

Synthesis and Characterization of Schiff-Base-Containing Polyimides

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ABSTRACT: Benzyl bithiosemicarbazone and its complexes with nickel (NiLH₄) and copper (CuLH₄) were used as diamine monomers for the synthesis of new Schiff-base polyimides. The solution polycondensation of these monomers with the aromatic dianhydrides afforded metal-containing Schiff-base polyimides with inherent viscosities of 0.98–1.33 dL/g (measured in *N*-methyl-2-pyrrolidone at 25°C). The polyimides were generally soluble in a wide range of solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, tetrahydrofuran, dimethyl sulfoxide,

tetrachloroethane, hexamethylene phosphoramidate, *N*-methyl-2-pyrrolidone, ethyl acetate, and pyridine at room temperature. The initial degradation temperatures of the resultant polyimides fell in the range of 220–350°C in nitrogen with char yields ranging from 36 to 64% at 700°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2496–2501, 2010

Key words: polycondensation; polyimides; synthesis; thermal properties

INTRODUCTION

Aromatic polyimides (PIs) are well known as high-performance polymeric materials. However, most aromatic PIs have poor processability because of high softening temperatures and no solubility.¹ Therefore, many attempts have been made to improve the processability of aromatic PIs with several different approaches, such as the introduction of pendent groups onto the polymer chains and the incorporation of noncoplanar structural units into the main chain, while their excellent level of thermal and mechanical properties is maintained.^{2–10} To achieve such a goal, of course, it is necessary to design and synthesize new monomers—diamines, dianhydrides, or both—that can fulfill this requirement. Polymers with a Schiff-base structure (polyazomethine), which have many special properties, have been drawing the attention of researchers for more than 50 years. A variety of polymers with a Schiff-base structure have been synthesized, characterized, and investigated with respect to their properties.^{11–20} A major obstacle to characterizing and developing these conjugated aromatic Schiff-base PIs with high thermal stability has been their lack of solubility in common organic solvents. Schiff-base metal complexes are a broad class of compounds that have received much less attention for incorporation into macromolecules.^{21–24} Seckin et al.²² reported the preparation of

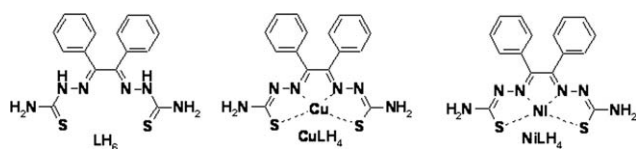
a partially soluble Schiff-base PI from 2,6-bis[1-(*p*-dimethylaminophenylimino)ethyl pyridine and used it for the selective extraction of some metals. Bella et al.²⁴ reported the synthesis and preparation of an insoluble PI film containing a Schiff-base complex of a bis(salicylaldiminato)Ni^{II}-functional amino derivative in the main chain. Researchers have demonstrated that the introduction of metals into polyurea,²⁵ bismaleimides,²⁶ and PIs²⁷ improves the thermal stability, and their initial decomposition temperatures show a relationship with the introduced metals. Bithiosemicarbazones can act as tetradentate ligands and can be coordinated with nickel and copper ions via N₂S₂ or N₄ atoms. We have reported the preparation of polyamides from a copper complex of benzyl bithiosemicarbazone (LH₆) with different dicarboxylic acids in a previous publication.²¹ To the best of our knowledge, no article has dealt with the preparation of PIs from LH₆ and its complexes with copper and nickel. In this article, we report the synthesis and characterization of new PIs based on thiosemicarbazone with a Schiff-base structure containing copper and nickel. The PIs were characterized with elemental analysis, solubility and viscosity measurements, Fourier transform infrared (FTIR), ¹H-NMR, and measurements of the thermal properties and thermal stability.

EXPERIMENTAL

Materials

Benzyl, thiosemicarbazide, pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetracarboxylic acid

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Scheme 1 Chemical structures of the monomers.

dianhydride (BPDA), and other reagents and solvents were purchased from Fluka (Germany) and used without purification.

Instruments

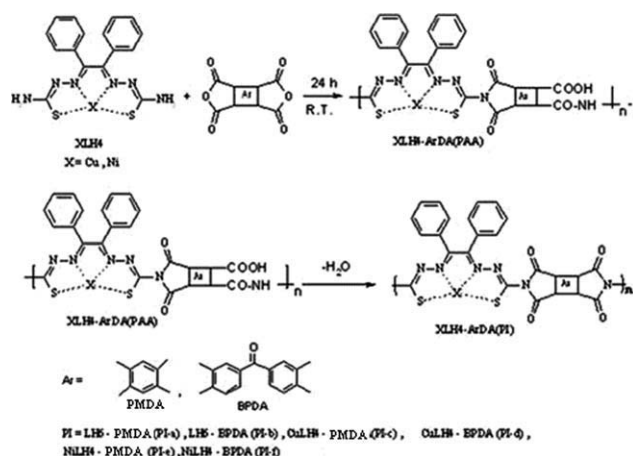
$^1\text{H-NMR}$ spectra were recorded on a Bruker (United States) Advance DRX 500-MHz instrument with hexadeuterated dimethyl sulfoxide as the solvent and tetramethylsilane as the internal standard. FTIR spectra were recorded with a Bruker Vector 22 spectrometer on KBr pellets. A Leco CHN-600 analyzer was used for elemental analysis. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed with a PerkinElmer Pyris instrument and a Mettler-Toledo (United States) 822^e instrument, respectively. The inherent viscosities of the polymers were determined in a solution of *N*-methyl-2-pyrrolidone (0.5 g/dL) at 25°C with an Ubbelohde viscometer. Copper and nickel were measured with a Shimadzu (Japan) model 170a atomic absorption apparatus. The total sulfur was measured with a Tanaka (Japan) model RX-360 SH apparatus.

Monomer synthesis

LH_6 and its complexes (CuLH_4 and NiLH_4) were prepared and their structural compositions were confirmed with procedures reported in previous publications.^{28–30} The chemical structures of the monomers are shown in Scheme 1.

PI synthesis

The chemical structures and the general procedure for the preparation of the PIs are presented in Scheme 2. The synthesis of the PIs (typically according to ref. 31) was carried out as follows: A 100-mL, two-necked, round-bottom flask equipped with a magnetic stirrer bar, a nitrogen gas inlet tube, and a calcium chloride drying tube was charged with 2 mmol of the diamine monomer (LH_6 , CuLH_4 , or NiLH_4) and 20 mL of dry *N*-methyl-2-pyrrolidone. The mixture was stirred at 0°C for 0.5 h. Then, 2 mmol of a dianhydride (PMDA or BPDA) was added, and the mixture was stirred at 0°C for 1 h. The temperature was raised to room temperature, and the solution was stirred for 24 h. Poly(amic acid) (PAA) was precipitated by the flask contents



Scheme 2 Preparation reactions for the PIs (R.T. = room temperature).

being poured into 200 mL of a 3 : 1 volume mixture of water and methanol. Then, it was filtered, washed with hot water, and dried overnight *in vacuo* at 40°C. The yields were over 88%. Chemical cyclization was applied for the conversion of PAA to PI: Into a 100-mL, two-necked, round-bottom flask equipped with a magnetic stirrer bar, a nitrogen gas inlet tube, and a reflux condenser was placed 1.0 g of PAA dissolved in 5 mL of *N,N*-dimethylacetamide and 5 mL of dry acetic anhydride, and 2.5 mL of pyridine was added. The mixture was stirred for 0.5 h, then slowly heated to 140°C, and held for 6 h

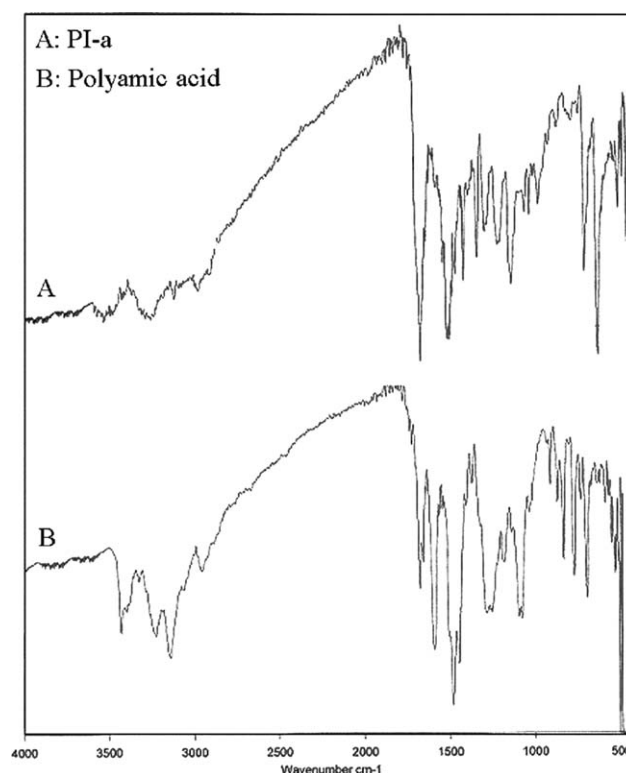


Figure 1 FTIR spectra of PAA and PI-a.

TABLE I
FTIR and ¹H-NMR Characteristics of the PIs

Code	IR (KBr, cm ⁻¹)	¹ H-NMR (DMSO- <i>d</i> ₆ , δ, ppm)
PI-a	3455 (CH, aromatic), 1625 (C=O), 1520 (C=N), 1315 (C-N)	7.9 (2H, NH), 7.2–7.8 (16H, aromatic)
PI-b	3255 (CH, aromatic), 1625 (C=O), 1615 (C=N), 1325 (C-N)	7.9 (2H, NH), 7.2–7.8 (16H, aromatic)
PI-c	3470 (CH, aromatic), 1701 (C=O), 1620 (C=N), 1367 (C-N)	7.25–7.40 (12H, aromatic)
PI-d	3470 (CH, aromatic), 1701 (C=O), 1620 (C=N), 1367 (C-N)	7.2–7.45 (16H, aromatic)
PI-e	3443 (CH, aromatic), 1689 (C=O), 1623 (C=N), 1370 (C-N)	7.1–7.27 (12H, aromatic)
PI-f	3455 (CH, aromatic), 1625 (C=O), 1615 (C=N), 1325 (C-N)	7.06–7.18 (16H, aromatic)

DMSO-*d*₆ = hexadeuterated dimethyl sulfoxide.

at this temperature. After that, the mixture was cooled and poured into water; it then was filtered, washed with hot water and methanol, and dried overnight *in vacuo* at 120°C. The yields were over 89%. The PIs obtained from CuLH₄ were black, and those from NiLH₄ were dark green. The inherent viscosities of the PIs were subsequently determined at a concentration of 0.5 g/dL at 25°C. The PIs, shown in Scheme 2, have been designated as follows: PI-a for LH₆+PMDA, PI-b for LH₆+BPDA, PI-c for CuLH₄+PMDA, PI-d for CuLH₄+BPDA, PI-e for NiLH₄+PMDA, and PI-f for NiLH₄+BPDA.

RESULTS AND DISCUSSION

Synthesis and characterization of the monomers

The monomer LH₆ and its complexes with copper and nickel were prepared according to the standard procedures reported in previous publications.^{28–30} The structural compositions of the monomers were determined by elemental analysis as well as FTIR and ¹H-NMR, and the results were in agreement with those reported in the literature. The ¹H-NMR spectra of both complexes were very similar; the signals of hydrogen atoms of the secondary amine at 8.8 ppm disappeared, and the signal corresponding to the terminal amine hydrogen atoms shifted to a high field (from 6.6 to 7.5 ppm). This agrees with the fact that the primary amines were not bonded to copper or nickel ions, and the ligand was didepro-

nated. Thus, these complexes were used as diamine monomers for the synthesis of the PIs.

Synthesis and characterization of the PIs

The PIs were synthesized through the reaction of the aromatic dianhydrides PMDA and BPDA with the diamine monomers, as shown in Scheme 2. The polymerization proceeded in two steps in a homogeneous solution. The synthesis of poly(amic acids) was typically carried out in *N*-methyl-2-pyrrolidone at 0°C for 1 h and then at room temperature for 24 h. The formation of PAA was confirmed by IR spectroscopy, as shown in Figure 1. PAA exhibited absorption bands in the region of 3500–3100 cm⁻¹ due to the amino (NH) and hydroxyl (OH) groups and amide carbonyl absorption at 1680 cm⁻¹. Chemical cyclization was carried in *N,N*-dimethylacetamide at 140°C for the conversion of PAA to PI in the presence of acetic anhydride and pyridine. The formation of PI was confirmed by FTIR, H-NMR, and elemental analysis, and the data from these tests are listed in Tables I and II. The elemental analysis values of all the PIs were generally in good agreement with the calculated values of the proposed structures. The dehydration cyclization of PAA to form an imide ring was confirmed by the disappearance of the band at 1680 cm⁻¹ (related to C=O of amic acid) and the appearance of a new characteristic absorption of the imide ring at 1725 cm⁻¹, as shown for PI-a in Figure 1. The disappearance of the amide and carbonyl bands indicated a virtually complete

TABLE II
Results of the Elemental Analysis of the PIs

Code	Calculated (%)						Found (%)					
	C	H	N	S	Cu	Ni	C	H	N	S	Cu	Ni
PI-a	57.9	2.6	15.6	11.9	—	—	57.8	2.5	15.8	12.0	—	—
PI-b	61.6	2.8	13.0	9.96	—	—	61.4	2.9	12.9	10.1	—	—
PI-c	52.0	2.0	14.0	10.6	10.6	—	52.2	2.1	13.8	9.9	9.8	—
PI-d	56.2	2.2	11.9	9.1	9.1	—	55.8	2.1	11.6	9.2	8.2	—
PI-e	52.4	2.02	14.1	10.7	—	9.9	52.7	2.2	13.8	10.5	—	8.9
PI-f	56.6	2.3	12.0	9.1	—	8.4	55.9	2.2	12.3	9.2	—	8.1

TABLE III
Solubility, Inherent Viscosities, and Yields of the PIs

PI	NMP	DMF	DMSO	TCE	Py	THF	H ₂ SO ₄	HMPA	DMAc	Acetone	Inherent viscosity (dl/g) ^a	Yield (%) ^b
PI-a	+	+	+	±	+	±	+	+	+	±	1.1	92
PI-b	+	+	+	±	+	±	+	+	+	±	0.98	92
PI-c	+	+	±	±	+	±	+	+	+	±	1.3	89
PI-d	+	+	±	±	+	±	+	+	+	±	0.98	88
PI-e	+	+	±	±	+	±	+	+	+	±	1.33	91
PI-f	+	+	±	±	+	±	+	+	+	±	1.03	92

The solubility was tested with 2.5 g of the polymer in 100 mL of the solvent. + = soluble; ± = partially soluble; DMAc = *N,N*-dimethylacetamide; DMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide; HMPA = hexamethylene phosphoramide; NMP = *N*-methyl-2-pyrrolidone; Py = pyridine; TCE = tetrachloroethane; THF = tetrahydrofuran.

^a Measured in NMP at 25°C (concentration = 0.5 g/dL).

^b Calculated on the basis of the amount of PAA used in the cyclization process.

conversion of the PAA precursor into PI. ¹H-NMR spectra of PI-a and PI-b exhibited a signal at 7.9 ppm related to the proton of the secondary amine. The aromatic protons at about 7.2 ppm in the ¹H-NMR spectra confirmed the imidic structure of the polymers.

Solubility of the PIs

One of the major objectives of this study was to produce Schiff-base PIs with improved solubility. The solubility of the PIs was measured at 0.5 g/dL and 25°C in various solvents, and the results are listed in Table III. All the PIs were readily soluble in polar aprotic solvents such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, pyridine, and hexamethylene phosphoramide without the need for heating, whereas PI-a and PI-b were also soluble in dimethyl sulfoxide. Also, with heating, they were soluble in less efficient solvents such as tetrahydrofuran and acetone. The good solubility behavior of these aromatic PIs in conventional organic solvents can be explained by the enhance-

ment of solubility induced by the side phenylene groups of the diamine component, which increased the disorder in the chains and hindered dense chain stacking, thereby reducing interchain interactions. The inherent viscosities of the PIs were in the range of 0.98–1.33 dL/g, and this revealed the high molecular weights of the polymers.³²

Thermal properties of the PIs

The thermal properties of the monomers were investigated with DSC at a heating rate of 10°C/min in a

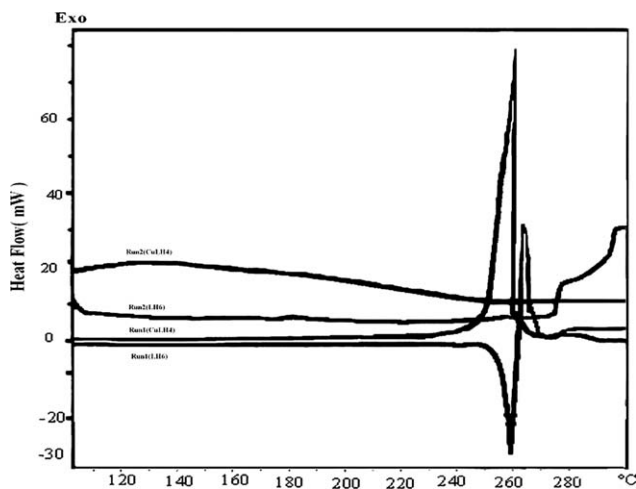


Figure 2 DSC thermograms of the first and second runs of LH₆ and CuLH₄.

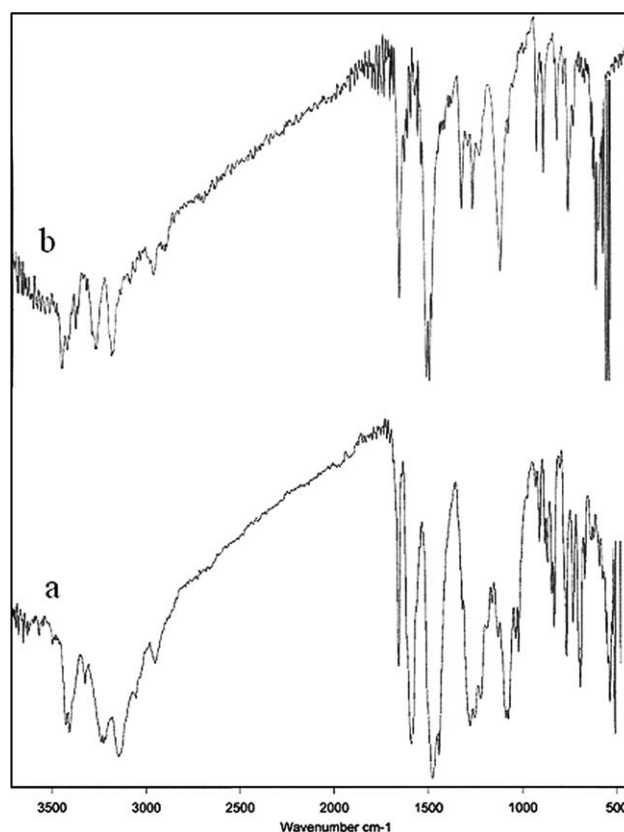


Figure 3 FTIR spectra of LH₆: (a) before heating and (b) after heating at 250°C.

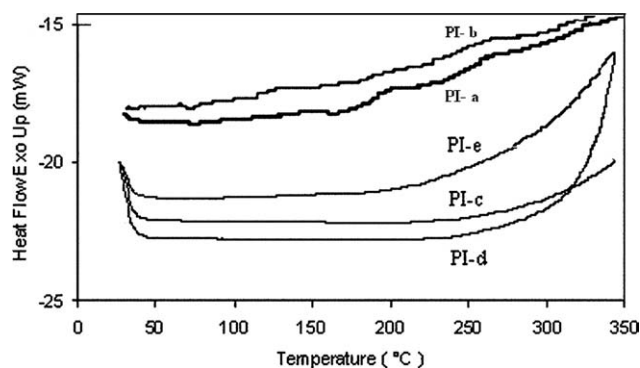


Figure 4 DSC thermograms of the PIs.

nitrogen atmosphere, and the thermograms are shown in Figure 2. The DSC curve of LH₆ showed endothermic and exothermic peaks at 260°C, which could be due to melting and decomposition. DSC curves of the complexes of CuLH₄ and NiLH₄ also showed exothermic peaks in the range of 250–260°C, indicating the decomposition of the compounds before melting. The FTIR spectrum of LH₆ was taken after the sample was heated at 250°C, and the results are shown in Figure 3. A comparison of the FTIR spectra before and after heating showed a small difference in the region of 3420–3250 cm⁻¹ related to NH and NH₂ groups and very clear differences in the region of 1610–1585 cm⁻¹ related to the azomethine (>C=N–N) group.

DSC thermograms of the PIs are shown in Figure 4. The thermal behavior data for all the polymers are presented in Table IV. DSC thermograms of all the PIs started to show exothermic peaks above 250°C, which could be due to the beginning of thermal decomposition. The beginning of thermal degradation of the PIs, indicated by their DSC curves, occurred in the same temperature ranges in which the exothermic peaks of the monomers appeared. The thermal degradation of the PIs could be a result of thermal breakdown of the azomethine linkage in the polymer chains. The thermal stability of the PIs was also evaluated by means of TGA, and the thermograms are shown in Figure 5. The PIs

TABLE IV
Thermal Analysis of the PIs

PI	T _i (°C) ^a	T ₁₀ (°C) ^b	Char yield (%)
PI-a	250	270	36
PI-b	220	240	28
PI-c	260	300	54
PI-d	300	330	64
PI-e	320	350	42
PI-f	350	370	50

T_i = initial decomposition (degradation) temperature; T₁₀ = temperature of 10% weight loss; Char Yield (%) = at 700°C under N₂.

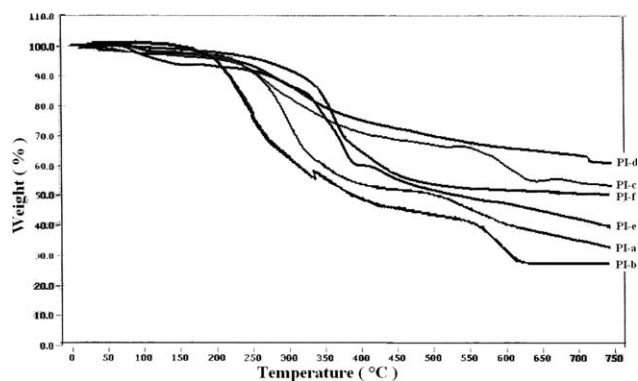


Figure 5 TGA thermograms of the PIs.

exhibited their initial decomposition temperature in the range of 220–350°C. The initial decomposition temperatures of PI-a and PI-b, which were prepared from LH₆ and the dianhydrides, were lower than the initial decomposition temperatures of those PIs prepared by the reaction of metal complexes of LH₆. The presence of metals in the polymer chain not only increased the maximum degradation temperature but also increased the initial degradation temperature. The initial decomposition temperature of aromatic PIs is usually higher than 400°C. The reason that the thermal stability of the prepared PIs was not as high as that of classical PIs^{1–4} could be the presence of the azomethine linkage in the polymers backbone. The maximum degradation temperature for most of the prepared PIs was between 600 and 750°C. The thermal stability of the PIs was also evaluated in terms of the 10% weight loss and residual weight at 700°C, as shown in Table IV. A comparison of the maximum degradation temperatures and residual weights (at 700°C) of the polymers showed that the introduction of the metal ions was especially effective at improving the thermal stability of the PIs. The PIs prepared from the reaction between the complexes and the dianhydrides showed over 50% residual weight at 700°C, whereas those obtained from LH₆ showed 25% residual weight at 700°C. This difference in the char yields could be attributed to the influence of the incorporation of metal into the polymer backbone. The glass-transition temperatures of Schiff-base PIs with similar dianhydrides in the polymer backbone have been reported to be higher than 240°C.²² Therefore, the glass-transition temperatures of these PIs should be lower than their decomposition temperatures.

CONCLUSIONS

Because the LH₆ ligand offers suitable sites for metal, a series of Schiff-base PIs containing copper and nickel in the main chain were prepared in a two-step procedure via the reaction between

diamine monomers and two commercially available aromatic dianhydrides. The PIs were characterized, and their physical properties, such as the solubility and viscosity, thermal properties, and thermal stability were studied. The introduction of phenyl side groups into the structures of the diamine monomers resulted in amorphous PIs with very good solubility in organic aprotic solvents such as *N*-methyl-2-pyrrolidone. The results obtained from DSC and TGA measurements indicated that the prepared PIs started to degrade at temperatures above 250°C. The presence of an azomethine linkage in the polymer backbone could be responsible for the moderate thermal stability of the polymers. On the basis of these results, the presence of metal ions in these new Schiff-base PIs improved their thermal stability by increasing the initial and maximum degradation temperatures.

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