

Synthesis and Liquid-Crystal-Aligning Properties of Novel Aromatic Poly(amide imide)s Bearing *n*-Alkyloxy Side Chains

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ABSTRACT: Novel aromatic poly(amide imide)s (*m*-PAIs, *m* = 8, 12, 16) containing preformed isophthalamide unit and pendent *n*-alkyloxy ($-O-n-C_mH_{2m+1}$, *m* = 8, 12, 16) side chains were prepared in thin films by polymerization of pyromellitic dianhydride (PMDA) with *N,N'*-bis(4-aminophenyl)-5-(*n*-alkyloxy)isophthalamides (*m*-DAs) obtained from *N,N'*-bis(4-nitrophenyl)-5-(*n*-alkyloxy)isophthalamides (*m*-DNs). The *m*-PAI films were tough, flexible and transparent with inherent viscosities in the 1.25–1.67 dL/g range in DMAc and soluble in DMAc and NMP on heating. In TGA *m*-PAIs began to degrade around 440°C and in DSC no phase transitions were detected. In X-ray diffractometry

the *m*-PAIs appeared amorphous with loosely developed layered crystalline structure. In liquid crystal (LC)-aligning performance measured using 4-*n*-pentyl-4'-cyanobiphenyl (5CB) on thin film surfaces rubbed with standard velvet fibers, the *m*-PAIs showed homogeneous LC alignment parallel to the rubbing direction with 2.5–17.5° pretilt angles, depending on the rubbing density and *n*-alkyloxy side chain length. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1793–1801, 2007

Key words: poly(amide imide)s; aromatic di(amide amine)s; *n*-alkyloxy side chains; liquid crystal alignment; Pretilt angle

INTRODUCTION

Aromatic poly(amide imide)s (PAIs) are an important class of high performance polymers having excellent thermal resistance and a favorable balance of physical and chemical properties.^{1,2} Commercial PAIs have been developed as engineering thermoplastic materials, for example, Torlon[®] (Amoco Chemical), and used as electrical wire enamels, adhesives, and various injection and extrusion molding products. They inherit desirable characteristics balanced between those of polyimides and polyamides, showing thermal stability and processability superior to those of polyamides and polyimides, respectively. To further improve processability and solubility of PAIs, several approaches have been used, which include introduction of flexible or asymmetric linkages in the backbone, introduction of bulky pendent groups, and so forth.^{3–10}

The attachment of flexible side chains has been drawing particular interest in polyimide synthesis because it increases not only the processability of polyimides^{11–13} but also the pretilt angle of liquid crystal (LC) molecules when their thin films are used

as LC-aligning layers after they are rubbed.^{14–16} The pretilt angle is the primary parameter determining the optoelectrical performance of thin-film transistor liquid crystal display (LCD) devices. The LCD devices of 90°- or 270°-twisted nematic mode are currently used in industry to manufacture many mobile electronic appliances such as notebook computers and telephone sets. For excellent optical performance with wide viewing angles, high contrast, and fast response time LCD, devices require a pretilt angle greater than 5°.^{17,18}

The present study aims at investigating the effects of introducing pendent flexible *n*-alkyloxy side chains on physical and LC-aligning properties of aromatic PAIs, laying particular emphasis on achieving LC pretilt angles higher than 5° on their rubbed thin films. For this, a series of new poly[*p*-phenyleneimino-5-(*n*-alkyloxy)isophthaloylimino-*p*-phenylene-pyromellitimide]s (*m*-PAIs, *m* = 8, 12, 16) having alternating amide and imide units in their backbone was synthesized by polycondensation of pyromellitic dianhydride (PMDA) with *N,N'*-bis(4-aminophenyl)-5-(*n*-alkyloxy)isophthalamides (*m*-DAs) containing preformed amide linkages and pendent *n*-alkyloxy side chains. As a reference material for characterizing chemical structure and delineating side chain effects, the poly(*p*-phenyleneiminoisophthaloylimino-*p*-phenylene-pyromellitimide) (H-PAI) without *n*-alkyloxy

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side chains was synthesized by polycondensation of PMDA with *N,N'*-bis(4-aminophenyl)isophthalamide (H-DA). After characterizing chemical and morphological structures by spectroscopic and X-ray-diffractometric means solution behaviors, thermal properties and LC-aligning abilities of *m*-PAIs were measured and discussed in respect with their chemical structure.

EXPERIMENTAL

Materials

Isophthaloyl chloride (Aldrich), Pd on charcoal (10%, Aldrich), hydrazine hydrate (Loba Chemie), 4-*n*-pentyl-4'-cyanobiphenyl (5CB, Aldrich) and Disperse Blue 1 dichroic dye (Aldrich) were used as received. *N,N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were distilled over calcium hydride under reduced pressure. PMDA (Aldrich) was sublimed under reduced pressure before use. 4-Nitroaniline (Loba Chemie) was recrystallized from water/ethanol (1/2 v/v) mixture. Triethylamine, *N,N*-dimethylformamide (DMF) and ethanol of reagent grade were purified prior to use in accordance to the literature procedures.¹⁹ 5-(*n*-Alkyloxy)isophthalic acids were prepared as per literature procedure.²⁰ Other organic solvents and inorganic acids and alkalis were used as received unless otherwise described.

Measurements

Inherent viscosities were measured with 0.5% (w/v) solution of polymers in DMAc at 30°C using an Ubbelohde viscometer. FTIR spectra were recorded using PAI films on a Perkin-Elmer 599B spectrophotometer. ¹H-NMR spectra were recorded on a Bruker NMR spectrophotometer at 200 or 500 MHz in DMSO-*d*₆ at room temperature. Solubility of PAIs was determined at 3 wt % concentration in various solvents at room temperature or on heating. Wide-angle X-ray diffractograms were obtained in transmission mode with Ni-filtered Cu *K* α radiation on a Rigaku Geiger Flex Dmax 2500 X-ray diffractometer. Thermogravimetric analyses (TGAs) were performed on Perkin-Elmer TGA-7 analyzer at 10°C/min scan rate in nitrogen atmosphere. Differential scanning calorimetric (DSC) analysis was performed on Perkin-Elmer DSC-7 at 20°C/min heating rate under nitrogen stream. Elemental analyses (EAs) were performed by an Elemental Vario El microanalyzer at the Korea Basic Science Institute, Daegu, Korea.

Synthesis of diamine monomers

Synthesis of *N,N'*-bis(4-nitrophenyl)-5-(*n*-alkyloxy)isophthalamides (*m*-DNs)

Into a 250-mL three-necked round-bottom flask equipped with a dropping funnel and a reflux con-

denser were placed a 5-(*n*-alkyloxy)isophthaloyl chloride or isophthaloyl chloride (0.013 mol) and DMAc (75 mL) and the mixture was magnetically stirred at room temperature for complete dissolution. To this solution Et₃N (3.15 g, 0.031 mol) in DMAc (5 mL) and 4-nitroaniline (4.28 g, 0.031 mol) in DMAc (10 mL) were dropped in sequence and then stirred for 24 h at room temperature. DMAc was removed by distillation under reduced pressure and the residue was poured into a large excess of methanol/water mixture (1/1 v/v) (200 mL). The solids precipitated out were isolated by filtration and washed twice with 50 mL water. The crude product was dried and purified by recrystallization from a mixture of methanol/DMF (1/2 v/v).

N,N'-Bis(4-nitrophenyl)isophthalamide (H-DN). Yield: 87%. M.P. >350°C (Lit. 377, dec.).²¹ IR (KBr pellet, cm⁻¹): 3378 (NH), 1682 (C=O), 1534 and 1340 (NO₂). ¹H-NMR (DMSO-*d*₆, δ ppm): 7.76 (1H, t, ArH *meta* to both C=O), 8.09 (4H, d, ArH *meta* to NO₂), 8.20 (2H, d, ArH *ortho* to NO₂), 8.29 (4H, d, ArH *ortho* to NO₂), 8.58 (1H, s, ArH *ortho* to C=O), 10.89 (2H, br. s, NH).

N,N'-Bis(4-nitrophenyl)-5-(*n*-octyloxy)isophthalamide (8-DN). Yield: 85%. M.P. 262°C. IR (KBr pellet, cm⁻¹): 3378 (NH), 1682 (C=O), 1534 and 1340 (NO₂), 1244 (Ar—O—C). ¹H-NMR (DMSO-*d*₆, δ ppm): 0.85 (3H, t, CH₃), 1.25–1.57 (10H, m, CH₂), 1.65–1.89 (2H, m, CH₂), 4.13 (2H, t, OCH₂), 7.74 (2H, s, ArH *ortho* to ether), 8.10 (4H, d, ArH *meta* to NO₂), 8.16 (1H, s, ArH *ortho* to C=O), 8.26 (4H, d, ArH *ortho* to NO₂), 10.92 (2H, br. s, NH).

N,N'-Bis(4-nitrophenyl)-5-(*n*-dodecyloxy)isophthalamide (12-DN). Yield: 88%. M.P. 251–252°C. IR (KBr pellet, cm⁻¹): 3378 (NH), 1682 (C=O), 1534 and 1340 (NO₂), 1244 (Ar—O—C). ¹H-NMR (DMSO-*d*₆, δ ppm): 0.85 (3H, t, CH₃), 1.21–1.58 (18H, m, CH₂), 1.65–1.89 (2H, m, CH₂), 4.15 (2H, t, OCH₂), 7.75 (2H, s, ArH *ortho* to ether), 8.08 (4H, d, ArH *meta* to NO₂), 8.16 (1H, s, ArH *ortho* to C=O), 8.26 (4H, d, ArH *ortho* to NO₂), 10.90 (2H, br. s, NH).

N,N'-Bis(4-nitrophenyl)-5-(*n*-hexadecyloxy)isophthalamide (16-DN). Yield: 90%. M.P. 153–154°C. IR (KBr pellet, cm⁻¹): 3378 (NH), 1682 (C=O), 1534 and 1340 (NO₂), 1244 (Ar—O—C). ¹H-NMR (DMSO-*d*₆, δ ppm): 0.94 (3H, t, CH₃), 1.21–1.57 (26H, m, CH₂), 1.65–1.89 (2H, m, CH₂), 4.15 (2H, t, OCH₂), 7.75 (2H, s, ArH *ortho* to ether), 8.08 (4H, d, ArH *meta* to NO₂), 8.15 (1H, s, ArH *ortho* to C=O), 8.25 (4H, d, ArH *ortho* to NO₂), 10.90 (2H, br. s, NH).

Synthesis of *N,N'*-bis(4-aminophenyl)-5-(*n*-alkyloxy)isophthalamides (*m*-DAs)

Into a 250-mL three-necked round-bottom flask equipped with a dropping funnel and a reflux condenser were placed ethanol (150 mL), an *m*-DN or

H-DN (0.01 mol), and palladium on charcoal (Pd/C, 10 wt %, 0.19 g, 3 wt % based on dinitro compound). Hydrazine hydrate (15.88 g, 0.32 mol) was added dropwise over a period of 15 min and the mixture was refluxed for 24 h. The reaction mixture was filtered to remove Pd/C and the filtrate was evaporated to dry products in vacuum. The crude products were recrystallized twice from methanol to obtain white crystals.

N,N'-Bis(4-aminophenyl)isophthalamide (H-DA). Yield: 75%. M.P. 245°C (Lit. 242).²¹ IR (KBr pellet, cm^{-1}): 3400–3250 (NH_2 , NH), 1646 (C=O). $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 4.94 (4H, br. s, NH_2), 6.57 (4H, d, ArH *ortho* to NH_2), 7.37 (4H, d, ArH *meta* to NH_2), 7.61 (1H, t, ArH *meta* to both C=O), 8.03 (2H, d, ArH *para* to C=O), 8.43 (1H, s, ArH between two C=O), 10.0 (2H, br. s, CONH).

N,N'-Bis(4-aminophenyl)-5-(*n*-octyloxy)isophthalamide (8-DA). Yield: 78%. M.P. 190°C. IR (KBr pellet, cm^{-1}): 3400–3250 (NH_2 , NH), 1646 (C=O), 1250 (Ar—O—C). $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm; Fig. 1): 0.89 (3H, t, CH_3), 1.15–1.55 (10H, m, CH_2), 1.60–1.80 (2H, m, CH_2), 4.13 (2H, t, OCH_2), 4.96 (4H, br. s, NH_2), 6.60 (4H, d, ArH *ortho* to NH_2), 7.40 (4H, d, ArH *meta* to NH_2), 7.60 (2H, s, ArH *ortho* to ether), 8.05 (1H, s, ArH *ortho* to C=O), 9.99 (2H, br. s, CONH).

N,N'-Bis(4-aminophenyl)-5-(*n*-dodecyloxy)isophthalamide (12-DA). Yield: 73%. M.P. 101°C. IR (KBr pellet, cm^{-1}): 3400–3250 (NH_2 , NH), 1646 (C=O), 1250 (Ar—O—C). $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 0.90 (3H, t, CH_3), 1.15–1.57 (18H, m, CH_2), 1.60–1.80 (2H, m, CH_2), 3.91 (2H, t, OCH_2), 4.96 (4H, br. s, NH_2), 6.60 (4H, d, *ortho* to NH_2), 7.29 (4H, d, ArH *meta* to NH_2), 7.60 (2H, s, ArH *ortho* to ether), 8.04 (1H, s, ArH *ortho* to C=O), 9.96 (2H, br. s, CONH).

N,N'-Bis(4-aminophenyl)-5-(*n*-hexadecyloxy)isophthalamide (16-DA). Yield: 76%. M.P. 87–88°C. IR (KBr pellet, cm^{-1}): 3400–3250 (NH_2 , NH), 1646 (C=O), 1250 (Ar—O—C).

$^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 0.96 (3H, t, CH_3), 1.00–1.55 (26H, m, CH_2), 1.65–1.80 (2H, m, CH_2), 3.91

(2H, t, OCH_2), 4.96 (4H, br. s, NH_2), 6.55 (4H, d, ArH *ortho* to NH_2), 7.39 (4H, d, ArH *meta* to NH_2), 7.60 (2H, d, ArH *ortho* to ether), 8.02 (1H, s, ArH *ortho* to C=O), 9.96 (2H, br. s, CONH).

Polymerization and film preparation

In a 50-mL three-necked round-bottom flask equipped with a nitrogen inlet and a thermometer an *m*-DA or H-DA (2 mmol) was dissolved in dry DMAc (10 mL) under magnetic stirring in nitrogen atmosphere. This solution was cooled to 10°C and PMDA (0.436 g, 2 mmol) was added in portions and then it was allowed to react for 18 h at room temperature. Poly(amic acid) solutions thus obtained were spread onto a glass plate, dried at 80°C and then thermally imidized to thin films by heating successively in vacuum at 100°C, 200°C, and 250°C for 1 h at each temperature.

Poly(*p*-phenyleneiminoisophthaloylimino-*p*-phenylenepyromellitimide) (H-PAI): IR (film, cm^{-1}): 3305 (NH), 1776 and 1715 (C=O, imide I), 1660 (C=O, amide), 1371 (C—N, imide II), 1248 (Ar—O—C), 737 (imide ring).

Poly(*p*-phenyleneimino-5-(*n*-octyloxy)isophthaloylimino-*p*-phenylenepyromellitimide) (8-PAI): IR (film, cm^{-1}): 3300 (NH), 1773 and 1712 (C=O, imide I), 1655 (C=O, amide), 1371 (C—N, imide II), 1242 (Ar—O—C), 737(imide ring). Elemental analysis (EA, wt. %): Calculated for $\text{C}_{38}\text{H}_{32}\text{N}_4\text{O}_7$ (repeat unit); C 69.5, H 4.9, N 8.5, O 17.0 and found; C 69.0, H 5.0, N 8.3, O 19.7.

Poly(*p*-phenyleneimino-5-(*n*-dodecyloxy)isophthaloylimino-*p*-phenylenepyromellitimide) (12-PAI): IR (film, cm^{-1}): 3295 (NH), 1771 and 1713 (C=O, imide I), 1656 (C=O, amide), 1370 (C—N, imide II), 1236 (Ar—O—C), 735 (imide ring). EA (wt %): Calculated for $\text{C}_{42}\text{H}_{40}\text{N}_4\text{O}_7$ (repeat unit); C 70.7, H 5.6, N 7.8, O 15.7 and found; C 68.8, H 5.8, N 7.7, O 17.6.

Poly(*p*-phenyleneimino-5-(*n*-hexadecyloxy)isophthaloylimino-*p*-phenylenepyromellitimide) (16-PAI): IR (film, cm^{-1}): 3294 (NH), 1770 and 1713 (C=O, imide I), 1655 (C=O, amide), 1369 (C—N, imide II), 1236 (Ar—O—C), 736 (imide ring). EA (wt %): Calculated for $\text{C}_{46}\text{H}_{48}\text{N}_4\text{O}_7$ (repeat unit); C 71.8, H 6.3, N 7.3, O 14.5 and found; C 71.0, H 6.4, N 7.2, O 16.6.

LC cell fabrication and pretilt angle measurement

PAI alignment layers were prepared by spin-coating 2 wt % *m*-PAI solutions in NMP at 3500 rpm for 50 s onto clean indium tin oxide-deposited glass substrates (1.7 cm \times 3.4 cm) and by subsequent drying. *m*-PAI films thus obtained were rubbed at varying rubbing density (*L/l*) using a laboratory rubbing machine (Wande) with a roller covered by a rayon velvet fabric (Yoshikawa, YA-20-R). The rubbing density (*L/l*)^{22–24} was varied by changing the cumulative rubbing time for a constant rubbing depth of 0.15 mm:

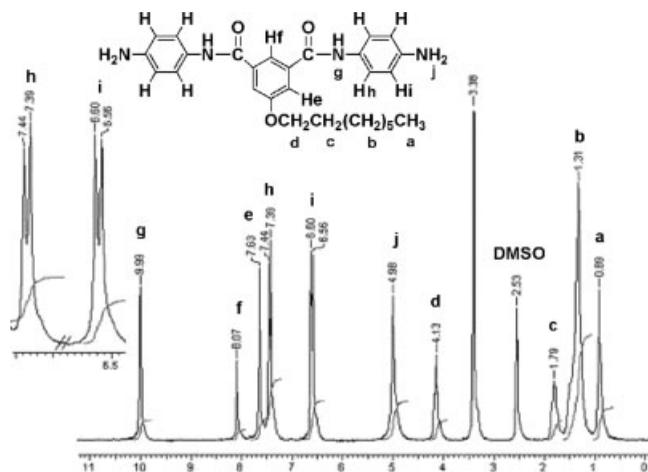


Figure 1 $^1\text{H-NMR}$ spectrum of 8-DA in DMSO- d_6 .

$L/l = N[(2\pi rn/60v) - 1]$, where L (mm) is the total length of the rubbing cloth which contacts a certain point of the m -PAI films, l (mm) is the contact length of the rubbing roller circumference, N is the cumulative number of rubbings, v (cm/s) is the velocity of the substrate stage, n (rpm) and r (cm) are the speed and radius of the rubbing roller, respectively.

To prepare the cells for testing LC alignment behavior, two pieces of the rubbed substrates were assembled in the antiparallel rubbing direction using 50 μm thick spacers and filled with 4-pentyl-4'-cyano-biphenyl (5CB) containing 1.0 wt % Disperse Blue 1 dichroic dye by the capillary method. Then the LC cells were heat-treated for 3 min at 40 $^{\circ}\text{C}$, a temperature higher than the nematic-to-isotropic transition temperature of 5CB, to remove any flow-induced memory arising from the 5CB injection process.

Optical phase retardations to determine LC aligning direction were conducted using a phase retardation analyzer equipped with a photoelastic modulator (Hinds Instruments, PEM 90) bearing a fused silica head, a He-Ne laser with a 632.8 nm wavelength (Spectra Physics, 106-1), a pair of polarizers (Oriol, 27,300), a photodiode detector (UDT Sensors, PIN-10DL), and a pair of lock-in amplifiers (Stanford Research Systems, SR510). The pretilt angles were measured from the fabricated LC cells by a crystal rotation method using a laboratory apparatus equipped with a goniometer, a photodiode detector, a He-Ne laser with 632.8 nm wavelength (Spectra Physics, 106-1), a polarizer-analyzer pair, and a sample stage rotating in out-of-plane direction.

RESULTS AND DISCUSSION

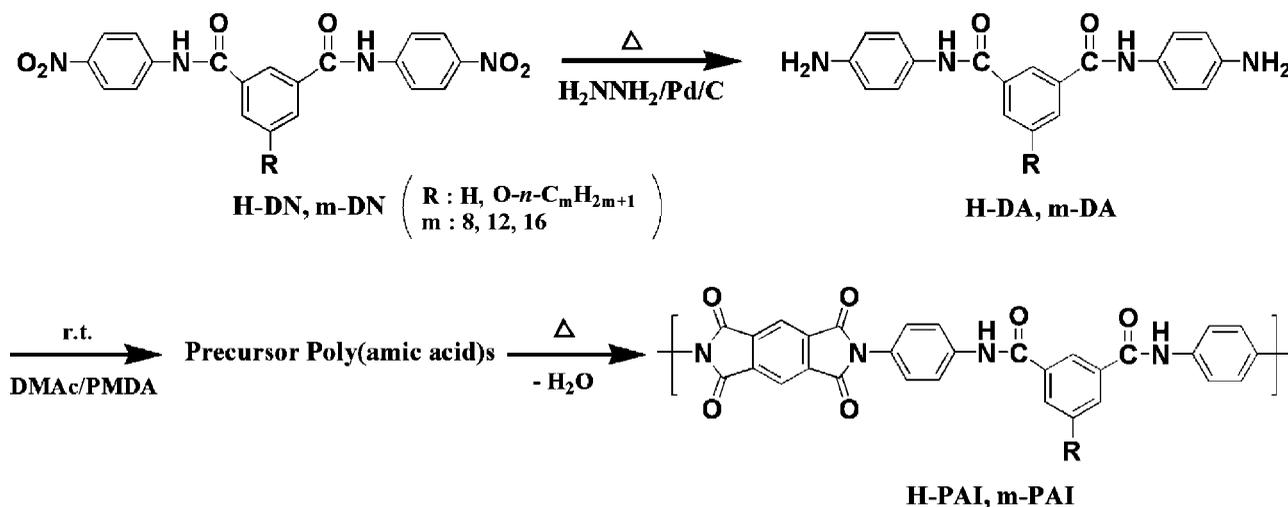
Synthesis of monomers

A series of new aromatic diamine monomers containing preformed amide linkages and pendent n -alkyl-

oxy side chains (m -DAs, $m = 8, 12, 16$) were prepared by condensing 5-(n -alkoxy)isophthaloyl chlorides with stoichiometric amounts of 4-nitroaniline in the presence of Et_3N as HCl scavenger and subsequent catalytic reduction of the corresponding dinitro intermediates (m -DNs, $m = 8, 12, 16$) using hydrazine hydrate, as shown in Scheme 1. An aromatic dinitro compound can be hydrogenated using various reducing agents,²⁵ but in the present work hydrazine hydrate/Pd/C was found to give high yields of the m -DA monomers.

In experimental section (monomer synthesis), melting points and IR and $^1\text{H-NMR}$ spectral data of the dinitro intermediates and the diamine monomers are summarized; $^1\text{H-NMR}$ spectrum of 8-DA monomer is reproduced in Figure 1 as a representative example of m -DAs together with assignment of all the absorption peaks. As can be seen from the characterization data and Figure 1 for 8-DA, all the IR and $^1\text{H-NMR}$ spectral absorptions interpreted are exactly coincident with the chemical structures of the dinitro intermediates and diamine monomers shown in Scheme 1, and it can be concluded that our monomer synthesis was successful.

Melting points of both m -DNs and m -DAs are much lower than that of H-DN and H-DA without side substituent, respectively, and decrease with increasing n -alkoxy side chain length. This is the effect of long side chains incorporated onto the DN and DA because the flexible side chains act as an internal plasticizer toward rigid aromatic backbone at high temperatures close to melting points. The gradual depression of melting points of m -DNs and m -DAs with increasing n -alkoxy side chain length is related with gradual increase in side chain contents providing increased internal plasticization. Such effect should be observable also in m -PAIs having rigid backbones and flexible side chains.



Scheme 1 Synthesis of N,N' -bis(4-aminophenyl)-5-(n -alkoxy)isophthalamide monomers and their polymerization with PMDA.

TABLE I
Solution Behavior and Thermal Stability of Poly(amide imide)s

PAI	η_{inh}^a (dL/g)	Solubility				Thermal stability			
		DMAc	NMP	DMF	MC	T_i (°C)	T_{10} (°C)	W_m (%)	W_{ip} (%)
H-PAI	0.50 ^b	–	–	–	–	515	525	–	–
8-PAI	1.25	+	+	±	±	440	460	37	39.7
12-PAI	1.52	+	+	±	±	440	450	42	44.5
16-PAI	1.67	+	+	±	±	445	450	46	48.6

^a Measured from 0.5 g/dL *m*-PAI solution in DMAc at 30°C.

^b Measured from 0.5 g/dL poly(amic acid) solution in DMAc at 30°C.

+, soluble on heating; ±, partially soluble on heating; –, insoluble; MC, *m*-cresol; T_i , onset temperature of degradation; T_{10} , temperature at 10% weight loss; W_m , weight loss (wt %) measured in the low temperature degradation step; W_{ip} , theoretical (*n*-alkyloxy)isophthaloyl group content of *m*-PAIs (wt %).

Synthesis of polymers

Poly(amide imide)s are commonly prepared either by polyamidation of an imide-unit-containing monomer or by polyimidization of an amide-unit-containing monomer. In this work, the new poly(*p*-phenyleneimino-5-(*n*-alkyloxy)isophthaloylimino-*p*-phenylene-pyromellitimide)s (*m*-PAIs, *m* = 8, 12, 16) were synthesized by polyimidization of PMDA with *N,N'*-bis(*p*-aminophenyl)-5-(*n*-alkyloxy)isophthalamide monomers (*m*-DAs, *m* = 8, 12, 16) containing preformed amide linkages and pendent *n*-alkyloxy side groups. Thus *m*-DA monomers were first polymerized with PMDA at room temperature to obtain the corresponding poly(amic acid)s and the precursors were cast into thin films and then thermally imidized to *m*-PAIs. To vividly show the effect of *n*-alkyloxy side chains of *m*-PAIs on their properties, the poly(*p*-phenyleneiminoisophthaloylimino-*p*-phenylene-pyromellitimide) (H-PAI) without side chain was synthesized as reference material from PMDA and *N,N'*-bis(4-aminophenyl)isophthalamide (H-DA) by the same method of polycondensation and film fabrication as that for *m*-PAIs synthesis.

During the entire polymerization time all the poly(amic acid)s remained homogeneous in DMAc and gradual increase in viscosity could be noticed. To obtain PAIs in 20–30 μm thick films the poly(amic acid) precursors dissolved in DMAc were spread onto clean glass plates and thermally imidized by heating successively at 100°C, 200°C, and 250°C for 1 h at each temperature under reduced pressure. The films were detached from glass plates by soaking into dilute ammonia water and washing thoroughly with water. The films thus obtained were all very tough, flexible and transparent, and they were used for structural characterization and properties measurement.

Inherent viscosities of *m*-PAIs measured in DMAc were in the 1.25–1.67 dL/g range (Table I), indicating that *m*-PAIs of reasonably high molecular weights were obtained by the polymerization. The H-PAI was not soluble in DMAc and other solvents, and its in-

herent viscosity had to be measured for its precursor poly(amic acid).

When a diamine or dianhydride monomer with an *n*-alkyl side group higher than *n*-dodecyl group is polymerized, it is frequently difficult to obtain polymers with high molecular weights on account of the steric hindrance exerted by the highly bulky *n*-alkyl groups.^{24,26} However, in our *m*-DA monomers the bulky groups are positioned so far away from their amino groups that initiate polymerization through their nucleophilic attack at C=O groups of PMDA that they did not exert any negative steric effect for obtaining *m*-PAIs with high molecular weights.

The H-PAI and *m*-PAIs obtained in thin films were characterized by IR spectroscopy and elemental analysis (EA). As to see from experimental section, the C, H, N, and O contents determined for the polymers coincide well with those theoretically calculated. In Figure 2 is reproduced a representative FTIR spectrum of 8-PAI. The bands at 1773 cm⁻¹ (C=O symmetric stretching of imide I), and 1712 cm⁻¹ (C=O asymmetric stretching), 1371 cm⁻¹ (C–N stretching of imide II) and 737 cm⁻¹ (imide ring deformation) confirmed the formation of imide rings. The absorp-

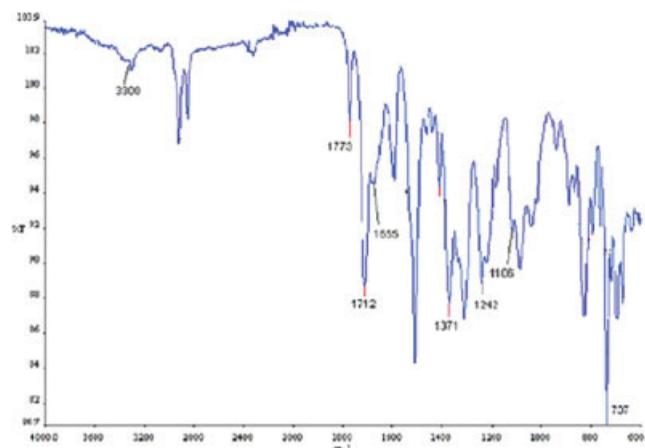


Figure 2 IR spectrum of 8-PAI film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tion bands at 3300 cm^{-1} and 1655 cm^{-1} correspond to N—H and C=O of the amide linkage, respectively. The peak at 1242 cm^{-1} was assigned to Ar—O—C— linkage. In addition, as to see from Figure 2, no absorption ascribable for COOH remaining unimidized can be identifiable. These spectral and EA results indicate that chemical structures of our new *m*-PAIs are identical with those shown in Scheme 1, meaning that our polymers synthesis was successful.

Solubility of polymers

PAI films were tested for solubility at 3 wt % concentration in various polar aprotic solvents and the results are summarized in Table I. As can be seen from Table I, *m*-PAIs were not soluble in DMSO, but on heating they were fully soluble in NMP and DMAc and partially soluble in DMF and *m*-cresol. Once the *m*-PAIs were dissolved by heating, they did not reprecipitate at room temperature. However, H-PAI was not soluble in any of the solvents even on heating.

Solubility of aromatic polymers depends strongly on their chemical structure. Repeat unit of our new *m*-PAIs possessing wholly aromatic backbone comprises a very rigid pyromellitimide ring and two stiff *p*-phenylene units as well as two primary amide links that can exert strong interchain hydrogen bonding. This aspect should contribute to making *m*-PAIs hardly soluble in organic solvents. However, the *m*-PAIs contain also a 120° -kinked isophthaloyl unit and flexible *n*-alkyloxy side chains, both of which should contribute to making *m*-PAIs easily soluble. In addition, the internally plasticizing effect of flexible *n*-alkyloxy side chains on the rigid PAI backbone, which was discussed already, functions as a great factor in enhancing solubility of *m*-PAIs. Hence, solubility of the *m*-PAIs should be determined by the ultimate counterbalance between the negative and positive factors. The higher solubility of *m*-PAIs than that of H-PAI indicates that the positive factors exert higher effect than the negative factors.

For a polymer film to be useful as an LC aligning layer, it should be completely inert to the LC molecules to be used in making LC cells. To check the inertness thin *m*-PAI films were soaked in the LC 4-*n*-pentyl-4'-cyanobiphenyl (5CB) for 24 h at room temperature and their swellability and weight differences before and after soaking were checked. No trace of swelling and weight difference of the films were noticed, indicating that our new *m*-PAIs can be safely used to fabricate LC cells using 5CB for measuring LC aligning direction and pretilt angle.

X-ray diffraction studies of polymers

Morphology of H-PAI and *m*-PAIs was examined by wide-angle X-ray diffractometry and their diffracto-

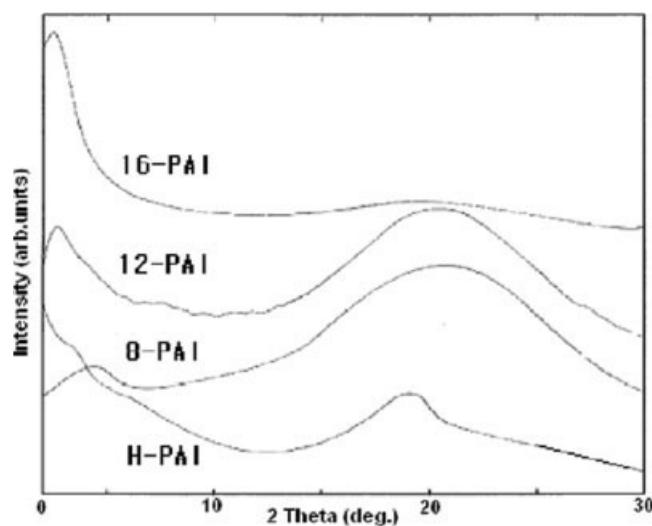


Figure 3 Wide-angle X-ray diffractograms of poly(amide imide)s.

grams are reproduced in Figure 3. It shows that all the polymers exhibit no sharp peaks but only very broad halos in the wide-angle region ($2\theta \approx 15\text{--}22^\circ$), indicating that the polymers are virtually amorphous in their structure. Even though the polymers contain rigid units making favorable for crystallization, the amorphous nature measured experimentally must be attributed to the 120° bent isophthaloyl unit contained in the repeat unit of the polymers, which strongly hinders the chains from packing.

Figure 3 shows also that in the small-angle region ($2\theta \approx 2\text{--}6^\circ$) any intensity maximum is not observable in H-PAI, whereas peaks are identifiable in *m*-PAIs, though fairly broad. The smallest-angle peak of rigid-rod polymers with flexible side chains is the most characteristic of layered crystal structure, in which the Braag *d* spacing increases with increasing side chain length.^{24,27} In Figure 3 it is actually to confirm that the smallest-angle peak shifts to lower angle and hence the Braag *d* spacing increases with increasing side chain length. Even though the increase in the *d* spacings could not be quantitatively analyzed because the smallest-angle peaks appeared too diffuse, the increase signifies that our new *m*-PAIs have layered crystalline structure in solid state.

From Figure 3 it is to see again that the smallest-angle peaks of *m*-PAIs appear fairly diffuse even though 12- and 16-PAI give a bit sharper peak than 8-PAI. Formation of a layer structure is a result of microphase separation between flexible aliphatic *n*-alkyloxy part and rigid aromatic backbone part. 12-PAI and 16-PAI are higher in flexible *n*-alkyloxy side chain content than 8-PAI, and the interaction between their flexible parts should be stronger than that of 8-PAI, indicating that in 12- and 16-PAIs a layer structure is more tightly developed than in 8-PAI. Similar

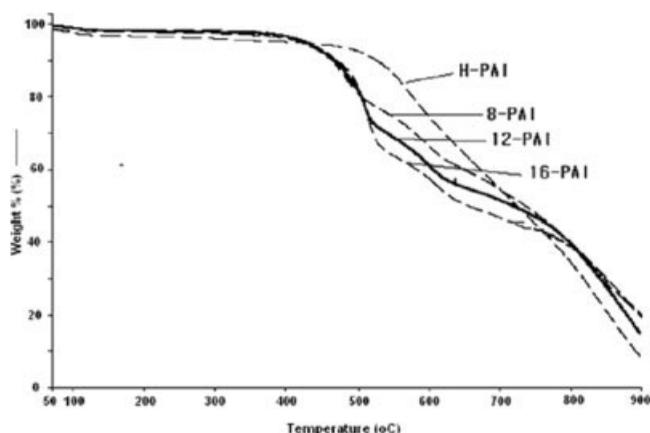


Figure 4 TGA curves of poly(amide imide)s.

observations have been reported for other rigid rod polymers having long flexible side chains.^{24,27–30}

Thermal properties of polymers

Thermal stability of poly(amide imide)s was investigated by TGA at 10°C/min heating rate in nitrogen and their thermograms are reproduced in Figure 4 and numerical values are summarized in Table I. As can be seen from Figure 4, *m*-PAIs begin to degrade around 440°C, meaning that they are excellent in performance as a high-temperature polymer. In Figure 4 is also to see that *m*-PAIs start to degrade at much lower temperature than H-PAI (515°C), meaning that due to the thermally labile *n*-alkyloxy groups *m*-PAIs are much inferior in thermal stability to H-PAI. Such depression in thermal resistance is observed commonly in many rigid aromatic polymers with flexible aliphatic side chains.^{27–30}

Figure 4 shows further that thermal degradation of *m*-PAIs occurs in a stepwise manner, in one step in 440–615°C range and in the other in 615–800°C range. To know which part of the *m*-PAIs degrades away in the lower-temperature step, we calculated theoretical contents of (*n*-alkyloxy)isophthaloyl groups and compared with the weights lost in the step, as shown in Table I. As can be seen from Table I, both the numerical values are fairly well coincident within experimental error. This result indicates that on pyrolysis of *m*-PAIs (*n*-alkyloxy)isophthaloyl groups degrade off first in the 440–615°C range. The lower thermal resistance of (*n*-alkyloxy)isophthaloyl groups is easy to understand because *n*-alkyloxy groups are inherently labile and the 120°-bent isophthaloyl group is not resonance-stabilized with other group contained in the repeat unit of *m*-PAIs.

Thermal phase transitions of poly(amide imide) samples were examined by DSC at scan rates 3°C/min and 10°C/min in nitrogen. Even on repeated scans up to degradation temperatures no samples

showed any T_g s. Such result is probably ascribable for the involvement of the hydrogen bonding, which enhances the interchain attraction so strongly that the local mobility of polymer chains becomes allowable only at higher temperatures than their degradation temperatures. Similar behavior has also been observed in rigid polypyromellitimides with two carboxyl groups in their repeat unit.^{31–33}

Liquid crystal-aligning property

To make thin films for use in fabricating LC cells 2 wt % *m*-PAI solutions in NMP were spin-coated on clean ITO glass substrates and thermally imidized after solvent evaporation. The films were rubbed at the rubbing densities controlled from 60 to 240 by a cumulative number of rubbings. LC cells were fabricated by assembling two pieces of the rubbed films in the anti-parallel rubbing direction using 50- μ m thick spacers and filled with 5CB containing 1.0 wt % Disperse Blue 1 dichroic dye by the capillary method.

Using the cells LC aligning directions were first measured by polar diagrams taken from the optical retardations measured upon in-plane-rotating the LC cells, and in Figure 5 is shown a diagram for the LC cell fabricated with 8-PAI film rubbed at a density of 120 as a representative example. From Figure 5 it is clearly to see that the intensity changes smoothly along the cell rotation angle without any sudden jump or drop and reaches a maximum at 90° and 270° and a minimum at 0° and 180° to the rubbing direction. This signifies that the LC molecules are aligned uniform along the rubbing direction of *m*-PAI films. The 12- and 16-PAIs rubbed at any rubbing densities

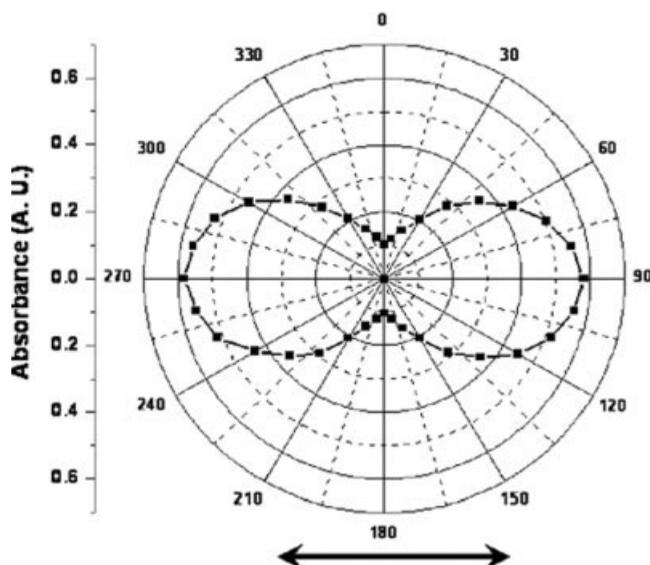


Figure 5 Polar diagram obtained from the LC cell fabricated with 8-PAI film rubbed at a density 120 (Arrow: rubbing direction).

gave the polar diagrams very similar in shape to that of Figure 5. The LC alignment direction parallel to the rubbing direction is easy to understand since some parts of main chains and the flexible *n*-alkyl side chains residing on film surface are deformed and reoriented more or less along the rubbing direction by the mechanical shear of the rubbing, and thereby the interaction between LC molecules and reoriented segments of *m*-PAIs is increased in parallel direction. This increased interaction causes the parallel LC alignment.

The pretilt angle (α) values of 5CB on the rubbed *m*-PAI film surfaces were measured by the crystal rotation method as a function of rubbing density and the results are plotted for each *m*-PAI in Figure 6. Pretilt angle measurement of H-PAI was excluded because any rigid aromatic polymers without flexible side chain are already known to give much lower α value than 5° .²² From Figure 6 it is first to see that at low rubbing densities up to 120 all *m*-PAIs exhibit α 's (9.6 – 17.6°) distinctively higher than 5° . These enhanced angle values are attributable for the effect of incorporated *n*-alkyloxy side chains, which generate their additional interaction with flexible *n*-pentyl moiety of 5CB.

Figure 6 shows also that at rubbing density 120 α of 5CB increases with *n*-alkyloxy side chain length. Although the mechanism of the LC alignment on rubbed surfaces of rigid aromatic polymers with flexible *n*-alkyl side chains is still not fully understood yet, both the van der Waals interaction²² between flexible *n*-pentyl part of 5CB and *n*-alkyl moieties of *m*-PAIs and the polar interaction^{21,34} between cyano group of 5CB and polar groups in the polymer backbone must simultaneously play critical roles in determining the α values. In general the effect of backbone

polar groups is known to be more contributive to α than the hydrophobic interaction of flexible side chains.^{21,34} However, it was recently found that in determining α 's of 5CB on the rubbed surfaces of the poly[3,6-di[4-(*n*-alkyloxy)phenoxy]pyromellitimide)s with flexible *n*-alkyl side chains longer than *n*-octyl, the side chains exert far more dominant effect on elevating α values than the polar imide groups.³⁵ Our *m*-PAIs possess all *n*-alkyl side chains longer than or equal to *n*-octyl in their repeat unit, and the strong hydrophobic interaction leads our *m*-PAIs to giving quite higher α values than 5° when rubbed below the density 120.

In Figure 6 it is to see further that the pretilt angles of all *m*-PAIs decrease at higher rubbing densities than 120 and the decrease is the most remarkable in 16-PAI. It is easy to understand that *m*-PAI with longer side chains will become more ductile and deform more easily by rubbing than *m*-PAI with shorter side chains. Therefore it is reasonable to assume that once a long side chain which has stronger interaction with rigid aromatic backbone than a short side chain is reoriented completely or nearly completely parallel to rubbing direction by a severe rubbing, it must give an $\alpha = 0^\circ$ or nearly 0° (actually 2.5° in 12-PAI and 3.6° in 16-PAI). On the contrary, a short side chain which has only weak interaction with rigid backbone cannot be reoriented completely or nearly completely parallel to rubbing direction by the same severe rubbing, and it will give an α value distinctively greater than 0° (9.5° in 8-PAI). Such behavior is actually observed at the rubbing density of 240. This result indicates that to achieve the pretilt angles higher than 5° , films of 12- and 16-PAIs should not be rubbed at a density higher than 120.

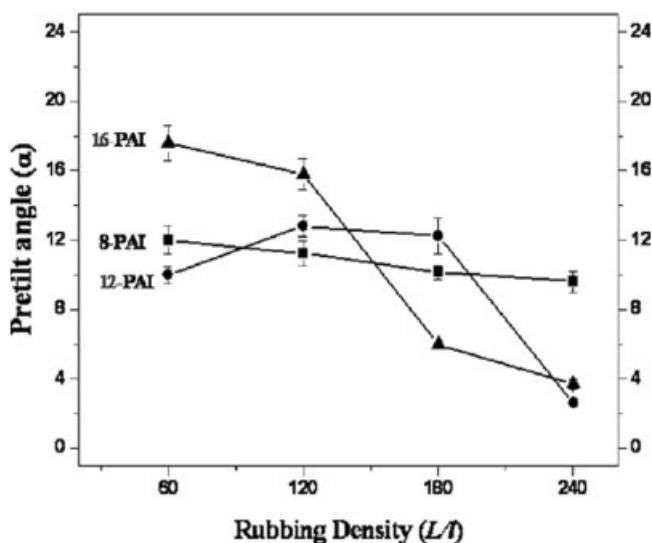


Figure 6 Pretilt angle of LCs on the rubbed surface of *m*-PAIs as a function of rubbing density.

CONCLUSIONS

A series of new aromatic *m*-PAIs possessing preformed isophthalamide unit and pendent flexible *n*-alkyloxy side chains with varying lengths was synthesized by the two step polymerization of *m*-DA monomers with PMDA. The *m*-PAIs obtained had reasonably high molecular weights and revealed considerably higher solubility in polar aprotic solvents on heating than the analogous poly(amide imide) without *n*-alkyloxy side chain (H-PAI). Tough, transparent and flexible films could be cast from solution of *m*-PAIs in NMP or DMAc. In TGA *m*-PAIs revealed somewhat lower thermal stability than H-PAI and showed two-step degradation behavior. In the lower-temperature range the (*n*-alkyloxy)isophthaloyl groups were believed to degrade off. X-Ray diffractograms revealed that *m*-PAIs are essentially amorphous and form only loosely developed layered structures in the solid state. On rubbed surfaces *m*-PAIs

exhibited uniform LC alignment parallel to the rubbing direction with pretilt angles in the 2.5–17.5° range, depending upon the rubbing density and the *n*-alkyloxy side chain length. When rubbed below a density of 120, *m*-PAIs show much higher pretilt angle values than 5°. The angles decreased with increasing rubbing density, and to achieve the angles higher than 5° the films of 12- and 16-PAIs should be rubbed at a density lower than 120. Overall, the *m*-PAIs synthesized in this study exhibited good properties suitable for applications in thin-film transistor LCDs.

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