Noncoplanar Rigid-Rod Aromatic Polyhydrazides Containing Tröger's Base

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ABSTRACT: A new Tröger's base-containing aromatic dihydrazide, 2,8-bis(carboxylic)-6H, 12H-5,11-methanodibenzo-[b,f] [1,5]-diazocine dihydrazide, was prepared by the condensation of ethyl *p*-aminobenzoate with hexamethylenetetramine in the presence of trifluoroacetic acid, followed by converting to the dihydrazide with a high yield and high purity. A series of novel aromatic polyhydrazides were prepared from the Tröger's unit containing dihydrazide and various aromatic diacyl chlorides via low-temperature solution polycondensation in quantitative yields. All the polyhydrazides were amorphous and readily soluble at room temperature in polar organic solvents such as *N*,*N*-dimethylacetamide and *N*-methyl-2-pyrrolidone. These polymers could be solution cast into transparent, tough, and flexible films with good mechanical properties. They had useful levels of thermal stability associated with good glass transition temperatures (163–172°C), 10% weight-loss temperatures in excess of 460°C, and char yields at 800°C in nitrogen higher than 39%. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 282–288, 2011

Key words: high performance polymers; Tröger's base; amorphous; heteroatom-containing polymers

INTRODUCTION

Polyhydrazide materials are of great interest, because they enhance dyeability of synthetic fibers, improve elasticity over other polymer types, and their use in reverse osmosis separations.[1,2] The polyhydrazides are high performance materials that have ability to spin to high modulus fibers and could be used as a reinforced plastics and tire cords.[3] In particular, they are soluble polymers with potential to convert to other highly thermally stable polymers like polyoxadiazoles and polytriazoles.[4,5]

Aromatic polyhydrazides (that are classified under a category of heat resistance materials) are usually made by reacting diacyl chloride with dihydrazide at low temperature or Yamazaki's phosphorylation method using dihydrazide and dicarboxylic acid.[3,6]

The rigid V-shaped Tröger's base unit suppresses coplanar structures, lower regularity, and molecular ordering.[7] Also, the Tröger's base (that is unable to undergo pyramidal inversion) is interesting because of their potential to function as artificial receptors.[8] There are some reports in the literature on different applications of polymers containing Tröger's base, which have conformationally and geometrically well-defined linker.[9,10]

Because this unit has good ability to prevent the close packing of chains and decreases interchain interaction, it has been suggested that synthetic polymers, containing Tröger's unit, can be dissolved by organic solvents. Thus, the presence of the V-shaped Tröger's unit in the final macromolecules was thought to lead to obtain amorphous polyhydrazides, which have high solubility in organic solvents, low softening temperatures, good thermal and mechanical properties, and easy melt processability.

In the present article, we report the synthesis of noncoplanar rigid-rod aromatic polyhydrazides containing Tröger's base. The thermal and mechanical properties, crystallinity, and solubility are also reported.

EXPERIMENTAL

Materials and measurements

Materials

Solvents and chemicals were either prepared in our laboratory or purchased from Fluka (Switzerland) and Merck (Germany) chemical companies. Isophthalic acid, terphetalic acid, 4,4′-bis(ether benzoic acid), 4,4′-dicarboxy diphenyl solfune, methanol, and hydrazine hydrate were purified and dried by the standard procedures.

N-methyl pyrrolidone (NMP) was distilled over calcium hydride and stored over molecular sieves

before use. Lithium chloride was dried under vacuum at 150°C for 6 h. Diacyl chloride compounds were synthesized by reported standard procedures.

Techniques

The infrared spectra were recorded using a JASCO 680 FTIR spectrophotometer with KBr pellet. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained using Bruker Avance 400 and 500 MHz spectrometer operating on monomer and polymer solution in CDCl$_3$ and DMSO-d_6; using tetramethylsilane as an internal standard. Inherent viscosities were measured with a Cannon–Fenske viscometer for a polymer solution of 0.5 g/dL in NMP at 25°C. Calorimetric analysis was performed on 10–15 mg of sample using a NETZSCHDSC200 F3 differential scanning calorimeter (DSC) from 60 to 260°C and with a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was carried out under nitrogen at a heating rate of 10°C/min from 25 to 800°C. CHNS analysis was performed with a CHNS-932, Leco. An Instron universal tester model 1130 with a load cell 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm min^{-1} was used for this study. Measurements were performed at room temperature with film specimens (6-cm long, 0.5-cm wide, and about 0.05–0.06-mm thick). The X-ray diffraction patterns are recorded by using a Philips Xpert MPD diffractometer equipped with a Cu Kα anode (λ = 1.51418 Å).

Monomer synthesis

2,8-Bis(ethoxycarbonyl)-6H,12H-5,11-methanodibenzo-[b,f][1,5] diazocine (1). A mixture of ethyl *p*-aminobenzoate (1 g, 6 mmol) and hexamethylenetetramine (0.8 g, 6 mmol) in trifluoroacetic acid (TFAA) (20 mL) was stirred at 60–70°C. After 60 h, TFAA was removed by distillation. The residue was taken in 15 mL of water, poured into a separatory funnel, and basified by the addition of liquid NH$_3$. The aqueous layer was then extracted with CH$_2$Cl$_2$ (3 × 60 mL). The combined organic phases were dried (MgSO$_4$), filtered, and concentrated *in vacuo* to give the crude product as a yellow glass foam. The crude product was purified by column chromatography using ethyl acetate in CHCl$_3$ (10% v/v) as the eluent to give the product. **(1)** (Yield 22%, 0.4 g), mp: 126–127°C.[8] ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.86 (d, 2H, Ar, *J* = 8.4 Hz), 7.67 (s, 2H, Ar), 7.20 (d, 2H, Ar, *J* = 8.4 Hz), 4.77 (d, 2H, CH$_2$, *J* = 16.6 Hz), 4.35 (m, 4H, CH$_2$), 4.32 (s, 2H, CH$_2$), 4.29 (d, 2H, CH$_2$, *J* = 16.6 Hz), and 1.38 (t, 6H, CH$_3$, *J* = 7.1 Hz) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 165.7, 152.3, 128.7, 127.2, 126.1, 124.7, 66.6, 60.5, 58.6, and 14.3 ppm; FTIR (KBr) ν = 2984, 2955, and 1711(C=O), 1609, 1285, 1186, 1104,

and 1024 cm^{-1}; UV λ$_{max}$: (log ε) 284 (4.33) and 250 (4.39) [*c* 1.09 × 10^{-4}*M*, CHCl$_3$].

2,8-Bis(carboxylic)-6H,12H-5,11-methanodibenzo-[b,f][1,5]-diazocine dihydrazide (2). The 100-mL bottom flask with a magnetic stirring bar was charged with 2,8-bis (ethoxycarbonyl)-6*H*,12*H*-5,11-methanodibenzo-[*b,f*][1,5]-diazocine (1) (0.183 g, 0.5 mmol), hydrazine hydrate (2.6 mL, 53.5mmol), and EtOH (2.5 mL) and then refluxed overnight. Compound **(2)** was precipitated by cooling down the solution to 0°C, after filtering resulted white solid.

(Yield 94%, 0.16 g); FTIR (KBr): 3298, 3200 (NH), and 1645 (C=O) cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 9.49 (s, 2H, NH), 7.53 (d, 2H, Ar, *J* = 8 Hz), 7.39 (s, 2H, Ar), 7.13 (d, 2H, Ar, *J* = 8.3 Hz), 4.63 (d, 2H, CH$_2$, *J* = 16.67 Hz), 4.34 (s, 4H, NH$_2$), 4.22 (s, 2H, CH$_2$), and 4.15 (d, 2H, *J* = 16.67 Hz) ppm; ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 166.49, 151.56, 129.2, 128.6, 126.9, 126.5, 125.38, 66.7, and 58.9 ppm. Anal. Calcd. (%) For C$_{17}$H$_{18}$N$_6$O$_2$: C, 60.34; H, 5.36; N, 24.84; Found: C, 60.12; H, 5.49; N, 24.61.

Synthesis of polyhydrazides

A typical procedure: a solution of 2,8-bis(carboxylic)-6*H*,12*H*-5,11-methanodibenzo-[b,f][1,5]-diazocine dihydrazide **(2)** (0.1 g, 0.3 mmol), NMP (5 mL), and LiCl (0.02 g) was placed in an ice-cooled reaction flask adapted with stirrer, nitrogen inlet, and drying tube. The materials were dissolved, and diacyl chloride compound (0.3 mmol) was added over a period of 15 min at 0°C in three portionwise. The reaction mixture was stirred overnight, and the polymer was cooled and precipitated with methanol. The isolated polymer was washed with ethanol. Then, it was dried in a vacuum oven.

(PH1). (Yield 95%); FTIR (KBr): ν = 3247 (NH), 1655, and 1610 (C=O) cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 10.21 (s, 2H, NH), 9.99 (s, 2H, NH), 8.08 (s, 4H, Ar), 7.65 (d, 2H, Ar, *J* = 7.6 Hz), 7.42 (s, 2H, Ar), 7.14 (d, 2H, Ar, *J* = 8 Hz), 4.70 (d, 2H, CH$_2$, *J* = 16 Hz), and 4.28 (d, 4H, CH$_2$, *J* = 17.5 Hz) ppm; η$_{inh}$: 0.35 dL/g; Anal. Calcd. (%) For C$_{25}$H$_{20}$N$_6$O$_4$: C, 64.10; H, 4.30; N, 17.94; Found: C, 63.89; H, 4.48; N, 17.81.

(PH2). (Yield 96%); FTIR (KBr): ν = 3242 (NH), 1652, and 1608 (C=O) cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 10.53 (s, 2H, NH), 10.32 (s, 2H, NH), 8.38 (s, 1H, Ar), 8.04 (d, 2H, Ar, *J* = 7.7 Hz), 7.68 (d, 2H, Ar, *J* = 8.3 Hz), 7.60 (t, 1H, Ar, *J* = 7.7 Hz), 7.53 (s, 2H, Ar), 7.22 (d, 2H, Ar, *J* = 8.35 Hz), 4.71 (d, 2H, CH$_2$, *J* = 16.7 Hz), and 4.26 (d, 4H, CH$_2$, *J* = 17.5 Hz) ppm; η$_{inh}$: 0.29 dL/g; Anal. Calcd. (%) For C$_{25}$H$_{20}$N$_6$O$_4$: C, 64.10; H, 4.30; N, 17.94; Found: C, 63.92; H, 4.39; N, 17.81.

(PH3). (Yield 94%); FTIR (KBr): ν = 3378(NH), 1654 (C=O), and 1157 (S=O) cm^{-1}; ^{1}H-NMR (400 MHz,
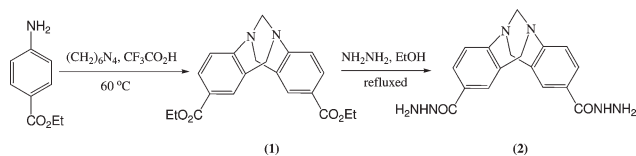
Scheme 1 Monomer synthesis.

DMSO-d_6): δ = 10.75 (s, 2H, NH), 10.45 (s, 2H, NH), 8.18 (d, 4H, Ar, J = 8.8 Hz), 8.15 (d, 4H, Ar, J = 8.8 Hz), 7.73 (d, 2H, Ar, J = 8.4 Hz), 7.60 (s, 2H, Ar), 7.30 (d, 2H, Ar, J = 4 Hz), 4.77 (d, 2H, J = 16 Hz), and 4.33 (d, 4H, J = 17.2 Hz) ppm; η_{inh}: 0.32 dL/g; Anal. Calcd. (%) For $C_{31}H_{24}N_6O_6S$: C, 61.18; H, 3.97; N, 13.81; S, 5.27; Found: C, 60.92; H, 4.19; N, 13.59; S, 5.19.

(PH4).. (Yield 95%); FTIR (KBr): ν = 3398, 3255(NH), 1648, 1609 (C=O), 1487, 1242 (C—O—C), and 1105(C—O) cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 10.43 (s, 2H, NH), 10.30 (s, 2H, NH), 7.97 (d, 2H, Ar, J = 7.6 Hz), 7.73 (d, 2H, Ar, J = 7.6 Hz), 7.57 (s, 2H, Ar), 7.26 (d, 4H, Ar, J = 8 Hz), 7.17 (d, 4H, Ar, J = 7.6 Hz), 4.73 (d, 2H, CH$_2$, J = 16.4 Hz), and 4.27 (d, 4H, CH$_2$, J = 17.2 Hz) ppm; η_{inh}: 0.30 dL/g.

RESULTS AND DISCUSSION

Monomer synthesis

A new aromatic dihydrazide bearing Tröger's moieties were synthesized according to the synthetic route depicted in Scheme 1. More particularly, ethyl *p*-aminobenzoate reacted with hexamethylenetetramine in the presence of TFAA to afford diester. **(1)** Compound **(1)** was converted to the dihydrazide by reacting with hydrazine hydrate. The structure of the dihydrazide was confirmed by elemental analysis, infrared, ^{1}H-NMR, and ^{13}C-NMR spectroscopies.

The FTIR spectrum of dihydrazide monomer shows the characteristic absorption bands of hydrazide groups at 3298, 3200 cm^{-1} (NH—NH$_2$), and 1645 cm^{-1} (C=O stretching), confirming the presence of hydrazide groups in the structure. ^{1}H-NMR spectrum of dihydrazide showed signals between δ = 7.12 and 7.55 ppm due to aromatic protons. The characteristic resonance of CH$_2$ (N—CH$_2$—N) singlet at 4.22 ppm, peak at 4.15 and 4.63 ppm is assigned to CH$_2$ protons bonded to benzene rings, and the protons of the hydrazide group (—NH—NH$_2$) were seen as two singlets at δ = 4.34 ppm and 9.49 ppm due to two NH$_2$ protons and one NH proton, respectively. (Fig. 1) Also, the ^{13}C-NMR spectrum of dihydrazide (Fig. 2) shows nine signals attributed to the nine carbons of the structure. It was revealed that aromatic carbons ranged from about 125–151 ppm. Carbonyl carbons of hydrazide group resonate in downfield region above 166 ppm. Also, —CH$_2$— car-

bons resonate in upfield region; around 58 and 66 ppm. These spectra are in agreement with the predicted structures of the monomer. The chemical structure of dihydrazide is also verified from the elemental analysis results, and the data correspond well with the calculated values.

Polymer synthesis

Among several different reaction pathways that have been developed for polyhydrazide synthesis,[1–6] low-temperature polycondensation by the reaction of diacyl chloride with dihydrazide is the most popular method. The polyhydrazides were synthesized through reaction of dihydrazide with diacyl chloride by low-temperature solution polymerization in dry NMP containing 5% LiCl (Scheme 2). The resulting polymers were characterized by FTIR, ^{1}H-NMR, viscosity, solubility, elemental analysis, and thermal analysis. The data of polymerization of polyhydrazide is given in Table I. The polyhydrazides were obtained in high yields in the range of 94–96%. FTIR spectra of polymers showed carbonyl absorptions in the range of 1648–1655 cm^{-1}, peculiar to carbonyl stretching of hydrazide groups; and NH stretching in the range of 3242–3398 cm^{-1}. The lowering in the usual carbonyl frequency is due to hydrogen bonding.

The typical ^{1}H-NMR of PH2 (Fig. 3) shows signals at 10.53 and 10.32 ppm corresponding to (NH—NH) protons of hydrazide group. Aromatic protons appeared in the range 7.22–8.38 ppm, whereas aliphatic —CH$_2$— group signal is appeared in the range 4.69–4.72 and 4.24–4.27 ppm. Thus, the NMR data
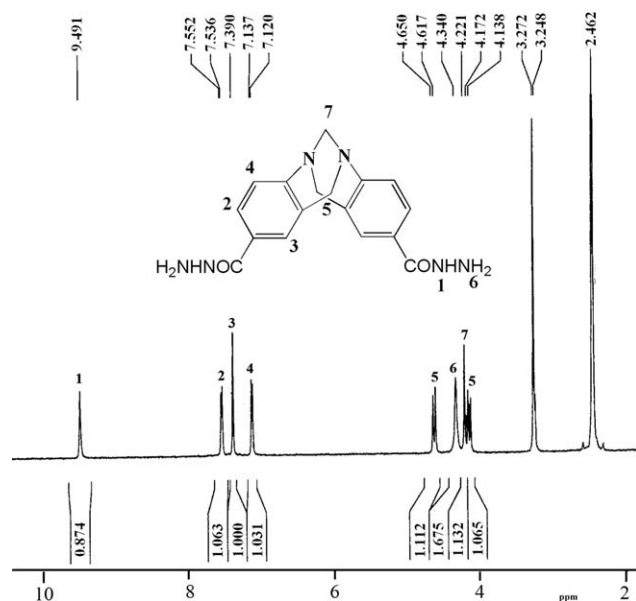

Figure 1 ^{1}H-NMR spectrum of (A) 2,8-bis(carboxylic)-6H,12H-5,11-methanodibenzo-[b,f][1,5]-diazocine dihydrazide (2).
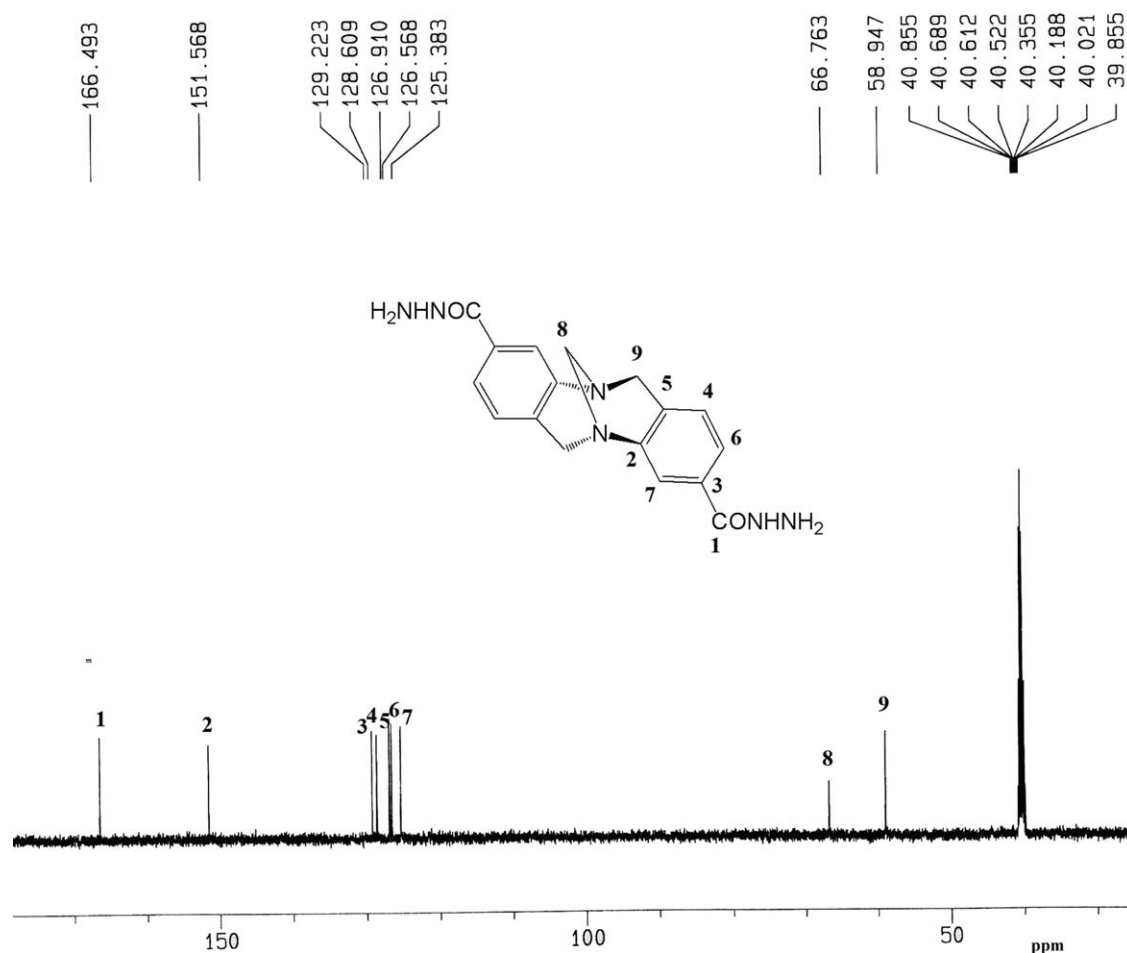
Figure 2 ^{13}C-NMR spectrum of (A) 2,8-bis(carboxylic)-6H,12H-5,11-methanodibenzo-[b,f][1,5]-diazocine dihydrazide (2).

confirm the assigned polymer structure indicating the incorporation of respective repeating units in the polymer chain.

The results of solubility tests of polyhydrazides are listed in Table II. As expected, all polymers showed excellent solubility and were readily soluble at room temperature in polar solvents such as NMP, DMAc, DMF, and DMSO, and in hot m-cresol. The relatively higher solubility associated with these polymers are believed to be related to the presence of the V-shape rigid, bulky Tröger's unit, which prevent the close packing of chains and decrease interchain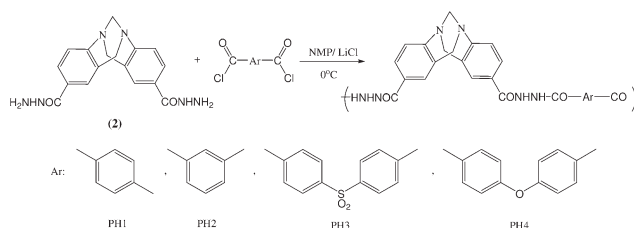 interaction. This noncoplanarity affects the crystallinity by weakening van der Waals forces and by lowering the symmetry of repeated units.

The wide-angle X-ray diffraction patterns of PH1 and PH2 over the 2θ range of 5°–45° are shown in Figure 4. Both the polyhydrazides revealed an essentially amorphous pattern. Obviously, the V-shape Tröger's unit hindered chain packing and reduced the level of crystallinity. The amorphous nature of these polymers was also reflected in their good solubility.

Scheme 2 Polymer synthesis.

TABLE I
Synthetic Conditions, Inherent Viscosities, and Film Quality of Polyhydrazides

Polymer code	Yield (%)	η_{inh} (dL/g)^a	Film quality
PH1	96	0.29	Flexible, transparent
PH2	95	0.35	Flexible, transparent
PH3	94	0.32	Flexible, transparent
PH4	95	0.30	Flexible, transparent

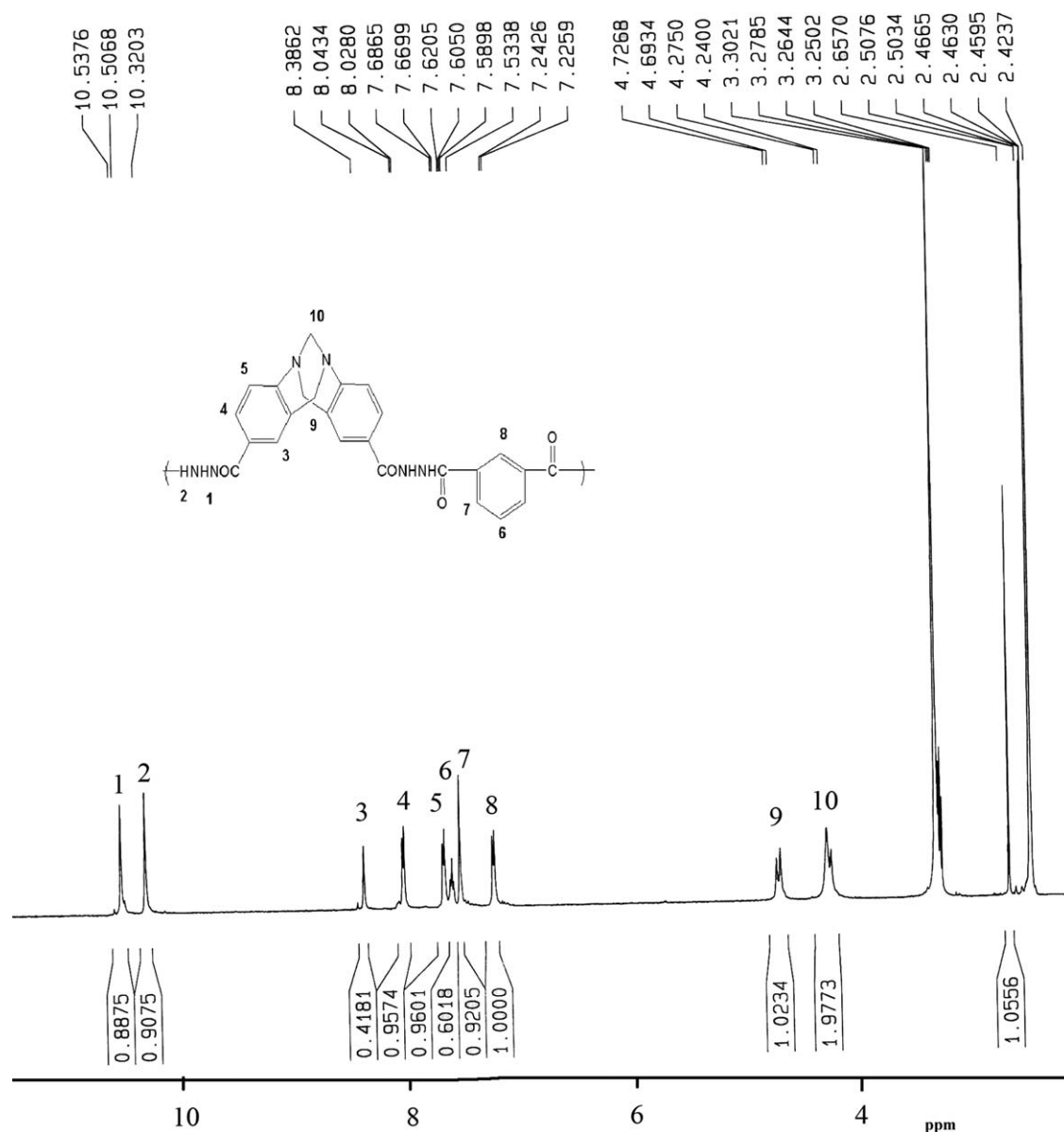^{a} Measured at a concentration of 0.5 g dL^{-1} in NMP at 25°C.

Figure 3 ^{1}H-NMR spectrum of PH2.

As can be seen from Table I, all the polyhydrazides could be solution-cast into flexible films. PH1 and PH2 were subjected to tensile testing, and the results are summarized in Table III. Their tensile strengths, elongations to break, and tensile modulus were in the range 77, 74 MPa, 12, 9% and 2.7, and 2.0 GPa, respectively. At this moment of time, there are only few reports about mechanical properties of polyhydrazides.[11,12] As can be seen from Table III, PH1 and PH2 showed better mechanical properties than the polymers reported in the literature.

The thermal behavior of all polyhydrazides was investigated by means of TGA and DSC in nitrogen. The relevant results are reported in Table IV. The T_g values are influenced by several factors, for example, chain symmetry and interchain interactions, but they primarily depend on chain flexibility. Thus, the polyhydrazides derived from V-shape aromatic dihydrazide showed relatively lower T_g's when compared with common polyhydrazides (Fig. 5). Figure

TABLE II
Solubility Behavior of Polyhydrazide

Polymer code	Solvent[a]				
	NMP	DMAc	DMF	DMSO	m-Cresol
PH1	+[b]	+	+	+	+h[b]
PH2	+	+	+	+	+h
PH3	+	+	+	+	+h
PH4	+	+	+	+	+h

[a] NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethyl formamide; DMSO, dimethyl sulfoxide.
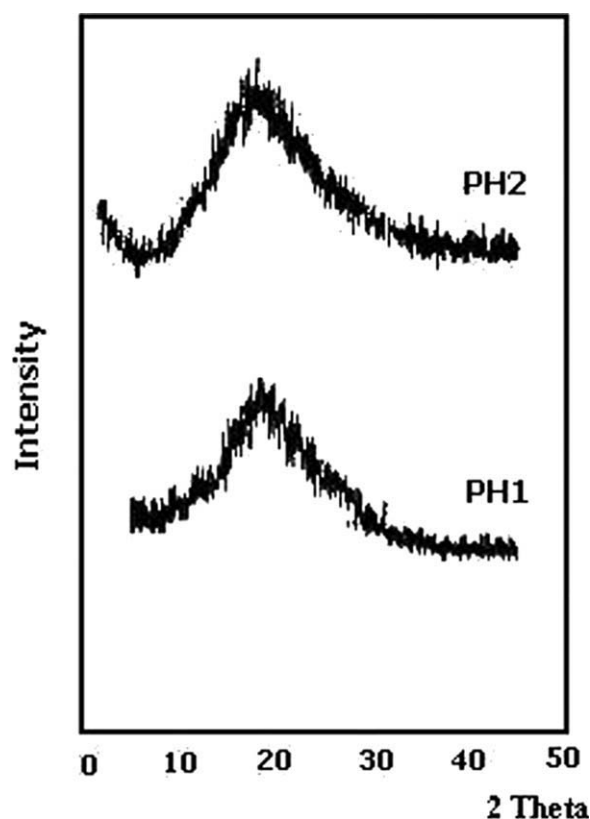[b] +, soluble at room temperature; +h, soluble on heating at 100°C.

Figure 4 Wide-angle X-ray diffractograms of typical pair of polyhydrazides.

6 shows some typical TGA curves measured in nitrogen for the polyhydrazides. The TGA tracings profile of polyhydrazides showed that they exhibited the main endothermal cyclodehydration reaction of the hydrazide group, which was occurring with water evolution in the range of 328–343°C.[13,14] The last break in the TGA curve occurred at around 440–520°C and corresponded to decomposition of poly(1,3,4-oxadiazole) formed *in situ*.

CONCLUSIONS

A series of novel polyhydrazide bearing V-shape Tröger's unit were successfully prepared from 2,8-bis (carboxylic)-6*H*,12*H*-5,11-methanodibenzo-[*b,f*][1,5]-diaz-

TABLE III
Tensile Properties of Polyhydrazides

Polymer code	Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)
PH1	77	9	2.7
PH2	74	12	2.0
Reference 11	69–73	4.6–5.3	2.2–2.3
Reference 12	67–74	8–11	1.8–1.9

Films were cast from slow evaporation of polymer solutions in DMAc. The cast films were dried under vacuum at 150°C for 6 h before tensile test.

TABLE IV
Thermal Behavior Data of Polyhydrazides

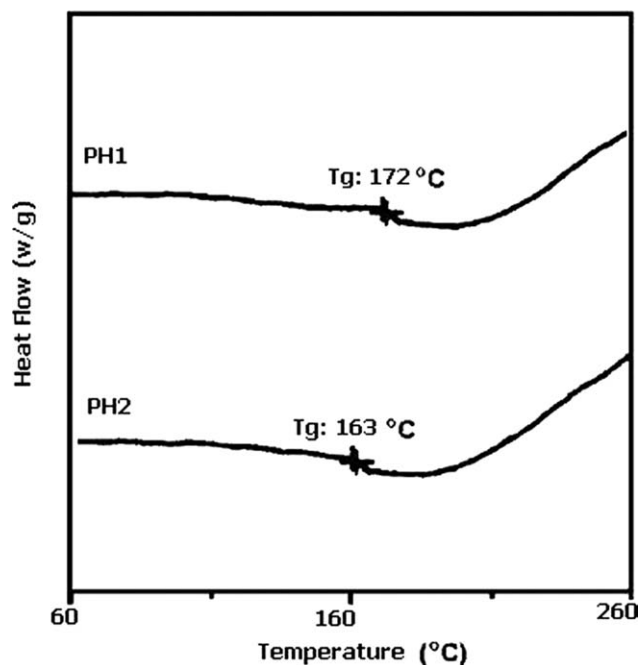| Polymer code	T_g (°C)	$T_{10\%}$	Char yield (%)
PH1	172	460	39
PH2	163	450	51

Figure 5 DSC curves of PH1 and PH2 with a heating rate of 10°C/min in nitrogen.

ocine dihydrazide with diacyl chlorides via the low-temperature solution polycondensation. Polyhydrazides containing Tröger's base suppress coplanar structures, lower regularity, and molecular ordering. All the
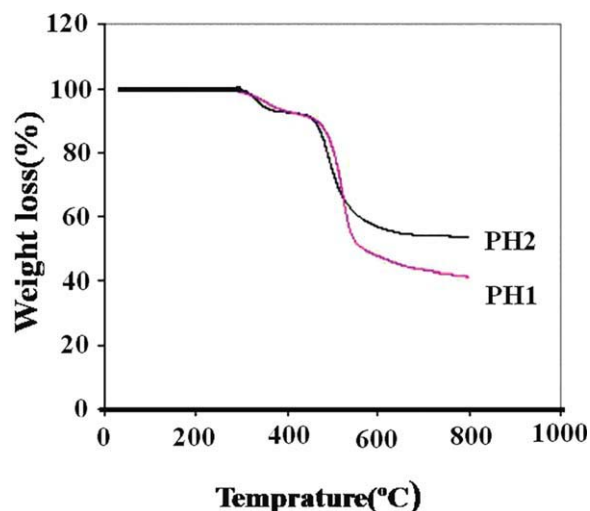

Figure 6 TGA's of polyhydrazides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymers were amorphous and soluble in various polar organic solvents such as NMP, DMAc, DMF, DMSO, and *m*-cresol. Most of them could be solution-cast into flexible, transparent (almost colorless), and tough films. The polyhydrazides had T_g's in the range of 163–172°C and could be thermally cyclodehydrated into the corresponding polyoxadiazole in the region of 328–343°C. The large window between the T_g and the decomposition temperature could be advantageous in the processing of these polymers.

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