

Organosoluble and Thermally Stable of Benzazole-Containing Poly(Imide-Urea)s: One-Pot Synthesis and Characterization

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Abstract

The preparation of new types of poly(imide-urea)s (PIUs) with high thermal stability and improved solubility was investigated. Three series of aromatic poly(imide-urea)s (PIU_O**a-c**, PIU_S**a-c**, and PIU_N**a-c**) bearing pendent benzoxazole, benzothiazole or benzimidazole rings were prepared by one-pot polycondensation reaction of three bis(imide-carboxylic acid)s, 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzoxazole (**1_O**), 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzothiazole (**1_S**), or 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzimidazole (**1_N**) with various kinds of aromatic diamines (**a-c**). The effects of the benzazole pendent groups on the polymer properties such as solubility and thermal stability were investigated by comparison of the polymers. All of the resulting polymers exhibited excellent solubility in common polar solvents. The glass transition temperature of the polymers determined by DSC thermograms were in the range 192°C - 236°C. The temperatures at 10% weight loss from their TGA curves were found to be in the range 390°C - 441°C in nitrogen.

Keywords: Poly(Imide-Urea)s, Structure-Property Relation, Thermal Properties, Benzazole Pendent Groups

1. Introduction

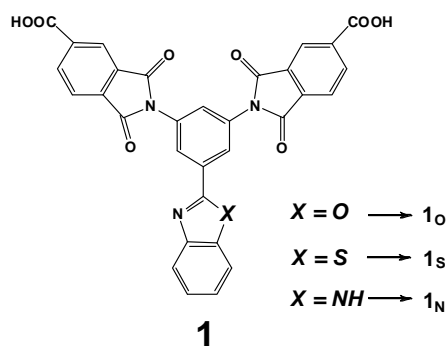
Aromatic polyimides (PIs) are well known as materials of high performance were developed in the early 1960s and since then have been of great technological importance because of their outstanding thermal stability and chemical resistance, together with their balanced electric and mechanical properties [1,2]. Because many of them are insoluble and infusible, however, their applications in some fields were limited. It is well known that the poor properties of PIs have a close connection with its chemical composition and chain structure, in other words, the chemical composition and chain structure of PIs will be a head ingredient leading them to infusible within processing temperature and insoluble in organic solvents. Thus, incorporating new functionalities to make polyimides more tractable without decreasing their many desirable properties has become one important target of polyimides' chemistry [3,4]. So far, many efforts on chemical modifications of polyimides structure have been made to enhance their processability and solubility while other advantageous polymer properties are retained either by introducing flexible linkages, bulky groups, or

molecular asymmetry into the polymer backbone [5-19]. Among these approaches, the method of incorporating bulky, rigid benzazole hetero rings as pendent groups into the polymer backbone has become very attractive [20-23]. The advantages of this method include two main parts: (1) close chain packing and intermolecular interactions of the resulting polyimide are restricted, and this results in relatively high polymer solubility, and (2) the main chain rigidity of the polyimide can be maintained by restricting the segmental mobility, in addition, these benzazole hetero rings are thermally stable, and these allow the polyimide to have a high glass-transition temperature (T_g) and excellent thermal properties.

As reported in our previous publications [22,23], three bis(imide-carboxylic acid)s, 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzoxazole (**1_O**), 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzothiazole (**1_S**), and 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzimidazole (**1_N**) were synthesized via a two-stage procedure that included the condensation reaction between 2-aminophenol, 2-aminothiophenol, or *m*-phenylenediamine and 3,5-diaminobenzoic acid in the presence of polyphosphoric acid (PPA) in 190°C, followed by their reaction two mole

equivalents of trimellitic anhydride in refluxing glacial acetic acid, and were used to prepare aromatic poly(amide-imide)s containing benzazole hetero rings pendent groups in the backbones.

Because of the bulky heat-resistant structure of the components **1_O**, **1_S**, and **1_N** as pendent groups, the resulting polymers exhibited reduced chain-packing efficiency and intermolecular interactions such as hydrogen bonding. Therefore, several organosoluble poly(amide-imide)s with moderate T_g s and high thermal stability could be achieved by the incorporation of the benzazole pendent units in the main chain. These results prompted us to use bis(imide-carboxylic acid) monomers (**1_O**, **1_S**, and **1_N**), and to study the properties of the poly(imide-urea)s obtained by direct polycondensation of them with aromatic diamines (**a-c**).



2. Experimental

2.1. Materials

Diphenyl azidophosphate (DPAP) purchased from Merck and used as received. Dimethyl sulfoxide (DMSO, Merck) and triethylamine (TEA, Merck) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. 2,6-Diaminopyridine (**a**, Merck) was purified by sublimation before use. Aromatic diamines including 5-(2-benzoxazole)-1,3-phenylenediamine (**b**, mp 226°C - 230°C), and 5-(2-benzothiazole)-1,3-phenylenediamine (**c**, mp 167°C - 171°C) were prepared in our laboratory according to the method previously reported [22].

2.2. Synthesis of the Monomer

Bis(imide-carboxylic acid) monomers **1_O**, **1_S**, and **1_N** were synthesized by the condensation of 5-(2-benzoxazole)-1,3-phenylenediamine, 5-(2-benzothiazole)-1,3-phenylenediamine, and 5-(2-benzimidazole)-1,3-phenylenediamine, with two mole equivalents of trimellitic anhydride in glacial acetic acid, respectively, according to our previous works [22,23].

2.3. Synthesis of Poly(Imide-Urea)s (PIUs)

The general procedure to prepare the poly(imide-urea)s is as follows: into a 50 mL two-neck round-bottom flask equipped with a drying tube-capped reflux condenser, magnetic stirrer, and dropping funnel were placed bis(imide-carboxylic acid) **1_O** (0.172 g, 0.30 mmol) in DMSO (2.0 mL). Then, DPAP (0.7 mL) and triethylamine (0.8 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. 2,6-Diaminopyridine (**a**) (0.032 g, 0.30 mmol) in DMSO (2.5 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 40°C to afford 0.103 g (51%) of PIU_{Oa} as dark brown powder.

The inherent viscosity of the poly(imide-urea)s obtained in *N,N*-dimethylacetamide (DMAc) was 0.22 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

FT-IR (KBr, cm^{-1}): 3352, 3190 (br, m), 1778 (sh, w), 1724 (sh, s), 1677 (sh, s), 1616 (sh, m), 1595 (sh, w), 1502 (sh, m), 1449 (sh, m), 1349 (sh, s), 1206 (sh, w), 1163 (sh, w), 1096 (sh, m), 1035 (sh, w), 924 (sh, w), 893 (sh, w), 763 (sh, w), 725 (sh, m), 675 (sh, w).
¹H-NMR (DMSO-*d*₆; δ , ppm): 8.81 ppm (4H of ureylene linkages), 7.44 - 8.46 ppm (separate peak blocks, 16H of aromatic rings). Elemental analysis: calculated for C₃₆H₂₀N₈O₇ (676)_n: C, 63.72%; H, 2.27%; N, 16.51%. Found: C, 63.21%; H, 2.24%; N, 16.09%.

The above one-pot polyaddition reaction was chosen as a procedure for preparation of the other PIUs.

2.4. Measurements

Inherent viscosities (η_{inh}) of polymers were determined for solution of 0.5 g/dL in DMAc at 30°C using a Canon-Fenske viscometer. ¹H-NMR spectra were recorded on a Bruker AV-500 FT-NMR spectrometer in DMSO-*d*₆ at 25°C with frequencies of 500.13 MHz. FT-IR spectra were recorded on a Bruker Tensor-27 spectrometer for the measurement of infrared absorption spectra for monomers and polymers. The spectra of solids were obtained using KBr pellets. Melting points (mp) were determined with a Buchi 535 melting point apparatus. Thermogravimetric analyses (TGA) was conducted with a Du Pont 2000 thermal analysis under nitrogen atmosphere (20 cm³/min) at a heating rate of 20°C/min. Differential scanning calorimeter (DSC) was recorded on a Perkin Elmer pyris 6 DSC under nitrogen atmosphere.

(20 cm³/min) at a heating rate of 20 °C /min.

3. Result and Discussion

3.1. Synthesis and Characterization

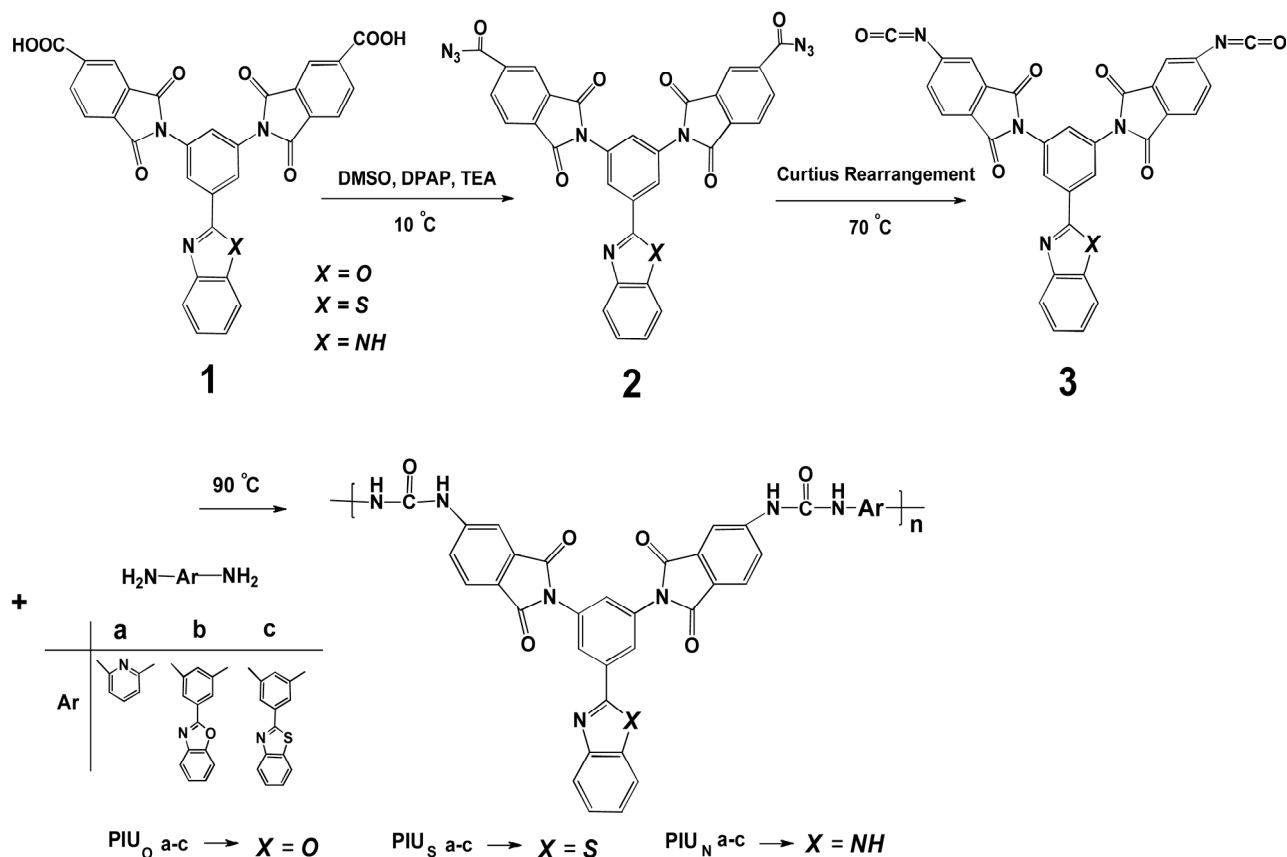
Bis(imide-carboxylic acid) monomers such as **1_O**, **1_S**, and **1_N** were synthesized by the condensation reaction between the appropriate aromatic diamine, 5-(2-benzoxazole)-1,3-phenylenediamine, and 5-(2-benzothiazole)-1,3-phenylenediamine, 5-(2-benzimidazole)-1,3-phenylenediamine, and two mole equivalents of trimellitic anhydride in glacial acetic acid, respectively. The details of this synthesis route and the characterization data were reported in our previous works [22,23].

Three series of aromatic poly(imide-ureas) (PIUs) having benzoxazole, benzothiazole, and benzimidazole pendent group were prepared by the diphenyl azido-phosphate (DPAP) activated one-pot polycondensation reaction of three bis(imide-carboxylic acid) monomers, 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzoxazole (**1_O**), 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzothiazole (**1_S**), and 2-[3,5-bis(*N*-trimellitimidoyl)-phenyl]benzimidazole

(**1_N**) with various aromatic diamines (**a-c**).

As shown in **Scheme 1**, bis(imide-carboxylic acid) monomers, **1** were converted to bis(imide-carbonyl azide) components, **2** using DPAP in DMSO as the reaction solvent. The thermal decomposition of the *in situ* obtained bis(imide-carbonyl azide) **2** via Curtius rearrangement gave the corresponding diisocyanates **3**. In continuation of this reaction, compounds **3** have been reacted with various aromatic diamines (**a-c**) to prepare the final benzazole-based poly(imide-ureas) (PIUs).

The reactions including diisocyanate formation and polyaddition readily proceeded in a dark yellow to brown homogeneous solution for all polymers preparation. The poly(imide-ureas) were prepared in total yields of about 60% starting from bis(imide-carboxylic acids) **1**. These low yields are reasonable because the yields of the Curtius rearrangement reactions are known generally not to be very high [24]. 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



Scheme 1. One-pot synthetic route to prepare new poly(imide-ureas).


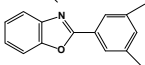
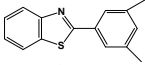

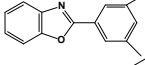
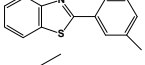

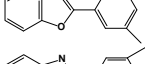
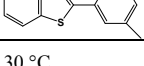
reported in literature [25]. As listed in **Table 1**, the resulting dark yellow to brown poly(imide-urea)s possessed inherent viscosities ranging between 0.10 dL/g and 0.22 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 °C.

Because, the inherent viscosity is a criterion for the es-

timination of molecular weight [23] the prepared PIUs showed reasonable molecular weights.

Also, structural features of these poly(imide-urea)s were verified by IR and proton NMR spectroscopy. Representative FT-IR spectrum of PIUs**b** is shown in **Figure 1**. It displays characteristic absorption bands for

Table 1. Some characterization data of the resulting poly(urea-imide)s.

Polymer code	bis(imide-carboxylic acid)s	Diamine structure	Yield (%)	η_{inh}^a (dL/g)	Color and appearance
PIU _{Oa}	1_O		51	0.22	dark brown powder
PIU _{Ob}	1_O		56	0.17	peal brown powder
PIU _{Oc}	1_O		50	0.15	brown powder
PIU _{Sa}	1_S		61	0.19	greenish powder
PIU _{Sa}	1_S		54	0.20	brown powder
PIU _{Sa}	1_S		63	0.17	greenish powder
PIU _{Na}	1_N		57	0.15	black powder
PIU _{Na}	1_N		43	0.10	peal brown powder
PIU _{Na}	1_N		54	0.13	black powder

^aMeasured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

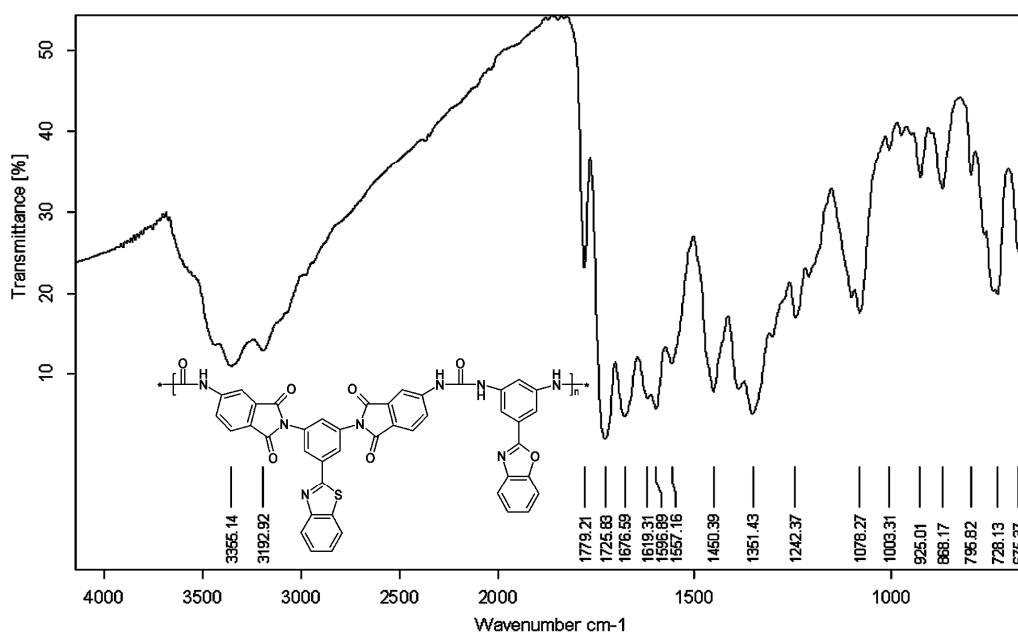


Figure 1. FTIR spectrum of PIUsb**.**

the imide ring at around 1779 and 1725 cm^{-1} (imide-I), which is indicative of the asymmetrical and symmetrical C=O stretching vibration, and at 1351 (imide-II), 1078 (imide-III) and 728 cm^{-1} (imide-IV) whereas the imide-I, -III, -IV bands were assigned to axial, transverse, and out-of-plane vibrations of the cyclic imide structure, respectively [22,28]. The N-H stretching band of the urea could be observed around 3200 - 3350 cm^{-1} , and the C=O stretching band of urea groups at 1676 cm^{-1} , the C=N stretching band benzothiazole groups at 1619 cm^{-1} and the N-H bending and C-N stretching bands at 1557 cm^{-1} could also be observed. Other PIUs had similar functional groups.

In general, the $^1\text{H-NMR}$ spectra of the resulting poly(imide-urea)s are divided two parts, with the first showing the urea-group protons in the most downfield region (around 8.60 - 9.05 ppm), and the second, reso-

nance signals of aromatic protons in the region of about 7.25 - 8.53 ppm. On the basis of the description above, we can conclude that the PIUs have the expected structures. For example, the $^1\text{H-NMR}$ spectrum of PIU_{0a} is presented in **Figure 2**. The $^1\text{H-NMR}$ spectrum of PIU_{0a} shows four protons at 8.81 δ that are assigned to hydrogen atoms of ureylene linkages, aromatic protons at 7.44 - 8.46 δ with expected multiples and integration is consistent with the expected structure of the compound.

3.2. Properties of the Poly(Imide-Urea)s

The solubility of all poly(imide-urea)s was tested qualitatively in various organic solvents, with the results summarized in **Table 2**. One of the aims of the present investigation was the enhancement of the polymer solubility by introducing voluminous pendent groups

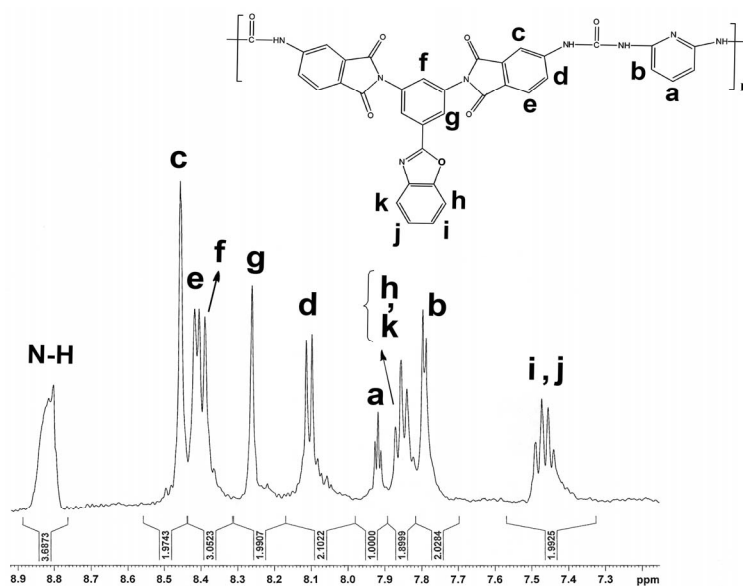


Figure 2. $^1\text{H-NMR}$ spectrum of PIU_{0a} (500 MHz, DMSO- d_6).

Table 2 Solubility of the poly(imide-urea)s.

Polymer code	Solvent ^a							
	DMAc	DMSO	DMF	NMP	<i>m</i> -cresol	THF	Py	CF
PIU _{0a}	+	+	+	+	+h	-	+h	-
PIU _{0b}	+	+	+	+	+	+h	+h	-
PIU _{0c}	+	+	+	+	+	+h	+	+h
PIU _{3a}	+	+	+	+	+	-	-	-
PIU _{3b}	+	+	+	+	+	+h	+	+h
PIU _{3c}	+	+	+	+	+	+h	+	+h
PIU _{Na}	+	+	+	+	+h	-	+h	-
PIU _{Nb}	+	+	+	+	+h	-	+h	-
PIU _{Nc}	+	+	+	+	+	-	+h	-

^a Qualitative solubility was determined by dissolving 10 mg of poly(imide-urea)s in 1 ml of solvent at room temperature or upon heating; + : soluble at room temperature; +h : soluble on heating; and - : insoluble even on heating; DMAc: *N,N*-dimethylacetamide; DMSO: dimethyl sulfoxide; DMF: *N,N*-dimethylformamide; NMP: *N*-methyl pyrrolidone; THF: tetrahydrofuran; Py: pyridine; CF: Chloroform.

along the polymer backbone.

The poly(imide-urea)s, PIU_{0a-c} were readily soluble in polar aprotic solvents (DMF, NMP, DMAc, DMSO). They also dissolved in *m*-cresol and pyridine, while they were partially soluble in chloroform and tetrahydrofuran upon heating at about 70°C. Poly(imide-urea)s, PIU_{sa-c}, compared to PIU_{0a-c} displayed almost the same solubility in these solvents. In general, the flexible amide, ether, and urea linkages affect the solubility of a copolyimide to a great extent due to a solvation effect. Besides the solvation effects related to enthalpy factor, the good solubility of these polymers is also caused, mainly by the entropy advantage which resulted from bulky pendant groups in the polymer structures that lead to expansion of the macromolecular chains in their solution state. Furthermore, this block of copolyimides showed somewhat further solubility toward the above solvents compared with that of the other copolyimides with analogous structure [22,23,28,29]. The better solubility of poly(imide-urea)s, should be attributed to the interchain steric repulsion caused by the bulky benzoxazole, benzothiazole or benzimidazole side groups. The chain separation effect accounts for a weakening of the strong interactions through hydrogen bonding and the steric factor must be dominant because the other effects, such as dipole attraction or chain rigidity enhancement, should work against good solubility.

The thermal properties of the resulting poly(imide-urea)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 3**. The DSC profiles were achieved at a heating rate of 20°C/min in a nitrogen atmosphere in the temperature range from 100°C to 300°C. The DSC thermograms of the poly(imide-urea)s showed glass-transition temperatures (T_g 's) in the range between 192°C and 236°C. The nature of the diamine moiety played a significant role on the T_g values. These went down in the series as follows **b** > **c** > **a** (**Table 3**). This could be attributed to the incorporation of rigid benzoxazole or benzothiazole ring in diamine segments, which restricted the free rotation of the macromolecular chains leading to an enhanced T_g value. Upon comparing the chemical structures of the pendant groups, it is seen that benzoxazole was somewhat more T_g than benzothiazole [20,22]. **Figure 3** shows DSC curves of the polymers PIU_{0b}, PIU_{sb}, and PIU_{Nb}.

In order to compare the thermal properties, some homo and copolymers, including polyimide, polyurea, poly(imide-amide), poly(imide-ether), and poly(imide-amide-ether) with the structures shown in **Scheme 2** were considered.

Table 3. Thermal properties of the poly(imide-urea)s.

Polymer code	T_g^a (°C)	T_{10}^b (°C)	Char yield ^c (wt%)
PIU _{0a}	209	408	38
PIU _{0b}	236	441	47
PIU _{0c}	216	412	44
PIU _{sa}	194	390	30
PIU _{sb}	223	417	41
PIU _{sc}	219	394	38
PIU _{Na}	192	397	36
PIU _{Nb}	201	437	42
PIU _{Nc}	197	415	39

^a Form the second heating traces of DSC measurements with a heating rate of 20°C.min⁻¹ in nitrogen. ^b Temperature at which 10% weight loss was recorded by TGA at a heating rate of 20°C.min⁻¹ in nitrogen. ^c Char yield at 800°C.

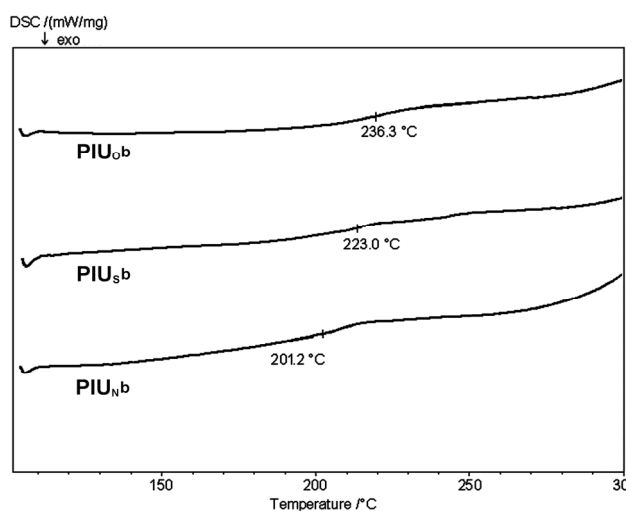
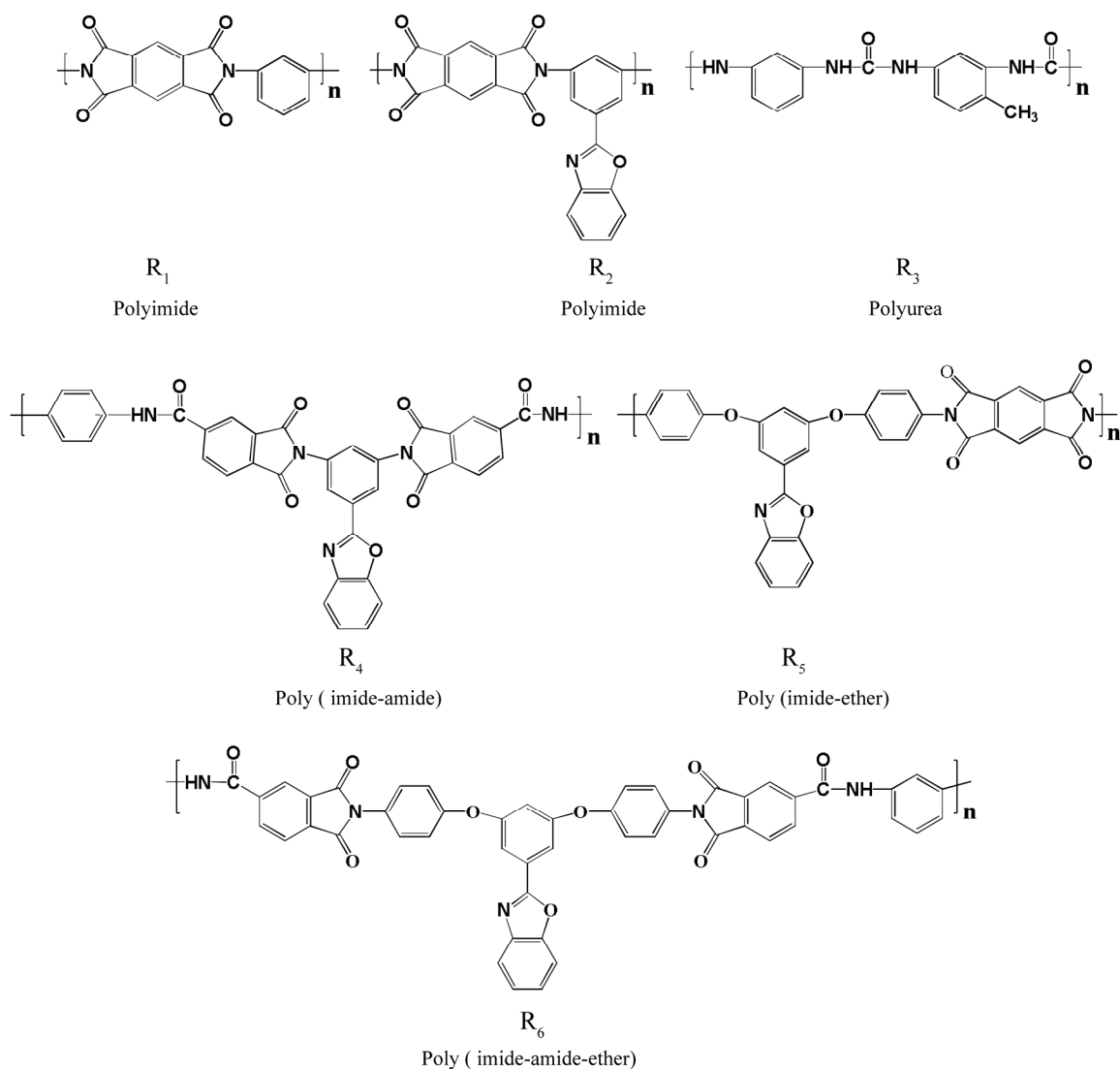


Figure 3. DSC thermograms of PIU_{0b}, PIU_{sb}, and PIU_{Nb}.

The thermal properties of these reference polymers are also listed in **Table 4**. All the poly(imide-urea)s exhibited lower T_g 's than the fully aromatic homopolyimide **R**₁, the poly(imide-amide) **R**₄, the poly(imide-ether) **R**₅, and the poly(imide-amide-ether) **R**₆ due to higher flexibility of the urea linkages than those of imide, amide and ether bonds.

Thermal stability of the polymers was evaluated by TGA in nitrogen at a heating rate of 20°C/min. The poly(imide-urea)s obtained were stable up to 400°C and lost 10% of their total weight between 390°C and 441°C, which showed a remarkably improvement of decomposition temperature in comparison with common homopolyurea **R**₃. There are similarities in the thermal stabilities of all PIUs. In fact, all of them showed two step thermal decomposition pattern in their thermograms. The temperature maximum decomposition of the first stage is



Scheme 2. The chemical structure of some reference polymers.

Table 4. Thermal properties of some reference polymers.

Polymer code	Polymer class	T_g (°C)	T_{10} (°C)	Char yield (wt%) ^a	Ref.
R ₁	Polyimide	412	551 ^c	57	20, 26
R ₂	Polyimide	— ^b	616 ^c	62	20
R ₃	Polyurea	— ^b	300	— ^b	27
R ₄	Poly(imide-amide)	— ^d	561	60	22
R ₅	Poly(imide-ether)	279	543	59	28
R ₆	Poly(imide-amide-ether)	263	513	52	29

^a Residual wt% at 800°C in nitrogen. ^b Was not reported. ^c Maximum polymer decomposition temperature. ^d No discernible transition was observed on the DSC traces.

at around 360°C - 385°C, which corresponds to the decomposition of the urea groups. The second-stage decomposition, started around 540°C - 570°C, is due to the

decomposition of the imide linkages. Therefore, the 10% weight loss temperatures are mainly caused by the decomposition of ureylene linkages. As shown in **Table 4**,

the poly(imide-urea)s exhibited less thermal stability than those of the homopolyimide **R**₁ and **R**₂, the poly(imide-amide) **R**₄, the poly(imide-ether) **R**₅, and the poly(imide-amide-ether) **R**₆. However, they showed higher T_{10%} values than the homopolyurea **R**₃. These observations might be attributed to the early degradation of the urea linkages than those of the imide, amide and even ether groups against high temperatures. Furthermore, when the heat-resistant benzoxazole or benzothiazole ring incorporated as pendent group to the diamines **c** and **b**, an obvious increase was observed for decomposition profiles aromatic PIU than unsubstituted diamine **a** in each series. Upon comparing the chemical structures of the pendent groups, it is seen that benzoxazole was somewhat more thermally stable than benzothiazole (**Table 3**).

4. Conclusions

The one-pot polyureylation reactions of bis(imide-carboxylic acid)s, namely, **1**_O, **1**_S, and **1**_N with a number of aromatic diamines (**a-c**) resulted in preparation of aromatic poly(imide-urea)s (PIU_{Oa-c}, PIU_{sa-c}, and PIU_{Na-c}). The main objectives of this study were to improve the solubility of homopolyimides as well as the thermal stability of homopolyurea by the introduction of both imide and urea linkages into the macromolecular chains. Most of the poly(imide-urea)s presented an excellent solubility in polar aprotic solvents such as, NMP, DMF, DMAc, and DMSO, while they were partially soluble in *m*-cresol and pyridine and also they were not soluble in less polar solvents such as chloroform and tetrahydrofuran at room temperature. The resulting poly(imide-urea)s showed a better solubility in common organic solvents than the polyimides, poly(imide-amide)s, and even poly(ether-imide)s with the same aromatic structure. Furthermore, the amorphous polymers obtained exhibited a desirable heat resistance in comparison with aromatic polyureas due to the presence of thermally stable imide groups as well as heat-resistant benzoxazole and benzothiazole rings into the fully aromatic structures.

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