and solubility of polyimides with the retention of their attractive properties by the introduction of new structures into polymer backbone [4-5] . Especially, the incorporation of alicyclic monomers or monomers containing bulky substituents have been found to be an effective approach to improve the solubility without the sacrifice of their excellent characteristics. Further, the pretilt angle is important

parameter for realization of defect free liquid crystal display[6]. Thus, numerous attempts had been carried out to investigate the relationship of the pretilt angle and the chemical structutre of polymers, which showed that the generation of the pretilt angles was highly depending on the interactions of the polyimides with liquid crystals[7-16]. However, the mechanism of the generation of the pretilt angle of the polymers has not been fully understood until now. Therefore, in this study, we would like to introduce the synthesis of novel soluble polyimides from the alicyclic dianhydride and new aromatic diamine with long alkoxy side chain to investigate the general properties such as thermal stability, solubility, transmittance, as well as the surface property for liquid crystal alignment layer. And we have also studied on the effect of long alkyl side chain on the pretilt angle.

EXPERIMENTAL

Materials. DOCDA(Tokyo Kasei Organic Chemicals) was recrystallized from the co-solvent of acetic anhydride and benzene. *N*-methyl-2-pyrrolidone (NMP) was dried over CaH_2 and distilled under the reduced pressure. *m*-Cresol was also distilled under the reduced pressure. *p*-PDA (99.6%, Mitsubishi Kasei) was used without further purification, because it was of highly purified grade for polyimide synthesis. 2,4-dinitrophenol (DNP, Aldrich Chemical Co., Inc., 97 %) and 1-iodohexadecane were used as received. The nematic liquid crystal used in this study was BL-002 purchased from Merck Ltd.

Measurement. Infra-red spectra were obtained with a Bio-Rad Digilab FIS-165 FT-IR spectrophotometer. The inherent viscosities of the polyimides were measured with a Ubbelohde viscometer at a concentration of 0.5 g/dL in NMP at 30℃. Thermogravimetric analysis (TGA) was done with a Du Pont Model 915 coupled with a Du Pont thermal analysis station 9900 at a heating

rate of 10℃/min under nitrogen atmosphere. The polyimide films were rubbed with nylon velvet cloth using a rubbing machine. The pretilt angle of liquid crystal with polyimide layer was measured by the crystal rotation method reported by A. Mosley.[6] The incident light was polarized at an angle of 45 ° with the respect to the axis of the liquid crystal alignment. The cell was rotated about an axis which was perpendicular to the rubbing direction through 120 °. And a plot of transmittance against angle of incidence was obtained, from which the pretilt angle was calculated. The dynamic advancing and receding contact angles were measured by Dynamic Contact Angle Analyzer (Khan, DCA-322) and the surface tension was determined by Rame-Hart telescopic goniometer and Gilmont syringe NRL.C.A. Goniometer (Model 100-00115) using water and diiodo methane.

Monomer Synthesis. The synthetic route of the diamine monomer is shown in scheme 1. 2,4-dinitro(n-hexadecaoxy)benzene was prepared by the reaction of the 1-iodohexadecane with DNP in DMAc in the presence of potassium carbonate at 60℃ . The obtained 2,4-dinitro(n-hexadecaoxy)benzene was reduced in Parr hydrogenator using palladium on carbon (5 % with palladium metal) as a catalyst

The synthetic route is as follows.

2,4-Dinitro-(n-hexadecaoxy)benzene (DN-L-16O). To a 250 ml reactor equipped with an agitator and nitrogen-inlet, nitrogen gas was slowly influxed as 2,4-dinitrophenol (7.36g, 0.04mole) was dissolved in 50 ml of DMAc. While influxing nitrogen gas, K_2CO_3 (6.99g, 0.05 mole), 1-iodohexadecane (19g, 0.05 mole) was slowly added and refluxed for 48 hours. The mixture was precipitated in excess distilled water. Thereafter, the solid material so filtered was recrystallized to obtain 2,4-dinitro-(n-hexadecanoxy)benzene (DN-L-16O) with the yield of 60.0 %.

2,4-Diamino-(n-hexadecaoxy)benzene (DA-L-16O). DN-L-16O (4.08g, 0.01 mole) was dissolved in 100ml of ethanol, after which was placed in a hydrogenator along with 2.0g of 5% Pd/C (catalyst for hydrogenation, in which the surface of the carbon powder has been coated at 5% with palladium metal). As such, the reduction reaction was carried out at 60℃ for 2 hours. After filtering of the reaction mixture, the solvent was removed by distillation under reduced pressure. The mixture was recrystallized using ethylacetate to yield 2,4-diamino-(n-hexadecanoxy)benzene (DA-L-16O) with the reaction yield of 70.0%.

Polymer synthesis. The soluble polyimides were prepared from DOCDA and the mixture of diamines by one step polymerization as shown in scheme 2. A typical polymerization procedure is as follows.

To a 500 ml reactor equipped with a mechnical stirrer, thermometer, nitrogen-inlet, dropping funnel and condenser, nitrogen gas was slowly influxed as p-phenylene diamine (*p*-PDA: 9.72g, 0.09 mole) and modified diamine DA-L-16O (3.48 g; 0.01mole) were dissolved in *m*-cresol. Thereafter, while influxing the nitrogen gas, DOCDA(26.4 g, 0.1 mole) was slowly added therein with the solid content of 15 wt%. The reaction mixture was heated to 70℃ and kept at that temperature for 2 hours and then the solution temperature was slowly raised to 200 ℃ and refluxed 4~6 hours. As an imidization catalyst, isoquinoline (~ 5 wt%) was used. After the reaction, the mixture was precipitated using the Waring Blender in excess methanol for several times. Then, the filtered polymer was washed with water and methanol for several times and dried under reduced pressure at 120℃ for 12 hours to yield a polyimide resin (SPI-2). The yield of polymerization was quantitative.

Fabrication of liquid crystal cell. The polyimide powder(0.3 g) was dissolved in 10 ml of co-solvents of γ-butyrolactone(85%) / NMP(10%) / 2-

butoxyethanol(5%) and spun onto cleaned indium tin oxide (ITO) coated glass substrates at 2,500 rpm for 25 seconds. After then, the coated layer was dried at 180℃ for 1 h. The obtained polyimide thin layer was rubbed with nylon velvet cloth using rubbing machine. The translation speed of the rubbing cloth and the rubbing pressure were kept to constant. The liquid crystal cell was assembled using two polyimide coated glass plates with antiparallel rubbing direction. In this study, Kapton® polyimide film (thickness : 56 ㎛) was used to control the cell gap. Nematic liquid crystal mixture (BL-002, Merck Ltd.) was injected by capillary method at isotropic temperature (72℃). And then, the characteristics of the liquid crystal cell were duly confirmed. The alignment property of liquid crystals was examined by a microscope with cross-polarizer, and the pretilt angles (θ p) of liquid crystal, BL-002 with polyimide layer were measured by the crystal rotation method, which equipment was fabricated in our laboratory.

RESULTS AND DISCUSSION

Monomer Synthesis. The synthetic route of the diamine monomer was shown in scheme 1. 2,4-Dinitro-(n-hexadecaoxy)benzene (DN-L-16O) was prepared by the reaction of the 1-iodohexadecane with 2,4-dinitrophenol in DMAc. The obtained 2,4-dinitro compound were reduced in Parr hydrogenator in the presence of palladium on carbon (5% with palladium metal) as a catalyst. The yields of the resulting diamines were about 60.0 %. The ^{1}H-NMR spectrum of the DA-L-16O is shown in Figure 1.

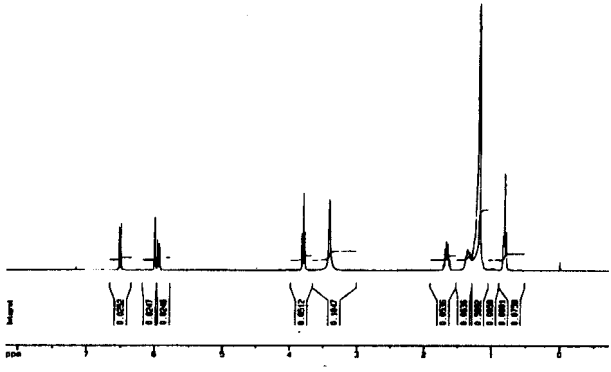
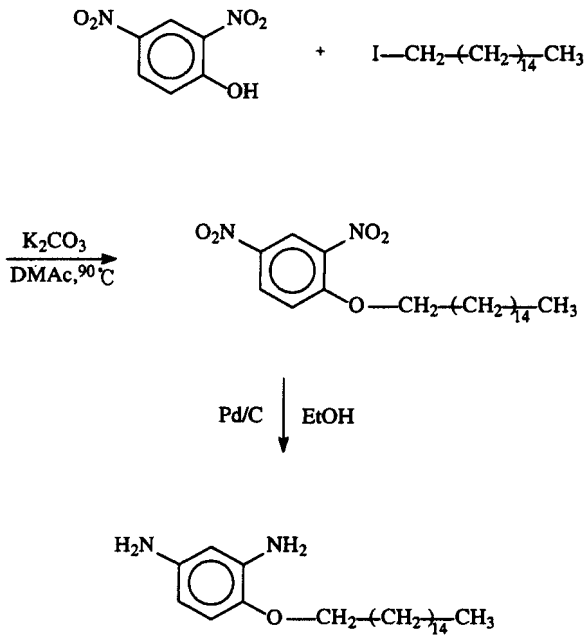


Figure 1. ^{1}H-NMR spectrum of DA-L-16O



scheme 1. Synthesis of DA-L-16O

Polymer Synthesis. A series of soluble polyimide was synthesized from DOCDA and two aromatic diamines changing mole fraction of p-PDA and DA-L-16O by one step thermal imidization reaction at high temperature as shown in scheme 2. The composition of modified diamine, DA-L-16O was varied 0~100 mol % to obtain the polyimides with different quantity of n-hexadecaoxy group. The result of the synthesis is summarized in Table 1 and the structures of the polyimide were confirmed by ^{1}H-NMR and FT-IR spectra. As shown in Figure 2, no amide and amic acid peaks were detected in ^{1}H-NMR spectrum of SPI-1, which revealed that the imidization reaction was performed completely. The inherent viscosities of the polyimides measured in NMP were in the range of 0.27~ 1.42 dL/g, which was decreased with the increase of the mole fraction of DA-L-16O. It can be seen that the steric hindrance of ortho-substituted modified diamines, DA-L-16O prevents the increase of moleculcar weight of the polyimides

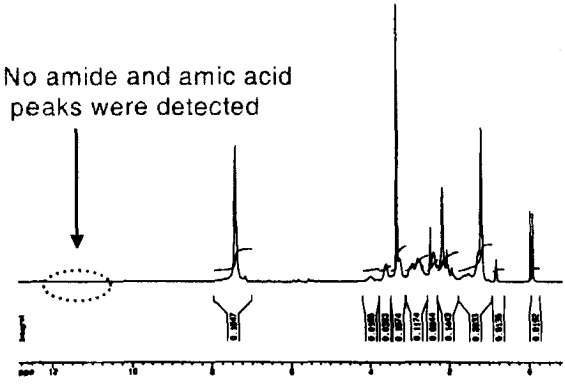
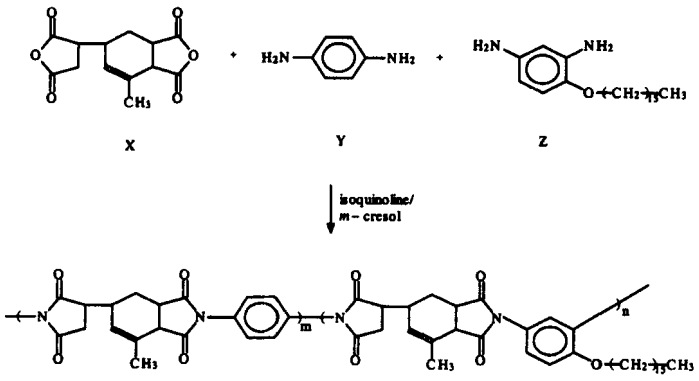


Figure 2. ^{1}H-NMR spectrum of SPI-1



Scheme 2. Synthesis of soluble polyimides

Mechanical property. It is well known that the tensile strength and the elogation required for enduring the rubbing process are about 1,000 kg/cm^2 and 15~30 %, respectively. Thus, we have measured the tensile strength and the elongation of the soluble polyimide films. The tensile strength was in the range of 817~1067 kg/cm^2, which was decreased with the increased of alkoxy density. And the elongations at break were ranged from 29 to 36 %.

Solubility. The thin film forming property is affected by various factors sush as the solubility of polymers, the surface tension of polymer solution and the vapor pressure of the using solvent. Especially, the good solubility for the solvents with low surface tension is very important to obtain the liquid crystal alignment layer with good planarity. As shown in Table 2, the increase of the quantity of n-hexadecaoxy side chain improved the solubility toward organic

solvents with low surface tension like cyclohexanone, which resulted in good thin film forming property. Furthermore, the good solubility in low boiling solvents can reduce the processing temperature.

Thermal stability. The thermal stabilities of the polyimides were evaluated by thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC) under nitrogen atmosphere. The results are also summarized in Table 1. The glass transition temperature of polyimides measured by DSC were ranged from 187 to 327 ℃, which were found to be controllable due to the fact that the glass transition temperature was indirectly proportional to the quantity of the n-hexadecaoxy group. That is, the Tgs of the polyimide without hexadecaoxy moiety (SPI-1) was about 327 ℃, which is surprisingly high as compared to those of others. However, as the amount of n-hexadecaoxy moiety increased, the Tgs decreased to 187 ℃. And, all the polyimides exhibited good thermal stability. Most of them were stable up to 350℃ under nitrogen atmosphere and the residual weight at 600℃ were above 20.0 %. On the other hand, the polyimides with long alkoxy side chain prepared in this study underwent two-step degradation at the temperature above 300℃ under air condition. It is assumed that the bond dissociation reaction between oxygen and carbon atoms of pendant n-hexadecaoxy group was occurred at high temperature. A typical TGA curve of polyimide (SPI-8) in air and nitrogen atmosphere is shown in Figure 3.

Transmittance. All the polymers prepared in this study showed high transmission above 90% in the wavelength of 400 ~ 700 nm. That is, alicyclic moiety of the polyimides increased the intermolecular chain distance and decreased the intermolecular interaction, which resulted in good optical transparency. Typical UV-visible spectra of the polyimide, SPI-1 with a concentration of 5 x 10^{-3}mol/L in NMP solution is shown in Figure 4.

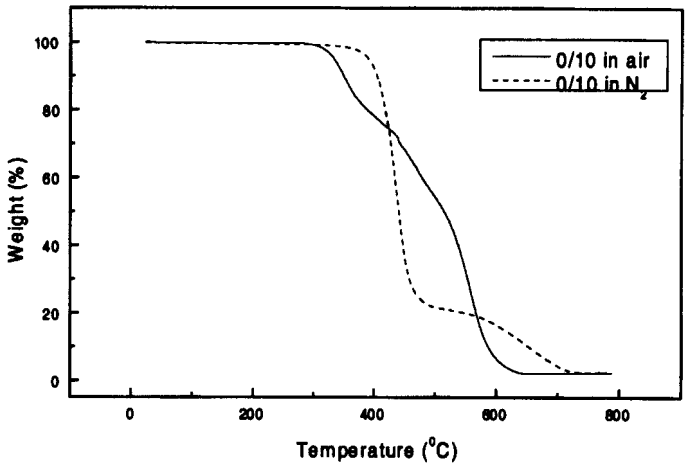


Figure 3. TGA curves of SPI-8

Effect of rubbing on the surface properties of polyimides with long alkoxy side chain ; As well known, the rubbing process is widely used technique to realize homogeneous alignment of liquid crystal molecules onto the polymer surface. Thus, a lot of studies have carried out in order to understand the physical mechanism responsible for the liquid crystal alignment on the polymer surface. In this study, a series of the soluble polyimides with well designed structures were synthesised and the effect of alkyl side chain density on the polarity of polyimide surface before and after rubbing was investigated by the mesurement of the dynamic water contact angle of the surface of polyimides. As the increase of the mole fraction of DA-L-16O, the water contact angles were increased both before and after rubbing, which is seemed to be due to the decrease of the polarity of the polyimide surface by the introduction of non-

polar n-hexadecaoxy side group. But, as the mole fraction of DA-L-16O exceeded 80 %, the water contact angles of the polyimides (SPI-6~8) exhibited simmilar values. It can be seen that all of the surface of polyimides were saturated by n-hexadecaoxy side group above the composition of 80 % of DA-L-16O. Furthermore, the rubbing process induced the increase of the polarity of the polyimide films except the polyimide, SPI-1. It reveals that the n-hexadecaoxy side group of the polyimide (SPI-2~8) was inserted into the polymer bulk during rubbing process, which resulted in the increase of the polarity of the polyimides containing long alkoxy side chain.

Effect of the alkoxy side chain on the pretilt angle ; It have been known that the pretilt angles might be affected by various factors, such as the surface morphology of alignment layer, the steric effect and electronic interaction of liquid crystal with alignment layer, etc. In this study, we have synthesized the polyimides with various content of n-hexadecaoxy side group and then investigated the relationship between the pretilt angles and the surface property of the polyimide film. The pretilt angles of liquid crystal, E-7 onto the surface of polyimides measured by crystal rotation method were in the range of 2~12° . According to the previous result,[17] the pretilt angle increased with the increase of the water contact angle of the polyimide films. However, as shown in Figure 6, the water contact angles of the polyimides were slightly increased at higher composition of 80 % of DA-L-16O, but the pretilt angles were remarkably increased compared to those of other polyimides. Therefore, it is believed that there are another important facters to affect the increase the pretilt angles, but which is not clear yet.

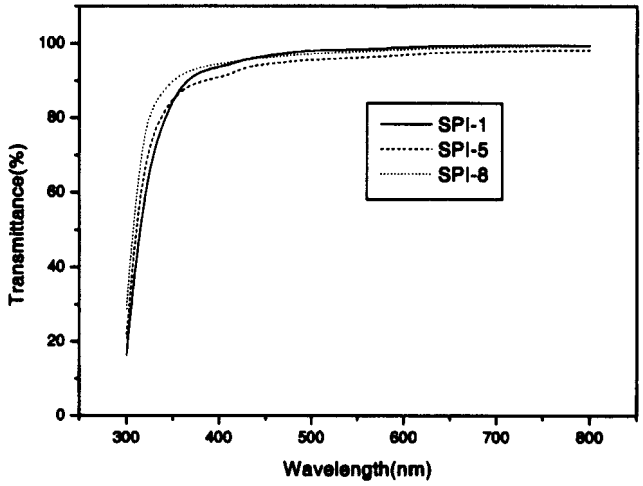


Figure 4. UV-Vis spectra of soluble polyimides

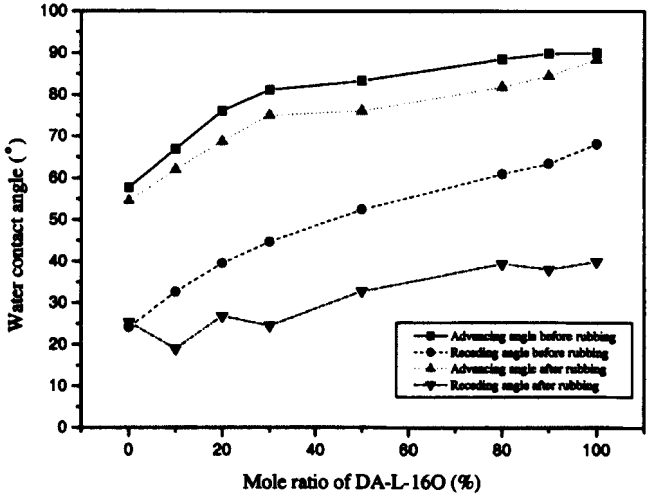


Figure 5. Change of the dynamic water contact angles with the mole percent of DA-L-16O before and after rubbing

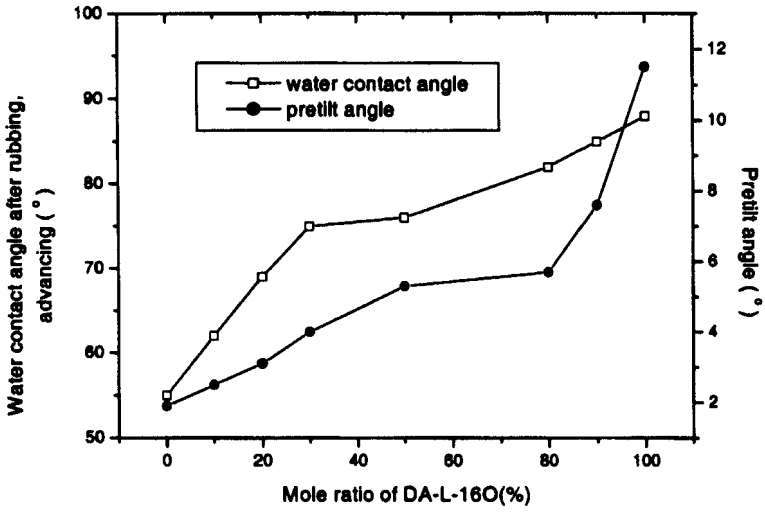


Figure 6. Relationship of the pretilt angle with water contact angle of soluble polyimides

CONCLUSION

A series of soluble polyimides containing with n-hexadecaoxy side chain was synthesized by one step polyimidization in *m*-cresol at high temperature. All of the polyimides have superior heat-resistance, good solubility, high mechanical strength, excellent liquid crytstal alignment property as well as high pretilt angles, which could be applicable as a liquid crystal alignment layer for the TFT TN LCD. The inherent viscosity, surface tension, glass transition temperature of polyimides were decreased with the increase of the composition of DA-L-16O, but the solubility was remarkably increased. And the pretilt angles were dependant on the water contact angle of the polyimide film. This results shows that liquid crystal alignment layer with desired properties could be prepared by the structural modification of polymers.

ACKNOWLEDGEMENT

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Table 1. Synthesis and Properties of the Soluble Polyimides

Polyimides	Mole percent of diamines (p-PDA/DA-L-16O)	Inherent viscosity (dl/g)	Tg (℃)
SPI-1	100/0	1.42	327[b]
SPI-2	90/10	0.78	313
SPI-3	80/20	0.67	276(264)[c]
SPI-4	70/30	0.69	(258)
SPI-5	50/50	0.65	227(226)
SPI-6	20/80	0.44	-
SPI-7	10/90	0.27	(192)
SPI-8	0/100	0.33	(186)

[a] measured at a concentration of 0.5 g/dl in N-methyl-2-pyrrolidone at 30 ℃.;

[b] from the second heating traces of DSC measurements conducted with a heating a rate of 10℃ /min. under nitrogen atmosphere.

[c] from MDSC(modulated DSC) measurements conducted with a heating a rate of 2℃/min. in nitrogen atmosphere.

Table 2. Solubility of the obtained Polyimides

Polymer	Solvents[a]							
	NMP	DMSO	DMAc	BUL	TCE	CHX	$CHCl_3$	THF
Surface tension (dyne/cm)	35	-	-	30	-	28	-	-
SPI-1	++	++	++	++	–	–	–	–
SPI-2	++	++	++	++	+-	–	–	–
SPI-3	++	++	++	++	++	–	–	–
SPI-4	++	++	++	++	++	+-	+-	–
SPI-5	++	++	++	++	++	++	+-	–
SPI-6	++	+	++	++	++	++	++	++
SPI-7	++	+	++	++	++	++	++	++
SPI-8	++	+-	++	+	++	++	++	++

[a] Abbreviations : NMP, *N*-methyl-2-pyrrolidone, DMSO; dimethylsulfoxide, DMAc; dimethylacetamide, BUL; γ -butyrolactone, TCE; 1,1,2,2-tetrachloroethane, CHX;cyclohexanone, THF; tetrahydrofuran

[b] Key : ++ ; soluble, + ; soluble on heating, +– ; partially soluble, –; insoluble

Table 3. Dynamic Water Contact Angle of the Polyimides[a]

Polymers	Contact angle before rubbing(°)		Contact angle after rubbing(°)	
	Advancing	Receding	Advancing	Receding
SPI-1	58	24	55	25
SPI-2	67	33	62	19
SPI-3	76	40	69	27
SPI-4	81	45	75	25
SPI-5	83	52	76	33
SPI-6	89	61	82	39
SPI-7	90	63	85	38
SPI-8	90	68	88	40

[a]determined by measuring the angle at the intersection of air/ water drop/surface of the polyimide film while advancing and receding water to from the drop.

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