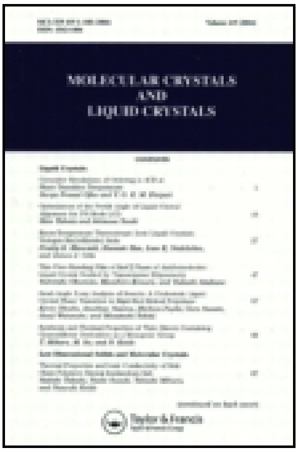

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Aromatic Polyimides Containing Pendant Alkyl Groups for Liquid Crystal Alignment Layers

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Aromatic Polyimides Containing Pendant Alkyl Groups for Liquid Crystal Alignment Layers

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A series of polyimides has been synthesized by polycondensation reaction of 3,3',4,4'-biphenyl tetracarboxylic acid dianhydride (BPDA) and corresponding diamines with various alkyl side chains via polyamic acid formation. The inherent viscosities of the polyamic acids measured in *N*-methyl-2-pyrrolidone (NMP) were in the range of 0.45 to 1.19 dL/g, which was decreased with the increase of alkyl chain length. The glass transition temperatures of the polyimides were in the range of 247.6~291.4°C. The effect of curing temperature on the pretilt angle of liquid crystals (BL-002. Merck Ltd.) with polyimides having alkyl side chains was investigated, which revealed that the increase of degree of imidization resulted in higher pretilt angles. On the other hand. the pretilt angles were decreased by the curing reaction above the temperature of 300 °C due to decomposition reaction of alkyl side chains. It was also found that the pretilt angles were varied with the length of alkyl side chains.

Keywords: alkyl side chains; effect of curing temperature; pretilt angle of liquid crystals; degree of imidization

INTRODUCTION

Aromatic polyimide has been noted for excellent thermal stabilities, mechanical properties as well as electro-optic properties, which resulted in a various applications.[1–2] One of the typical application is liquid crystal alignment layer for active matrix liquid crystal displays owing to its excellent thermo-mechanical properties. chemical resistance, and good liquid crystal aligning capability. It is well known that several important properties were required for liquid crystal alignmnet layer such as large pretilt angle, high voltage holding ratio as well as good

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* Correspondence Author.

transparency. Especially, the pretilt angle (θp) deeply relates with electro-optic properties of liquid crystal devices.

Therefore, numerous attempts have been made to investigate the relationship of the pretilt angle with the structure of polymers. One of them was the introduction of long alkyl side chains into the polymer backbone to give a large pretilt angle.[3–9] It was reported that the liquid crystal alignment capability as well as the generation of pretilt angles were highly depending on the interactions of the polyimides with liquid crystals because the liquid crystal alignment on rubbed polyimide surface was a phenomena at the interface. However, the mechanism of generation of pretilt angle of polyimides with alkyl side chain has not been fully understood until now. Therefore, in this study, we have synthesized a series of new polyimide alignment layers with various pendant alkyl groups to investigate the relationship of pretilt angle with the length of alkyl side chains as well as the curing temperature. All of the polyimides were prepared by two step thermal imidization from 3,3',4,4'-biphenyl tetracarboxylic acid dianhydride (BPDA) and several modified aromatic diamines containing various alkyl substituents via polyamic acid formation reaction. And the general properties of obtained polyimide alignment layers were investigated in detail.

EXPERIMENTAL

Materials

BPDA (99.6%, Mitsubishi Kasei) was used without further purification. because it was of highly purified grade for polyimide synthesis. *N*-methyl 2-pyrrolidone(NMP) and *N,N*-dimethylacetamide(DMAc) were distilled over CaH_2, under reduced pressure. 3,5-Dinitrobenzoyl chloride (DBC, Aldrich Chemical Co., Inc., 97 %) and 8 kinds of n-alkylamines were used as received. The nematic liquid crystal used in this study was BL-002 purchased from Merck Ltd.

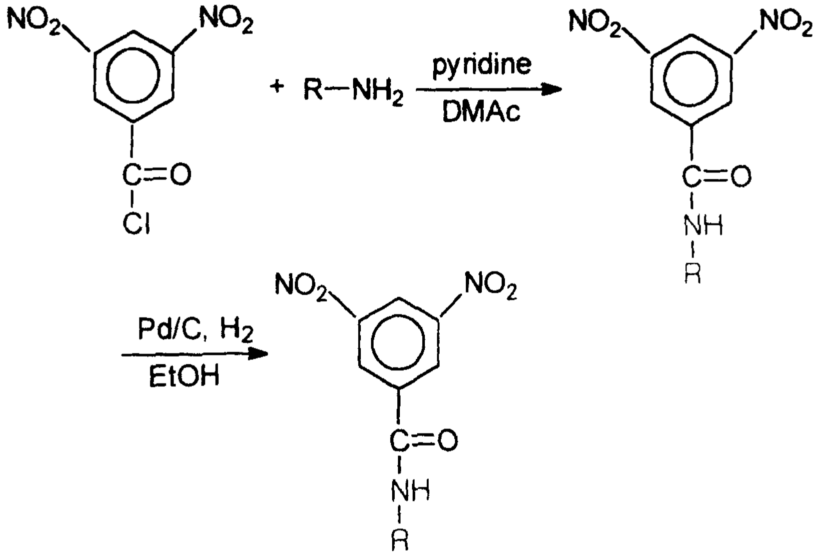
Measurement

Infra-red spectra were obtained with a Bio-Rad Digilab FIS-165 FT-IR spectrophotometer. The inherent viscosities of the polyamic acids were measured with a Ubbelohde viscometer at a concentration of 0.5 g/dL in NMP at 30°C. The melting points of the prepared diamines were determined by differential scanning calorimeter (DSC, Du Pont Model 910). 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°C/min under nitrogen atmosphere. The polyimide films were rubbed with nylon velvet cloth using a rubbing machine. The pretilt angles of liquid crystal with polyimide layer were measured by the crystal rotation method.

Monomer Synthesis

The synthetic route of the diamine monomers is shown in scheme 1. Several kind of 3,5-dinitrobenzamide derivatives containing various pendant alkyl groups were prepared by the reaction of the corresponding n-alkylamines with DBC in the presence of pyridine in DMAc. The obtained 3,5-dinitro compounds were reduced in Parr hydrogenator using palladium on carbon (5% with palladium metal) as a catalyst. The yields of the resulting diamines were above 68.0 %. The results of synthesis are summarized in Table Iand the typical ^{1}H-NMR spectrum of the DA-16AM is shown in Figure 1.

A typical synthetic route is as follows.



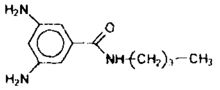
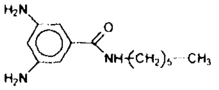
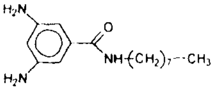
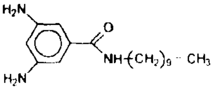
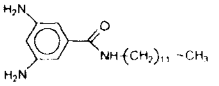
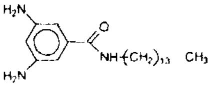
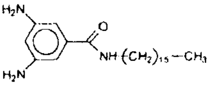
R : n-C_4H_9, n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, n-$C_{14}H_{29}$, n-$C_{16}H_{33}$

SCHEME 1 Synthesis of monomers

3,5-Dinitro-(n-hexadecyl)-benzamide (DN-16AM)

To a 50 ml reactor equipped with an agitator and nitrogen-inlet, nitrogen gas was slowly influxed as n-hexadecylamine (2.41 g, 0.01 mole) and pyridine (0.79 g, 0.01 mole) were dissolved in 15ml of DMAc. While influxing nitrogen gas, DBC (2.31 g, 0.01 mole) in the solid phase was slowly added. After the mixture was stirred for 20 h at room temperature, the mixture was precipitated in excess water. Thereafter, the solid material was washed with sodium bicarbonate and diluted hydrochloric acid solutions for more than three times. after which was dried under reduced pressure at 40°C. The crude product was recystallized from ethyl acetate to give 3.97 g (yield: 91.0 %) of white crystal. The same process was carried out with changing the number of carbon atom in the alkyl group by means of substituting n-hexadecylamine with n-butylamine. n-hexylamine, n-octylamine, n-decylamine, n-dodecylamine, or n-tetradecylamine.

TABLE I Synthesis of Aromatic Diamines Containing Various Pendant Alkyl Groups

Monomers	Structure	Yields (%)	Melting point[a] (℃)
DA-4AM		95.7	82.6
DA-6AM		96.0	100.4
DA-8AM		89.5	91.3
DA-10AM		84.0	95.1
DA-12AM		85.3	94.7
DA-14AM		83.0	98.0
DA-16AM		68.0	109.8

[a] Measured by DSC.

3,5-Diamino-(n-hexadecyl)-benzamide (DA-16AM)

DN-16AM (4.36 g, 0.01 mole) was dissolved in 50ml of ethanol, after which was placed in a hydrogenator along with 1.0 g of Pd/C (catalyst for hydrogenation, in which the surface of the carbon powder has been coated at 5% with palladium metal). The reduction reaction was carried out at 60°C for 3 h under the hydrogen pressure of 50 psi. After filtering the reaction mixture, the obtained solid was recrystallized under ethyl acetate/hexane co-solvent to yield DA-16AM with the reaction yield of 68.0%. The above process was carried out with changing the number of carbon atom in the alkyl group by means of substituting DN-16AM with DN-4AM, DN-6AM, DN-8AM, DN-10AM, DN-12AM, DN-14AM. The yields based on the number of carbon atom in the alkyl group were 95.7 % for DN-4AM, 96.0% for DN-6AM, 89.5% for DN-8AM, 84.0 % for DN-1OAM, 85.3% for DN-12AM, 83.0 % for DN-14AM, respectively.

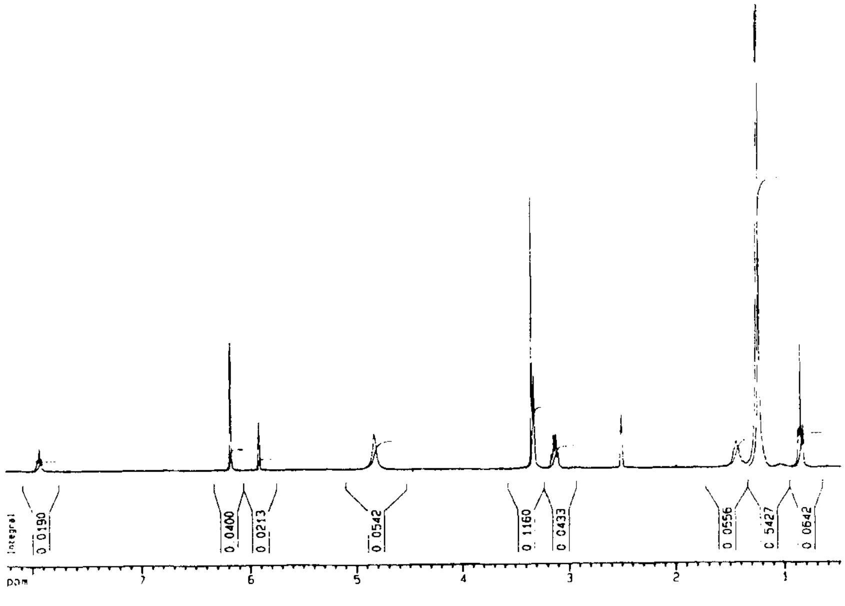
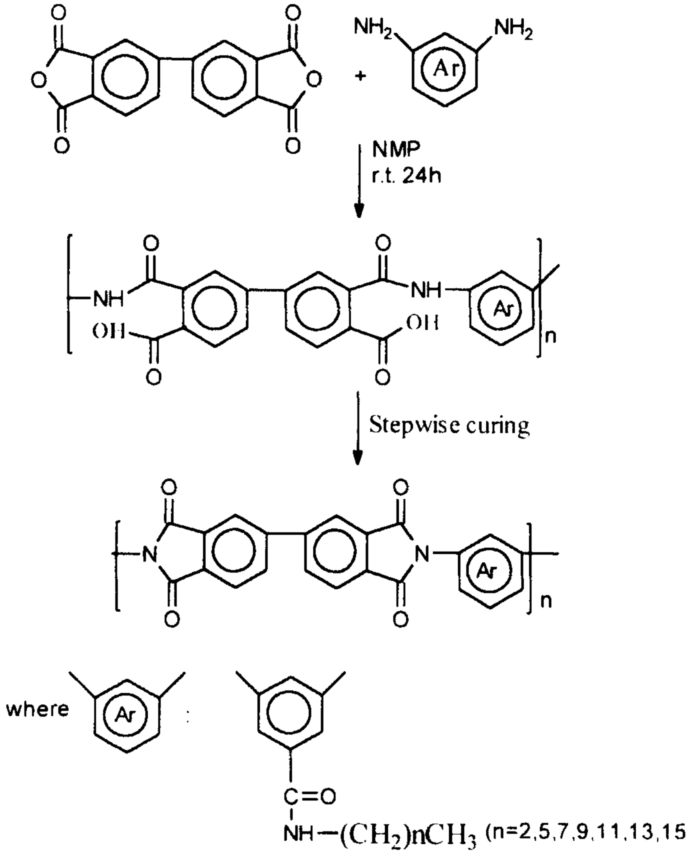


FIGURE 1 ^{1}H-NMR spectrum of DA-16AM (solvent: DMSO-d_6)

Polymer synthesis

The polyimide thin layer was prepared from BPDA and corresponding diamines by two step thermal imidization reaction via polyamic acid formation as shown in scheme 2. As shown in Table II.the inherent viscosities of the polyamic acid measured in NMP were in the range of 0.45 ~ 1.19 dL/g, which was decreased with the increase of alkyl chain length. The glass transition temperature of polyimides measured by DSC were ranged from 247.6 to 291.4 °C, which were found to be controllable due to the fact that the glass transition temperature was indirectly proportional to the length of alkyl substituents. That is, the introduction of long alkyl side group increased the inter-chain distance, which decreased the Tgs as compared to that of unsubstituted one. A typical polymerization procedure is as follows.



SCHEME 2 Synthesis of polyimides

To a solution of DA-16AM (10 mmol, 3.76 g) in 60 mL of freshly distilled NMP, BPDA(10 mmol, 2.94 g) was added at 0~10 °C under nitrogen atmosphere. The reaction mixture was stirred for 24 h at room temperature.

Fabrication of liquid crystal cell

The polyamic acid solution was diluted with NMP to 3~4 wt % and spun onto cleaned indium tin oxide (ITO) coated glass substrates at 2,500 rpm for 25 seconds. After spin coating of polyamic acid onto ITO glass. the imidization reaction was performed at 80°C in vacuo for 1 h and the obtained partially imidized polyimide film was further cured at 150°C and 250 °C each for 1 h under nitrogen atmosphere. 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 μm) was used to control the cell gap. Nematic liquid crystal mixture (BL-002, Merck Ltd.) was injected by capillary method at isotropic temperature (72°C). 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 (θp) of liquid crystal, BL-002 with polyimide layer were measured by the crystal rotation method, which equipment was fabricated in our laboratory.

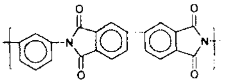
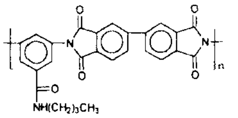
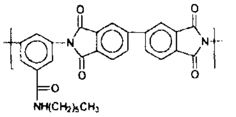
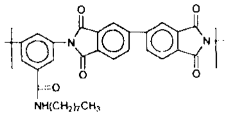
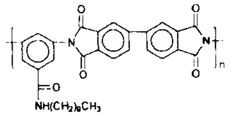
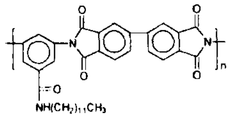
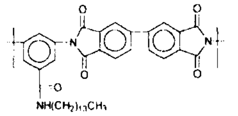
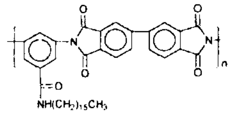
RESULTS AND DISCUSSION

Effect of curing temperature on the pretilt angle

It have been well known that the pretilt angles might be affected by various factors, such as surface morphology of alignment layer, steric effect and electronic interaction of liquid crystal with alignment layer, etc. In this study, we have synthesized a series of novel polyamic acid with various alkyl pendant groups and then cured them at different imidization temperature to investigate the relationship between the pretilt angles and the structure of side chain polymers. As well known, the degree of imidization was increased with increasing curing temperatures, which was usually confirmed by FT-IR spectroscopy. The degree of imidization (D. I) was calculated using eq. 1 where A_{1780} stands for the absorbance of characteristic imide I band and A_{1090} is the absorbance of aromatic -C-H (in plane) band. A fully imidized sample (Ref-PI-7) was prepared by the thermal imidization at 350°C for 1.0 h as a reference film.

$$\text{D.I.}(\%) = \frac{\left(\frac{A_{1780}}{A_{1090}}\right)\ \text{sample film}}{\left(\frac{A_{1780}}{A_{1090}}\right)\ \text{Reference film}}$$

TABLE II Synthesis of Polyimides Containing Pendant Alkyl groups

Polymer	Monomers		Structures	η_{inh}^{c} (dL/g)	Tg[d] (℃)	Pretilt angle[e] (°)
PI(c)-1[a]	m-PDA[b]	BPDA		1.23	336.5	3.3
PI(c)-2	DA-4AM	BPDA		1.19	291.0	8.3
PI(c)-3	DA-6AM	BPDA		0.75	256.9	10.0
PI(c)-4	DA-8AM	BPDA		0.60	245.5	10.3
PI(c)-5	DA-10AM	BPDA		0.74	245.1	10.6
PI(c)-6	DA-12AM	BPDA		0.75	243.1	8.8
PI(c)-7	DA-14AM	BPDA		0.52	247.6	7.8
PI(c)-8	DA-16AM	BPDA		0.45	-	6.0

[a] The imidization reaction was performed at 80℃ in vacuo for 1 h and the obtained partially imidized polyimide film was further cured at 150℃ and 250 ℃ each for 1 h under nitrogen atmosphere.

[b] m-PDA; m-phenylene diamine

[c] Inherent viscosity measured at 30℃ in NMP at a concentration of 0.5 g/dL.

[d] Measured by DSC at a heating rate of 10 ℃/min under nitrogen atmosphere.

[e] Measured by crystal rotation method ($-60° < \theta < 60°$).

In this study, the imidization reaction was performed by various curing schedules to obtain the polyimides with different imidization degree. The curing conditons and the prepared polyimides[PI(a~d)-7] are as follows.

Polyimides	*Curing conditions*
PI(a)-7	at 80°C for lh in vacuo
PI(b)-7	at 80°C for 1h in vacuo → 150°C for 1h under nitrogen atmosphere
PI(c)-7	at 80°C for 1h in vacuo → 150°C, for 1h → 250°C, for 1h under nitrogen atmosphere
PI(d)-7	at 80°C for 1h in vacuo → 150°C, for 1h → 250 °C, for 1 h → 300 °C, for 1h under nitrogen atmosphere
Ref-PI-7	at 80°C for 1h in vacuo → 150 °C. for 1h → 250 °C, for 1h → 300 °C for 1h → 350°C, for 1h under nitrogen atmosphere

As the imidization temperature increased, the intensity of the absorption band (imide I) at 1777~1779 cm^{-1} was gradually increased as compared to that of aromatic -CH band at 1082~1091 cm^{-1}. The dependence of pretilt angle on the curing temperature and degree of imidization is shown Figure 2.

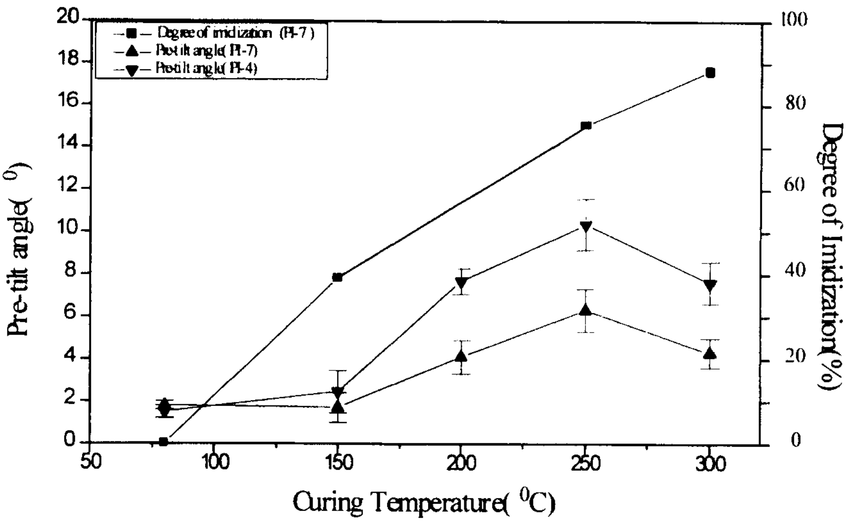


FIGURE 2 Relationship between the pretilt angle of polyimides [PI(a~d)-4, PI(a~d)-7] and the degree of imidization

As can be seen in Figure 2, the pretilt angles considerably increased with the increase of the curing temperature and reached maximum value at 250°C. However, further increase of curing temperature, the pretilt angles slowly decreased in spite of higher degree of imidization, which is contrary to the results of previous study reported by K.W. Lee et al.[10] They reported that the increase of imidization degree of polyimides imparted higher pretilt angles due to the weaker electronic interaction of liquid crystals with polymer surface. However, for the polyimides containing long alkyl side chains prepared in this work, the decomposition reaction of pendant alkyl group was occurred at higher curing temperature than 300°C, which was confirmed by FT IR spectroscopy as well as TGA analysis. As shown in FT-IR spectra of Figure 3, the intensity of C-H stretching band of alkyl side chain at 2850~2930 cm^{-1} compared to that of aromatic -CH band at 1082~1091 cm^{-1} was slowly decreased with increase of the curing temperature. And then, it was remarkably decreased at above the temperature of 300°C. A typical TGA curve of polyimide [PI(c)-7] is shown in Figure 4.

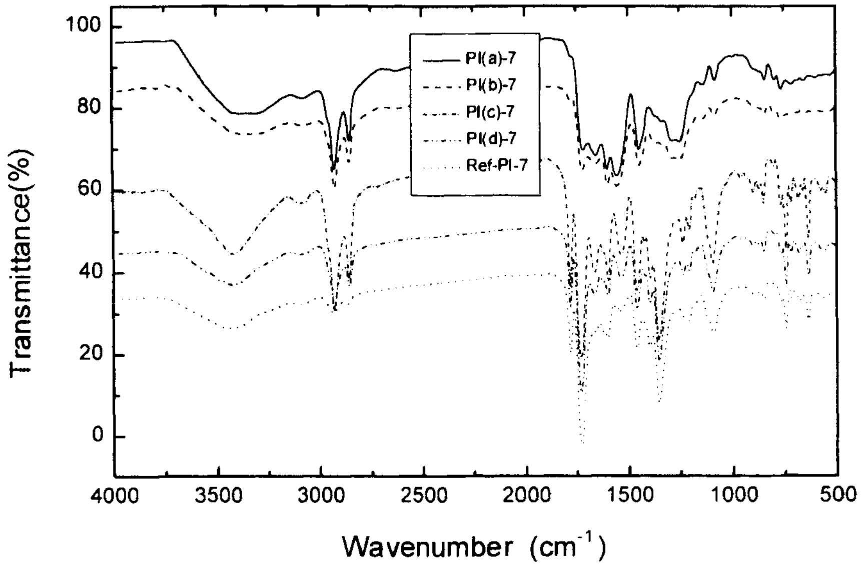


FIGURE 3 FT-IR spectra of polyimide[PI(a~d)-7] cured at different temperatures

As shown in Figure 4, PI(c)-7 underwent two-step degradation at the temperature above 300°C under nitrogen atmosphere. The percent of weight loss (a) of PI(c)-7 during first degradation step was 29.3 %, which is very simmilar to that of theoretical weight percent of pendant tetradecyl group (30.2%). It is assumed that the bond dissociation reaction between nitrogen and carbon atoms of pendant tetradecyl benzamide group was occurred at high temperature curing. That is, as the increase of curing temperature, the degree of imidization was increased, on the other hand, the content of alkyl side chain in polyimide was decreased at the temperature of hihger than 300°C, As'shown in Figure 2 and 4, when the imidization reaction was performed at the temperature of 250°C. The degree of imidization was relatively high (about 80%) and decomposition reaction of pendant alkyl group was hardly occurred, which resulted in highest pretilt angles.

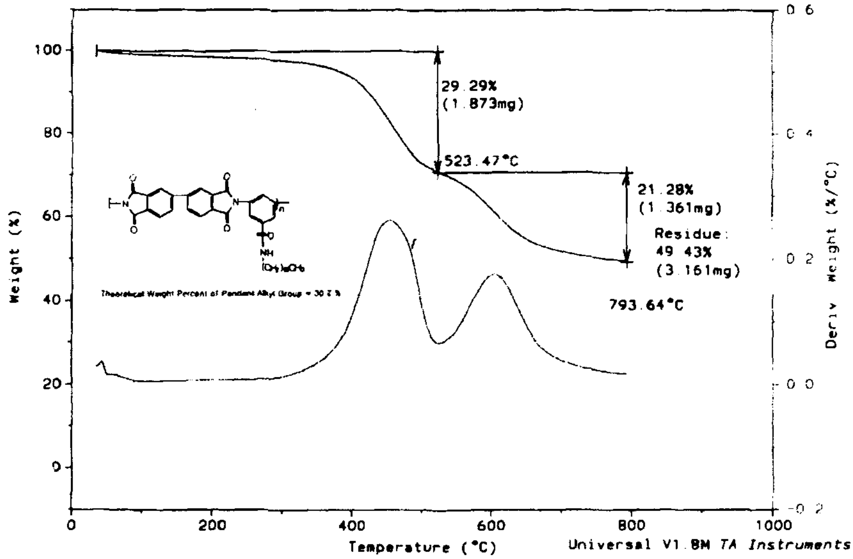


FIGURE 4 Typical TGA curve of polyimide [PI(c)-7]

Effect of alkyl chain length on the pretilt angle

Figure 5 has shown the variation of the pretilt angles with the chain length of the pendant alkyl groups in polyimides. According to the preliminary experiment, the final curing temperature of all polyimides was fixed to 250°C to obtain the highest pretilt angles. As shown in Figure 5. the pretilt angles of the liquid crystal initially was increased by the introduction of pendant alkyl groups, which was increased from 3.3 up to 10.2°. As reported by the previous researchers the introduction of non-polar alkyl substituents resulted in low surface tension and electronic interaction, which might increase the pretilt angles. On the other hand, the pretilt angle was reached the highest value for the polyimide [PI(c)-5] having decyl side group and then decreased with increase of number of carbon in alkyl side chain. It might be assumed that the introduction of alkyl side chains longer than decyl group formed the different surface morphology with those of polyimide [PI(c)-1~ PI(c)-5], which strongly affected on the generation of the pretilt angles.

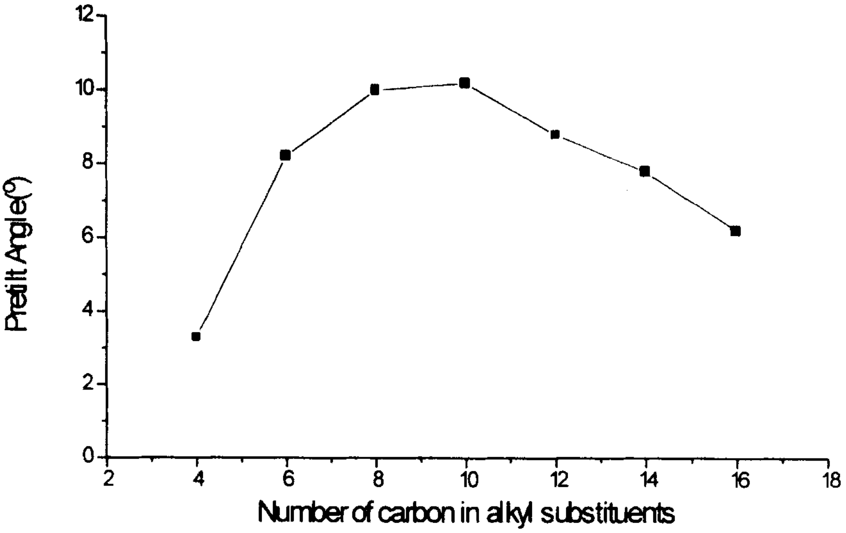


FIGURE 5 Variation of the pretilt angles with the chain length of pendant alkyl groups

CONCLUSION

All of the polyimides containing various pendant alkyl groups exhibited good thermal stability and liquid crystal alignment property. The polyimides with alkyl side chains prepared in this study have superior heat-resistance, excellent liquid crtstal alignment property as well as high pretilt angles, which could be applicable as a liquid crystal alignment layer for the TFT-LCD. Further, the pretilt angles were varied with the length of alkyl side chains as well as the degree of imidization. Especially, the increase of the alkyl chain density resulted in the increase of the pretilt angle, which might be due to the decrease of the surface tension of polyimide film. This results reveals that liquid crystal alignment layer with desired properties could be prepared by the structural modification of polymers.

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