Synthesis and Characterization of Novel Schiff-Base Polyamides from Copper/Benzil Bisthiosemicarbazone Complexes

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ABSTRACT: A new copper-containing Schiff-base diamine, benzil bis(thiosemicarbazonato)copper(II) (CuLH$_4$), was synthesized in two steps from benzil bisthiosemicarbazone (LH$_6$). The ligand LH$_6$ and the complex CuLH$_4$ were characterized with Fourier transform infrared spectroscopy, ^{1}H-NMR, and elemental analysis. CuLH$_4$ was used to prepare novel polyamides. The low-temperature solution polycondensation of the complex CuLH$_4$ with various aromatic and aliphatic diacid chlorides afforded copper-containing Schiff-base polyamides with inherent viscosities of 0.25–0.36 dL/g in *N,N*-dimethylformamide (DMF) and 0.75 dL/g in H$_2$SO$_4$ at 25°C. The polyamides were generally soluble in a wide range of solvents, such as DMF, *N,N*-dimethylacetamide, tetrahydrofuran, dimethyl sulfoxide, ethyl acetate, tetrachloroethane, hexamethylene phosphoramide, *N*-methylpyrrolidone, and pyridine. Thermal analysis showed that these polyamides were practically amorphous, decomposed above 270°C, and exhibited 50% weight loss at and above 400°C. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2388–2394, 2008

Key words: polyamides; polycondensation; step-growth polymerization; thermal properties

INTRODUCTION

Wholly aromatic polyamides are difficult to process because of their high melting and/or glass-transition temperatures and/or their limited solubility in common organic solvents, which is caused by the chain stiffness and intermolecular hydrogen bonding between amide groups.[1,2] The ordering and variation of the backbone in synthetic polymers have profound effects on their end properties. The inherent problems of wholly aromatic polyamides have been studied by many researchers.[3–9]

Polymers with a system of conjugated —C═C— and —C═N— bonds in their main chain have been drawing the attention of researchers because of their importance in many areas.[10–14] Among these polymers, Schiff-base polymers, which are characterized by the presence of HC═N linkages, are of considerable interest and are produced by the polycondensation of diamines with various dicarbonyl compounds. They have thermal stability similar to that of polyamides and have been used as solid stationary phases for gas chromatography.[15] The high thermal stability of fully aromatic poly(Schiff base)s is due to the great number of aromatic rings and the extent of electronic conjugation over the entire molecule, which lead to polymers with high conducting properties. To lower the transition temperatures and to improve the solubility, several methods are used, such as copolymerization and the introduction of bulky alkyl, alkoxy, or aryl groups into the aromatic rings or into the polymer backbone.[14,16] Schiff-base polymers have been reported to be useful catenation ligands, and the coordination polymeric Schiff bases have been extensively studied.[17–20] A particularly important group of such ligands includes those containing thiosemicarbazone moieties because complexes formed with many of the first-row transition metals have shown a wide range of properties, including biological properties.[21–26] Thiosemicarbazones are versatile ligands bearing suitable donor atoms for coordination to metals. Although different coordination modes have been reported, they usually act as bidentate ligands through their azomethyne nitrogen and thiocarbonyl sulfur atoms. Thiosemicarbazones have also been reported as light stabilizers for the photochemical stabilization of polyamide fiber materials or blends thereof with other fiber materials.[27,28]

It is well known that pendant bulky aryl groups should improve the thermal stability of polymers with an increase in the glass-transition temperature and also push the neighboring polymer chains apart to reduce the hydrogen bonding at the amide linkage, leading to amorphous or lowered crystallinity because of the less packed structure.

In this article, we report the synthesis of novel Schiff-base polyamides with pendant bulky aryl groups containing copper ions by the low-tempera-

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ture polycondensation reaction of diacid chlorides such as terephthaloyl dichloride, isophthaloyl dichloride, sebacoyl dichloride, adipoyl dichloride, and pyridine-2,6-dicarboxylic acid with a new diamine, a benzil bis(thiosemicarbazonato)copper(II) (CuLH$_4$) complex from benzil bisthiosemicarbazone (LH$_6$). The physical properties of the polymers, including the characterization, inherent viscosity (η_{inh}), solubility, and thermal properties, are also reported. We will also report other properties of these polyamides in a future publication.

EXPERIMENTAL

Materials and instruments

Benzil, thiosemicarbazide, and other reagents and solvents were purchased from Fluka (Switzerland) and used without purification.

^{1}H-NMR spectra were recorded on a Bruker Advance DRX 500-MHz instrument (Germany) with deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane as the internal standard. Fourier transform infrared spectra were recorded with a Bruker Vector 22 spectrometer (Germany) on KBr pellets. A Leco CHN-600 analyzer (USA) was used for elemental analysis. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were performed with PerkinElmer Pyris (USA) and Mettler–Toledo 822^e instruments (USA), respectively. η_{inh} (η_{inh} = Ln η_{rel}/C) of the polymers was determined for 0.5 g/dL solutions in N-methylpyrrolidone (NMP) or in H$_2$SO$_4$ at 25°C with an Ubbelohde viscometer (Witeg, Germany); where η_{inh} is inherent viscosity, η_{rel} is relative viscosity, and c is concentration. Copper was measured by atomic absorption with a Shimadzo model 170a (Japan) apparatus. Total sulfur was measured with a Tanaka model RX-360 SH (Japan) apparatus.

Preparation of the monomers

LH_6[29]. Thiosemicarbazide (3.64 g, 40.30 mmol) was dissolved in 40 mL of methanol, 40 mL of 2N HCl, and 1 mL of concentrated HCl and then added to a suspension of benzil (4.24 g, 20.20 mmol) in 50 mL of methanol with a few drops of concentrated HCl. The mixture was stirred for 6 h at room temperature. The yellow solid was filtered off, washed with methanol, and dried in a vacuum oven at 70°C for 2 h. The yellow solid product in a yield of 75% started to melt and decompose at about 240°C. The chemical structure of LH$_6$ is shown in Scheme 1.

IR (cm^{-1}): 3420, 3250, 3150 (NH, NH$_2$), 1610 (CN), 1585 (NH$_2$), 848 (CS). ^{1}H-NMR (CDCl$_3$, δ, ppm): 8.8 (2H, s), 7.6 (6H, m), 7.4 (4H, m), 6.6 (4H, s).

$CuLH_4$. With a standard method in the literature,[30] copper(II) acetate monohydrate (144 mg, 0.722 mmol) was added to a solution of LH$_6$ (257 mg,
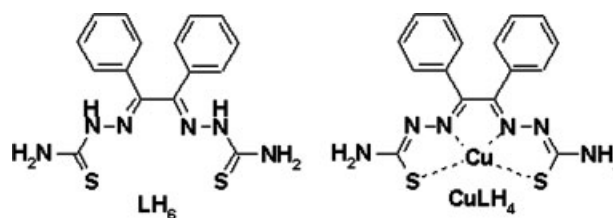
Scheme 1 Chemical structures of the ligand LH$_6$ and the complex CuLH$_4$.

0.722 mmol) in ethanol (15 mL). The mixture was heated under reflux for 5 h and then cooled, and the resulting solid was collected, washed with ether, and dried in a vacuum oven at 70°C to produce CuLH$_4$ as a dark brown powder in a 48% yield. The chemical structure of CuLH$_4$ is shown in Scheme 1.

IR (cm^{-1}): 3419, 3241 (NH, NH$_2$), 1626, 1600, 1569 (CN), 3419, 3343, 3150 (CH), 449, 428 (N—M, S—M). ^{1}H-NMR (DMSO-d_6, δ, ppm): 7.5 (4H, NH$_2$, s), 7.1–7.3 (10H, Ph, m).

Preparation of the model compound (MO). A flask was charged with a mixture of CuLH$_4$ (0.418 g, 1 mmol), 10 mL of dimethylacetamide (DMAc), and triethylamine (0.8 μL). 4-Nitrobenzoyl chloride (0.371 g, 2 mmol), dissolved in DMAc, was added dropwise to the stirred solution at 0°C under N$_2$. Stirring of the mixture was continued for 3 h at the ambient temperature under N$_2$, and then it was poured into water. The red solid was filtered off and washed with a solution of NaHCO$_3$. The pure product was obtained by recrystallization from 1,2-dichloroethane and then dried in a vacuum oven at 60°C.

IR (cm^{-1}): 1570, 1320 (NO$_2$), 3450, 3270 (NH, NH$_2$), 1670 (C=O), 1570 (C=N). ^{1}H-NMR (DMSO-d_6, δ, ppm): 9.3 (NH amide, 2H), 8.8–9 (CH, Ph, 18H).

Preparation of the polyamides

Poly[benzil bis(thiosemicarbazonato)copper]terephthalate (PBCT). A typical procedure for the preparation of the polyamides is given in Scheme 2. A two-necked flask, equipped with a dropping funnel and gas inlet tube, was charged with a mixture of CuLH$_4$ (0.836 g, 2 mmol), 20 mL of DMAc, and triethylamine (0.8 mL). Terephthaloyl chloride (0.406 g, 2 mmol), dissolved in 20 mL of DMAc, was added dropwise to the stirred solution at 0°C under N$_2$. The mixture was subsequently stirred at the ambient temperature for 5 h under N$_2$, and then it was poured into cold water. The reddish, solid product was separated by filtration and washed with a solution of NaHCO$_3$. Then, the red, solid product was dried in a vacuum oven at 70°C. A purified sample was obtained by Soxhlet extraction from methanol for 24 h.

IR (cm^{-1}): 3450, 3270 (NH, NH$_2$), 1680 (C=O), 1570 (C=N). ^{1}H-NMR (DMSO-d_6, δ, ppm): 9–9.4 (NH amide, 2H), 8.2–8.8 (CH aromatic, 14H).
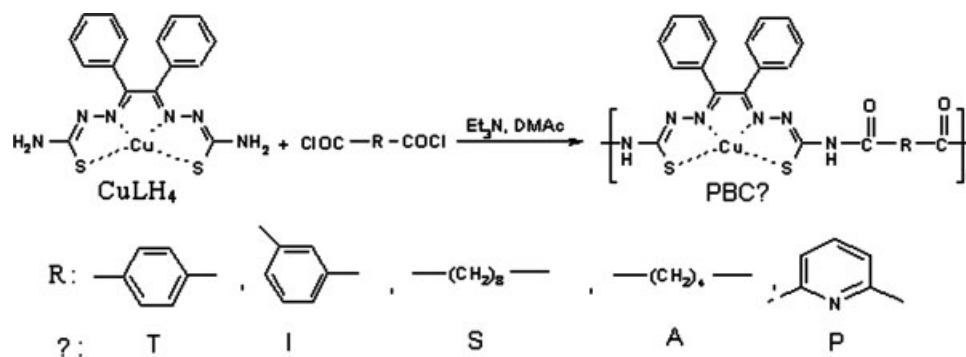
Scheme 2 Reaction procedure for the preparation of the polyamides.

Other polyamides, except poly[benzil bis(thiosemicarbazonato)copper]pyridine dicarboxylate (PBCP), were also prepared by the same procedure with CuLH$_4$ and different diacid chlorides as follows:

1. Isophthaloyl chloride for the preparation of poly [benzil bis(thiosemicarbazonato)copper]isophthalate (PBCI; a red, solid product).
   IR (cm^{-1}): 3450, 3270 (NH, NH$_2$), 1680 (C=O), 1570 (C=N). ^{1}H-NMR (DMSO-d_6, δ, ppm): 9.4 (NH amide, 2H), 9–9.3 (CH aromatic, 14H).
2. Sebacoyl chloride for the preparation of poly [benzil bis(thiosemicarbazonato)copper]sebacoylate (PBCS; a red, solid product).
   IR (cm^{-1}): 3450, 3270 (NH, NH$_2$), 3150 (C—H), 1680 (C=O), 1570 (C=N). ^{1}H-NMR (DMSO-d_6, δ, ppm): 9.4 (NH amide, 2H), 8.1–8.6 (CH aromatic, 10H), 2.4–2.6 (CH$_2$ aliphatic, 16H).
3. Adipoyl chloride for the preparation of poly [benzil bis(thiosemicarbazonato)copper]adipoylate (PBCA; a red, solid product).
   IR (cm^{-1}): 3450, 3260 (NH, NH$_2$), 3150 (C—H), 1680 (C=O), 1570 (C=N). ^{1}H-NMR (DMSO-d_6, δ, ppm): 9.5 (NH amide, 2H), 8.1–8.9 (CH aromatic, 10H), 1.2–1.4 (CH$_2$ aliphatic, 8H).
4. Pyridine 2,6-dicarboxylic acid, for the preparation of PBCP (a gray, solid product), was used

in the polycondensation reaction with CuLH$_4$ in a mixture of NMP and pyridine (30/6 v/v) as the solvent at 110°C for different periods of time. The η$_{inh}$ values of the polyamide, measured in H$_2$SO$_4$, were 0.5, 0.75, and 0.78 for reaction times of 4, 8, and 15 h, respectively.
IR (cm^{-1}): 3500–3330 (NH, NH$_2$), 1670 (C=O), 1570 (C=N).

RESULTS AND DISCUSSION

IR and elemental analysis

The monomer LH$_6$ and its complex with copper, CuLH$_4$, were prepared according to procedures reported in the literature.[29,30] The Fourier transform infrared spectroscopy and elemental analysis data for LH$_6$ and its copper complex of this study are in good agreement with the results reported in the literature. The results of elemental analysis are given in Table I. Only two regions of the IR spectra are of particular interest: 3000–3500 (NH$_2$ asymmetric and symmetric stretching) and 1500–1700 cm^{-1} (double-bond region). In the complex, the number of bands corresponding to υ(N—H) vibrations have decreased because of deprotonation, and the others appear at

TABLE I
Characteristic Features of the Monomer and Polyamides

Complex code	η$_{inh}$ (dL/g)[a]	Yield (%)	Calcd (%)					Found (%)				
			C	H	N	S	Cu	C	H	N	S	Cu
LH$_6$	—	75	53.93	4.49	23.59	17.97	—	54.15	4.49	23.29	—	—
CuLH$_4$	—	48	45.91	3.35	20.12	15.31	15.3	45.87	3.38	19.87	—	15.41
MO	—	97	50.14	3.06	15.59	8.92	8.92	50.65	3.11	16.02	—	8.25
PBCT	0.28	95	52.36	3.27	15.27	11.71	11.71	51.97	3.49	15.44	11.35	10.85
PBCI	0.25	95	52.36	3.27	15.27	11.71	11.71	52.13	3.16	14.95	—	10.95
PBCS	0.36	96	53.24	5.12	14.33	10.95	10.95	53.52	5.23	14.95	—	11.51
PBCA	0.25	94	49.82	4.15	15.85	12.12	12.12	50.20	4.05	15.36	12.75	13.11
PBCP	0.55[b]	90	50.11	3.11	17.78	11.66	11.66	49.95	3.21	18.06	—	11.35

[a] Measured in NMP at 25°C (concentration = 0.5 g/dL).
[b] Measured in H$_2$SO$_4$ at 25°C (concentration = 0.5 g/dL).

TABLE II
Solubility of the Polyamides

Polymer code	NMP	DMF	DMSO	TCE	Py	THF	H2SO4	HMPA	DMAC	Ethyl acetate
PBCT	+	±	+	±	+	+	+	+	+	−
PBCI	+	±	+	±	+	+	+	+	+	−
PBCS	+	+	+	+	+	+	+	+	+	−
PBCA	+	+	+	+	+	+	+	+	+	−
PBCP	±	±	±	±	+	±	+	+	±	−

The solubility was tested with 0.5 g of the polymer in 100 mL of the solvent. + = soluble; ± = partially soluble; − = insoluble; HMPA = hexamethylene phosphoramide; Py = pyridine; TCE = tetrachloroethane.

higher frequencies, probably because the intramolecular hydrogen bonding has decreased. The shift in the $\upsilon(C{=}N)$ band is a clear sign of coordination via the azomethine nitrogen atom.

In ^{1}H-NMR spectra of the complex $CuLH_4$, the signal of the hydrogen atoms of the secondary amine has disappeared, and the signal corresponding to the terminal amine hydrogen atoms has shifted to a high field. These facts agree with the fact that in the $CuLH_4$ complex, the ligand is deprotonated.

The IR spectrum of MO showed amide bands at 3270 (N—H stretching), 1670 (C=O stretching), and 1550 cm^{-1} (combined N—H bending and C=N stretching).

The polyamides (PBCT, PBCI, PBCS, and PBCA) were synthesized by the polycondensation reaction of aromatic and aliphatic diacid chlorides (Scheme 2) with the complex $CuLH_4$ with triethylamine as the base. The reactions were carried out in a DMAc solution of the diacid chloride and $CuLH_4$ in a nitrogen atmosphere and at room temperature. The polymerizations proceeded in a homogeneous solution, and the yields of the polyamides were quantitative. The pyridine-based polyamide PBCP (Scheme 2) was synthesized by the polycondensation reaction of pyridine 2,6-dicarboxylic acid with $CuLH_4$ in an NMP–pyridine solution in a nitrogen atmosphere and at a temperature of 110°C. The elemental analysis values of all the polyamides (Table I) were generally in good agreement with the calculated values of the proposed structures. As a representative example, the complete elemental analysis of PBCT was as follows: C, 51.97% (calcd 52.36%); H, 3.49% (calcd 3.27%); N, 15.44% (calcd 15.27%); S, 11.2% (calcd 11.7%); and Cu, 10.8% (calcd 11.7%). The polyamides were also characterized with IR and ^{1}H-NMR spectrometry. The presence of the amine band at 3450 cm^{-1} (terminal NH_2) and the amide bands at about 3270 (N—H stretching), 1620 (C=O stretching), and 1530 cm^{-1} (N—H bending and C=N stretching) in the IR spectra and the amidic proton at about 9.4 ppm in the ^{1}H-NMR spectra of all the prepared polyamides confirmed the amidic structure of the polymers.

η_{inh} of the polyamides was determined for extracted and dried polymers in NMP or sulfuric acid solutions, depending on the solubility of the polyamide. For the same or similar types of linear polymers, the viscosity value was proportional to the molecular mass. The η_{inh} values of the polyamides PBCT, PBCI, PBCS, and PBCA, obtained in NMP solutions, were in the range of 0.25–0.36 dL/g. Because of the poor solubility of the polyamide PBCP in N,N-dimethylformamide (DMF), the viscosity of this polymer was obtained in H_2SO_4; it was 0.55 dL/g for the polyamide prepared after 4 h of amidation and increased to 0.75 dL/g after 8 h. For the PBCP prepared beyond 8 h, the reaction time had little effect on η_{inh} (Table I). For example, the polyamide PBCP had η_{inh} values of 0.75 and 0.78 dL/g after 8 and 15 h of reaction, respectively.

One of the major objectives of this study was to produce modified Schiff-base polyamides with improved solubility. The solubility of these polyamides was determined for the powdery samples in excess solvents, and the results are listed in Table II. All the polyamides except PBCP were readily soluble in common polar aprotic solvents without the need for heating. Also, with heating, they were soluble in a less efficient solvent such as tetrahydrofuran (THF). Among these polymers, only PBCP, which was obtained by a reaction with pyridine 2,6-dicarboxylic acid, was not easily dissolved in most of the organic solvents tested. The good solubility behavior of most of the prepared polyamides can be explained by the enhancement of solubility induced by the side phenylene groups of the diamine moiety and by the lower interaction between the chains, except for PBCP, which had poor solubility; this indicates that the presence of the pyridine rings in the polymer chains increased the interaction between the chains and decreased flexibility.

The thermal behavior of LH_6 and the polyamides was studied with DSC and TGA. The DSC thermograms of the ligand LH_6 for the first and second runs are shown in Figure 1. The first-run DSC curve of LH_6 shows a melting temperature at 260°C, and immediate decomposition of the compound follows. The second DSC run of the same sample did not show any thermal event up to 300°C, and this confirms the decomposition of the compound at 260°C
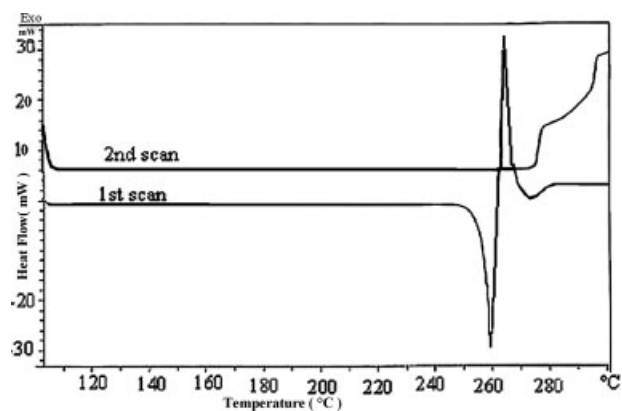
Figure 1 DSC thermograms of the ligand (LH$_6$).

during the first run. DSC thermograms of the complex CuLH$_4$ up to 350°C are shown in Figure 2. As shown in the first DSC scan, the complex showed only an exothermic peak in the temperature range of 250–260°C without showing a melting peak. The exothermic peak at 260°C disappeared completely in the second DSC scan. The decomposition of the complex CuLH$_4$ occurred at almost the same temperature as that for the decomposition of the ligand LH$_6$, as shown in Figure 1.

The thermal properties of the prepared polyamides were also evaluated by means of DSC and TGA. Representative DSC thermograms are shown in Figures 3 and 4 for the polyamides PBCA and PBCT prepared from aliphatic and aromatic diacid dichlorides, respectively. None of the polyamides showed a crystallization temperature or melting point. All the polyamides showed similar patterns of thermal properties in DSC scans under a nitrogen atmosphere. Slow heating up to 200°C did not show any transition, and this was followed by cooling to room temperature, which removed all the moisture absorbed by the polyamides because of the presence of polar amide linkages. The first DSC scan up to 300°C showed a strong exothermic peak at 260°C

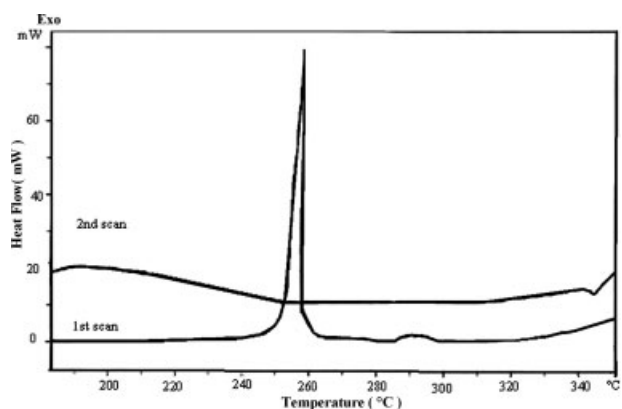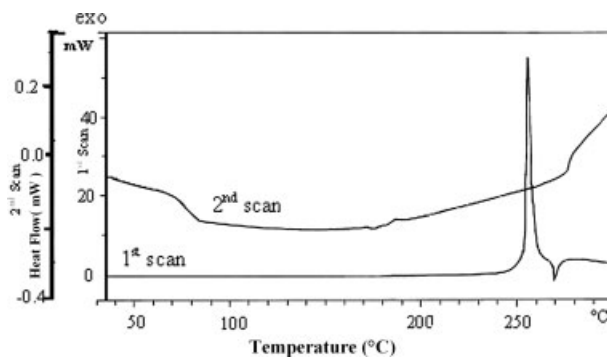**Figure 3** Representative DSC thermograms of the aliphatic polyamide PBCA.

that disappeared completely in the second DSC scan. The exothermic peak of the polyamides at 260°C occurred at exactly the same temperature as those for the decomposition of the ligand LH$_6$ and the complex CuLH$_4$.

The representative TGA (the weight percentage vs the temperature) and differential thermogravimetry (DTG; the derivative weight percentage vs the temperature) curves are shown in Figure 5. The temperatures of the 50% weight loss and remaining polyamides at 680°C in a nitrogen atmosphere are given in Table III. All the polymers and the MO showed similar patterns of thermal stability with no weight loss below 260°C in nitrogen, and this implied that no thermal decomposition occurred. However, as the temperature increased beyond 260°C, the polymers showed rapid thermal decomposition. The 50% weight loss of all the polymers except PBCP was around 400°C, as shown in Table III. These features were attributed to the occurrence of thermal decomposition of the azomethine bridges in the monomers and in the polymer chains. The DSC curves for the pyridine-based polyamide PBCP up to 450°C are shown in Figure 6. The initial DSC scan of the polyamide PBCP sample showed a strong endothermic
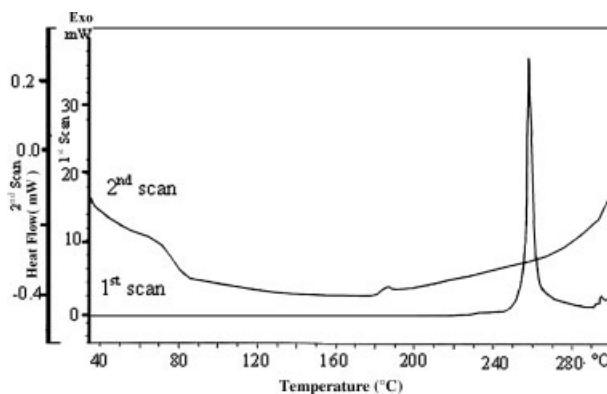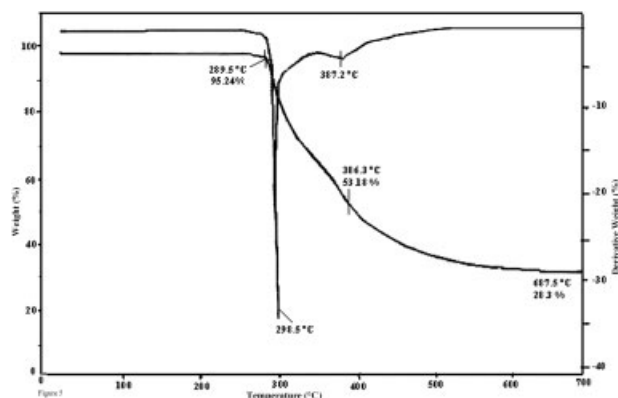

Figure 2 DSC thermograms of the complex CuLH$_4$.

Figure 4 Representative DSC thermograms of the aromatic polyamide PBCI.

Figure 5 Representative TGA and DTG curves of the polyamide PBCT.

Figure 6 DSC thermograms of the polyamide PBCP.

peak at 150°C, and there were also smaller endothermic peaks in the temperature range of 250–320°C. The second DSC scan of the same sample displayed a transition at 230°C followed by a very small and sharp exotherm peak at 260°C. The large endothermic peak observed at 150°C in the first DSC scan disappeared completely in the second DSC run. The disappearance of this endothermic peak at 150°C was surprising and could not be explained, unless it was due to the continuation of endothermic step-growth polymerization between the oligomers. The reproducibility of the DSC analysis was found to be excellent, as evidenced by the scanning of three specimens from each of three different batches.

The TGA curve of the polyamide PBCP in Figure 7 shows that this polyamide absorbed noticeable amounts of moisture, which appeared as small weight losses in the range of 50–150°C. The polyamide PBCP showed three gradual steps of minor weight loss: 15% at 270°C, a total of 25% at 520°C, and a total of 30% at 680°C. The small exothermic peak in the second DSC scan at 270°C was consistent with the 15% weight loss shown in the TGA curve. The polyamides PBCT, PBCI, PBCS, and PBCA retained 30% of their original weight at 680°C in

nitrogen. The pyridine-based polyamide PBCP showed residual weight retention much higher than that of the other polyamides. PBCP retained 70% of its original weight at 680°C in nitrogen. The higher thermal stability of PBCP in comparison with the other prepared polyamides, which was in agreement with the lower solubility and higher viscosity, could be due to the higher interaction between the polymer chains. None of the polyamides exhibited a glass-transition temperature or melting point up to 300°C. In all cases, a sharp exothermic peak was observed above 260°C. In the TGA traces of the polymers, the major weight loss was observed above 270°C. Both these features were attributed to the occurrence of the azomethine linkage in the polymer chains. It can be concluded from these observations that the decomposition of the polyamides starts at this temperature in air, with the exception of PBCP, which starts at much higher temperatures. The azomethine linkages in the polymer chain are probably weak linkages at which thermal dissociation occurs, which is accompanied by the evolved volatile products and smell of sulfur derivatives. Hence, the strong and sharp exotherm of the DSC trace of each

TABLE III
Thermal Analysis of the Polyamides

Compound code	$T_{50\%}$ (K)[a]	CY (%)[b]
LH$_6$	—	—
CuLH$_4$	—	—
MO	400	—
PBCT	400	28.3
PBCI	400	29.3
PBCS	400	30
PBCA	400	29.5
PBCP	520[c]	70

[a] Temperature at 50% weight loss.
[b] Char yield at 680°C.
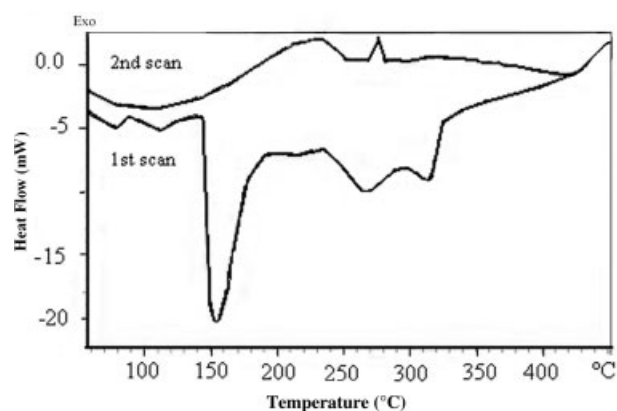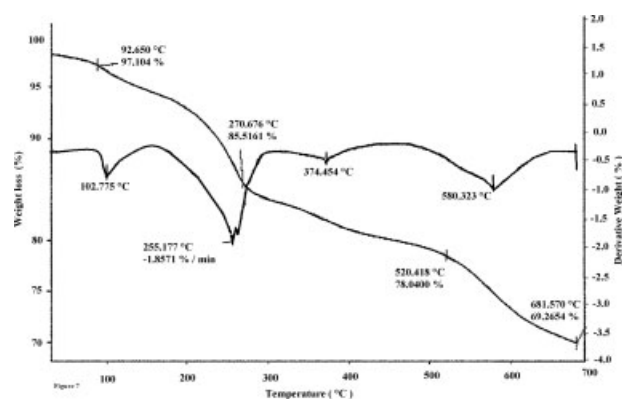[c] Twenty-five percent weight loss.

Figure 7 TGA and DTG curves of the polyamide PBCP.

polyamide was associated with the evolution of volatiles.

CONCLUSIONS

A series of Schiff-base polyamides with bulky aryl side groups coordinated with Cu(II) in the main chain were prepared through the reactions of different diacid dichlorides and a dicarboxylic acid with $CuLH_4$. The molar ratio of the diacid dichloride or dicarboxylic acid to $CuLH_4$ was 2 : 2, and the reactions were carried out at the ambient temperature for 5 h under an atmosphere of N_2, except in the case of dicarboxylic acid; that reaction was carried out at 110°C for 4–15 h. The polyamides were fully characterized, and their thermal properties were studied. The introduction of phenyl side groups into the structure of the diamine resulted in amorphous polyamides with very good solubility in aprotic solvents such as NMP. By DSC, none of the prepared polyamides exhibited a melting point before the decomposition temperature was reached. The introduction of azomethine units into the main chain of the polyamides showed a sharp exothermic peak in the DSC scan at 260–270°C (except for PBCP), which disappeared in the second scan. In the TGA traces of all polyamides (except PBCP), a major weight loss was observed above 270°C. Both these features were attributed to the occurrence of thermal breakdown in the azomethine units and production of volatile species. The polyamide PBCP was an exception among the polymers studied, in that it had less solubility and higher viscosity and thermal stability, which could be due to the higher intermolecular interactions between the chains due to the presence of pyridine.

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