Synthesis and Properties of New Soluble Triphenylamine-Based Aromatic Poly(amine amide)s Derived from *N,N′*-Bis(4-carboxyphenyl)-*N,N′*-diphenyl-1,4-phenylenediamine

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ABSTRACT: A new triphenylamine-containing aromatic dicarboxylic acid, *N,N′*-bis(4-carboxyphenyl)-*N,N′*-diphenyl-1,4-phenylenediamine, was synthesized by the condensation of *N,N′*-diphenyl-1,4-phenylenediamine with 4-fluorobenzonitrile, followed by the alkaline hydrolysis of the intermediate dinitrile compound. A series of novel triphenylamine-based aromatic poly(amine amide)s with inherent viscosities of 0.50–1.02 dL/g were prepared from the diacid and various aromatic diamines by direct phosphorylation polycondensation. All the poly(amine amide)s were amorphous in nature, as evidenced by X-ray diffractograms. Most of the poly(amine amide)s were quite soluble in a variety of organic solvents and could be solution-cast into transparent, tough, and flexible films with good mechanical properties. They had useful levels of thermal stability associated with glass-transition temperatures up to 280 °C, 10% weight-loss temperatures in excess of 575 °C, and char yields at 800 °C in nitrogen higher than 60%. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 41: 94–105, 2003

Keywords: aromatic poly(amine amide)s; new diacid monomers; triphenylamine unit; solubility; thermal properties; amorphous; high-performance polymers; polycondensation

INTRODUCTION

Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, rigidity of the backbone and strong hydrogen bonding result in high melting temperatures or glass-transition temperatures (T_g's) and limited solubility in most organic solvents.[1,2] These properties make them generally intractable or difficult to process, restricting their applications. Therefore, a great deal of effort has been expended to improve the processing characteristics of the relatively intractable polymers.[3–14] These studies include introducing flexible segments into the polymer chain; replacing symmetrical aromatic rings with unsymmetrical ones, which leads to a reduction in crystallinity; introducing bulky pendant groups to minimize crystallization; and forming a noncoplanar structure, thereby making crystallization impossible. Generally, it is

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known that one of the successful approaches for increasing the solubility and processability of polyamides without sacrificing high thermal stability is the introduction of bulky pendant phenyl groups into the polymer backbone.[15–17] Nevertheless, little is known to date about aromatic polyamides having phenyl–pendant aromatic amine units in the polymer backbone, that is, poly(amine amide)s. The only examples are poly(amine amide)s derived from 4,4′-diaminotriphenylamine[17] and *N,N′*-bis(4-aminophenyl)-*N,N′*-diphenyl-1,4-phenylenediamine.[18] As a continuation of these studies, we have designed new triphenylamine-based poly(amine amide)s with a 1,4-phenylene backbone to elucidate the effect of the backbone structure on the properties of poly(amine amide)s. This work deals with the synthesis and basic characterization of novel aromatic poly(amine amide)s derived from *N,N′*-bis(4-carboxyphenyl)-*N,N′*-diphenyl-1,4-phenylenediamine (**3**), a triphenylamine-containing dicarboxylic acid monomer extended from *N,N′*-diphenyl-1,4-phenylenediamine (**1**). The incorporation of bulky, propeller-shaped triphenylamine moieties would interrupt the intermolecular hydrogen bonding of the polyamides and generally disturb the coplanarity of the aromatic unit, reducing the stacking efficiency and crystallinity. This should enhance solubility and maintain a high T_g through decreased segmental mobility due to steric hindrance. In addition, it is quite likely that the triphenylamine-based poly(amine amide)s will possess electrochemical and photochemical properties as well as high thermal stability because of the triphenylamine conjugated system. Therefore, these triphenylamine-based poly(amine amide)s may be applied in organic electroluminescent elements because light-emitting triarylamine derivatives[19–21] and triarylamine-based polymers[22–25] are reputed to be hole-transporting layer materials and are showing increasing potential as active components for a wide range of electronic and optoelectronic devices.

EXPERIMENTAL

Materials

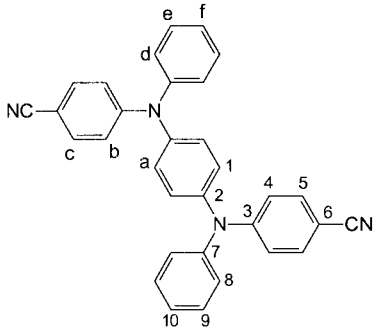
N,N′-Diphenyl-1,4-phenylenediamine (**1**; Tokyo Chemical Industries), 4-fluorobenzonitrile (Tokyo Chemical Industries), and triphenyl phosphite (TPP) were used without further purification. Commercially obtained anhydrous calcium chloride was dried *in vacuo* at 150 °C for 6 h. Dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. *p*-Phenylenediamine (**4a**; Tokyo Chemical Industries) and *m*-phenylenediamine (**4b**; Tokyo Chemical Industries) were purified by vacuum distillation before use. Bis[4-(4-aminophenoxy)phenyl] ether (**4g**; mp = 128–129 °C) was prepared by the aromatic nucleophilic substitution reaction of 4,4′-oxydiphenol and *p*-chloronitrobenzene in the presence of potassium carbonate and by the subsequent reduction of the intermediate bis(*p*-nitrophenoxy) compound with hydrazine monohydrate as the reducing reagent and with palladium on charcoal (Pd/C) as the catalyst.[26] All other diamines, including 4,4′-oxydianiline (**4c**), 4,4′-methylenedianiline (**4d**), 1,4-bis(4-aminophenoxy)benzene (**4e**), 4,4′-bis(4-aminophenoxy)biphenyl (**4f**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**4h**), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**4i**), and 9,9-bis(4-aminophenyl)fluorene (**4j**) were purchased from Tokyo Chemical Industries and used as received.

Monomer Synthesis

N,N′-*Bis(4-cyanophenyl)*-N,N′-*diphenyl-1,4-phenylenediamine (2)*

A mixture of 6.00 g (0.250 mol) of sodium hydride in 250 mL of DMSO was stirred at room temperature. To the mixture, 32.54 g (0.125 mol) of **1** and 30.40 g (0.251 mol) of 4-fluorobenzonitrile were added in sequence. The mixture was heated with stirring at 140 °C for 10 h under nitrogen and then precipitated into 2 L of cold water. The products was filtered and recrystallized from toluene to give 45.1 g (78% yield) of yellowish needles [mp = 221–222 °C by differential scanning calorimetry (DSC) at a scan rate of 2 °C/min].

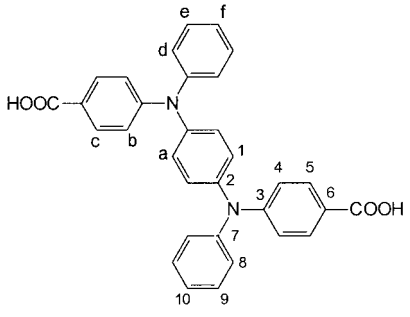
IR (KBr): 2216 cm^{-1} (C≡N). ^1H NMR [400 MHz, deuteriochloroform ($CDCl_3$), δ]: 6.98 (d, 4H, Hb), 7.08 (s, 4H, Ha), 7.15–7.19 (m, 6H, Hd + Hf), 7.36 (t, 4H, He) 7.44 (d, 4H, Hc). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.6 (C^3), 145.9 (C^7), 142.9 (C^2), 133.5 (C^5), 130.2 (C^9), 127.2 (C^8), 126.6 (C^4), 125.7 (C^{10}), 120.1 (C^1), 119.8 (C≡N), 103.2 (C^6). ELEM. ANAL. Calcd. for $C_{32}H_{22}N_4$ (462.55): C, 83.09%; H, 4.79%; N, 12.11%. Found: C, 83.19%; H, 4.83%; N, 12.22%.



N,N′-*Bis(4-carboxyphenyl)*-N,N′-*diphenyl-1,4-phenylenediamine (3)*

A mixture of 50.0 g of potassium hydroxide and 29.0 g of the obtained dinitrile compound **2** in 200 mL of ethanol and 200 mL of distillated water was stirred at approximately 100 °C until no further ammonia was generated. The time taken to reach this stage was about 5–6 days. The solution was cooled, and the pH value was adjusted by dilute hydrochloric acid to near 3. The yellowish precipitate formed was collected by filtration, washed thoroughly with water, and dried *in vacuo* to give 31.1 g (yield = 99%) of diacid **3** (mp = 318–321 °C by DSC at 2 °C/min).

IR (KBr): 1676 (C═O), 2700–3400 cm^{-1} (O—H). ^1H NMR [400 MHz, perdeuteriodimethyl sulfoxide (DMSO-d_6), δ]: 6.93 (d, 4H, Hb), 7.11 (s, 4H, Ha), 7.15–7.19 (m, 6H, Hd + Hf), 7.39 (t, 4H, He) 7.80 (d, 4H, Hc). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 166.8 (C═O), 151.2 (C^3), 145.9 (C^7), 142.3 (C^2), 130.8 (C^5), 129.8 (C^9), 126.7 (C^4), 126.7 (C^8), 124.7 (C^{10}), 122.6 (C^6), 119.2 (C^1). ELEM. ANAL. Calcd. for $C_{32}H_{24}N_2O_4$ (500.55): C, 76.78%; H, 4.83%; N, 5.60%. Found: C, 76.17%; H, 4.79%; N, 5.33%.



Polymer Synthesis

Typical procedures for the synthesis of triphenylamine-based poly(amine amide) **5b** are as follows. A mixture of 0.2163 g (2.0 mmol) of diamine **4b**, 1.0011 g (2.0 mmol) of diacid **3**, 0.4 g of calcium chloride, 1.4 mL of TPP, 1.5 mL of pyridine, and 6 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol, giving rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried *in vacuo* at 100 °C; the yield was 1.071 g (99%). The inherent viscosity (η_{inh}) of the obtained poly(amine amide) **5b** was 0.50 dL/g, measured at a concentration of 0.5 g/dL in dimethylacetamide (DMAc) containing 5 wt % LiCl at 30 °C.

IR (film): 3310 (N—H stretching), 1657 cm^{-1} (amide carbonyl). ELEM. ANAL. Calcd. for $(C_{38}H_{28}N_4O_2)_n$ $(572.42)_n$: C, 79.70%; H, 4.93%; N, 9.78%. Found: C, 76.99%; H, 4.64%; N, 9.43%.

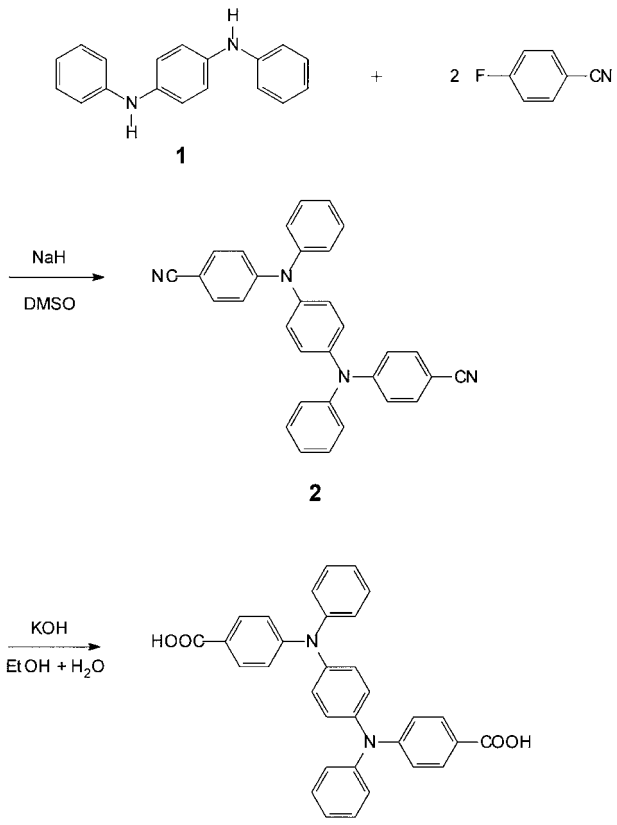
Preparation of the Films

A polymer solution was made by the dissolution of about 0.7 g of the poly(amine amide) sample in 10 mL of DMAc or NMP. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight to slowly release the solvent, and then the film was stripped off from the glass substrate and further dried *in vacuo* at 160 °C for 8 h. The obtained films were about 90–120 μm thick and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Measurements

IR spectra were recorded with a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were performed with a PerkinElmer model 2400 CHN analyzer. ^1H and ^{13}C NMR spectra were measured on a JEOL EX 400 spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent and with tetramethylsilane as the internal reference. The η_{inh} values were determined at a concentration of 0.5 g/dL in DMAc/5 wt % LiCl with a Cannon-Fenske viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on 3–5-mg samples heated in flowing nitrogen or air (30 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC instrument in flowing nitrogen (20 cm^3/min) at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a

scan rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer with nickel-filtered Cu Kα radiation (40 kV, 15 mA), and the scanning rate was 2°/min. Measurements were performed with film specimens about 0.1 mm thick. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined by means of gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Waters apparatus [with tetrahydrofuran (THF) as an eluent]. An Instron 1130 universal tester with a load cell of 5 kg was used to study the stress–strain behavior of the samples at a crosshead speed of 5 mm/min. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 0.1 mm thick), and an average of at least five individual determinations was used.



Scheme 1

RESULTS AND DISCUSSION

Monomer Synthesis

The new polymer-forming triphenylamine-containing aromatic dicarboxylic acid **3** was successfully synthesized by the alkaline hydrolysis reaction of the dinitrile compound **2**, which resulted from the condensation reaction of **1** with 4-fluorobenzonitrile in DMSO in the presence of sodium hydride, according to the synthetic routes outlined in Scheme 1. The aromatic fluoro-displacement reaction of 4-fluorobenzonitrile with the amine ion of **1** treated by sodium hydride was generally more preferable than using potassium carbonate for the preparation of dinitrile compound **2** with a higher yield. Elemental analysis, IR, and ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify the structures of the intermediate dinitrile compound **2** and the dicarboxylic acid monomer **3**. The IR spectra (Fig. 1) of dinitrile compound **2** gave a cyano group characteristic band at 2126 cm^{-1} (stretching). After hydrolysis, the characteristic absorption of the cyano group disappeared, and the carboxylic acid group showed a typical carbonyl absorption band at 1676 cm^{-1} (C═O stretching) together with the appearance of broad bands around 2700–3400 cm^{-1} (O—H stretching). The structures of **2** and **3** were also confirmed by high-resolution NMR spectra. The ^{1}H and ^{13}C NMR spectra of these compounds are given in Figures 2 and 3. The assignments of each carbon and proton also are given in the figures, and these spectra are in good agreement with the proposed molecular structures. The ^{13}C NMR spectra confirm that the cyano groups were completely converted into the carboxylic acid groups by the disappearance of the resonance peak for the cyano carbon at 119.8 ppm and by the appearance of the carbonyl peak at 166.8 ppm. Other important evidence of this change is the shifting of the carbon resonance signals of C^6 adjacent to the cyano or carboxyl group. The C^6 of dinitrile **2** resonated at a higher field (103.2 ppm) than the other aromatic carbons because of the anisotropic shielding by the π electrons of C≡N. After hydrolysis, the resonance peak of C^6 shifted to a lower field (122.6 ppm) because of the lack of an anisotropic field.

Polymer Synthesis

A series of new triphenylamine-based aromatic poly(amine amide)s, **5a–5j**, containing *p*-phe-

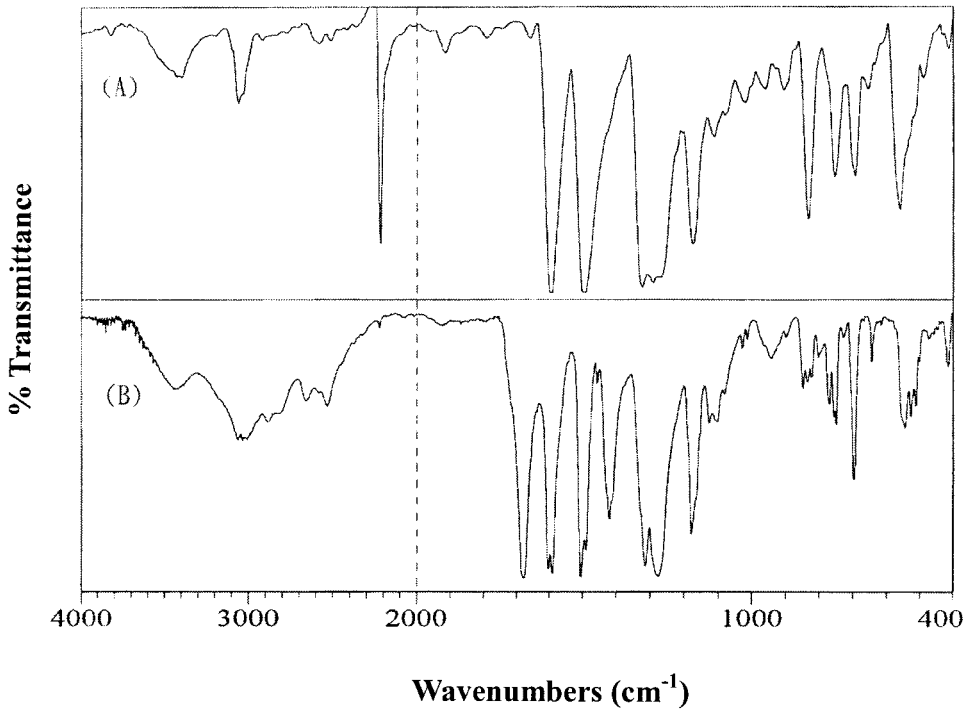


Figure 1. IR spectra of (A) dinitrile **2** and (B) diacid **3**.

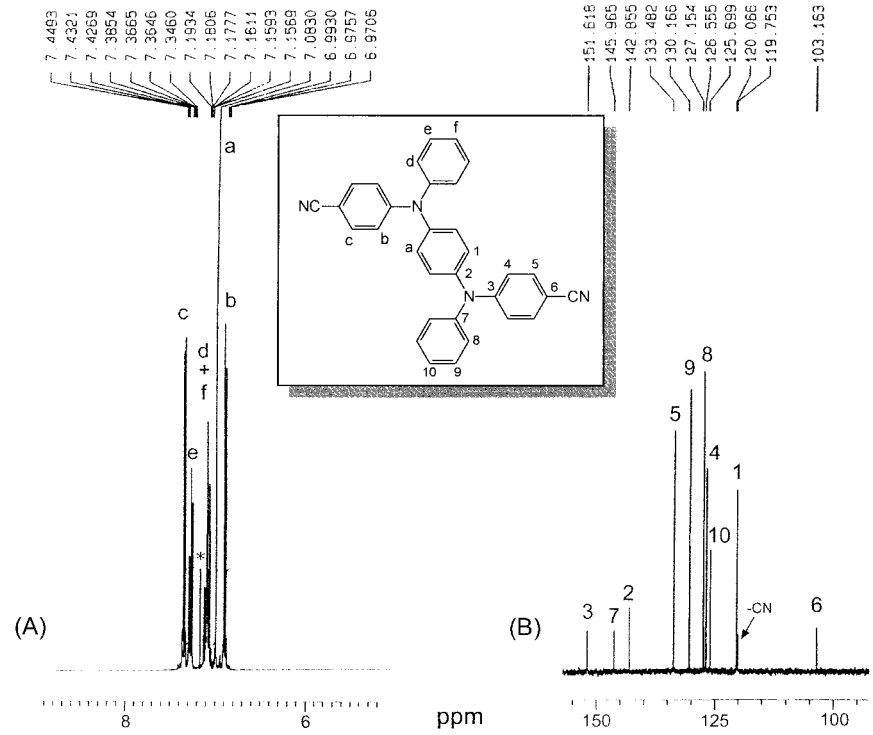


Figure 2. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of dinitrile **2** in $CDCl_3$. * indicates a signal arising from $CHCl_3$.

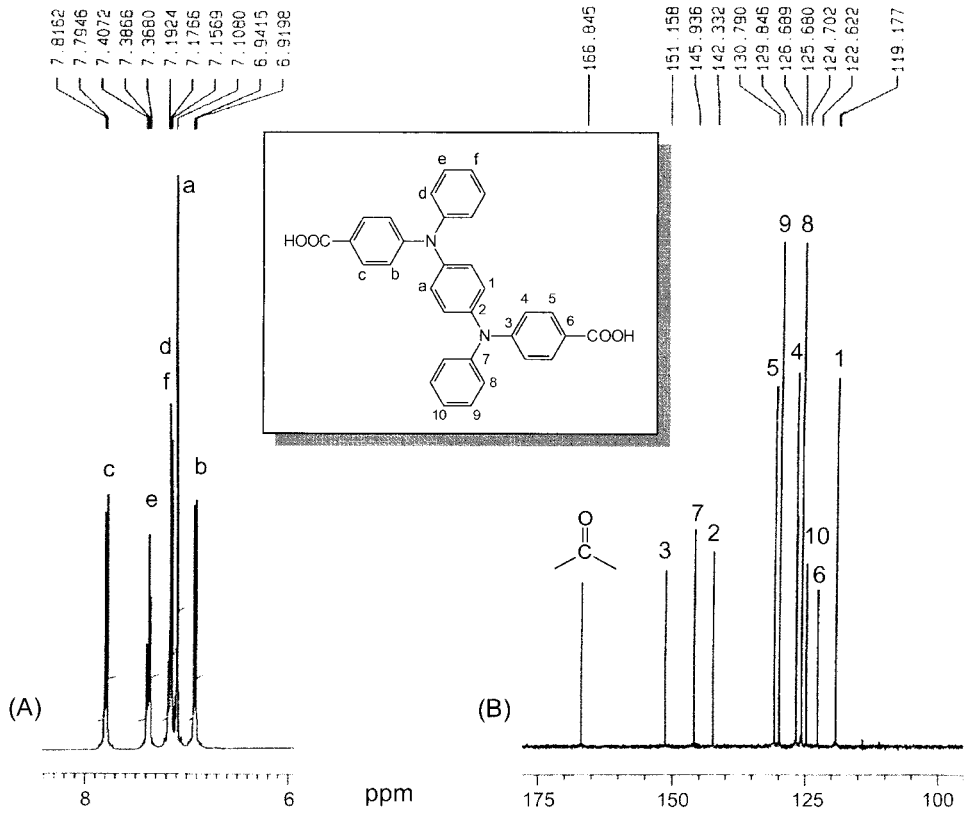


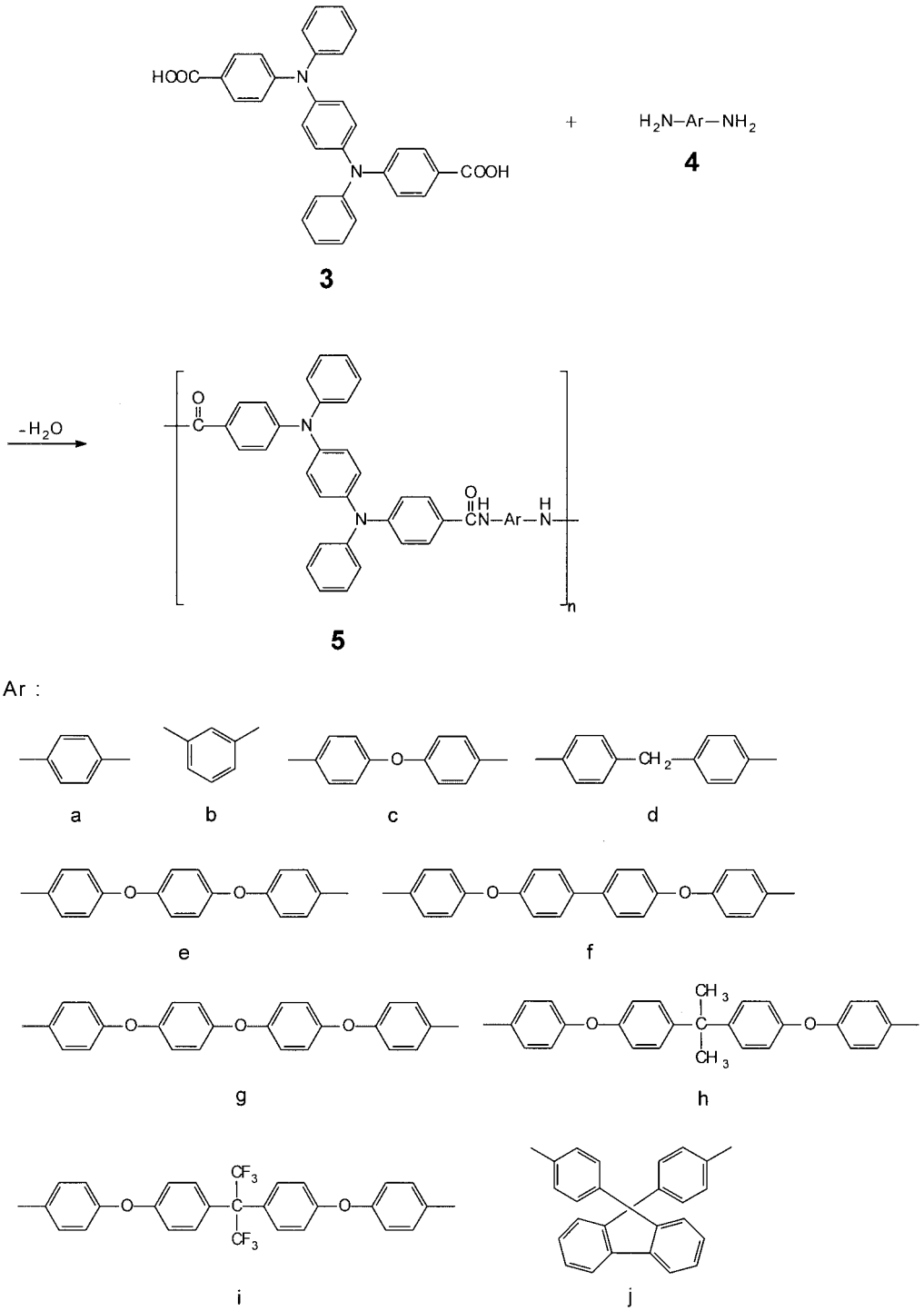
Figure 3. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of diacid **3** in DMSO-d_6.

nylene units were prepared from the diacid **3** and various aromatic diamines (**4a–4j**) by the direct polycondensation reaction[27] with TPP and pyridine as condensing agents (Scheme 2). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough, fiberlike form when the resulting polymer solutions were slowly poured with stirring into methanol. These poly(amine amide)s were obtained in almost quantitative yields, with η_{inh} values in the range of 0.50–1.02 dL/g measured in DMAc/5 wt % LiCl, as shown in Table 1. All the polymers except poly(amine amide) **5a** could be solution-cast into flexible and tough films, and this was indicative of the formation of high molecular weight polymers. The GPC chromatogram of poly(amine amide) **5i** showed that the M_w and M_n values were 56,000 and 37,000, respectively, relative to standard polystyrene, and the M_w/M_n ratio was 1.5. The IR spectra of the poly(amine amide)s, which showed characteristic amide absorptions near 3400–3300 and 1657 cm^{-1}, supported the formation of the amide linkages (Fig. 4).

Properties of the Polymers

The X-ray diffraction studies of the triphenylamine-based poly(amine amide)s indicated that all the polymers were essentially amorphous. The solubility behavior of these polymers was tested qualitatively, and the results are listed in Table 1. All the poly(amine amide)s except polymer **5a**, derived from rigid and symmetrical **4a**, were soluble in polar solvents such as NMP and *m*-cresol. Most of them were also soluble in DMAc, dimethylformamide (DMF), and hot DMSO. Polymer **5i** with the hexafluoroisopropylidene group was soluble even in less polar THF. Their high solubility and amorphous nature can be attributed to the introduction of bulky, twisted, three-dimensional triphenylamine units along the polymer backbone. Therefore, the excellent solubility makes these polymers potential candidates for practical applications in spin-on and casting processes.

As mentioned previously, except for **5a**, all the poly(amine amide)s could be solution-cast into smooth, flexible, and tough films. These films were subjected to tensile testing, and the results



Scheme 2

are given in Table 1. The tensile strengths, elongations to break, and initial moduli of these films were 88–110 MPa, 8–12%, and 1.81–2.72 GPa, respectively.

DSC and TMA were used to evaluate the thermal transitions of these poly(amine amide)s. Each sample was subjected to two subsequent DSC heating runs at 20 °C/min, the first from 40 to 400 °C, after which the sample was cooled down with a programmed cooling rate of −200 °C/min to 40 °C, followed by a second heating run with an end temperature of 400 °C. The first run was intended

Table 1. Inherent Viscosities, Solubilities and Thin-Film Tensile Properties of the Poly(amine amide)s

Polymer	η_{inh} (dL/g)[a]	Solubility[b]						Tensile Properties of the Polymer Films[c]		
		NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Tensile Strength (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
5a	0.69	−	−	−	−	+h	−	–	–	–
5b	0.50	+	+	+	+h	+	−	101	9	2.49
5c	0.69	+	+	+	+h	+	−	107	9	2.38
5d	0.57	+	+	+	+h	+	−	94	8	2.15
5e	0.68	+	+h	−	−	+	−	95	10	1.81
5f	1.02	+	−	−	+h	+	−	110	10	2.31
5g	0.69	+	+	+	+h	+	−	99	12	2.19
5h	0.69	+	+	+	+h	+	−	90	12	1.85
5i	0.69	+	+	+	+	+	+	88	11	2.30
5j	0.57	+	+	+	+	+	−	108	8	2.72

[a] Measured at a concentration of 0.5 g/dL in DMAc/5 wt % LiCl at 30 °C.
[b] + = soluble at room temperature; +h = soluble on heating; − = insoluble even on heating.
[c] Films were cast by the slow evaporation of polymer solutions in DMAc. The film specimens were dried *in vacuo* at 160 °C for 6 h before the tensile test.

to eliminate any possible volatiles such as the absorbed moisture and residual solvent in the samples. Reheating produced neat DSC thermograms in the second run, and a clear heat capacity jump attributable to a glass transition could be observed in every case, with the exception of rigid **3j**. As shown in Table 2, the poly(amine amide)s **5a–5i** had T_g's of 195–280 °C, following the de-

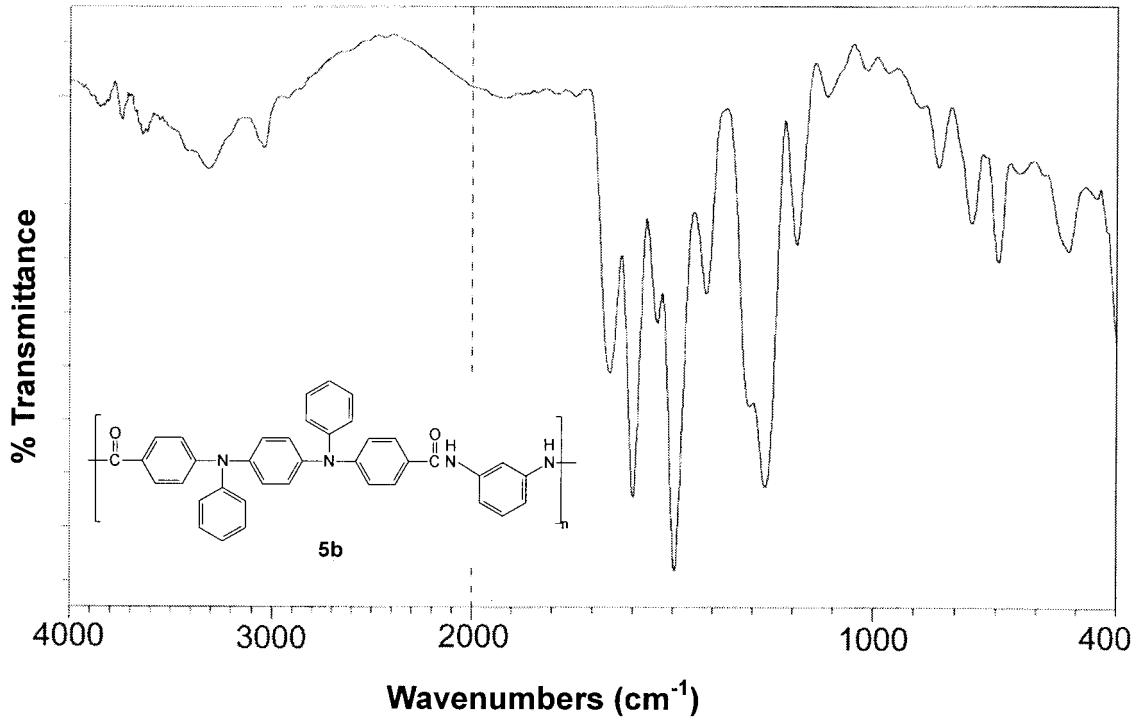


Figure 4. IR spectrum of poly(amine amide) **5b**.

Table 2. Thermal Properties of the Poly(amine amide)s

Polymer	T_g(°C)[a]	T_s (°C)[b] after Annealing for 30 min		T_d at 5 wt % Loss (°C)[c]		T_d at 10 wt % Loss (°C)[c]		Char Yield (wt %)[d]
		250 °C	300 °C	In N_2	In Air	In N_2	In Air	
5a	280	270	287	490	504	573	565	69
5b	221	236	274	511	519	649	613	83
5c	222	257	273	548	529	620	612	78
5d	211	221	268	525	539	600	615	80
5e	200	221	244	530	528	575	615	71
5f	213	242	260	547	526	607	618	70
5g	204	215	218	550	524	583	590	60
5h	195	210	215	542	523	601	594	74
5i	207	240	244	549	514	602	582	70
5j	—[e]	322	328	555	550	593	617	76

[a] The midpoint temperature of the baseline shift on the DSC heating trace at a scan rate of 20 °C/min in nitrogen after rapid cooling from 400 °C.
[b] Taken as the onset temperature of the probe displacement on the TMA trace. The film samples were heated at 250 or 300 °C for 30 min before the TMA test.
[c] Recorded via TGA at a heating rate of 20 °C/min and at a gas-flow rate of 40 cm^3/min.
[d] Residual weight percentage at 800 °C under a nitrogen flow.
[e] No discemible transition was observed by DSC.

creasing order of chain flexibility. All the polymers showed no melting endotherms up to the decomposition temperatures (T_d's) on the DSC thermograms. This result also supports the amorphous nature of these triphenylamine-containing poly(amine amide)s. The softening temperatures (T_s's; also called the apparent T_g's) of the poly(amine amide) film samples were determined by the TMA method with a loaded penetration probe and were taken from the onset temperatures of the probe displacement on the TMA traces. Figure 5 shows typical TMA curves of poly(amine amide) **5b**. The T_s values of the poly(amine amide) films annealed at 250 and 300 °C were recorded in the ranges of 210–322 and 215–328 °C, respectively. As expected, the heat treatment of these polymer films at an enhanced temperature led to an increase in T_s because of more compact molecular packing and aggregation. In almost all cases, the T_s values obtained by TMA were higher than the T_g values measured by the DSC experiments. These differences may be attributed to the different heating histories and the distinct natures of these two testing methods.

The thermal stability of these poly(amine amide)s was studied by TGA. The TGA curves of a representative poly(amine amide) **5b** in both air and nitrogen atmospheres are shown in Figure 6. Some thermal behavior data determined from original thermograms are also tabulated in Table 2. In general, all the poly(amine amide)s exhibited good thermal stability with insignificant weight loss up to 450 °C in nitrogen or air. The 10% weight-loss temperatures of the poly(amine amide)s in nitrogen and in air were recorded in the ranges of 573–649 and 565–618 °C, respectively. The amount of carbonized residue (char yield) at 800 °C of these poly(amine amide)s in a nitrogen atmosphere was higher than 60% and up to 83%. The high char yields of these poly(amine amide)s can be ascribed to their high aromatic contents.

CONCLUSIONS

A new triphenylamine-containing aromatic dicarboxylic acid (**3**) was synthesized in good yields and high purity from readily available reagents. A series of high molecular weight poly(amine amide)s were readily prepared from the diacid and various aromatic diamines by the direct phosphorylation polycondensation reaction. Because of the presence of the bulky triphenylamine unit, all the poly(amine amide)s were amorphous, had good solubility in many polar aprotic solvents,

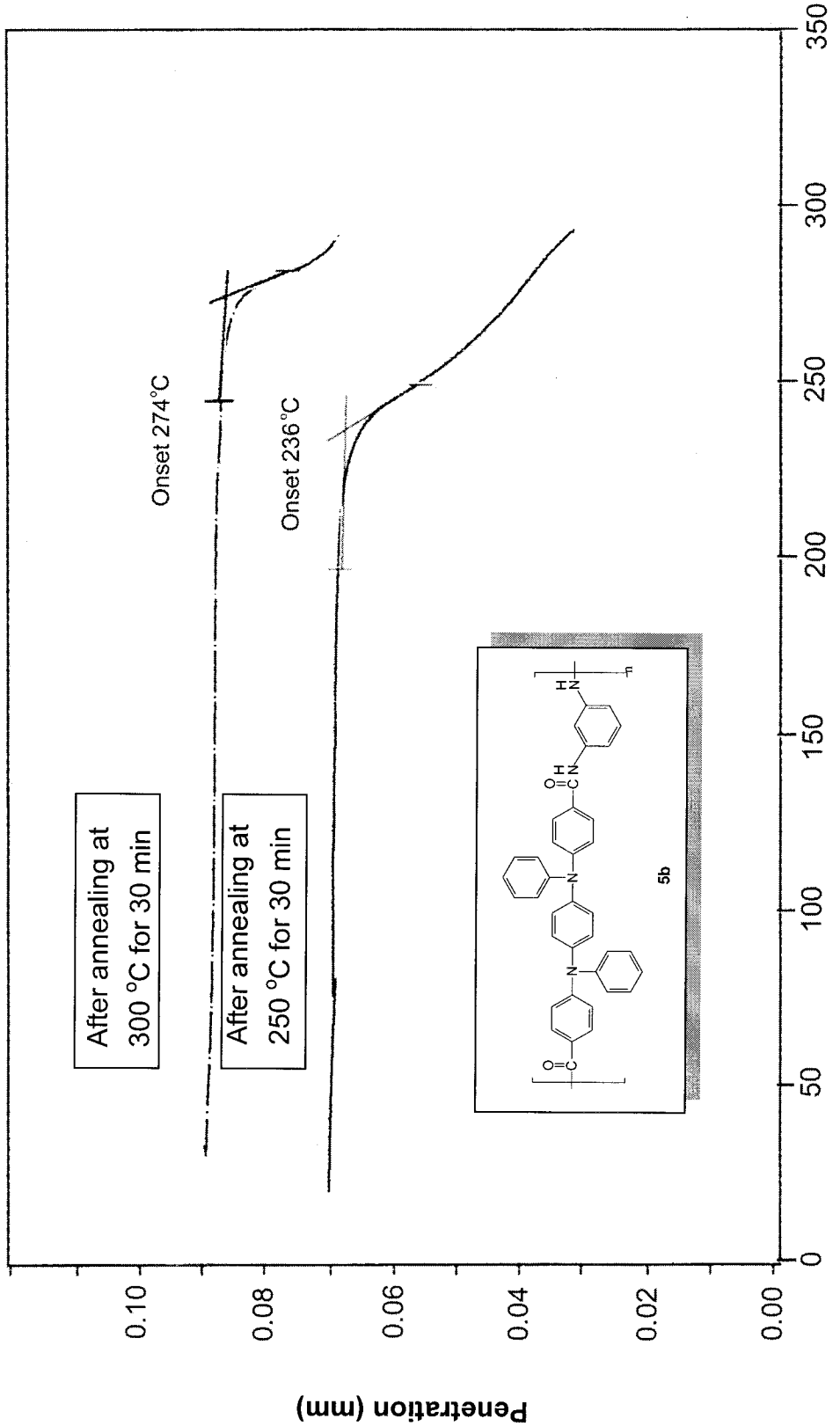


Figure 5. TMA thermograms of a film sample of poly(amine amide) **5b** at a heating rate of 10 °C/min.

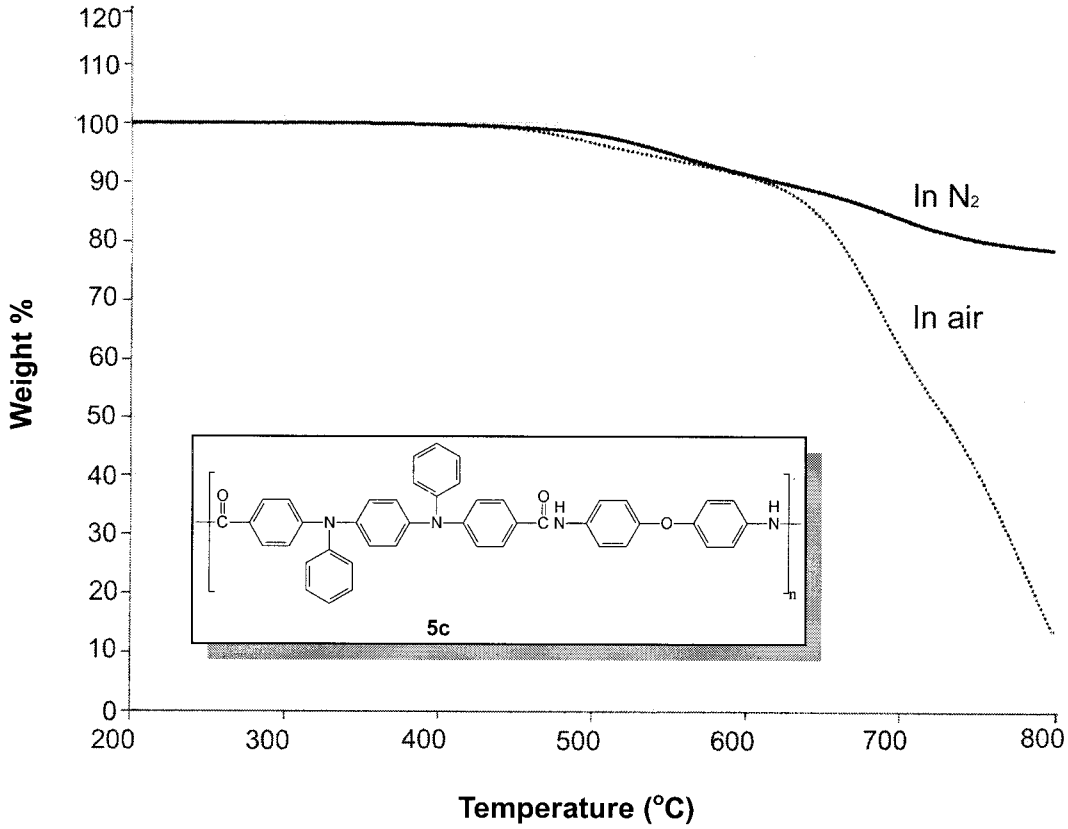


Figure 6. TGA thermograms of poly(amine amide) **5c** at a scan rate of 20 °C/min.

and exhibited excellent thin-film-forming capability. Good solubility, moderate T_g or T_s values, and good thermal stability and mechanical properties make these triphenylamine-based poly(amine amide)s promising processable high-performance polymeric materials.

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REFERENCES AND NOTES

1. Cassidy, P. E. Thermally Stable Polymers; Marcel Dekker: New York, 1980.
2. Yang, H. H. Aromatic High-Strength Fibers; Wiley: New York, 1989.
3. Imai, Y. High Perform Polym 1995, 7, 337.
4. Imai, Y. React Funct Polym 1996, 30, 3.
5. Imai, Y.; Park, K. H. Polym Mater Encycl 1996, 1, 404.
6. Liou, G. S.; Hsiao, S. H. J Polym Sci Part A: Polym Chem 2001, 39, 1786.
7. Hsiao, S. H.; Li, C. T. Macromolecules 1998, 31, 7213.
8. Liou, G. S. J Polym Sci Part A: Polym Chem 1998, 36, 1937.
9. Eastmond, G. C.; Paprotny, J.; Irwin, R. S. Polymer 1999, 40, 469.
10. Yang, C. P.; Hsiao, S. H.; Yang, H. W. Macromol Chem Phys 1999, 200, 1528.
11. Espeso, J. F.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. J Polym Sci Part A: Polym Chem 2000, 38, 1014.
12. Espeso, J. F.; Ferrero, E.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. J Polym Sci Part A: Polym Chem 2001, 39, 475.
13. Liaw, D. J.; Hsu, P. N.; Chen, J. J.; Liaw, B. Y.; Hwang, C. Y. J Polym Sci Part A: Polym Chem 2001, 39, 1557.
14. Kakimoto, M.; Yoneyama, M.; Imai, Y. J Polym Sci Part A: Polym Chem 2000, 38, 3911.
15. Jeong, H. J.; Oishi, Y.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1991, 29, 39.
16. Xie, M.; Oishi, Y.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1991, 29, 55.
17. Oishi, Y.; Ishida, M.; Kakimoto, M.; Imai, Y.; Kurosaki, T. J Polym Sci Part A: Polym Chem 1992, 30, 1027.

18. Liou, G. S.; Hsiao, S. H.; Ishida, M.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 2002, 40, 2810.
19. Ko, C. W.; Tao, Y. T. Synth Met 2002, 126, 37.
20. Koene, B. E.; Loy, D. E.; Thompson, M. E. Chem Mater 1998, 10, 2235.
21. Shirota, Y.; Okumoto, K.; Inada, H. Synth Met 2000, 111, 387.
22. Wu, A.; Kakimoto, M.; Imai, Y. Supramol Sci 1996, 3, 3.
23. Lu, J.; Hlil, A. R.; Sun, Y.; Hay, A. S. Chem Mater 1999, 11, 2501.
24. Li, H.; Geng, Y.; Tong, S.; Tong, H.; Hua, R.; Su, G.; Wang, L.; Jing, X.; Wang, F. J Polym Sci Part A: Polym Chem 2001, 39, 3278.
25. Pu, Y. J.; Soma, M.; Tsuchida, E.; Nishide, H. J Polym Sci Part A: Polym Chem 2000, 38, 4119.
26. Hsiao, S. H.; Chen, Y. J. J Polym Res 2000, 7, 205.
27. Yamazaki, N.; Matsumoto M.; Higashi, F. J Polym Sci Polym Chem Ed 1975, 13, 1373.