

New Organosoluble and Thermally Stable Poly(urea-imide)s Prepared from One-Pot Polyaddition Reactions

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ABSTRACT: A new class of aromatic poly(urea-imide)s having biphenylene pendant group was prepared by the diphenyl azidophosphate (DPAP) activated one-pot polyaddition reaction of a preformed imide ring-containing dicarboxylic acid, 4-*p*-biphenyl-2,6-bis(4-trimellitimidophenyl)pyridine (**1**) with various aromatic diamines. A model compound was also synthesized by the reaction of diimide-dicarboxylic acid **1** with two mole equivalents of aniline. In this direct method the polymers were prepared by polyaddition reactions of the *in situ*-formed diisocyanate with the aromatic diamines. The inherent viscosities of the polymers were measured in the range of 0.11–0.15 dL g⁻¹. The ultraviolet λ_{max} values of the poly(urea-imide)s were also determined.

Furthermore, crystallinity of the resultant polymers was evaluated by wide-angle X-ray diffraction method, and they exhibited nearly a noncrystalline nature. All of the resulting polymers exhibited excellent solubility in common polar solvents. The glass transition temperatures of the polymers determined by DSC thermograms were in the range 241–272°C. The temperatures at 10% weight loss from their TGA curves were found to be in the range 406–437°C in nitrogen. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 727–735, 2008

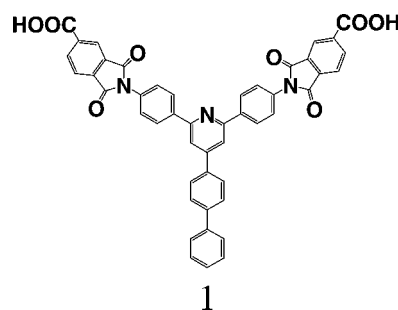
Key words: noncrystalline polymers; structure–property relation; thermal properties; viscosity; differential scanning calorimetry

INTRODUCTION

Aromatic homopolyimides are characterized by their outstanding chemical and thermal properties.¹ This class of polymers with linear backbones such as the one derived from pyromellitic dianhydride and *p*-phenylene diamine are often difficult to process because of their insolubility in organic solvents.^{2,3} In general, the two key factors in designing soluble and processable aromatic polyimides are (i) introducing other functional groups such as amide,^{4–8} ester,^{9–13} urethane,^{14–18} and urea^{19–23} accompanied by the imide group into the macromolecular chain, consequently preparing copolyimides instead of homopolyimides, (ii) placing bulky pendant groups along the main chain of the polymer.^{24–29} Therefore, the design and synthesis of purely aromatic monomers that will lead to processable polyimides is desirable.

In our previous studies, a pyridyl-based fully aromatic dicarboxylic acid bearing two preformed imide rings, 4-*p*-biphenyl-2,6-bis(4-trimellitimidophenyl)pyridine (**1**), was synthesized by the consecutive steps including the modified-Chichibabin synthesis³⁰ to prepare 4-*p*-biphenyl-2,6-bis(4-nitrophenyl)pyridine with the use of biphenyl-4-carboxaldehyde and 4-nitroacetophenone, reduction of the dinitro obtained by hydrazine hydrate and palladium on

charcoal to synthesize 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine, and finally the condensation reaction between the diamine obtained and two mole equivalents of trimellitic anhydride in dry DMF and toluene.



Diimide-dicarboxylic acid **1** was used for the preparation of corresponding aromatic alternating poly(amide-imide)s,³¹ poly(ester-imide)s,³² and poly(urethane-imide)s.³³ The results clearly showed the copolymers obtained from the above monomer have both good solubility in a variety of organic solvents and high thermal stability. It was also found that the incorporation of biphenylene as a bulky pendant group into the copolyimides backbone could substantially decrease their crystallinity and increase their solubility in tested organic solvents. In addition to the above-mentioned copolyimides, the monomer containing biphenylene pendant group seems to be a good choice for the preparation of various soluble

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and thermally stable aromatic poly(urea-imide)s via one-pot polyaddition reactions.

Alongside these studies, in this article we wish to report the synthesis and characterization of a new class of poly(urea-imide)s by the diphenyl azidophosphate (DPAP) activated direct polyaddition method as a convenient technique to achieve polyaddition reactions including polyureas and polyurethanes formation. Moreover, with due attention to the previous reports about the synthesis and properties of the other copolyimides including poly(amide-imide)s, poly(ester-imide)s, and poly(urethane-imide)s, it seems to be useful information from this matter that which alternating group has how much effect on the properties of the copolyimides. In fact, this object could be interesting research along the previous studies related to the field of aromatic copolyimides. Therefore, some properties of the resulting pyridyl-based aromatic poly(urea-imide)s such as solution viscosity, crystallinity situation, solubility behavior in common organic solvents, glass transition temperatures, and thermal stability were investigated. Solubility and heat resistance of the copolyimides were compared with those of copolymers with the similar main chain prepared in our previous works.^{31–33}

EXPERIMENTAL

Materials

All initial chemicals were purchased either from Merck or Fluka chemical except DPAP that was prepared from Sigma-Aldrich chemical and used as obtained without further purification. Aromatic diamines including *p*-phenylenediamine (**4a**), 2,6-diaminopyridine (**4b**), 1,5-diaminonaphthalene (**4c**), 4,4'-diaminodiphenylether (**4d**) were purified by sublimation before use. The 2,2'-bis(*p*-aminophenoxy)biphenyl (**4e**), and 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine (**4f**) were synthesized as described previously.^{8,31} *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. The other solvents including dichloromethane, toluene, and acetone as well as triethylamine were used as obtained without further purification.

Synthesis of the monomer

Imide ring-containing dicarboxylic acid, 4-*p*-biphenyl-2,6-bis(4-trimellitimidophenyl)pyridine (**1**), was synthesized by the condensation reaction between 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine

and two mole equivalents of trimellitic anhydride (TMA) in dry DMF and toluene as reaction solvents according to the procedure reported previously.³¹

Synthesis of the model compound

Into a hot flow-dried flask were placed diimide-dicarboxylic acid **1** (0.191 g, 0.25 mmol) and DMSO as reaction solvent (1.5 mL) with a stir bar. Then, DPAP (0.6 mL) and triethylamine (0.7 mL) were added to the initial contents at once. The final mixture was stirred 2 h at 10°C and then for 3 h at 70°C until evolution of nitrogen gas stopped. After both steps, the reaction progress was checked by TLC plates. Aniline (0.046 g, 0.5 mmol) in DMSO (1.5 mL) was added dropwise to the reaction mixture, and the final mixture was heated for 12 h at 90°C. After cooling, the reaction solution obtained was poured slowly into stirred methanol (50 mL) to give rise to a crude precipitate, which was collected by filtration, washed thoroughly with methanol, hot water, and ether, respectively, and dried under reduced pressure at 50°C to afford 0.167 g (71%) of model compound (m.p. = 243–246°C). The ultraviolet maximum wavelength (λ_{max}) of the diimide-diurea obtained was found in 388 nm. FTIR (KBr): 3250–3450 (m), 2962 (w), 1778 (w), 1721 (s), 1674 (m), 1600 (m), 1544 (w), 1516 (m), 1498 (m), 1443 (w), 1374 (s), 1320 (w), 1261 (m), 1186 (w), 1092 (m), 1025 (m), 948 (w), 831 (m), 757 (w), 691 (w) cm^{-1} . ¹H NMR (δ , ppm, DMSO- d_6): 9.20–860 ppm (4H of ureylene linkages), 8.40–6.95 ppm (35H of aromatic rings).

Preparation of the poly(urea-imide)s

A typical example of the polyaddition reactions was as follows: into a hot flow-dried two-necked flask equipped with a drying tube-capped reflux condenser, magnetic stirrer, and dropping funnel were placed diimide-dicarboxylic acid **1** (0.191 g, 0.25 mmol) in DMSO (1.5 mL). Then, DPAP (0.6 mL) and triethylamine (0.7 mL) were added to the initial contents of the flask. The final mixture was stirred 2 h at about 10°C and then for 3 h at 70°C until evolution of nitrogen gas stopped. 1,4-Phenylene diamine (**4a**) (0.027 g, 0.25 mmol) in DMSO (2.0 mL) was added dropwise to the initial reaction mixture, and the final mixture was heated for 12 h at 90°C. The viscous polymer solution obtained was trickled on stirred methanol to give rise to a crude precipitate, which was collected by filtration, washed thoroughly with methanol, hot water, and ether, respectively, and dried under reduced pressure at 50°C to afford 0.123 g (57%) of **5a** as brown solid.

The inherent viscosity of the polyurea-imide obtained in DMAc was 0.13 dL g^{-1} , measured at a

concentration of 0.5 g dL⁻¹ at 30°C. The ultra-violet maximum wavelength (λ_{max}) of the polymer solution in DMSO appeared in 383 nm. FTIR (KBr): 3200–3500 (m), 2925 (w), 1774 (w), 1718 (s), 1674 (m), 1608 (m), 1559 (w), 1516 (s), 1499 (m), 1443 (w), 1374 (s), 1319 (w), 1250 (w), 1186 (w), 1089 (m), 1025 (w), 948 (w), 835 (m), 766 (w), 689 (w) cm⁻¹. ¹H NMR (δ , ppm, DMSO-d₆): 9.25–8.60 ppm (4H of ureylene linkages), 8.40–6.47 ppm (separate peak blocks, 29H of aromatic rings).

The above one-pot polyaddition reaction was chosen as a procedure for preparation of the other poly(urea-imide)s.

Measurements

Inherent viscosities were measured using an Ubbelohde viscometer with polymer solutions in chloroform at a concentration of 0.5 g dL⁻¹ at 30°C. Melting points were determined in open capillaries with a Buchi 535 melting point apparatus. Ultraviolet maximum wavelength (λ_{max}) values were determined with a GBC model 916 ultraviolet-visible (UV-vis) instrument in DMSO at a concentration of 0.1 mg mL⁻¹. ¹H NMR spectra were recorded on a Bruker Advanced DPX-250 250-MHz spectrometer in DMSO-d₆ at 25°C with frequencies of 250.13 MHz. Tetramethylsilane was used as an internal standard. FTIR spectra were recorded on a Perkin Elmer RX I FTIR spectrometer. The spectra of solids were obtained using KBr pellets. Wide-angle X-ray diffraction (WXR) patterns were performed at room temperatures with film specimens on a D8 Advance Bruker X-ray diffractometer with Ni-filtered Cu K α radiation (30 kV, 25 mA). Differential scanning calorimetric (DSC) and thermal gravimetric analysis (TGA) were performed on a Mettler TA4000 System under nitrogen atmosphere at a heating rate of 10°C min⁻¹. The DSC traces were obtained from heating, rapidly cooling, and reheating of samples at a range of 50–400°C. The range FS of 20 mW for DSC and 10 mG for TGA were used.

RESULTS AND DISCUSSION

Synthesis

The imide ring-containing dicarboxylic acid **1** was synthesized by the condensation reaction between the appropriate aromatic diamine, 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine, and two mole equivalents of TMA in dry DMF and toluene using a Dean-Stark trap. The details of this synthesis route and the characterization data was reported in our previous work.³¹

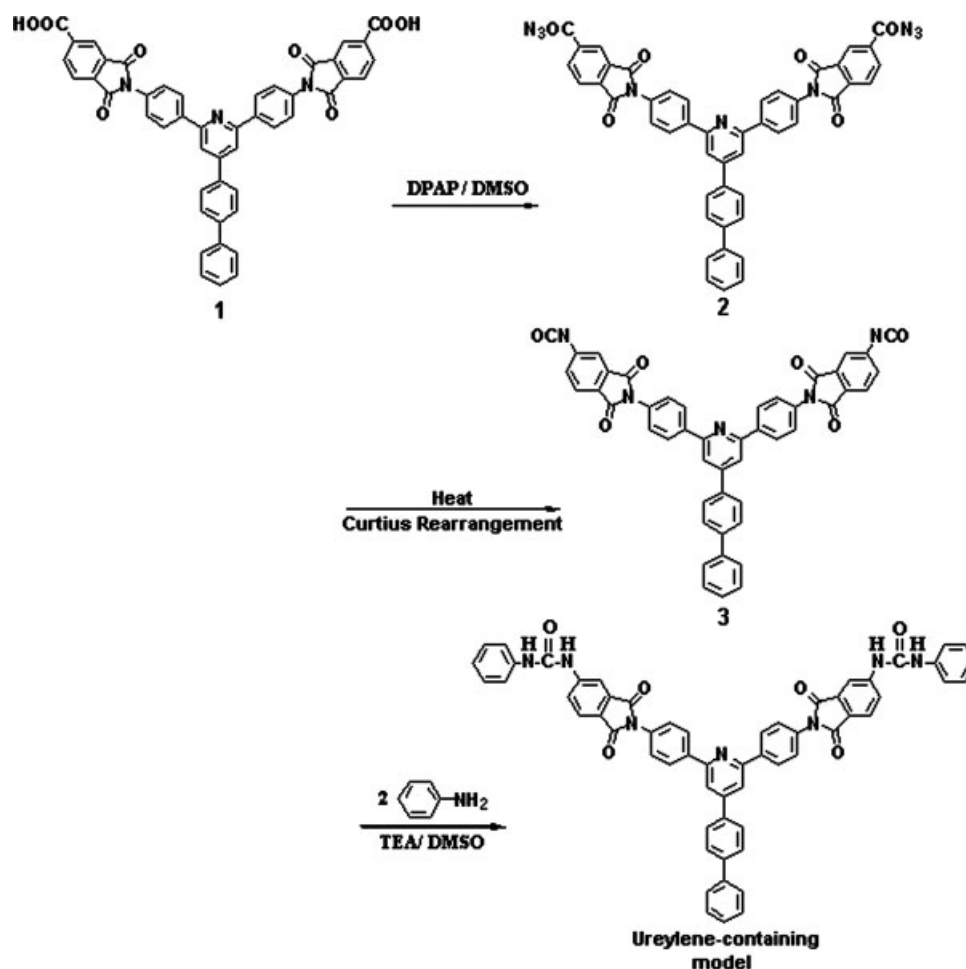
An ureylene-containing model compound was then prepared by the reaction of compound **1** with

two mole equivalents of aniline by means of DPAP in DMSO as the reaction solvent. The model compound synthesis permitted an optimization in the polymerization conditions. Furthermore, its spectral data could be compared with the data of poly(urea-imide)s prepared subsequently. In this synthesis method for avoidance of amidation as a side reaction, the acyl azide **2** which is derived from the carboxyl component has to be converted to isocyanate **3** prior to the addition of the amino component. By employing this procedure, the model compound with ureylene linkages only could be prepared from dicarboxylic acids and aniline. Diimide-dicarboxylic acid **1** was converted to diimide-di(carbonyl azide) **2** using DPAP in DMSO. The thermal decomposition of diimide-di(carbonyl azide) **2** via Curtius rearrangement gave the corresponding diisocyanate **3**. In continuation of this reaction, compound **3** has been reacted with aniline to prepare the model compound. The synthetic route chosen for the preparation of the model compound is shown in Scheme 1.

The structure of the ureylene-containing model compound was confirmed by FTIR and ¹H NMR spectroscopic methods. The FTIR spectrum showed a broad band in the region of 3250–3450 cm⁻¹ assigned to stretching vibration of the ureylene N–H bonds. The characteristic absorptions of the carbonyl groups occurred around 1775, 1720 (asymmetric and symmetric imide C=O stretching, respectively), and 1675 (ureylene C=O stretching) cm⁻¹. The ¹H NMR spectrum showed N–H proton signal in about 9.20–8.60 ppm. The aromatic ring protons appeared in the region of about 8.40–6.95 ppm.

In continuation, a series of new alternating aromatic poly(urea-imide)s, **5a–5f**, containing biphenylene pendant groups was directly synthesized starting from diimide-dicarboxylic acid **1** and various aromatic diamines **4a–4f** in equivalent amounts via the conditions used to prepare the model compound. The synthesis of new poly(urea-imide)s **5a–5f** is illustrated in Scheme 2.

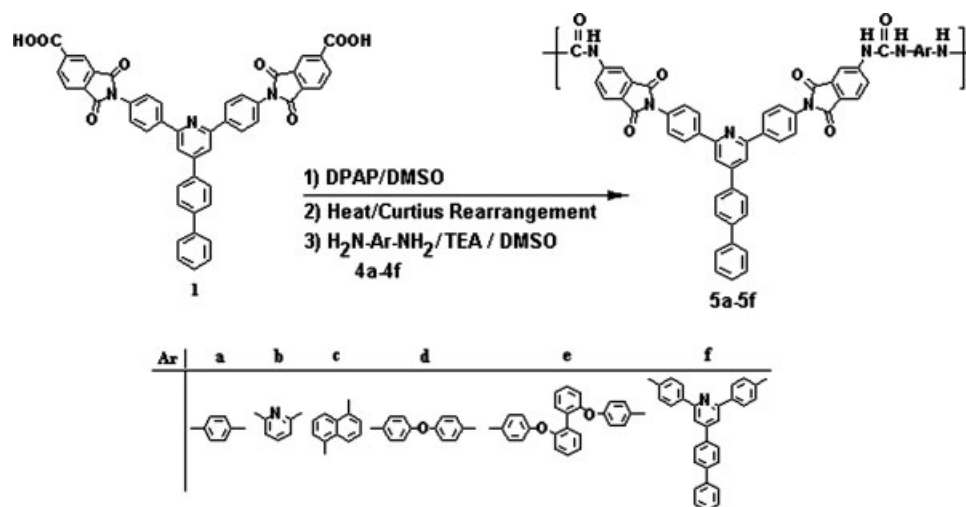
As stated for the case of the model compound synthesis, diimide-dicarboxylic acid **1** was converted to diimide-di(carbonyl azide) **2** using DPAP in DMSO. Then, the thermal decomposition of the *in situ*-obtained diimide-di(carbonyl azide) **2** via Curtius rearrangement gave the corresponding diisocyanate **3**. In continuation of this step, compound **3** confronted aromatic diamines **4a–4f** to prepare the final poly(urea-imide)s. The reactions including diisocyanate formation and polyaddition readily proceeded in a yellow to brown homogeneous solution for all polymers preparation. The poly(urea-imide)s were prepared in total yields of about 60% starting from diimide-dicarboxylic acid **1**. These low yields are reasonable because the yields of the Curtius rearrangement reactions are known generally not to be



Scheme 1 Synthesis route to prepare the model compound.

very high.^{34,35} Moreover, some impurities containing unfunctionalized or monofunctionalized species are generated in these reactions, which their presence in the polymerization flask causes a significant decrease in molecular weight of the final products. The details

about various aspects of this one-pot polyaddition were reported in literature.³⁶ As listed in Table I, the resulting yellow to brown poly(urea-imide)s possessed inherent viscosities ranging between 0.11 and 0.15 dL g⁻¹, measured in DMAc at a concentration



Scheme 2 One-pot polyaddition reactions to prepare new poly(urea-imide)s 5a–5f.

TABLE I
Some Characterization Data of Various Poly(urea-imide)s

Polymer code	Yields (%)	η_{inh}^a (dL g ⁻¹)	λ_{max}^b (nm)	Color	IR (C=O) (cm ⁻¹)		
5a	57	0.13	383	Pale yellow	1774	1718	1675
5b	56	0.12	381	Dark brown	1775	1719	1675
5c	59	0.13	376	Dark brown	1775	1719	1678
5d	61	0.15	387	Brown	1774	1718	1677
5e	56	0.11	372	Pale yellow	1775	1719	1675
5f	59	0.13	385	Yellow	1774	1718	1776

^a Measured in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C.

^b Measured in DMSO at a concentration of 0.1 mg mL⁻¹.

of 0.5 g dL⁻¹ at 30°C. The viscosity measurements provide an approximate estimate about the molecular weights by applying the Mark-Huwinck equation. In other words, molecular weights can be studied viscometrically and their measures increase when the values of viscosity increase. Although an exact opinion about molecular weights is not possible using this simple technique because of the structural effects on macromolecular expansion in solution state, it can be considered that the molecular weights of the polymers obtained are satisfactory by comparing these viscosity data with those of reported for the similar chemical structures having known molecular weights.

Furthermore, the ultraviolet maximum wavelengths (λ_{max} 's) of the polymers depending upon π to π^* allowed transitions were also determined and ranged between 372 and 387 nm. Generally, the highly conjugated aromatic structures of the obtained polymers lead to various absorption bands in their UV-vis spectra, as a number of broad and sharp peaks, which could be attributed to the various of allowed and forbidden electron transitions.

Also, the structure of the above-mentioned poly(urea-imide)s were confirmed by FTIR and ¹H NMR spectroscopy methods. The Fourier transform IR spectra of the polymers showed a wide band in the region of 3200–3500 cm⁻¹ assigned to stretching vibration of the urea N–H bonds. The characteristic absorptions of the carbonyl groups occurred around 1775, 1720 (asymmetric and symmetric imide C=O stretching, respectively), and 1675 (urea C=O stretching) cm⁻¹ (Table I). The ¹H NMR spectra of the resulting poly(urea-imide)s showed N–H proton signal in about 9.25–8.60 ppm. The aromatic ring protons appeared in the region of about 8.40–6.75 ppm. On the basis of the description above, we can conclude that the polymers have the expected structures.

To compare the solubility behavior and thermal properties of copolyimides with the same aromatic moieties, in addition to the poly(urea-imide) 5a synthesized here, three more copolyimides including poly(amide-imide), poly(ester-imide), and poly(urethane-imide) have been considered. These copoly-

imides were synthesized during our previous works,^{31–33} and their chemical structures are illustrated in Scheme 3.

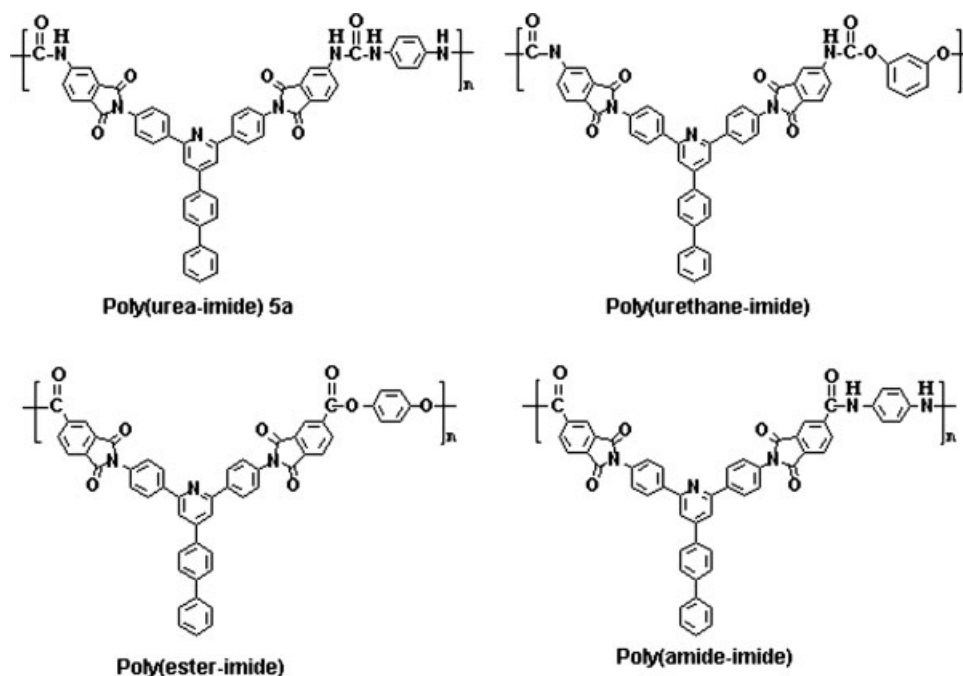
Crystallinity

The crystallinity of the prepared poly(urea-imide)s 5a–5f was measured by WXRd scans at room temperature with 2θ ranging from 5° to 45°.

In general, a rigid-rod aromatic homopolymer without bulky pendant groups or twisted structures shows crystalline pattern in its X-ray diffractogram due to the existence of the rigid planar segments in the macromolecular backbones that led to a better packing of the polymer chains. In our study, however, nearly no crystal diffraction was detected for most of the poly(urea-imide)s. This amorphous diffraction pattern is reasonable because the presence of the bulky biphenylene pendant group along the macromolecular chains decreases the intermolecular forces between the chains and induces looser chain packing causing a decrease in crystallinity of the polymers containing this group. Moreover, it could be resulted that a different diffuse diffraction pattern between the resulting polymers was revealed in the range 10°–30° depending on the structure. Among the polymers obtained, poly(urea-imide)s 5a, 5b, and 5d presented a less amorphous pattern because of their relatively ordered chemical structure. The poly(urea-imide) 5e having disorderly phenylene ether linkages as well as the poly(urea-imide) 5f, having high degree of bulky biphenylene pendant group along the main chain presented a significant decrease in crystallinity behavior. Instead, for example, the incorporation of *p*-phenylene units into the backbone of the polymer 5a resulted in low disorderly structure in comparison with the other ones, leading to a less decrease in crystallinity.

Solubility behavior

The solubility behavior of the resulting poly(urea-imide)s, 5a–5f, was studied qualitatively in a variety of common organic solvents with concentration of



Scheme 3 Copolyimides with the same aromatic moieties.

5 mg mL⁻¹ and the results were summarized in Table II.

These polymers could be easily dissolved in polar aprotic solvents such as *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc) at room temperature. Poly(urea-imide)s **5e** and **5f** were soluble even in pyridine as a moderate polar solvent at room temperature. On the other hand, all of them were insoluble in less polar solvents such as dichloromethane (DCM), toluene, and acetone at room temperature, but several of them were partially soluble upon heating in pyridine. Generally, the solubility behavior of all polymers was reflected in their crystallinity nature, which is in

agreement with the general rule that the solubility increases with decreasing crystallinity. According to this rule, for example, poly(urea-imide) **5f** possessing the least crystallinity because of its disordered chemical structure was readily soluble in all polar solvents used for this solubility test.

With an emphasis on the structures shown in Scheme 3 it may be stated that the relatively flexible amide, ester, urethane, and urea linkages affect the solubility of a copolyimide to a great extent due to a solvation effect. The poly(urea-imide) **5a** prepared herein, and the poly(urethane-imide) showed an excellent solubility in high polar solvents. On the other hand, only the poly(ester-imide) and somewhat the poly(urethane-imide) were soluble in less polar

TABLE II
Solubility of Various Copolyimides^a

Code	NMP	DMSO	DMF	DMAc	Pyridine	DCM	Toluene	Acetone
PAI	++	+	+	++	+	b	b	-
PEI	-	-	+	+	++	+	+	-
PUI	++	++	++	++	+	+	b	-
5a	++	++	++	++	-	-	-	-
5b	++	++	++	++	+	-	-	-
5c	++	++	++	++	-	-	-	-
5d	++	++	++	++	+	-	-	-
5e	++	++	++	++	++	-	-	-
5f	++	++	++	++	++	-	-	-

Solubility: ++, soluble at room temperature; +, soluble on heating; -, insoluble.

NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DCM, dichloromethane.

^a Qualitative solubility was tested with 5 mg of a sample in 1 mL of the solvent.

^b Was not checked.

TABLE III
Thermal Properties of Various Copolyimides^a

Code	T_g^b (°C)	T_{d10}^c (°C)	Char yield ^d (%)
Poly(amide-imide)	– ^e	495	55
Poly(ester-imide)	303	452	36
Poly(urethane-imide)	193	398	33
Poly(amide-imide) 5a	243	406	46
Poly(urea-imide) 5b	248	411	44
Poly(urea-imide) 5c	254	418	44
Poly(urea-imide) 5d	241	421	48
Poly(urea-imide) 5e	249	429	45
Poly(urea-imide) 5f	272	437	49

^a Data of PAI, PEI, and PUI from Refs. 30, 31, and 32, respectively.

^b From the second heating traces of DSC measurements with a heating rate of 10°C min⁻¹ in nitrogen.

^c temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C min⁻¹ in nitrogen.

^d Percentage weight of material left undecomposed after TGA analysis at maximum temperature 800°C in nitrogen.

^e Was not determined.

solvents. With due attention to the other findings of our previous studies,^{31–33} this observed solubility behavior in these four blocks of copolyimides can be generalized for the structures other than those shown in Scheme 3. These observations may be explained as follows: the strong solvation of ester linkages and somewhat urethane groups by pyridine and less polar solvents causes the better solubility of the poly(ester-imide)s and poly(urethane-imide)s in this class of solvents whereas the strong solvation of the amide, imide, and the urea linkages by high polar aprotic solvents improved the solubility of the poly(amide-imide)s and poly(urea-imide)s in NMP, DMAc, DMF, and DMSO. In addition to the solvation effects related to enthalpy factor, the good solubility of these copolyimides is also caused by the entropy advantage resulted from the bulky biphenylene pendant group in the polymer backbone that leads to expansion of the macromolecular chains in their solution state. This means that the organosoluble behavior of these copolyimides could also be attributed to the introduction of this bulky group that inhibited the close packing of the polymer chains.

Thermal properties

The thermal properties of the resulting poly(urea-imide)s were determined by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The thermal behavior data of the polymers are summarized in Table III.

A rapidly quenching from the elevated temperatures to room temperature yields predominately amorphous samples so that discernible baseline shifts could be easily measured in the DSC charts of

the second-heating trace. The DSC thermograms of the poly(urea-imide)s showed glass-transition temperatures (T_g 's) at about 250°C depending on the structure of aromatic diamine component, and the increasing order of T_g generally corresponded to an increase in the rigidity and bulkiness of the diamine monomer moiety. All the poly(urea-imide)s displayed distinct glass transitions on the second heating DSC traces and had T_g 's in the range of 241–272°C. These high glass transitions could be attributed to the incorporation of rigid wholly aromatic segments along the polymers backbone, which restricted the free rotation of the macromolecular chains leading to an enhanced T_g values. Polymer **5f** with a high degree of bulky biphenylene pendant group in the polymer chain exhibited the highest T_g value among these poly(urea-imide)s. Figure 1 shows DSC curves of the resulted polymers.

Moreover, among the copolyimides with the same aromatic moieties shown in Scheme 3, poly(urea-imide) **5a** had a more value of T_g than the poly(urethane-imide) but a less value than the poly(ester-imide). This observation might be resulted from both the inherent rigidity of the above functional groups and intermolecular interactions of the chains. In fact, value of the T_g 's was determined by the net effect of the mentioned factors.

The thermal stability of the obtained poly(urea-imide)s was also evaluated by TGA in nitrogen atmosphere at a heating rate of 10°C min⁻¹. There

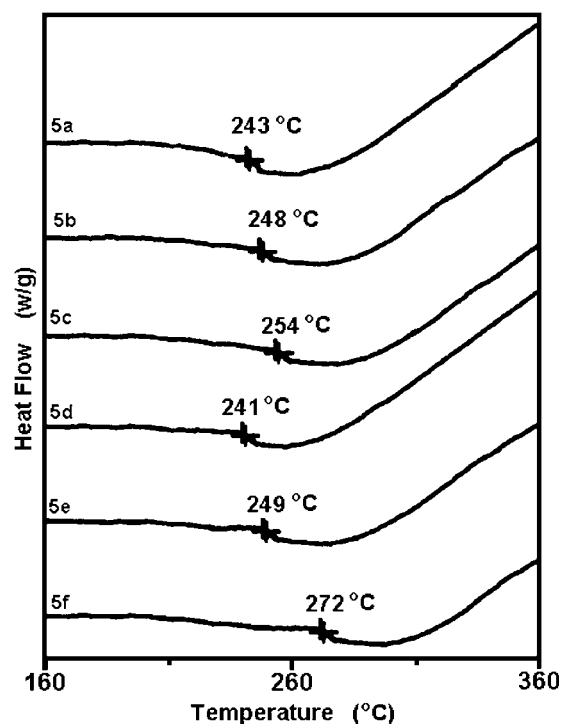


Figure 1 DSC thermograms of the poly(urea-imide)s **5a–5f** obtained.

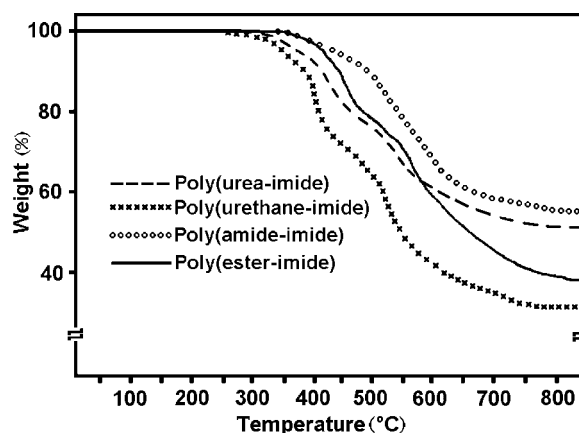


Figure 2 TGA thermograms of the copolyimides with the same aromatic moieties, shown in Scheme 3, at a heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen.

was no significant difference in thermal stability curves of the polymers. All of them showed two-step thermal decomposition pattern in their thermograms. Assuming a different stability of the urea and the imide units, the first stage of weight losses might be attributed to the early degradation of the urea linkages. Therefore, the 10% weight loss temperatures are mainly caused by the decomposition of ureylene linkages. Since the dipoles present at the urea groups are the weakest sites in terms of thermal stability, the rupture of the urea bonds occurs first. The decomposition temperatures for 10% weight loss ranged from 406 to 437°C . On the basis of these results, all the polymers showed nearly high thermal stability which this can be attributed to the heat resistant wholly aromatic structure of the macromolecular chains. Among the polymers, the poly(urea-imide) **5f**, derived from compound **1** and 4-*p*-biphenyl-2,6-bis(4-aminophenyl)pyridine (**4f**), exhibited the highest $T_{d10\%}$ value. For all polymers, percentage weight of material left undecomposed after TGA analysis at maximum temperature 800°C in nitrogen was about 45%.

Now, we would like to compare the decomposition behavior of the above poly(urea-imide)s with the other copolyimides including poly(amide-imide), poly(ester-imide), and poly(urethane-imide). As a logical comparison, we have to consider structures with identical aromatic moieties such as those drawn in Scheme 3. An obvious difference was not observed for decomposition profiles of the copolymers except for the poly(amide-imide) decomposition behavior. In fact, all the copolyimides except the poly(amide-imide) showed distinguished two-stage decomposition at elevated temperatures. These observations might be attributed to the early degradation of the ester, urethane, and ureylene linkages than the imide functional groups against high temperatures. However for the poly(amide-imide), this

thermal decomposition followed from a one-stage degradation behavior. With comparison between the results obtained from the thermal analyses, it can be concluded the better heat stability of a poly(amide-imide) copolymer than the other ones (Table III). For further evaluation of the heat stabilities, thermal decomposition plots of the copolyimides with the same aromatic segments are presented in Figure 2.

CONCLUSIONS

A series of new poly(urea-imide)s, **5a–5f**, having biphenylene pendant groups in the macromolecular chains derived from an imide ring-containing dicarboxylic acid **1** were synthesized by the DPAP-activated polyaddition reactions with various aromatic diamines in a medium consisting of DMSO and triethylamine. In this direct method, separate synthesis and purification of the intermediate diisocyanate was not necessary, and the polyaddition readily proceeded as a one-pot reaction starting from dicarboxylic acid **1**. Solubility and thermal stability of the resulting poly(urea-imide)s were the main properties that their relationship with the chemical structure of the polymers was investigated and compared with the other copolyimides including poly(amide-imide)s, poly(ester-imide)s, and poly(urethane-imide)s bearing the same aromatic moieties. All of the copolyimides had a noncrystalline nature because of the presence of the bulky biphenylene pendant group along the macromolecular chains. The poly(urea-imide) and poly(urethane-imide) had better solubility than the poly(amide-imide) and poly(ester-imide) in high polar solvents. Among these series of copolyimides, the poly(amide-imide) had more thermal stability than the rest.

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References

- Mittal, K. L. *Polyimides: Synthesis, Characterization and Applications*; Plenum: New York, 1984; Vols. 1/2.
- Feger, C.; Khojasteh, M. M.; Htoo, M. S. *Advances in Polyimide Science and Technology*; Technomic: Lancaster, 1993.
- Abadie, M. J. M.; Sillion, B. *Polyimides and Other High-Temperature Polymers*; Elsevier: New York, 1991; p 255.
- Yang, C. P.; Chen, Y. P.; Woo, E. M. *J Polym Sci Part A: Polym Chem* 2004, 42, 3116.
- Yang, C. P.; Su, Y. Y. *Macromol Chem Phys* 2005, 206, 1947.
- Saxena, A.; Prabhakaran, P. V.; Rao, V. L.; Ninan, K. N. *Polym Int* 2005, 54, 544.
- Behniafar, H.; Banihashemi, A. *Eur Polym Mater* 2004, 40, 1409.
- Banihashemi, A.; Behniafar, H. *Polym Int* 2003, 52, 1136.
- Banu, P.; Radhakrishnan, G. *J Polym Sci Part A: Polym Chem* 2004, 42, 341.

10. Behniafar, H.; Jafari, A. *J Appl Polym Sci* 2006, 100, 3203.
11. Mehdipour-Ataei, S.; Amirshaghghi, A. *J Appl Polym Sci* 2005, 96, 570.
12. Behniafar, H.; Habibian, S. *Polym Int* 2005, 54, 1134.
13. Behniafar, H.; Akhlaghinia, B.; Habibian, S. *Eur Polym Mater* 2005, 41, 1071.
14. Yeganeh, H.; Atai, M.; Hojati, T. P.; Jamshidi, S. *Macromol Mater Eng* 2006, 291, 883.
15. Qin, X.; Yang, X.; Wang, X.; Wang, M. *J Polym Sci Part A: Polym Chem* 2005, 43, 4469.
16. Park, M. H.; Jang, W.; Yang, S. J.; Shul, Y.; Han, H. *J Appl Polym Sci* 2006, 100, 113.
17. Liu, J.; Ma, D. *J Appl Polym Sci* 2002, 84, 2206.
18. Behniafar, H.; Haghghat, S.; Farzaneh, S. *Polymer* 2005, 46, 4627.
19. Liu, J.; Li, Z.; Luo, X.; Ma, D. *J Polym Sci Polym Phys* 2004, 42, 216.
20. Wang, H. H.; Wu, S. P. *J Appl Polym Sci* 1999, 74, 1719.
21. Yang, Y.; Zhi, Z.; Yang, X.; Lu, L.; Wang, X. *Eur Polym Mater* 1998, 34, 1893.
22. Park, K. H.; Tani, T.; Kakimoto, M.; Imai, Y. *Macromol Chem Phys* 1998, 199, 457.
23. Behniafar, H. *J Macromol Sci* 2006, 43, 813.
24. Kulkarni, M.; Kothawade, S.; Arabale, G.; Wagh, D.; Vijayamohanan, K.; Kulkarni, R. A.; Vernekar, S. P. *Polymer* 2005, 46, 3669.
25. Wang, L.; Chang, P.; Cheng, C. L. *J Appl Polym Sci* 2006, 100, 4672.
26. Kricheldorf, H. R.; Fan, S. C.; Vakhtangishvili, L.; Schwarz, G.; Fritsch, D. *J Polym Sci Part A: Polym Chem* 2005, 43, 6272.
27. Pal, R. R.; Patil, P. S.; Dere, R. T.; Salunkhe, M. M.; Maldar, N. N.; Wadgaonkar, P. P. *J Appl Polym Sci* 2005, 97, 1377.
28. Maya, E. M.; Lozano, A. E.; Campa, J. G.; Abajo, J. *Macromol Rapid Commun* 2004, 25, 592.
29. Imai, Y.; Itoya, K.; Kanamaru, M.; Kakimoto, M. A. *J Polym Sci Part A: Polym Chem* 2002, 40, 1790.
30. Weiss, M. *J Am Chem Soc* 1952, 74, 200.
31. Behniafar, H.; Banihashemi, A. *Polym Int* 2004, 53, 2020.
32. Behniafar, H.; Khaje-Mirzai, A. A.; Beit-Saeed, A. *Polym Int* 2007, 56, 74.
33. Behniafar, H. *J Appl Polym Sci* 2006, 101, 869.
34. Dong, H. S.; Jia, W.; Cui, J. D.; Wang, Q. L. *J Chin Chem Soc* 2003, 50, 1209.
35. Cram, D. J.; Bradshaw, J. S. *J Am Chem Soc* 1963, 85, 1108.
36. Nishi, N.; Tsunemi, M.; Nakamura, K.; Tokura, H. *Die Makromol Chem* 1991, 192, 1811.