

SYNTHESIS AND CHARACTERIZATION OF SCHIFF-BASE-CONTAINING POLYAMIDES

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Abstract A series of new Schiff base polyamides (PAs) were synthesized by polycondensation of benzilbisthiosemicarbazone diamine (LH₆) with different commercially available aliphatic and aromatic diacid chlorides. The monomer and all the PAs were characterized by FTIR, ¹H-NMR, and elemental analysis. The prepared polyamides showed inherent viscosities in the range of 0.30–0.36 dL/g in DMF at 25°C, indicating their moderate molecular weight. The PAs were completely soluble in aprotic polar solvents such as dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), tetrachloroethane (TCE), dimethylsulfoxide (DMSO) and also in H₂SO₄ and partially soluble in THF, acetone and chloroform at room temperature. Thermal analysis showed that these PAs were practically amorphous and exhibited 10% weight loss above 220°C.

Keywords: Polyamides; Schiff base polymers; Solubility; Thermal stability.

INTRODUCTION

Polymers with a system of conjugated —C=C— and —C=N— bonds in their main chain have been drawing the attention of researchers due to their importance in many aspects^[1–10]. Among these polymers, Schiff base polymers, which are characterized by the presence of HC=N linkages, are of considerable interest and have generally been produced by the polycondensation of diamines with various dicarbonyl compounds^[5–7, 11–15]. They have thermal stability similar to polyamides and have been reported to be useful as solid stationary phase for gas chromatography^[16], and as catenation ligand, where the coordination polymeric Schiff bases are extensively studied^[11, 12, 17, 18]. A considerable amount of work has been carried out in recent years in an effort to obtain high molecular weight conjugated Schiff base polymers. However, a major obstacle to characterizing and developing most conjugated aromatic poly(Schiff bases) with high thermal stability has been their insolubility in common organic solvents. In order to lower the transition temperatures and to improve their solubility, several methods have been reported to improve the processability of conjugated poly(Schiff bases) by modification and selection of polymer structure such as introduction of pendent groups (aromatic or alkyl groups) on to the polymer chain and incorporation of non-coplanar structural units in the main chain^[3, 4, 19–22]. Keeping in view the interesting properties of thiosemicarbazone Schiff base metal complexes that we have used as curing agents for epoxy resin^[23, 24], in this article, we report the synthesis and characterization of new Schiff base-containing PAs with improved solubility by the low temperature solution polycondensation of benzilbisthiosemicarbazone diamine (LH₆) with different diacid chlorides. The physical properties of polymers including characterization, inherent viscosity, solubility and thermal properties are also reported.

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EXPERIMENTAL

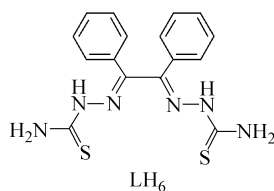
Materials and Instruments

Benzil, thiosemicarbazide, dicarboxylic acid dichlorides and solvents were purchased from Fluka Co., and used without further purification. $^1\text{H-NMR}$ spectra were recorded on a 500 MHz Bruker Advance DRX instrument using DMSO-d_6 as solvent and tetramethyl silane as an internal standard. FTIR spectra were recorded using a Bruker Vector 22 spectrometer on KBr pellets. The CHN-600 Leco analyzer was used for elemental analysis. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using Perkin-Elmer Pyris and Mettler Toledo 822°, respectively. Inherent viscosity ($[\eta]_{\text{inh}} = \ln \eta_{\text{rel}}/c$, at a concentration of 0.5 g/dL) was measured with an Ubbelohde suspended-level viscometer at 25°C in NMP solution. Total sulfur was measured using Tanaka Model RX-360 SH.

Monomer Synthesis

Synthesis of benzilbisthiosemicarbazone diamine (Scheme 1)^[25]

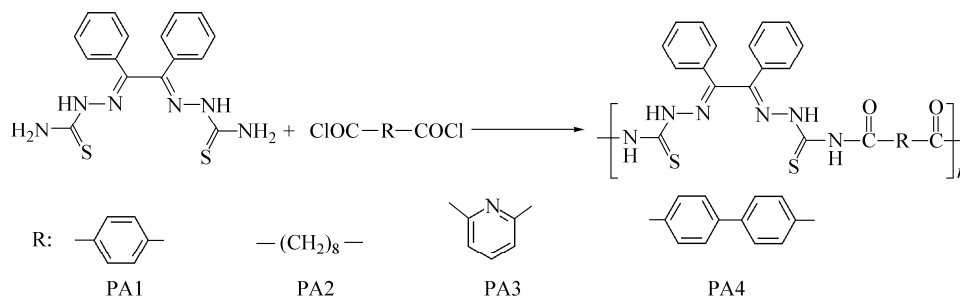
Into a 250 mL two necked round-bottomed flask with a magnetic stirrer bar, 3.64 g (40.30 mmol) thiosemicarbazide was dissolved in a mixture of 40 mL methanol, 40 mL of 2 mol/L HCl and 1 mL of concentrated HCl. A suspension of 4.24 g (20.20 mmol) benzil in 50 mL of methanol and few drops of concentrated HCl were added to the flask. The mixture was stirred at room temperature for 6 h. The yellow precipitate was filtered off, washed with methanol and dried in a vacuum oven at 70°C for 2 h. A yellow product was obtained in 75% yield with a melting point of 240°C. Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_6\text{S}_2$: C, 53.9%; H, 4.4%; N, 23.5%; S, 17.9%. Found: C, 54.1%; H, 4.4%; N, 23.2%; S, 17.8%. FTIR (KBr, cm^{-1}) at: 3420, 3250 and 3150 (NH, NH_2), 1610 (CN), 1680 (NH_2), 1580 (NH), 848 (CS). $^1\text{H-NMR}$ (CDCl_3 , δ) at: 6.7 (4H, NH_2), 7.3–7.6 (10H, aromatic), 9.1 (2H, NH).



Scheme 1 Structure of Schiff base diamine monomer (LH_6)

Polyamide Synthesis

A typical procedure for the preparation of PAs is given in Scheme 2. A 250 mL two-necked flask equipped with a dropping funnel, magnetic stirrer bar and gas inlet tube was charged with a mixture of 0.712 g (2 mmol) LH_6 , 20 mL dimethyl acetamide (DMAc) and 0.8 mL triethylamine (Et_3N). Then a solution of 2 mmol of a dicarboxylic acid dichloride (such as terephthaloyl chloride, sebacoyl chloride, pyridine-2,6-dicarbonyl chloride, or biphenyl-4,4'-dicarbonyl chloride) in 20 mL DMAc was added drop-by-drop to the mixture of the flask at



Scheme 2 Synthetic reaction and PAs designation

0°C under N₂. The mixture was subsequently stirred at ambient temperature for 5 h, and then it was poured into cold water. The yellow precipitate was separated by filtration, washed with NaHCO₃ solution and dried in a vacuum oven at 70°C. Purified polymer was obtained by hot extraction from methanol for 24 h. The yields were in the range of 92%–95%.

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

The monomer, LH₆, was prepared according to the procedure given in the literature^[25]. The characteristics data obtained from FTIR and ¹H-NMR spectra are in good agreement with the results reported in the literature^[23–25], and confirm the structure illustrated in Scheme 1. The particular interesting absorption bands in the FTIR spectrum of LH₆, Fig. 1(a), are: 3420–3150 cm⁻¹ (NH₂ and NH symmetric and asymmetric stretch), 1680 cm⁻¹ (NH₂) and 1610 (C=N). ¹H-NMR spectrum of LH₆ in Fig. 2 shows characteristics signals at: δ = 6.7 (4H) and 9.1 (2H) related to the protons of NH₂ and NH, respectively. Thermal behavior of LH₆ was studied by DSC, and the curves are shown in Fig. 3. As can be seen in this figure, the first DSC scan showed an unexpected thermal event at 260°C, appearing as endothermic and exothermic peaks, which was not observed during the second run.

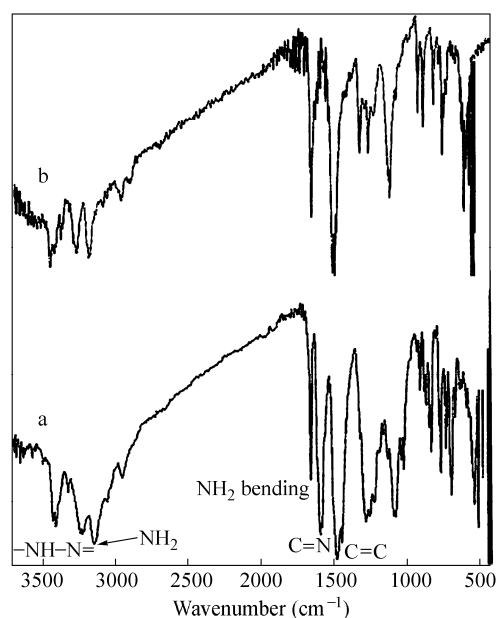


Fig. 1 FTIR spectra of LH₆: (a) before heating and (b) after heating at 250°C

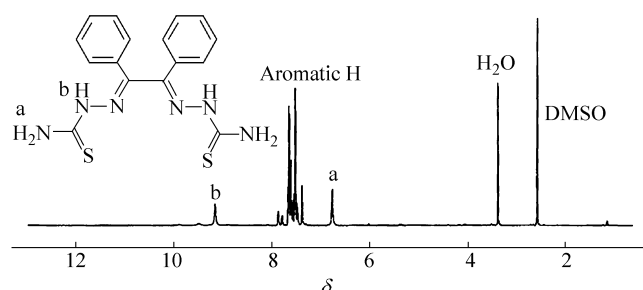


Fig. 2 ¹H-NMR spectrum of LH₆

Code	Yield (%)	T_g (°C)	FTIR (KBr, cm^{-1})	$^1\text{H-NMR}$ (DMSO- d_6 , δ)	Elemental analysis							
					Calculated				Found			
					C	H	N	S	C	H	N	S
PA1	95	95	3247 (NH), 1655 (C=O), 1608 (C=N), 872 (C=S).	11.02 (2H, NH), 9.13 (2H, NH), 7.29–8.20 (14H, phenyl)	59.2	5.0	17.2	13.1	59.4	4.9	17.1	13.3
PA2	92	80	3242 (NH), 1686 (C=O), 1608 (C=N), 816 (C=S).	11.01 (2H, NH), 9.12 (2H, NH), 7.30–7.57 (10H, phenyl) 1.41–2.12 (16H, aliphatic)	59.7	5.7	16.0	16.0	59.4	5.8	16.0	–
PA3	92	80	3242 (NH), 1634 (C=O), 1618 (C=N), 798 (C=S).	11.01 (2H, NH), 9.10 (2H, NH), 7.32–8.26 (13H, phenyl)	56.6	3.4	20.1	13.1	56.4	3.8	20.1	–
PA4	94	80	3361 (NH), 1665 (C=O), 1648 (C=N), 898 (C=S).	11.02 (2H, NH), 9.12 (2H, NH), 7.29–8.33 (18H, phenyl)	64.0	3.9	14.9	11.3	63.9	4.1	14.7	–

characteristic absorption bands in the regions of $3242\text{--}3361\text{ cm}^{-1}$, $1634\text{--}1165\text{ cm}^{-1}$ and $1608\text{--}1648\text{ cm}^{-1}$ which are related to the N—H, C=O and C—N stretching, respectively. $^1\text{H-NMR}$ spectra of the representative polyamide PA3, in Fig. 4, showed signals at $\delta = 9.12$ due to the proton of azomethine ($>\text{C}=\text{N}-\text{NH}-$), at $\delta = 11.01$ related to the proton of amide ($-\text{NH}-\text{CO}-$) group, and in the regions of $\delta = 7.30\text{--}7.57$ corresponding to aromatic protons. Disappearance of the signal at $\delta = 6.7$ related to the $-\text{NH}_2$ and the presence of amidic proton at *ca.* $\delta = 11.02$ confirmed the amidic structure of polymers.

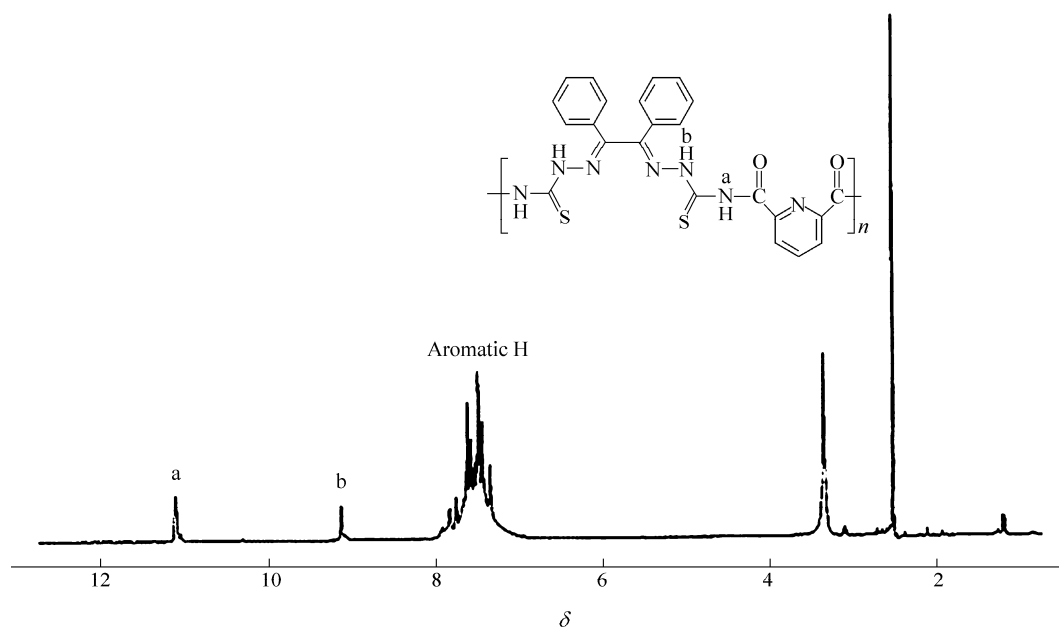


Fig. 4 $^1\text{H-NMR}$ spectrum of PA3 prepared from LH₆ and pyridine-2,6-dicarbonyl chloride

Solubility of PAs

One of the major objectives of this study was to produce Schiff base polyamides with improved solubility. The solubility of these polyamides was determined for the powdery samples, and the results are listed in Table 2. All PAs were readily soluble in common polar aprotic solvents without need for heating. Also, by heating they were soluble in a less efficient solvent such as THF. Among these polymers, the polyamide PA2 was more soluble in common solvents, and shorter time was needed for complete dissolution. For this polyamide, the presence of methylene groups increased flexibility and also disturbed the planarity of aromatic units which reduce the close packing. The good solubility behavior of the prepared polyamides can be explained through the enhancement of solubility induced by the particular functional groups such as azomethine linkage ($>\text{C}=\text{N}-\text{NH}-$) and the bulky side phenylene groups which reduced the close packing of the chains and decreased the interchain interactions.

Table 2. Solubility of the polyamides

PA	NMP	DMF	DMSO	TCE	THF	H ₂ SO ₄	HMPA	DMAC	Acetone	Ethanol
PA1	+	+	+	+	±	+	+	+	±	±
PA2	+	+	+	+	±	+	+	+	±	±
PA3	+	+	+	+	±	+	±	±	±	±
PA4	+	+	+	+	±	+	±	±	±	±

Soluble (+); partially soluble (±); insoluble (−); Solubility tested with 0.5 g of polymer in 100 mL of solvent; NMP = *N*-methylpyrrolidone; DMF = dimethylformamide; DMSO = dimethylsulfoxide; TCE = tetrachloroethane; Py = pyridine; THF = tetrahydrofuran; HMPA = hexamethylenephosphoramide; DMAC = dimethylacetamide

Thermal Properties of PAs

Thermal properties of the prepared polyamides were evaluated by means of DSC and TGA. DSC curves of the first run of all of the polyamides showed identical curves in comparison with the curve of the monomer LH₆. The representative DSC curves for the polyamides (PA1, PA2, and PA4) are shown in Fig. 5. The first DSC scan of all the polyamides showed the distinctive thermal transition above 200°C. This transition peak was not observed when samples were cooled to room temperature and rescanned up to 300°C, as shown in Fig. 5. The curves of the second runs showed endothermic steps varied from 80°C to 100°C depending on the diacid residue in the polymer backbone, which can be taken as the T_g of the polymers. The reason for the relatively low T_g s of these polyamides can be due to the low barrier for segmental mobility in the diamine residue of the polymer backbone and also the presence of the bulky pendent groups prevents the chains to pack closely which reduces the interchain interactions.

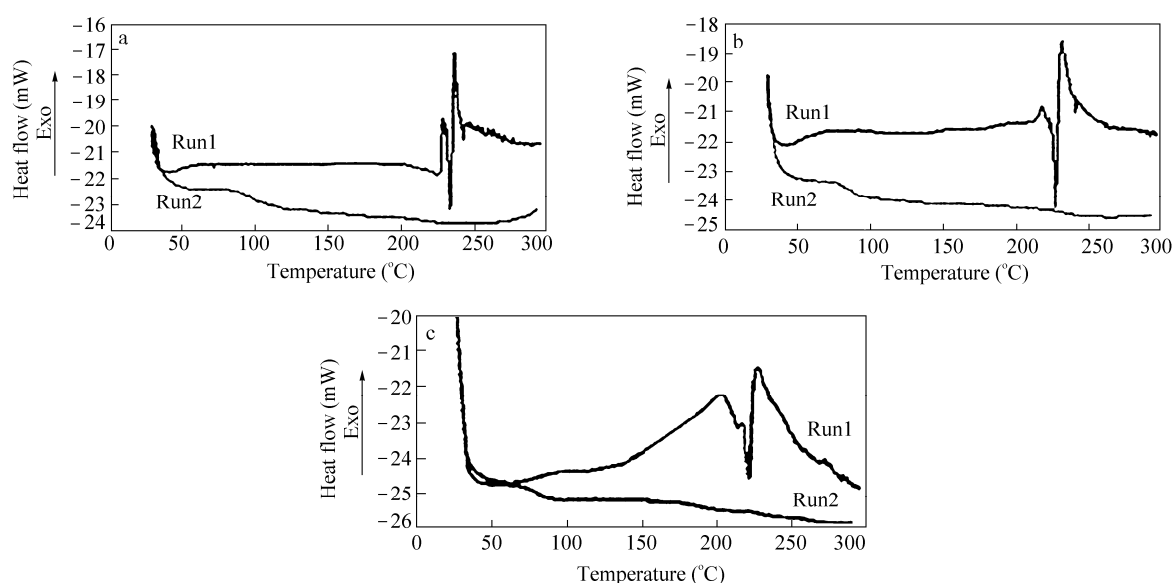


Fig. 5 DSC curves of the polyamides: (a) PA1, (b) PA2 and (c) PA4

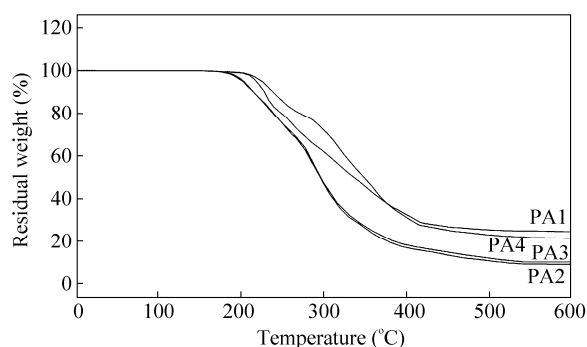


Fig. 6 TGA curves of PAs

Thermal stability of the polyamides has been evaluated by TGA measurements under N₂ atmosphere at the heating rate of 10 K/min, and the curves are shown in Fig. 6. All of the polyamides showed similar stability up to 200°C and started to lose weight above this temperature. Their 10% weight loss occurred in the region of 220–250°C. The char yields of the polymers at 600°C were in the range of 10%–22%. The chemical structure of the diacids did not have much effect on the initial decomposition temperatures of the polyamides. This can be

due to the fact that the main thermal breakdown of the polymer backbone occurs in the weaker bonds of the diamine residue. However, the thermal stability of the prepared Schiff base polyamides is close to the thermal stability of the same type of polymers which were reported by other researchers^[3, 8, 26].

CONCLUSIONS

Four new Schiff-base polyamides were prepared from the reaction of a new Schiff base diamine monomer (LH₆) with the commercially available dicarboxylic acid dichlorides. The introduction of the bulky phenyl side groups and polar azomethine linkage in the backbone of polymers resulted in the amorphous Schiff base polyamides with excellent solubility in the polar aprotic solvents. Thermal properties of these polyamides were investigated by DSC and TGA. The monomer LH₆ and the related polymers showed a thermal transition peak above 200°C during the first DSC scan. This was suggested to be due to thermal decomposition in the diamine residue in the polymer backbone. TGA thermograms also confirmed decomposition of polymers above 200°C.

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