High Glass Transitions of New Polyamides, Polyimides, and Poly(amide−imide)s Containing a Triphenylamine Group: Synthesis and Characterization

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ABSTRACT: A new triphenylamine-containing diamine monomer, 4,4′-diamino-3″,4″-dimethyltriphenylamine (DADT), was successfully synthesized by the cesium fluoride-mediated condensation of 3,4-dimethylaniline with 4-fluoronitrobenzene, followed by reduction. The monomer was reacted with various aromatic dicarboxylic acids and tetracarboxylic dianhydrides to produce a series of novel polyamides and polyimides, respectively. A new triphenylamine-containing dicarboxylic acid monomer, 4,4′-trimellitimido-3″,4″-dimethyltriphenylamine (TDT), was successfully synthesized by refluxing the diamine, DADT, with trimellitic anhydride in glacial acetic anhydride. A series of new poly(amide−imide)s were prepared from TDT with various diamines by the direct polycondensation. The polymers were obtained in quantitative yields with inherent viscosities of 0.61−2.28 dL g^{-1}. Most of the polymers dissolved in *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, pyridine, and cyclohexanone. These polymers, especially poly(amide−imide)s, showed high glass transition temperatures between 254 and 326 °C. These polymers were fairly stable up to a temperature around or above 400 °C and lost 10% weight in the range of 430−566 and 462−574 °C in nitrogen and air, respectively. These tough and flexible polymer films had a tensile strength of 82−145 MPa, an elongation at break of 5−11%, and a tensile modulus of 1.7−3.3 GPa. The UV−vis absorption spectra revealed that most of the polymers had absorption maxima around 303 nm. Cyclic voltammograms of the polyamides, polyimides, and poly(amide−imide)s showed an oxidation wave with a peak around 0.9, 1.1, and 1.3 V, respectively.

Introduction

Aromatic polyamides and polyimides are well-accepted thermally stable materials.[1] One of the problems in high-temperature polymers is their poor processability caused by low solubility in organic solvents and high melting or softening temperatures. Recently, considerable effort has been made to modify their chemical structure to change their properties with regard to a specific application or to a particular property. Several significant synthetic efforts have been centered on improving processability and solubility through the synthesis of new diamine or dianhydride monomers. The incorporation of bulky substituents[2−7] or bulky pendant groups[8−12] into rigid polymer backbones was very successful. It has been recognized that one of the successful approaches to increase solubility and processability of polyamides and polyimides without sacrificing their high thermal stability is the introduction of a pendant phenyl group into the polymer backbone.[13−15]

Organic charge-transporting materials are important for electrical and optical applications such as organic photoconductor, electroluminescence, and electrochromic devices.[16] To obtain charge-transporting polymers, recently, many investigators have prepared polymers containing triphenylamine units in the main chain.[17−22] Such electroactive sites can be provided by triphenylamines, which are electron-rich aromatics and readily oxidized to form radical cation conducting salts.[18] Son et al.[17] and Ogino et al.[22] have successfully prepared triphenylamine-containing polymers which had hole-transporting ability. Recently, Wu et al.[20,23] reported that the charge injection and electroluminescent efficiency were improved remarkably by the incorporation of the hole-transporting polyimide containing a triphenylamine group in the backbone. Therefore, the introduction of triphenylamine units into the polymer backbone would expect to be a potential structural modification to the rigid polymers such as polyamides, polyimides, and poly(amide−imide)s due to the presence of the bulky pendent phenyl group. In addition, the incorporation of triphenylamine groups in the polyamides and polyimides backbone would allow them to be used as potential hole-transporting materials.[21−23]

In the present article we report the synthesis of a series of new polyamides, polyimides, and poly(amide−imide)s bearing triphenylamine groups based on a new diamine, 4,4′-diamino-3″,4″-dimethyltriphenylamine. The general properties such as solubility, crystallinity, UV−vis spectra, and thermal, mechanical, and electrochemical properties of these polymers will be described herein.

Experimental Section

Materials. 3,4-Dimethylaniline (from ACROS), 4-fluoronitrobenzene (from ACROS), cesium fluoride (from ACROS), anhydrous potassium carbonate (from Merck), hydrazine monohydrate (from Merck), and 10% palladium on activated carbon (Pd−C, from Merck) were used as received. Trimellitic anhydride (from Merck) was purified by sublimation. *N*-Methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), and pyridine were purified by distillation under reduced pressure over calcium hydride before used in polymerization.

Monomer Synthesis (Scheme 1). 4,4′-Dinitro-3″,4″-dimethyltriphenylamine (DNDT). In a 50 mL three-neck

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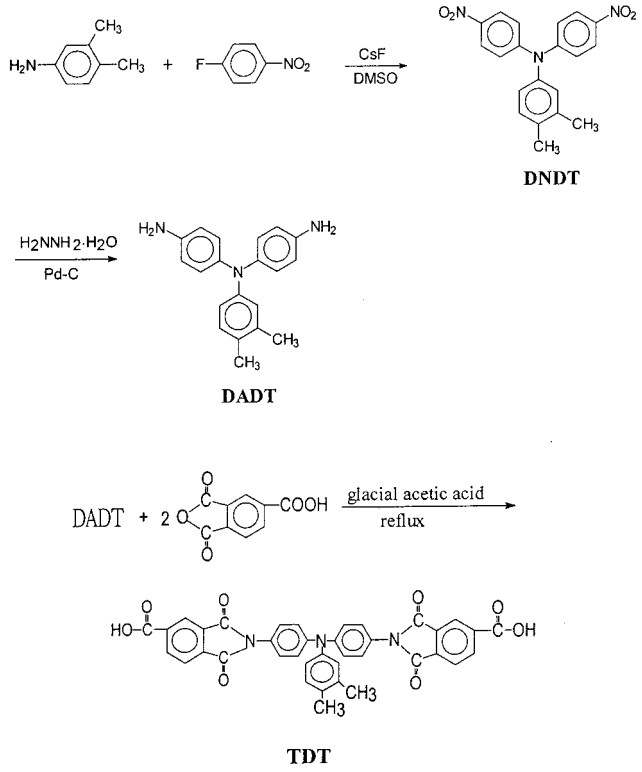
Scheme 1. Synthesis of Triphenylamine Containing Diamine (DADT) and Diimide−Dicarboxylic Acid (TDT)



round-bottom flask was placed 3,4-dimethylaniline (1.8 g, 14.9 mmol), 4-fluoronitrobenzene (4.23 g, 30 mmol), cesium fluoride (4.56 g, 30 mmol), and 15 mL of dimethyl sulfoxide (DMSO). The mixture was heated with stirring at 110 °C for 6 h under argon. The reaction mixture was cooled and then poured into 250 mL of ethanol. The yellow precipitate was collected by filtration and dried under vacuum. The product was purified by recrystallization from glacial acetic acid to afford 4,4′-dinitro-3″,4″-dimethyltriphenylamine (DNDT) in 85% yield; mp 203−204 °C. The IR spectrum (KBr) exhibited absorptions at 1571 and 1334 cm^{-1} (NO_2). ^1H NMR (DMSO-d_6, ppm): 8.17 (d, 4H), 7.27 (d, 1H), 7.18 (d, 4H), 7.06 (s, 1H), 6.99 (d, 1H), 2.25 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (DMSO-d_6, ppm): 152.9, 143.1, 142.9, 140.1, 136.9, 132.5, 129.4, 126.5, 125.9, 122.9, 19.1, 18.7.

Anal. Calcd for $C_{20}H_{17}O_4N_3$: C, 66.11%; H, 4.72%; N, 11.56%. Found: C, 65.87%; H, 4.62%; N, 11.43%.

4,4′-Diamino-3″,4″-dimethyltriphenylamine (DADT). Hydrazine monohydrate (3 mL) was added dropwise to a mixture of DNDT (2.0 g, 5.5 mmol), ethanol (30 mL), and a catalytic amount of 10% palladium on activated carbon (Pd−C, 0.03 g) at the boiling temperature. The mixture became homogeneous after 1 h, and the reaction was refluxed for 24 h. The mixture was then filtered to remove Pd−C. After cooling, the precipitated blue crystals were isolated by recrystallization. It was purified by recrystallized from ethanol and then sublimed before use in polymerization. The yield was 89%; mp 184−185 °C. The IR spectrum (KBr) exhibited absorptions at 3412, 3340, and 1601 cm^{-1} (N−H). ^1H NMR (DMSO-d_6, ppm): 6.83 (d, 1H), 6.74 (d, 4H), 6.52 (d, 5H), 6.43 (d, 1H), 4.86 (s, 4H), 2.07 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (DMSO-d_6, ppm): 149.1, 146.3, 138.4, 137.5, 131.0, 127.9, 127.3, 120.9, 117.1, 115.9, 19.7, 18.4.

Anal. Calcd for $C_{20}H_{21}N_3$: C, 79.17%; H, 6.98%; N, 13.85%. Found: C, 79.20%; H, 7.08%; N, 13.87%.

4,4′-Trimellitimido-3″,4″-dimethyltriphenylamine (TDT). A flask was charged with 1.49 g (4.9 mmol) of 4,4′-diamino-3″,4″-dimethyltriphenylamine (DADT), 2.08 g (10.80 mmol) of trimellitic anhydride, and 15 mL of glacial acetic acid. The heterogeneous mixture was stirred for 1 h and then refluxed for 12 h. The reaction mixture was filtered to yield an orange-yellow solid which was rinsed with methanol to remove acetic acid. The obtained crude product was washed several times with ethanol and then reprecipitated from tetrahydrofuran (THF) into *n*-hexane and dried in a vacuum at 100 °C for 24 h to afford a slightly yellow solid. The IR spectrum (KBr) exhibited absorptions at 2500−3475 (C(O)O−H), 1773, 1714, and 1379 cm^{-1} (imide). Yield: 85%, mp 346.3 °C (by DSC). ^1H NMR (DMSO-d_6): δ (ppm) = 8.36 (d, 2H), 8.24 (s, 2H), 8.01 (d, 2H), 7.37 (d, 4H), 7.16−7.10 (m, 5H), 7.00 (s, 1H), 6.90 (s, 1H), 2.19 (d, 6H). ^{13}C NMR (DMSO-d_6): δ (ppm) = 168.1, 168.0, 167.5, 148.3, 145.5, 139.4, 137.7, 136.8, 136.1, 134.3, 133.2, 132.2, 129.4, 128.3, 126.8, 124.9, 124.8, 124.5, 123.7, 19.3, 16.7.

Anal. Calcd for $C_{38}H_{25}O_8N_3$: C, 67.65%; H, 4.18%; N, 6.45%. Found: C, 67.28%; H, 4.33%; N, 6.13%.

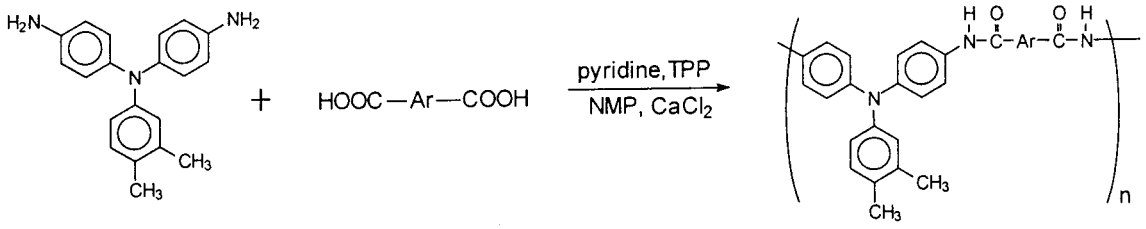
Preparation of Polymers (Schemes 2 and 3). Polyamide PA-1. A flask was charged with a mixture of diamine DADT (0.379 g, 1.25 mmol), terephthalic acid (0.208 g, 1.25 mmol), triphenyl phosphite (0.9 mL), pyridine (0.9 mL), *N*-methyl-2-pyrrolidinone (NMP, 4 mL), and calcium chloride (0.35 g). It was refluxed under argon atmosphere for 3 h. After cooling, the reaction mixture was poured into excess large amount methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried to afford **PA-1**. It was then washed with hot acetone using a Soxhlet extractor. All of the other polyamides (**PA-2**−**PA-6**) were prepared using similar procedures.

Polyimide PI-1. To a stirred solution of DADT (0.379 g, 1.25 mmol) in *N*,*N*-dimethylacetamide (DMAc, 5 mL) was gradually added pyromellitic dianhydride (0.272 g, 1.25 mmol). The mixture was stirred at room temperature for 2 h under an argon atmosphere to form viscous poly(amic acid) solution. Chemical imidization was also carried out by adding additional DMAc and a mixture of acetic anhydride (1 mL) and pyridine (0.5 mL) into the poly(amic acid) solution with stirring at room temperature for 1 h and then heating at 120 °C for 3 h. It was subsequently poured into methanol, and the brown solid precipitate was filtered off, washed with methanol and hot water, and dried to afford **PI-1** solid. Alternatively, the thermal imidization was also taken to produce polyimide film. The above-mentioned poly(amic acid) solution was spread on a glass plate, and the solvent was removed at 80 °C overnight. Imidization was carried out by thermal cyclodehydration of the poly(amic acid) film by sequential heating (2 h at 150 °C, 2 h at 200 °C, 3 h at 250 °C, and 2 h at 300 °C) under vacuum to convert the poly(amic acid) into polyimide. All of the other polyimides (**PI-2**−**PI-6**) were prepared using a similar procedure.

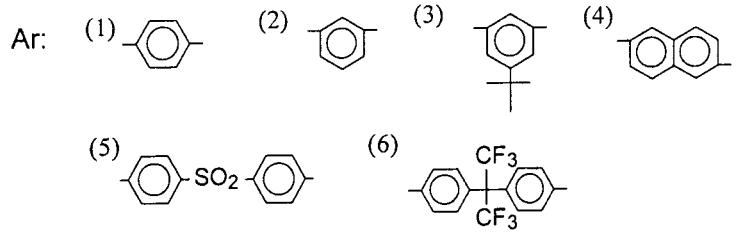
Poly(amide−imide) PAI-1. A mixture of 0.279 g (0.8 mmol) of diamine **DA-1**, 0.521 g (0.8 mmol) of diimide−dicarboxylic acid (TDT), 0.36 g of calcium chloride, 0.8 mL of triphenyl phosphite, 0.8 mL of pyridine, and 4 mL of NMP was refluxed for 3 h. After cooling, the reaction mixture was poured into a large amount methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100 °C under vacuum. Yield: 98%. The inherent viscosity of the polymer in DMAc was 0.87 dL g^{-1}, measured at a concentration 0.5 g dL^{-1} at 30 °C. The IR spectrum (KBr) exhibited absorptions at 3308 (N−H), 1766 (imide C═O), 1712 (C═O imide and amide), and 1373 cm^{-1} (C−N). All other PAIs (**PAI-2**−**PAI-7**) were prepared analogously.

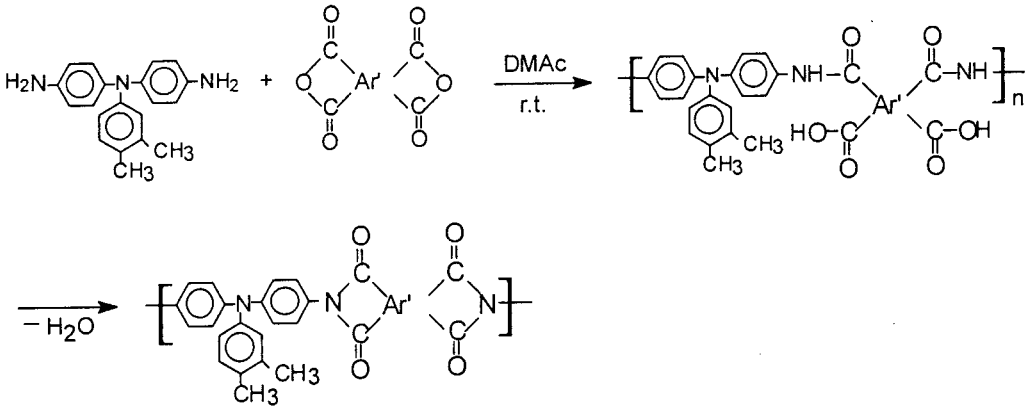
Measurements. Melting points were measured in capillaries on a Büchi apparatus (model BUCHI 535). IR spectra were recorded in the range 4000−400 cm^{-1} on a JASCO IR-700 spectrometer. ^{13}C and ^1H NMR spectra were obtained using a Joel EX-400 operating at 100.40 MHz for carbon and 399.65 MHz for proton. The inherent viscosities of all polyimides were measured using a Ubbelohde viscometer. Elemental analysis was made (Perkin-Elmer 2400 instrument). Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer (Philips model PW 1710) using Ni-filtered Cu−Kα radiation (35 kV, 25 mA). The scanning rate was 3 deg min^{-1}. The

Scheme 2. Preparation of Various Polyamides and Polyimides

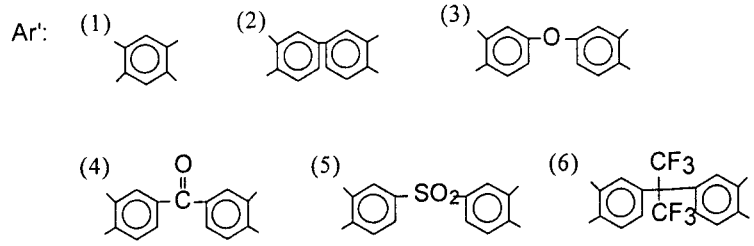


PA-1 − PA-6



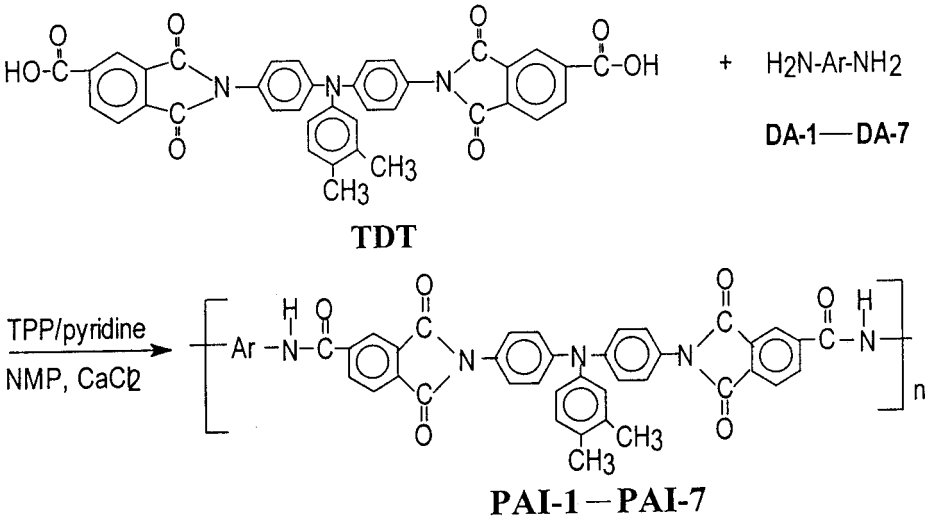


PI-1 − PI-6

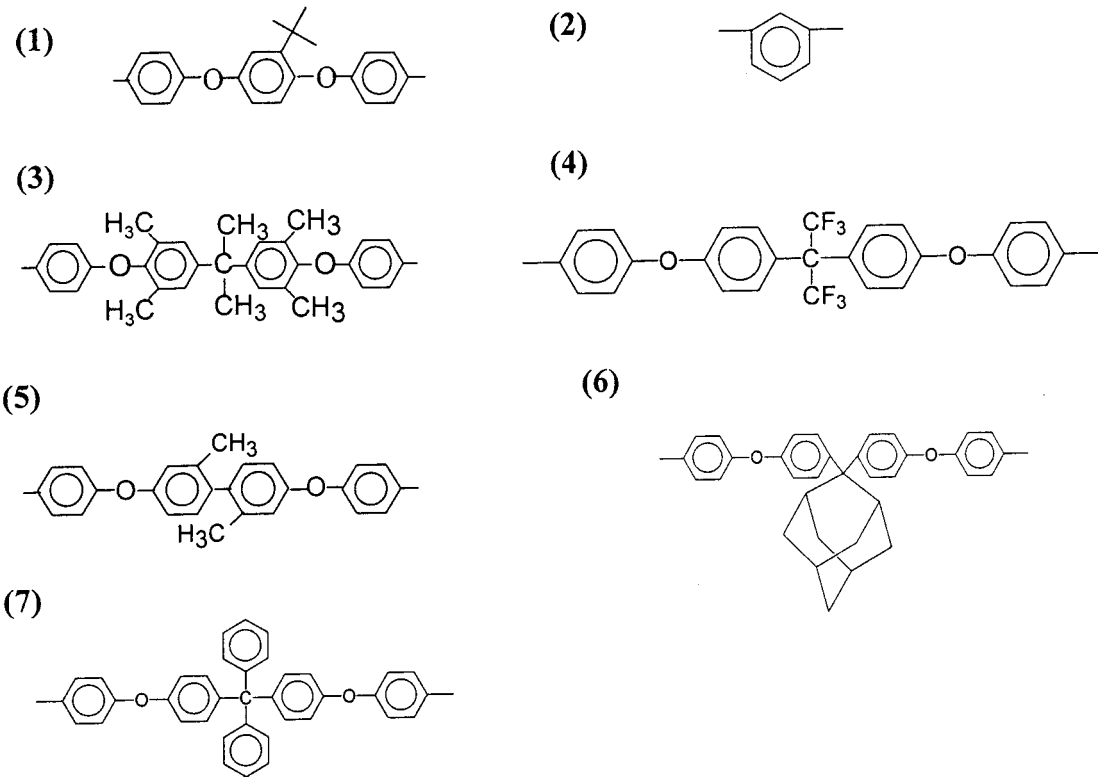


weight-average ($\overline{M_w}$) and number-average molecular weights ($\overline{M_n}$) were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns 300 × 7.7 mm (guard, 10^5, 10^4, 10^3, 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 mL min^{-1}) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard. UV spectra were obtained by a Varian DMS 300 UV−vis spectrophotometer. Thermogravimetric data were obtained on a Du Pont 2100 in flowing nitrogen or air (60 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a DuPont 2000 differential scanning calorimeter. Tensile properties were determined from stress−strain curves obtained with a Orientec Tensilon with a load cell of 10 kg. A gauge of 2.5 cm and a strain rate of 2 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (4 mm wide, 5 cm long, and ca. 0.1 mm thick). The redox behavior was investigated with cyclic voltammetry on an AUTOLAB instruments (PGSTAT30). It was conducted for the dipped polymer film on the platinum working electrode (WE) in dry acetonitrile containing tetrabutylammonium perchlorate (0.1 M) as an electrolyte. A platinum spiral was used as a counter electrode (CE). The scanning rate is 150 mV/s. The in-plane, linear coefficient of thermal expansion (CTE) was obtained from a TA TMA-2940 thermomechanical analyzer (10 °C min^{-1} from 25 to 300 °C, 10 mN). The CTE value on the temperature scale between 50 and 200 °C was recorded after an initial conditioning step (heating to 300 °C, hold 5 min, and cool). Dielectric constants were measured by the parallel plate

Scheme 3. Preparation of Various Poly(amide−imide)s



Ar:



capacitor method using a dielectric analyzer (TA instrument DEA 2970) on thin films. Gold electrodes were vacuum-deposited on both surfaces of dried films at 25 °C.

Results and Discussion

Synthesis of Monomers and Polymers. The synthetic route of the new triphenylamine-containing diamine monomer, 4,4′-diamino-3″,4″-dimethyltriphenylamine (DADT), is outlined in Scheme 1.

The dinitro compound (DNDT) was synthesized successfully by the cesium fluoride-mediated condensation of 3,4-dimethylaniline with 4-fluoronitrobenzene by using cesium fluoride as a base. The catalytic hydrogenation of the dinitro compound DNDT to the diamine compound DADT was accomplished by using hydrazine monohydrate as well as a catalytic amount of Pd−C. In general, reduction of the triphenylamine-containing nitro compounds to amino compounds has carried out using catalytic hydrogenation or treatment of the nitro compounds with acid as well as metal salt. We used the hydrazine/Pd−C system as reducing agent in the present work since it is a convenient and suitable method in the laboratory scale. It was noted that the hydrazine did not react with the triphenylamine group of the dinitro compound and was available for the preparation of diamine. The chemical structures of these newly synthesized compounds were confirmed by the good agreement of the elemental analysis values with those

of the calculated values. In addition, the IR and NMR spectra also supported the formation of the desired compounds having the proposed structures. The diamine monomer DAPT has a UV−vis absorption maximum at 303 nm. It was reported that the triphenylamine-containing compound has a UV absorption maximum around 306 nm.[18] The diimide−dicarboxylic acid (TDT) was obtained by reacting the diamine DADT with 2 mol equiv of trimellitic anhydride (TMA) in the refluxing glacial acetic acid. The diamine was reacted with TMA in glacial acetic acid to form an amic acid intermediate in homogeneous solution at room temperature. In a subsequent cyclodehydration which was carried out at reflux, the diimide−dicarboxylic acid was precipitated from the reaction mixture. The IR spectrum showed absorption bands around 2500−3500 (−OH, carboxylic acid), 1773 (imide C═O asymmetrical stretching), and 1714 cm^{-1} (imide C═O symmetrical stretching and acid C═O stretching), confirming the presence of imide ring and carboxylic acid groups in the structure. The ^1H NMR and ^{13}C NMR spectra data of TDT, listed in the Experimental Section, revealed that carbonyl carbons of carboxylic acid and imide groups resonate in the downfield at 168.1 and 167.5 ppm, respectively. The resonance signal at downfield regions (8.37−8.00 ppm) in the ^1H NMR is ascribed to the protons of trimellitimido group. The area of integration for the protons is in accordance with the assignment. These results provided clear evidence that the diimide−dicarboxylic acid monomer TDT prepared in this study is consistent with the proposed structure.

The preparation of these new polyamides (**PA-1**−**PA-6**) and polyimides (**PI-1**−**PI-6**) are shown in Scheme 2. Polyamides **PA-1**−**PA-6** were prepared from the diamine DADT with various aromatic dicarboxylic acids in NMP by the Yamazaki reaction conditions using triphenyl phosphite (TPP) and pyridine as condensing agents.[30] All polyamides remained soluble in the reaction medium, thus permitting an increase of their molecular weight and giving viscous solutions. The polyamides were produced with moderate to high inherent viscosities ranged from 0.64 to 2.28 dL g^{-1} (Table 1). The polymer **PA-4** exhibited the highest inherent viscosity due to the presence of the rigid naphthalene unit in the polymer backbone. The molecular weight of the polymers was high enough to obtain flexible and tough polymer films by casting from their NMP solutions. The polyimides **PI-1**−**PI-6** were prepared by the conventional two-step method which involved ring-opening polyaddition from equal molar amounts of diamine DADT with various aromatic dianhydrides to form poly(amic acid)s and subsequently cyclodehydration to polyimides. The chemical cyclodehydration of the poly(amic acid) was performed using a mixture of acetic anhydride and pyridine as dehydrating agents. The resulting polyimides **PI-3**, **PI-5,** and **PI-6** which could dissolve in DMAc had inherent viscosities of 0.61−0.98 dL g^{-1} (Table 1). Polymers **PI-5** and **PI-6** exhibited number-average molecular weight ($\overline{M_w}$) and weight-average molecular weight ($\overline{M_w}$) in the range of 41 000−68 000 and 93 000−138 000, respectively. Alternatively, the thermal cyclodehydration of the poly(amic acid) was occurred by heating the poly(amic acid) films to the temperature around 300 °C under vacuum to produce polyimide films. Most of these polyimide films showed tough and flexible nature except those of polymers **PI-1** and **PI-2**. The structures of the polymers were verified by IR spectroscopy. Specifically, polymer **PA-1** showed characteristic absorptions of amide groups occurred around 3300 and 1650 cm^{-1}, due to N−H stretching and carbonyl stretching, respectively. On the other hand, polyimide **PI-1** displayed absorptions at 1771, 1715, and 1370 cm^{-1} assigned to the imide structure.

Table 1. Inherent Viscosity and Molecular Weight of Various Polymers

polymer code	η_{inh}[a] (dL g^{-1})	$\overline{M_n} \times 10^{-4}$ [c]	$\overline{M_n} \times 10^{-4}$ [c]
PA-1	1.03	*d*	*d*
PA-2	0.78	*d*	*d*
PA-3	0.81	*d*	*d*
PA-4	2.28	*d*	*d*
PA-5	0.64	*d*	*d*
PA-6	0.68	*d*	*d*
PI-1	*b*	*d*	*d*
PI-2	*b*	*d*	*d*
PI-3	0.61	*d*	*d*
PI-4	*b*	*d*	*d*
PI-5	0.73	4.1	9.3
PI-6	0.98	6.8	13.8
PAI-1	0.87	3.9	6.1
PAI-2	1.28	*d*	*d*
PAI-3	1.01	*d*	*d*
PAI-4	0.98	3.7	7.4
PAI-5	1.18	*d*	*d*
PAI-6	0.97	*d*	*d*
PAI-7	0.82	2.0	3.4

[a] Measured in DMAc at a concentration of 0.5 g dL^{-1}at 30 °C. [b] Polymer could not be soluble in DMAc or NMP at room temperature. [c] Measured by GPC in THF; polystyrene was used as standard. [d] Polymer could not be soluble in THF at room temperature.

The poly(amide−imide)s (PAIs) were prepared from diimide−dicarboxylic acid (TDT) with various diamines (**DA-1**−**DA-7**) (Scheme 3). All of the polymerizations in NMP proceeded homogeneously, indicating that the polymers showed good solubility in the polymerization media. The PAIs were obtained almost in quantitative yields (yields were above 95%) and had inherent viscosity values ranging between 0.82 and 1.28 dL g^{-1} (Table 1). The polymers **PAI-1, -4,** and **-7** exhibited number-average and weight-average molecular weights in the range of 20 000−39 000 and 34 000−74 000, respectively. The structure of PAIs was confirmed by elemental analysis and IR spectroscopy. IR spectra of these PAIs revealed the characteristic absorptions of imide groups occurred at 1766, 1712, and 1373 cm^{-1}, and those of the amide group occurred around 3308 and 1668 cm^{-1}.

Polymer Characterization. The solubility behavior of the polyamides and polyimides in several organic solvents at 3.0% (w/v) is summarized in Table 2. Most of the polymers exhibited good solubility in a variety of solvents such as NMP, DMAc, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), pyridine, and cyclohexanone at room temperature or upon heating at 70 °C. This result demonstrated that the polymers containing triphenylamine unit displayed good solubility in the organic solvents owing to the presence of the bulky pendent dimethylphenyl group. A chain packing of the polymer chain is probably disturbed by the bulky pendent group. Consequently, the solvent molecules can easily penetrate to solubilize the polymer chain. Among these polyamides, **PA-1** and **PA-4** showed relatively lower solubility due to the presence of rigid phenylene and naphthalene units in their backbone. Among these polyimides, **PI-3**, **PI-5,** and **PI-6** containing kink units

Table 2. Solubility of Various Polymers

polymer code	solvent[a]				
	NMP	DMAc	DMF	DMSO	pyridine
PA-1	+	+−	+−	+−	+−
PA-2	++	++	++	++	++
PA-3	++	++	++	++	++
PA-4	+	+−	+−	+−	+−
PA-5	++	++	++	++	++
PA-6	++	++	++	++	++
PI-1	+−	+−	+−	+−	−
PI-2	−	−	−	−	−
PI-3	++	+	+	+−	++
PI-4	+−	+−	+−	−	+−
PI-5	++	++	++	++	++
PI-6	++	++	++	++	++
PAI-1	++	++	++	++	++
PAI-2	++	++	+	+−	+−
PAI-3	++	++	+	+	+
PAI-4	++	++	++	+	++
PAI-5	++	++	+	+−	+
PAI-6	++	++	+	−	++
PAI-7	++	++	++	−	+−

[a] Solubility: ++ = soluble at room temperature; + = soluble on heating at 60 °C; +− = partial soluble on heating at 60 °C; − = insoluble on heating at 60 °C. Abbreviations: NMP = *N*-methyl-2-pyrrolidinone; DMAc = *N*,*N*-dimethylacetamide; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide; THF = tetrahydrofuran.

showed better solubility than the others. The solubilities of the PAIs in several organic solvents at 3.0% (w/v) are also summarized in Table 2. Remarkably, all these PAIs were easily soluble at room temperature in aprotic polar solvents such as NMP, DMAc, DMF, and DMSO as well as in less polar solvents such as pyridine and tetrahydrofuran. It was noted that polymer **PAI-2** also showed good solubility in polar solvents although it was derived from rigid diamine without ether units. Among these PAIs, polymers **PAI-1**, **-4,** and **-7** containing *tert*-butyl substituent, hexafluoroisopropylidene, and diphenylmethylene units, respectively, showed better solubility than the other PAIs. It was reasonable, since the introduction of a monosubstituted monomer into the polymer chain decreased the order along the chain and enhanced solubility.[24,25] The hexafluoroisopropylidene and diphenylmethylene units are kink units which lowered the rigidity of the polymer backbone and enhanced the solubility of the polymers.[26,27]

The thermal properties of the polyamides and polyimides were evaluated by differential scanning calorimetry (DSC) as well as thermogravimetric analysis (TGA) and are tabulated in Table 3. The DSC thermograms of the polyamides and polyimides, except **PI-1** and **PI-2,** showed high glass transition temperatures in the range of 254−306 °C. One master plot of the DSC T_g scans of PA-5 (A) and PI-3 (B) is provided as Figure 1. The T_g order was comparable to the decreasing order of stiffness and polarity of the polymer backbones. Upon comparison of commercial available polyimides (Ultem 1000, T_g = 215 °C), polyamides [Arlene A (Mitsui Chemical), T_g = 125 °C, Amodel (Amoco), T_g = 120 °C, and Zytel HTN (DuPont), T_g = 135 °C], and poly(amide−imide)s (Amoco, T_g = 272 °C), it was observed that the TPA unit can effectively enhance the glass transition temperature of the polyamides, polyimides, and poly(amide−imide)s. The 10% weight loss temperature ($T_{d,10}$) as well as the anaerobic char yield at 800 °C in nitrogen, measured by TGA, is also summarized in Table 3. All of the polymers exhibited excellent thermal stability. They started to decompose around or above 450 °C and lost 10% weight between 430 and 566 °C and 462 and 574 °C in nitrogen and air atmosphere, respectively. It is interesting to find that most of the polymers showed higher $T_{d,10}$ value in air than in nitrogen atmosphere. The higher $T_{d,10}$ value in air may reflect oxidation of methyl groups in the polymer chain and then causes weight gain.[28] These polymers afforded high anaerobic char yield in the range of 63−72% at 800 °C in a nitrogen atmosphere. It implied that these polymers showed good thermal stability irrespective of introducing methyl groups in the polymer backbone. The PAI copolymers do not exhibit at T_g thermally due to the difference of heat capacity is not large enough to be detected. The thermal properties of the PAIs were evaluated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The results are also tabulated in Table 3. There was no distinct glass transition temperature that could be observed from the heating trace in the differential scanning calorimetry (DSC). Therefore, the T_g value of the polymers was determined by DMA using film species. The T_g values,

Table 3. Thermal Properties of Various Polymers

polymer code	T_g[a] (°C)	$T_{d,10}$[d] (°C)		CTE[e] (ppm/°C)
		in N_2	in air	
PA-1	277	470	491	87.1
PA-2	254	502	515	49.6
PA-3	265	500	528	66.0
PA-4	285	477	505	105.0
PA-5	277	460	462	70.4
PA-6	271	515	525	87.7
PI-1	[b]	558	557	*f*
PI-2	[b]	504	513	*f*
PI-3	285	543	526	62.1
PI-4	303	553	556	75.5
PI-5	306	566	574	55.8
PI-6	290	545	555	58.2
PAI-1	286[c]	441	512	52.3
PAI-2	277[c]	443	518	44.2
PAI-3	326[c]	452	542	53.8
PAI-4	294[c]	430	495	50.4
PAI-5	287[c]	437	529	38.1
PAI-6	325[c]	462	550	40.1
PAI-7	286[c]	447	543	31.9

[a] From DSC measurements conducted at a heating rate of 20 °C min^{-1}. [b] Could not be detected by DSC. [c] From DMA (dynamic mechanical analysis) measurements conducted at a heating rate of 5 °C min^{-1}. [d] Temperature at 10% weight loss ($T_{d,10}$) was determined by TGA at a heating rate of 20 °C min^{-1}. [e] Thermal expansion coefficient (CTE) was measured from TMA measurements conducted at a heating rate of 10 °C min^{-1} from 25 to 300 °C. [f] Polymers were too brittle to be measured.

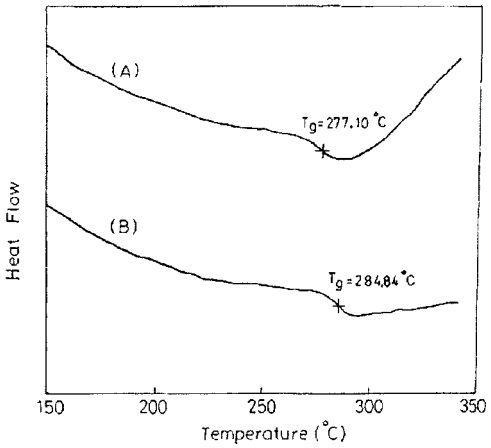


Figure 1. DSC scan diagram of polymers (A) **PA-5** and (B) **PI-3**.

Table 4. Mechanical and Dielectric Properties of Various Polymers

polymer code	tensile strength (MPa)	elongation at break (%)	tensile modulus (GPa)	dielectric constant (dry, 1 kHz)
PA-1	133	8	2.9	4.02
PA-2	90	5	2.2	4.21
PA-3	139	11	2.5	3.89
PA-4	145	6	3.3	4.66
PA-5	119	7	2.5	3.94
PA-6	113	11	2.6	3.81
PI-1	*a*	*a*	*a*	*a*
PI-2	*a*	*a*	*a*	*a*
PI-3	90	10	2.0	3.74
PI-4	82	9	2.2	3.57
PI-5	92	6	2.3	3.62
PI-6	108	6	2.2	3.89
PAI-1	89	7	1.7	3.67
PAI-2	114	11	2.3	4.93
PAI-3	102	9	2.0	4.22
PAI-4	95	8	1.9	3.61
PAI-5	108	10	2.1	4.64
PAI-6	97	7	1.9	3.92
PAI-7	85	6	1.7	3.67

[a] Polymers were too brittle to be measured.

measured by DMA, were found in the range of 277−326 °C. Among these PAIs, polymer **PAI-6** having bulky and stiff pendant adamantane group showed a high T_g value of 325 °C. In general, the chain rigidity was increased due to the pendent cardo group, which restricted the free rotation of the polymer backbone. Hence, the obtained polymers could show high glass transition temperature.[29] These polymers including polyamides, polyimides, and poly(amide−imide)s have CTEs of 31.9−105.0 (ppm/°C) (Table 3), because that polyimides (**PI-3**−**PI-6**) have bent ether units groups. These bent units loosen the films' packing.[34] In addition, producing a polyimide film from polyimide solution generally yields a lower CTE than from the corresponding poly(amic acid).[34] Concerning the CTEs of polyamide and poly(amide−imide), the value of CTEs is similar to commercial polyamide and poly(amide−imide). The mechanical properties of the polyamide and polyimide films are summarized in Table 4. The polymer films had a tensile strength of 82−145 MPa, an elongation at break of 5−11%, and a tensile modulus of 2.0−3.3 GPa. Most of the polymer films exhibited high tensile strength; thus, they could be considered as strong materials. It was observed that polymer **PA-4** with a rigid naphthalene unit showed the highest tensile strength and modulus. The mechanical properties of the PAI films are also collected in Table 4. The films had a tensile strength of 85−114 MPa, an elongation at break range of 6−11%, and a tensile modulus range of 1.7−2.3 GPa. Most of the polymer films exhibit high tensile strength, indicating that they are strong materials. It is interesting to find that polymer **PAI-7** with diphenylmethylene unit showed the lowest tensile strength and modulus due to the presence of the kink unit. In general, the presence of the kink unit lowers the rigidity of the polymer chain.[27,28] These polymers have a dielectric constant of 3.57−4.93. The value of the dielectric constant of polyimides (**PI-3**−**PI-6**) is similar to that of polyimide derived from polyalicyclic bicyclo[2.2.2]octane−2,3,5,6-tetracarboxylic 2,3:5,6-dianhydride.[33] Concerning the dielectric constant of polyamides and poly(amide−imide)s, the value of dielectric constant is similar to that of commercial polyamides and poly(amide−imide)s. The optical properties of the polyamides and polyimides,

Table 5. UV−vis Absorption of Various Polymers[a]

polymer code	λ_{max} (nm)	polymer code	λ_{max} (nm)
PA-1	*b*	**PI-5**	303
PA-2	334	**PI-6**	300
PA-3	345	**PAI-1**	324
PA-4	*b*	**PAI-2**	323
PA-5	300	**PAI-3**	327
PA-6	301, 335	**PAI-4**	320
PI-1	*b*	**PAI-5**	321
PI-2	*b*	**PAI-6**	322
PI-3	309	**PAI-7**	323
PI-4	*b*		

[a] UV−vis absorption of polymers was measured in NMP solution. [b] Polymer could not be dissolved in NMP.

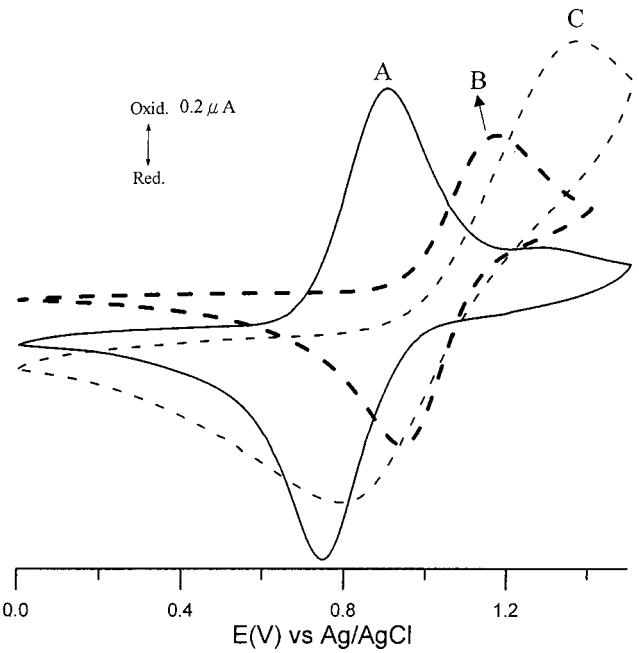


Figure 2. Cyclic voltammogram of polymers (A) **PA-5**, (B) **PI-5**, and (C) **PAI-2** I in acetonitrile with 0.1 M Bu_4NClO_4. Scanning rate 150 mV/s.

particularly their UV−vis absorption in NMP solution, were investigated. The UV absorption data of the polymers which could dissolve in NMP are listed in Table 5. The UV absorptions of poly(amide−imide)s have also been listed in Table 5. Most of the polymers including polyamides, polyimides, and poly(amide−imide)s had absorption maxima at 300−309 and 320−345 nm assignable to the $\pi \rightarrow \pi^*$ transition resulting from the conjugation between the aromatic rings and nitrogen atoms.[31] It could be observed that the absorption spectra of the polyamides displayed a red shift compared with those of polyamides. This supports that polyamides possesses a longer effective chromophore.[5]

Charge transport in organic materials is believed to be governed by the hopping process involving redox reaction of charge transport molecules. Cyclic voltammetry (CV) is a preliminary characterization method to determine the redox properties of polymeric materials. Figure 2 shows the representative cyclic voltammogram of polymers **PA-5**, **PI-5**, and **PAI-2**. One pair of redox waves was observed in these polymers. As shown in this figure, polyamide **PA-5** showed an oxidation wave of which a peak top is at 0.88 V (versus Ag/AgCl) and a reduction wave at 0.74 V. In contrast, polyimide **PI-5** showed a higher oxidation potential than the polyamides and showed a peak top at 1.18 V. It was observed

that polyamide (Figure 2, curve A) is more reversible than polyimide (Figure 2, curve B) and poly(amide−imide) (Figure 2, curve C) due to the large ability of electron donating of polyamide than polyimide and poly(amide−imide).[32] The difference of the oxidation potential between polyamides and polyimides is due to the fact that the oxidized triarylamine unit has an electrochemical effect on the adjacent units.[23] It was observed that the intensity of redox peaks decreased as cycle time increased, which can be explained by the dissolution of ionized polymer into the solvent. The polymer displayed an electrochromic property, as they were transformed from the orange neutral form to the blue oxidized form.

Conclusions

This study successfully prepared the new diamine DADT and diimide−dicarboxylic acid TDT containing a triphenylamine group. The polyamides and polyimides were prepared from DADT with various dicarboxylic acid and dianhydride, respectively, with moderate to high inherent viscosity. The diimide−dicarboxylic acid TDT reacted with various diamines, yielding various new poly(amide−imide)s. Most of the polyamides, polyimides, and poly(amide−imide)s exhibited good solubility, high glass transition temperature, thermal decomposition temperature, and tensile properties. Results presented herein also demonstrated that incorporating bulky dimethylphenyl group into polymer backbone enhanced the processability of the rigid polymer backbone while maintaining good thermal stability. Thus, the present polyamides, polyimides, and poly(amide−imide)s are considered as new promising processable high-temperature polymeric materials. The investigation of electrochemical properties suggests that most of these new polymers have a potential as the type of hole-transporting materials.

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Appendix

(A) 4,4′-Dinitro-3″,4″-dimethyltriphenylamine (DNDT). IR spectrum: 1571 and 1334 cm^{-1} (NO_2). ^1H NMR (DMSO-d_6, ppm): δ 8.17 (d, 4H), 7.27 (d, 1H), 7.18 (d, 4H), 7.06 (s, 1H), 6.99 (d, 1H), 2.25 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (DMSO-d_6, ppm): δ 152.9, 143.1, 142.9, 140.1, 136.9, 132.5, 129.4, 126.5, 125.9, 122.9, 19.1, 18.7.

(B) 4,4′-Diamino-3″,4″-dimethyltriphenylamine (DADT). IR spectrum: 3412, 3340, and 1601 cm^{-1} (N−H). ^1H NMR (DMSO-d_6, ppm): δ 6.83 (d, 1H), 6.74 (d, 4H), 6.52 (d, 5H), 6.43 (d, 1H), 4.86 (s, 4H), 2.07 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (DMSO-d_6, ppm): δ 149.1, 146.3, 138.4, 137.5, 131.0, 127.9, 127.3, 120.9, 117.1, 115.9, 19.7, 18.4.

(C) 4,4′-Trimellitimido-3″,4″-dimethyltriphenylamine (TDT). IR spectrum: 2500−3475 (C(O)O−H), 1773, 1714, 1379 cm^{-1} .^1H NMR (DMSO-d_6): δ (ppm) = 8.36 (d, 2H), 8.24 (s, 2H), 8.01 (d, 2H), 7.37 (d, 4H), 7.16−7.10 (m, 5H), 7.00 (s, 1H), 6.90 (s, 1H), 2.19 (d, 6H). ^{13}C NMR (DMSO-d_6): δ (ppm) = 168.1, 168.0, 167.5, 148.3, 145.5, 139.4, 137.7, 136.8, 136.1, 134.3, 133.2, 132.2, 129.4, 128.3, 126.8, 124.9, 124.8, 124.5, 123.7, 19.3, 16.7.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymer*; Dekker: New York, 1980; Chapter 4.
(2) Liaw, D.-J.; Liaw, B.-Y. *Macromol. Symp.* **1997**, *122*, 343.
(3) Jeong, H.-J.; Oishi, Y.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3193.
(4) Yagci, H.; Mathias, L. J. *Polym. Prepr.* **1998**, *39* (1), 262.
(5) Spiliopoulos, I. K.; Mikroyannidis, J. A.; Tsivgoulis, G. M. *Macromolecules* **1998**, *31*, 522.
(6) Liaw, D.-J.; Liaw, B.-Y.; Li, L.-J.; Sillion, B.; Mercier, R.; Thiria, R.; Sekiguchi, H. *Chem. Mater.* **1998**, *10*, 734.
(7) Sun, X.; Yang, Y.-K.; Lu, F. *Macromolecules* **1998**, *31*, 4291.
(8) Akutsu, F.; Inoki, M.; Araki, K.; Kasashima, Y.; Naruchi, K.; Miura, M. *Polym. J.* **1997**, *29*, 529.
(9) Lozano, A. E.; Abajo, J. de.; Campa, J. G. de la.; Preston, J. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1987.
(10) Park, K. H.; Tani, T.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1767.
(11) Kasashima, Y.; Kumada, H.; Yamamoto, K.; Akutsu, F.; Naruchi, K.; Miura, M. *Polymer* **1995**, *36*, 645.
(12) Yi, M.-H.; Huang, W.; Jin, M.-Y.; Choi, K.-Y. *Macromolecules* **1997**, *30*, 5606.
(13) Oishi, Y.; Ishida, M.; Kakimoto, M.; Imai, Y.; Kurosaki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1027.
(14) Liaw, D.-J.; Liaw, B.-Y.; Yang, C.-M. *Macromolecules* **1999**, *32*, 7248.
(15) Huang, S.-J.; Hoyt, A.-E. *Trends Polym. Sci.* **1995**, *3*, 262.
(16) Son, J.-M.; Nakao, M.; Ogino, K.; Sato, H. *Macromol. Chem. Phys.* **1999**, *200*, 65.
(17) Son, J.-M.; Mori, T.; Ogino, K.; Sato, H.; Ito, Y. *Macromolecules* **1999**, *32*, 4849.
(18) Tan, L.-S.; Srinivasan, K. R.; Bai, S.-J. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1909.
(19) Nishikata, Y.; Fukui, S.; Kakimoto, M.; Imai, Y.; Nishiyama, K.; Fujihira, M. *Thin Solid Films* **1992**, *210/211*, 296.
(20) Wu, A.; Jikei, M.; Kakimoto, M.; Imai, Y.; Ukishima, S.; Takahashi, Y. *Chem. Lett.* **1994**, 2319.
(21) Tak, Y.-H.; Mang, S.; Greiner, H.; Bassler, A.; Pfeiffer, S.; Horhold, H. H. *Acta Polym.* **1997**, *48*, 450.
(22) Ogino, K.; Kanegae, A.; Yamaguchi, R.; Sato, H.; Kurjata, J. *Macromol. Rapid Commun.* **1999**, *20*, 103.
(23) Wu, A.; Kakimoto, M. *Adv. Mater.* **1994**, *7*, 812.
(24) Heitz, W.; Niessner, N. *Makromol. Chem.* **1990**, *191*, 225.
(25) Schmidt, H. W.; Guo, D. *Makromol. Chem.* **1988**, *189*, 2029.
(26) Liaw, D.-J.; Wang, K.-L. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1209.
(27) Park, J. W.; Lee, M.; Lee, M.-H.; Liu, J.-W.; Kim, S.-D.; Chang, J.-Y. Rhee, S.-B. *Macromolecules* **1994**, *27*, 3459.
(28) Liaw, D.-J.; Liaw, B.-Y.; Chen, J.-R.; Yang, C.-M. *Macromolecules* **1999**, *32*, 6860.
(29) Korshak, V. V.; Vinogradova, S. V.; Vygodski, Y. S. *J. Macromol. Sci., Rev. Macromol. Chem.* **1974**, *C11*, 45.
(30) Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1373.
(31) Ogino, K.; Kanegae, A.; Yamaguchi, R.; Sato, H.; Kurjata, J. *Macromol. Rapid Commun.* **1999**, *20*, 103.
(32) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.
(33) Matsumoto, T.; Kurosaki, T. *Macromolecules* **1997**, *30*, 993.
(34) Trofimenko, S.; Auman, B. C. *Macromolecules* **1994**, *27*, 1136.

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