Novel Poly(amide-hydrazide)s and Copoly(amide-hydrazide)s from Bis-(4-aminobenzyl) Hydrazide and Aromatic Diacid Chlorides: Synthesis and Characterization

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ABSTRACT: A new aromatic diamine, viz., bis-(4-aminobenzyl) hydrazide (BABH), which contains preformed hydrazide and methylene linkage, was synthesized starting from α-tolunitrile. The BABH and intermediates involved in its synthesis were characterized by spectroscopic methods. Novel poly(amide-hydrazide)s were synthesized by low temperature solution polycondensation of BABH with isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC). Furthermore, two series of copoly(amide-hydrazide)s, based on different mol % of BABH and bis-(4-aminophenyl) ether (ODA) with IPC/TPC were also synthesized. Poly(amide-hydrazide)s and copoly(amide-hydrazide)s were characterized by inherent viscosity [η_{inh}], FTIR, solubility, X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The polycondensation proceeded smoothly and afforded the polymers with inherent viscosities in the range of 0.18–0.93 dL/g in (NMP + 4% LiCl) at 30°C ± 0.1°C. These polymers dissolved in DMAc, NMP or DMSO containing LiCl. The solubility of copolymers was considerably improved in line with less crystalline nature due to random placement of constituent monomers during the copolymerization. XRD data indicated that poly(amide-hydrazide)s from BABH alone and IPC/TPC had higher crystallinity than the corresponding copoly(amide-hydrazide)s derived from a mixture of BABH and bis-(4-aminophenyl) ether (ODA). Polymers showed initial weight loss around 160°C which is attributed to the cyclodehydration leading to the formation of corresponding poly(amide-oxadiazole)s. Copolyamide-hydrazides showed T_{max} between 400 and 540°C which is essentially the decomposition of poly(amide-oxadiazole)s. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2441–2450, 2010

Key words: poly(amide-hydrazide); bis-(4-aminobenzyl) hydrazide; x-ray diffractograms; thermogravimetric analysis (TGA); structure-property relations

INTRODUCTION

Many aromatic polymers because of high aromatic content display excellent thermal stability, excellent physico–mechanical properties and good chemical resistance. The high regularity and high rigidity of the backbone of aromatic polymer results in strong chain–chain interactions, high crystallinity, high melting points, and low solubility; often making the processing of such polymers difficult.[1] To improve the processability of the high performance aromatic polymers, we have synthesized in our previous work a wide variety of modified thermally stable and soluble polyimides, polyamides, polyhydrazides, polyesters and number of copolymers.[2–5]

Poly(amide-hydrazide)s are known for their excellent thermal, dimensional and hydrolytic stability, as well as good fiber properties.[6,7] Poly(amide-hydrazide)s were used to reinforce plastics and as a tire cord. They can be used in protective and decorative coatings, strengthening agents, textile finishing agents, binders for nonoven fabrics, high temperature fibers, etc. Poly(amide-hydrazide)s have been extensively studied to enhance dye ability of synthetic fibers; due to their fair absorption characteristics; to improve elasticity of polymer types[8–10] and have been cyclized to give poly(amide-oxadiazole)s[11,12] and poly(amide-triazole)s.[13,14] These polymers are precursors to synthetic desalination membranes[15] and also provide a synthetic base for the chelating polymers,[16] since the hydrazide group (—CO—NH—NH—CO—) can react to form a complex with metal ions. Hence, several novel wholly aromatic structures complexing with various transition metal salts were synthesized and used in metallized plastic application as film, electronic devices, sensors etc.[17,18] Poly(amide-hydrazide)s are generally

synthesized by the low temperature solution poly-condensation in a solvent such as N-methyl-2-pyrro-lidone (NMP)/N,N-dimethyl acetamide (DMAc) in the presence of an inorganic salt like lithium chlo-ride (LiCl).[19,20] Interfacial polycondensation of diacyl-hydrazide with aromatic diacid chlorides can yield high molecular weight polyhydrazides and poly(amide-hydrazide)s or they could be synthe-sized by the direct polycondensation reaction using aromatic dicarboxylic acids by Yamazaki's method.[21–23]

Earlier, we reported new soluble thermally stable polyhydrazides from novel phenylated dicarboxylic acid containing methylene linkage; 2,5-bis(4-carboxy-methylene phenyl) 3,4-diphenyl thiophene; and dif-ferent aromatic diacyl-dihydrazides by Yamazaki's direct phosphorylation method wherein the effect of incorporation of methylene linkages in polymer back-bone on thermal and processing characteristics was investigated.[22] The attachment of phenyl pendant groups and methylene linkages in main chain increased the polymer processability by decreasing crystallinity and consequently enhancing the solubil-ity. As a part of our continuing efforts, we now wish to report herein synthesis and characterization of new poly(amide-hydrazide)s and copoly(amide-hydrazide)s based on novel aromatic diamine con-taining preformed hydrazide linkage and methylene linkage; viz., bis-(4-aminobenzyl) hydrazide [BABH]. The polymers were characterized by inherent viscos-ity, IR spectroscopy, solubility, X-ray diffraction stud-ies, DSC, and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidone, N,N-dimethylacetamide, hexa-methyl phosphoramide, methanol, and hydrazine hydrate were purified and dried as per the standard procedures. 4-Nitro phenyl acetic acid, isophthalloyl chloride (IPC) and terephthalloyl chloride (TPC) were synthesized in the laboratory and were puri-fied by recrystalisation from dry solvents before use. Lithium chloride was dried under vacuum at 150°C for 6 h. Bis-(4-aminophenyl) ether (ODA); E-Merck product was crystallized from alcohol and vacuum dried.

Measurements

Inherent viscosity measurements were made with 0.5% (w/v) solution of polymer in (NMP + 4% LiCl) at 30°C ± 0.1°C using Ubbelohde suspended level viscometer. The solubility of polymers was deter-mined at 1 wt % concentration in various solvents at room temperature or by warming, if needed. IR

spectra were recorded as KBr pellet on Perkin–Elmer 599B spectrophotometer. Elemental analysis was per-formed with Perkin–Elmer model 2400 C, H, N, S analyzer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker NMR spectrometer (200 or 500MHz) in DMSO-d_6. All melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. X-Ray diffractograms of poly-mers were obtained on a Rigaku Dmax 2500 X-ray diffractometer using Cu Kα source of radiation (λ = 1.54 Å). TGA were performed on Perkin–Elmer TGA-7 analyzer at a heating rate of 10°C/min in nitrogen atmosphere. Differential scanning calorime-try (DSC) analyzes were performed on Perkin–Elmer DSC-7 at a heating rate of 20°C/ min.

Synthesis of BABH monomer

Synthesis of bis-(4-nitrobenzyl)hydrazide (BNBH)

Into a 250 mL three necked round bottom flask equipped with a magnetic stirrer, a calcium chloride guard-tube, a reflux condenser and a nitrogen gas inlet were placed 4-nitro phenyl acetohydrazide (V) (8.58 g, 0.044 mol), 4-nitro phenyl acetic acid (III) (7.96 g, 0.044 mol), LiCl (5.0 g, 8 wt % based on sol-vent NMP and pyridine mixture), triphenyl phos-phite (TPP) (16.38 g), pyridine (12.5 mL) and NMP (50 mL). The temperature of the reaction mixture was slowly raised to 100°C over a period of 30 min and the reaction mixture was stirred at this tempera-ture for 3 h under nitrogen flow. After cooling, the reaction mixture was poured into methanol (300 mL) with stirring to precipitate bis-(4-nitrobenzyl)hydra-zide (BNBH), which was filtered; washed with meth-anol, aq. sodium bicarbonate solution and then with water. Yield: 13.2 g (83.8%), m.p. 272–75 °C.

Elem. Anal. Calculated for $C_{16}H_{14}N_4O_6$: C-53.63, H-3.91, N-15.64%.

Found: C-53.30, H-3.78, N-15.78%.

Synthesis of bis-(4-aminobenzyl) hydrazide (BABH)

Reduction of BNBH by NaSH: Into a single necked 250 mL round bottom flask BNBH (4.29 g, 0.012 mol) in methanol (40 mL) was warmed to 50°C with stirring, and "NaSH solution" (2.24 g, 0.04 mol in 30 mL methanol; prepared from 10.8 g $Na_2S.9H_2O$ crys-tals) was added dropwise over a period of 30 min. The reaction mixture turned dark as reactant was added. Reaction mixture was heated to reflux for 30 min; then excess methanol was removed by distilla-tion. The residual concentrated solution was poured in ice-water (100 mL) with vigorous stirring. The precipitate (BABH) was filtered, washed with water, methanol acetone and dried. Yield 2.29 g (64%), m.p. 244–45°C.

Elemental Analysis calculated for $C_{16}H_{18}N_4O_2$: C-64.42, H-6.04, N-18.79%.

Found: C-64.10, H-5.97, N-18.38%.

Synthesis of Poly(amide-hydrazide) (PAHI-1)

Into a 100 mL three necked round bottom flask, equipped with a magnetic stirrer, a calcium chloride guard-tube and a nitrogen gas inlet were placed; BABH (0.298 g, 1 mmol), lithium chloride (0.24 g), DMAc (3 mL) and the reaction mixture was stirred to form a homogeneous solution. The reaction mixture was cooled to 0°C in ice-bath; and solid IPC (0.203 g, 1 mmol) was added in small lots over a period of 1 h. The reaction mixture was stirred in ice-bath for additional 2 h; at room temperature for 12 h, and then it was poured into rapidly stirred methanol (200 mL). The precipitated polymer was filtered, washed with methanol and dried under vacuum at 80°C for 6 h. The yield of poly(amide-hydrazide), PAHI-1 was 0.46 g (98.6%) and the inherent viscosity (in NMP + 4% LiCl) was 0.28 dL/g at 30°C ± 0.1°C.

Other poly(amide-hydrazide)s were prepared by similar procedure. Polymerization of BABH with IPC and TPC (PAHI-1 and PAHT-1, respectively) showed precipitation after 3 h. from the start of reaction and therefore these two polymers were synthesized in a (HMPA + 4% LiCl) solvent system also; where in polymerization proceeded smoothly in solution phase without precipitation of polymers during the polymerization period.

RESULTS AND DISCUSSION

A new aromatic diamine, BABH, containing preformed hydrazide unit and methylene linkage was synthesized as depicted in Scheme 1. To introduce two methylene groups in the aromatic diamine monomer; α-tolunitrile was chosen as the starting material which on nitration and subsequent hydrolysis gave 4-nitro phenyl acetic acid (III).[24] 4-nitro phenyl acetic acid was further converted to its corresponding methyl ester (IV) and then reacted with hydrazine hydrate to obtain 4-nitro phenyl aceto hydrazide (V).[24] Reaction of (V) with (III) in a Yamazaki's[23] phosphorylation method using TPP as condensing agent afforded bis(4-nitrobenzyl) hydrazide (BNBH) whereby two methylene groups and preformed hydrazide linkage were successfully incorporated in the aromatic diamine-BABH.

The reduction of BNBH to bis-(4-aminobenzyl) hydrazide (BABH) was accomplished by NaSH in hot methanol. BABH and intermediate BNBH involved in the synthesis, were characterized by spectroscopy; IR, ^{1}H, ^{13}C-NMR, and elemental analyzes. IR spec-
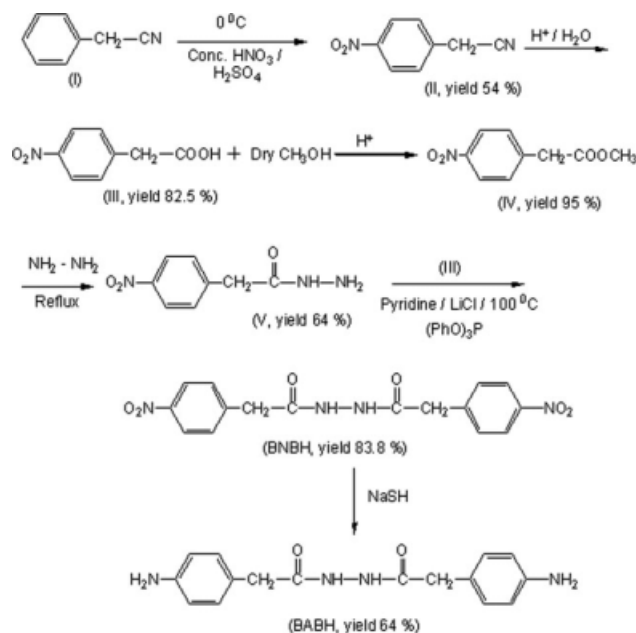
Scheme 1 Synthesis of bis-(4-aminobenzyl) hydrazide (BABH).

trum of BNBH showed characteristic absorptions at 1611 and 1349 ($-NO_2$), 3159 (hydrazide NH) and 2921, 3011 cm^{-1} (aliphatic and aromatic $-CH$, respectively) absorption. IR spectrum of BABH showed absorptions at 3408 and 3319 ($-NH_2$) as expected with the corresponding disappearance of absorptions at 1611 and 1349 cm^{-1} ($-NO_2$) indicating complete reduction of the nitro functionality to amine.

^{1}H-NMR spectrum of BNBH (Fig. 1) showed signals at 10.3 δ (s, hydrazide NH proton); doublet: 8.18 δ (d, aromatic $-CH$ ortho to nitro), 7.56 δ (d, aromatic $-CH$ ortho to $-CH_2$) and 3.66 δ (s, $-CH_2$). Similarly, ^{1}H-NMR spectrum of BABH (Fig. 2) showed signals at 9.90 δ (s, hydrazide NH proton), doublet: 6.92 δ (d, aromatic $-CH$ ortho to amine), 6.48 δ (d, aromatic $-CH$ ortho to $-CH_2$), 4.91 δ (broad, s, $-NH_2$) and 3.23 δ (s, $-CH_2$).

^{13}C-NMR spectrum of BNBH [Fig. 3(A)] showed signals at 167.86 δ ($-C=O$); 146.37 δ and 143.64 δ for tertiary aromatic carbon; 130.36 δ and 123.32 δ for secondary aromatic carbon; 39.71 δ for aliphatic carbon. These values also correlate with DEPT ^{13}C-NMR spectrum of BNBH [Fig. 3(B)]. ^{13}C-NMR spectrum of BABH [Fig. 4(A)] showed signal at 169.62 δ ($-C=O$); 147.04 δ and 122.59 δ for tertiary aromatic carbon; 129.41 δ and 113.76 δ for secondary aromatic carbon; 39.37 δ for aliphatic carbon. These values also correlate with DEPT ^{13}C-NMR spectrum of BNBH [Fig. 4(B)].

Micro analysis (Elemental analysis) results for C, H, N; in case of BNBH and BABH; were in good agreement with the theoretical values.
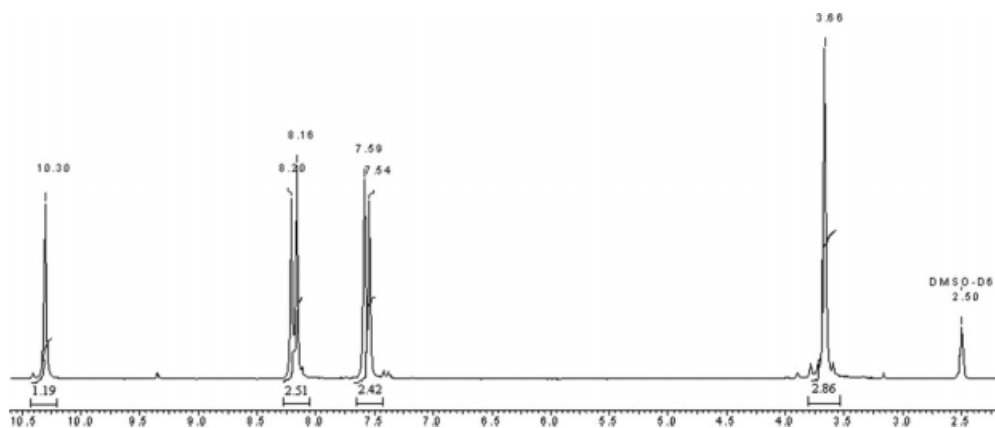
Figure 1 ^{1}H-NMR spectrum of BNBH in DMSO-d_6.

Poly(amide-hydrazide)s, and copoly(amide-hydrazide)s were prepared (Scheme 2) by reacting IPC/TPC with equimolar quantities of BABH or a mixture [BABH + ODA], wherein mol % of BABH was varied from 0 to 100%; which allowed to synthesize polymers with varying % of amide and hydrazide groups in the main polymer chain. Polymers PAI-5 and PAT-5, (00 mol % BABH); are aromatic polyamides of bis-(4-aminophenyl) ether (ODA) and IPC/TPC since there is no hydrazide-linkage incorporated in these polymers.

Polymers were synthesized by low temperature solution polycondensation method and inherent viscosities, except for PAHI-1 and PAHT-1, were in the range of 0.44–0.93 dL/g (Table I), indicating that the polymers had moderate to high molecular weights.

Poly(amide-hydrazide)s, PAHI-1 and PAHT-1, precipitated during polymerization after 3 h when DMAc was used as the solvent and polymers had inherent viscosities 0.13 and 0.11 dL/g respectively; with yield around 80%. Hence, these polymers, PAHI-1 and PAHT-1; were also prepared in (HMPA + 4% LiCl) solvent system wherein smooth polymerization in solution was evident (no precipitation of polymers was observed) thereby giving polymers with higher viscosities (0.28 and 0.18 dL/g respectively) in good yield (98% and 85%, respectively). This is reasonable because HMPA containing LiCl has higher polarity; due to more amide content (three) and added salt, compared to that of DMAc which has only one amide group. Hence polymers were more soluble in HMPA which allowed higher molecular weight built-up in solution form and as molecular weight increased the amount of polymers on coagulation increased since content of low molecular weight oligomers was reduced.

IR spectra of poly(amide-hydrazide)s and copoly(amide-hydrazide)s exhibited (Figs. 5 and 6) —NH— stretching vibration in the range of 3350–3180 cm^{-1} and hydrazide carbonyl absorption and amide carbonyl absorption (amide-I band) in the range of 1693–1650 cm^{-1} and amide-carbonyl at about 1598 cm^{-1} (amide-II band); therefore showing two carbonyl bands in the spectra. The lowering of the carbonyl frequency may be assigned to the hydrogen bonding. Overlapping of hydrazide carbonyl absorption and the amide-I band (at about
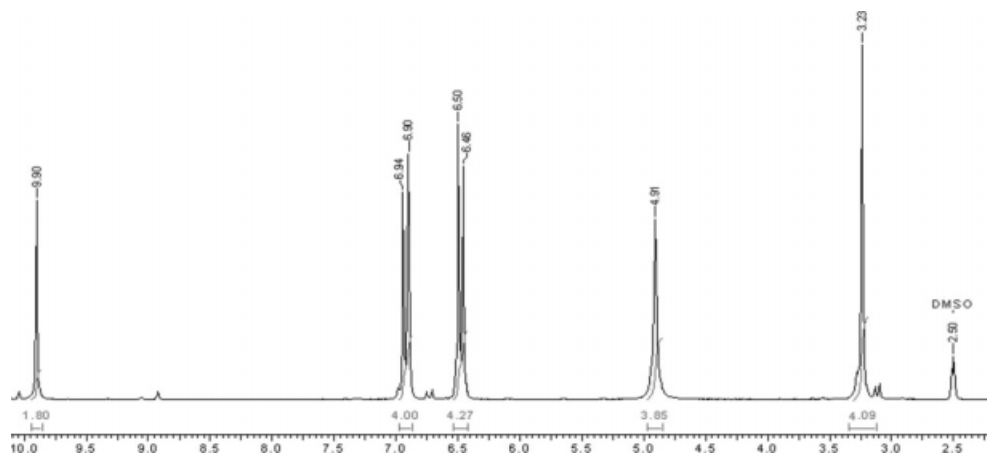

Figure 2 ^{1}H-NMR spectrum of BABH in DMSO-d_6.
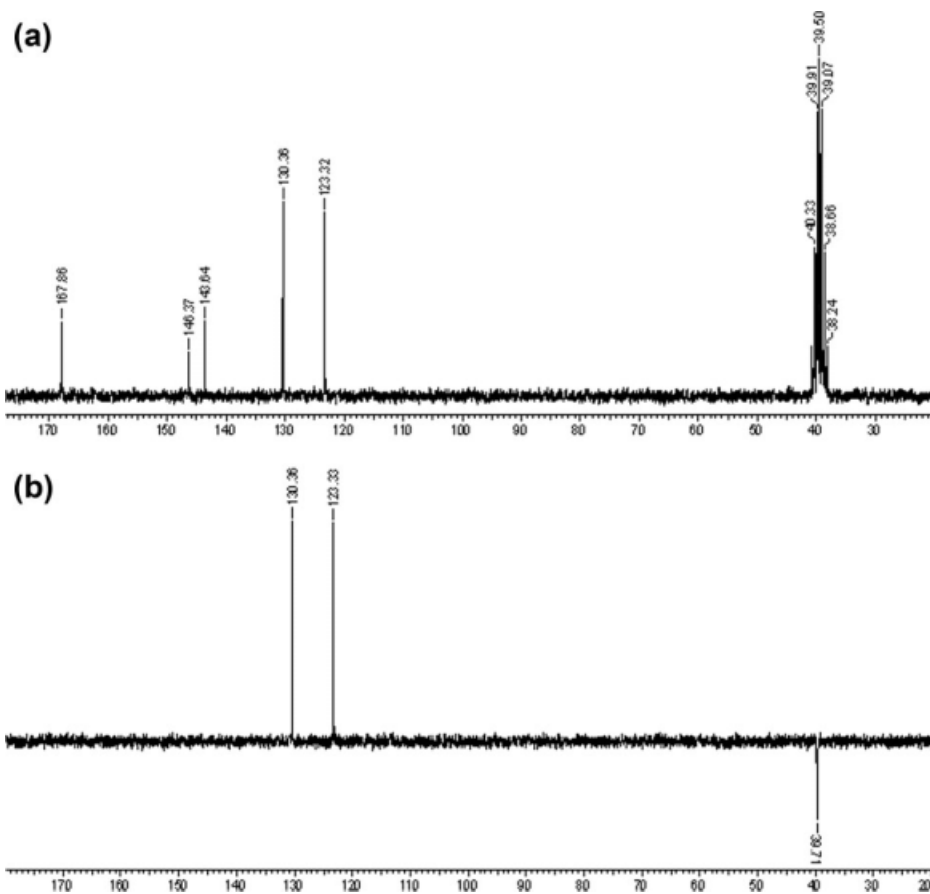
Figure 3   (a) ^{13}C-NMR spectrum of BNBH in DMSO-d$_6$. (b) ^{13}C-NMR (DEPT) spectrum of BNBH in DMSO-d$_6$.
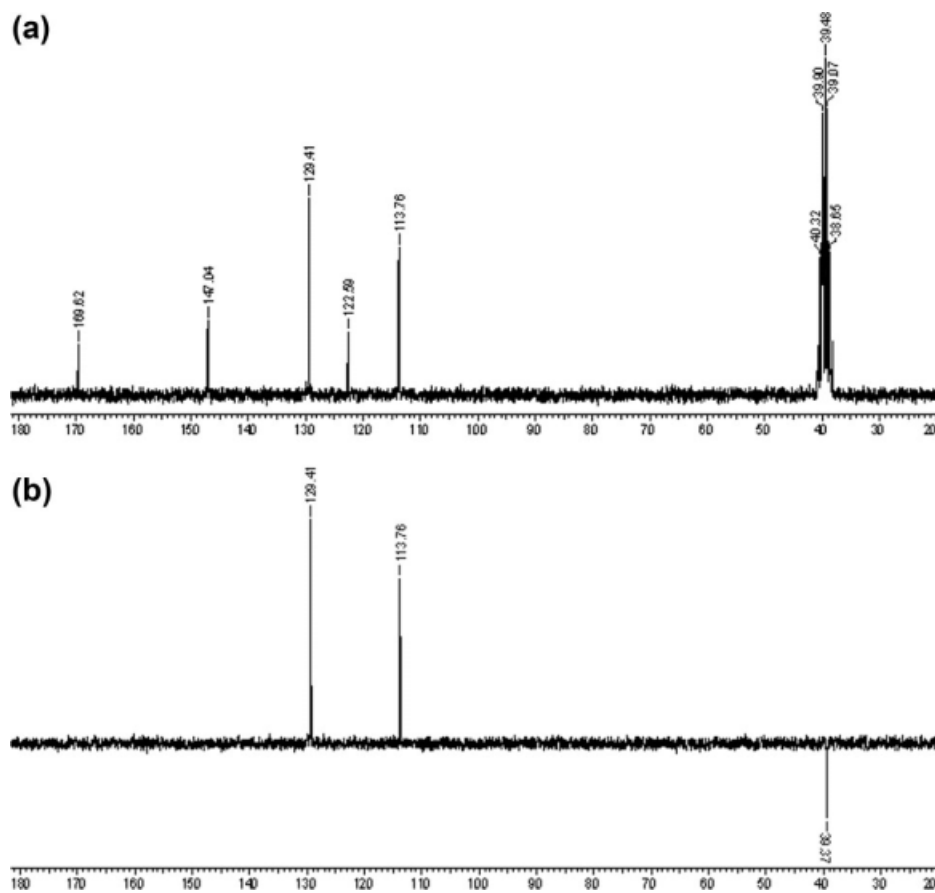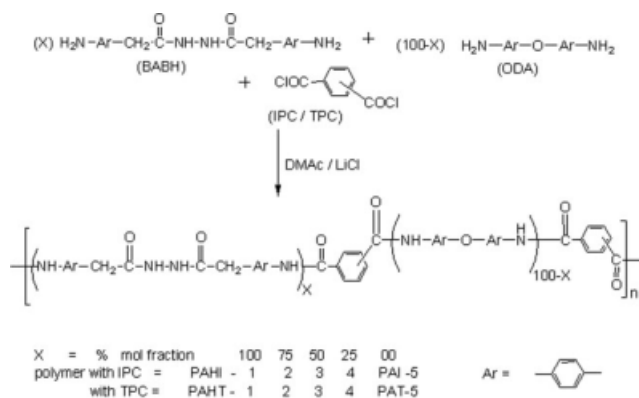

Figure 4   (a) ^{13}C-NMR spectrum of BABH in DMSO-d$_6$. (b) ^{13}C-NMR (DEPT) spectrum of BABH in DMSO-d$_6$.

Scheme 2 Synthesis of poly(amide-hydrazide)s and copoly(amide-hydrazide)s.

1652 cm^{-1}) is seen. The intensity of amide-II absorption band at 1598 cm^{-1} increased along the series with composition of copolymer; as the mol % of ODA in the polymer increased; from PAHI-1 to PAI-5. The absorption at 1270 and 1230 cm^{-1} in IR spectra of polymers PAHI-2 to PAI-5 is due to the ether linkage and the intensity of these absorption bands in the given series increased from PAHI-2 to PAI-5. This is obviously due to the increase in the mol % of ODA from PAHI-2 to PAI-5. Similar trend was observed in PAHT-2 to PAT-5 polymer series. Further these absorption bands (1270–1230 cm^{-1} due to ether linkage) are absent in the IR spectra of poly-(amide-hydrazide)s PAHI-1 and PAHT-1.

All polymers were soluble in conc. sulphuric acid whereas some copolymers dissolved in polar aprotic solvents namely NMP, DMAc and DMSO. It was observed that copolymer derived from IPC (PAHI-4) readily dissolved in hot DMSO and DMAc whereas corresponding TPC-based polymer (PAHT-4) was insoluble in the same solvents even under hot conditions. Similarly, polyamide polymers PAI-5 and PAT-5 exhibited better solubility in polar aprotic solvents than poly(amide-hydrazide) polymers. Among PAI-5 and PAT-5, the former had better solubility. PAI-5 dissolved in hot m-Cresol.

The degree of crystallinity in polymers was calculated by Nara and Komiya method.[25,26] A smooth curve was plotted which connected the baseline of the peaks in such a way that area above the curve represents the crystalline phase and area below the curve represents the amorphous phase. The total diffraction curve and the smooth curve were integrated separately to give total area under the curve and the area of amorphous phase. Area of crystalline phase was calculated by subtraction of area of amorphous phase from total diffraction area.

The degree of crystallinity (X_c) is calculated using the following equation,

$$X_c = \frac{A_c}{(A_c + A_a)} \times 100$$

where A_c is area of crystallized phase and Aa is area of amorphous phase in X-ray diffractogram.

X-ray diffractograms (Figs. 7 and 8) of poly(amide-hydrazide)s indicated higher crystallinity for the PAHI-1 and PAHT-1 than the other copolymers studied here. Thus PAHI-1 and PAHT-1 had degree of crystallinity, 24.67 and 24.28%, respectively; whereas copolymers had degree of crystallinity in

TABLE I
Synthesis of Poly(amide-hydrazide)s^a from BABH^b

Serial no.	Polymer code	Diamine mol (%)		Diacid chloride	Yield (%)	Inherent viscosity^c η_{inh} (dL/g)
		BABH	ODA			
1.	PAHI-1^d	100	00	IPC	98.6	0.28 (0.13)^e
2.	PAHI-2	75	25	IPC	93.6	0.79
3.	PAHI-3	50	50	IPC	98.2	0.93
4.	PAHI-4	25	75	IPC	97.2	0.67
5.	PAI-5^f	00	100	IPC	99.3	0.81
6.	PAHT-1^d	100	00	TPC	85.8	0.18 (0.11)^e
7.	PAHT-2	75	25	TPC	90.0	0.76
8.	PAHT-3	50	50	TPC	91.3	0.66
9.	PAHT-4	25	75	TPC	99.3	0.66
10.	PAT-5^f	00	100	TPC	98.5	0.44

^{a} Polymerization was carried out with 1 mmol of BABH and/or ODA and 1 mmol of IPC/TPC.
^{b} BABH, bis-(4-aminobenzyl) hydrazide.
^{c} Measured at concentration of 0.5 g/dL in (NMP containing 4% LiCl) at 30°C ± 0.1°C.
^{d} Precipitation of polymer observed during the early stage of polymerization.
^{e} η_{inh} for polymers prepared in DMAc.
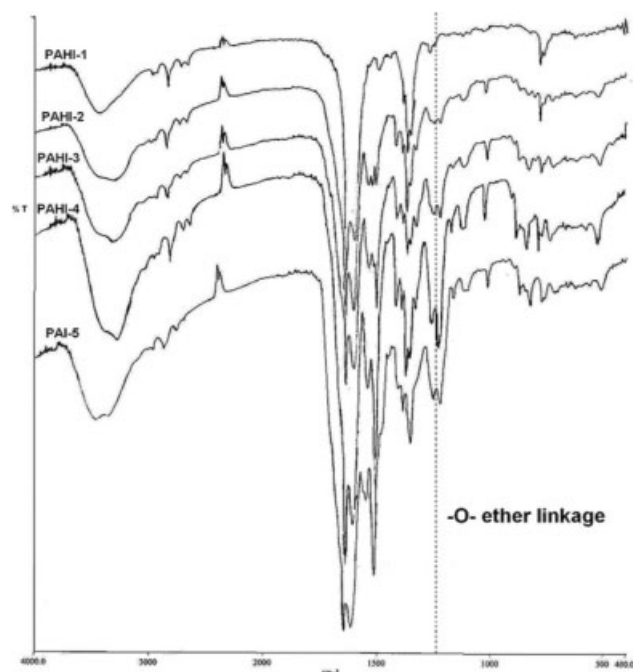^{f} Polyamide polymers.

Figure 5 IR spectra of polymers PAHI-1 to PAI-5.

the range 16.22– 21.77%. It was observed that copoly(amide-hydrazide)s showed decrease in crystallinity with incorporation of bis-(4-aminophenyl) ether. This could be explained, as the incorporation of bis-(4-aminophenyl) ether in copolymers increased; there was decrease in hydrazide-linkages in the copolymers, increase in the randomness due to copolymerization; thereby the degree of the hydrogen bonding in resulting copolymer decreased. The polyamides PAI-5 and PAT-5 had degree of crystallinity 24.83 and 29.64% respectively, agreeing with
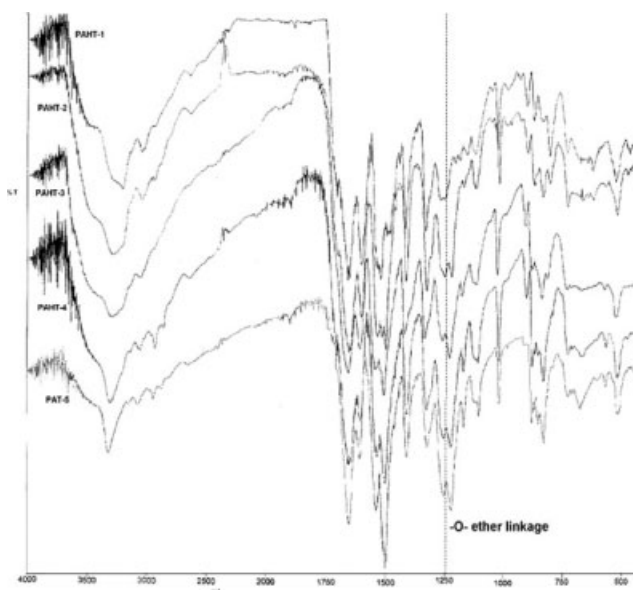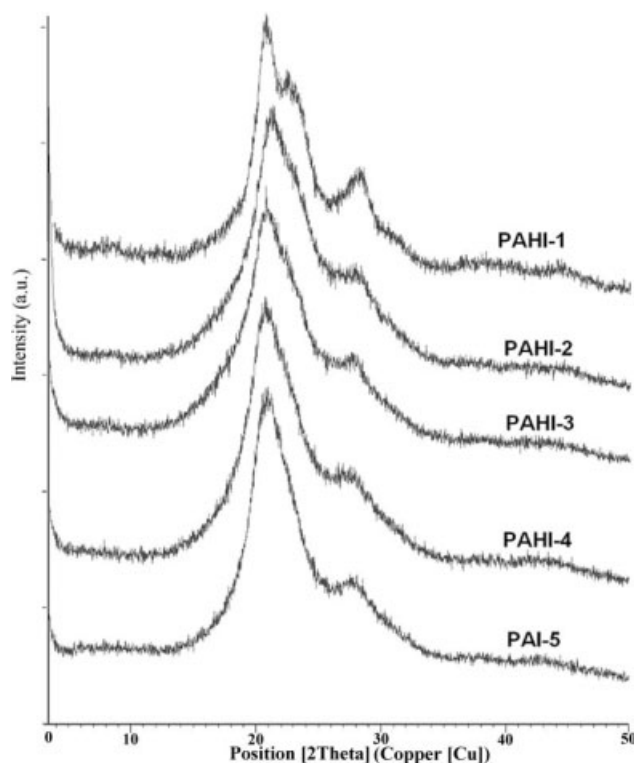

Figure 7 X-ray diffractograms of polymers PAHI-1 to PAI-5.

the concept that TPC- based (1,4-linked) polyamides have more crystallinity than that of IPC (1,3-meta catenated) derived polyamides. The average crystal
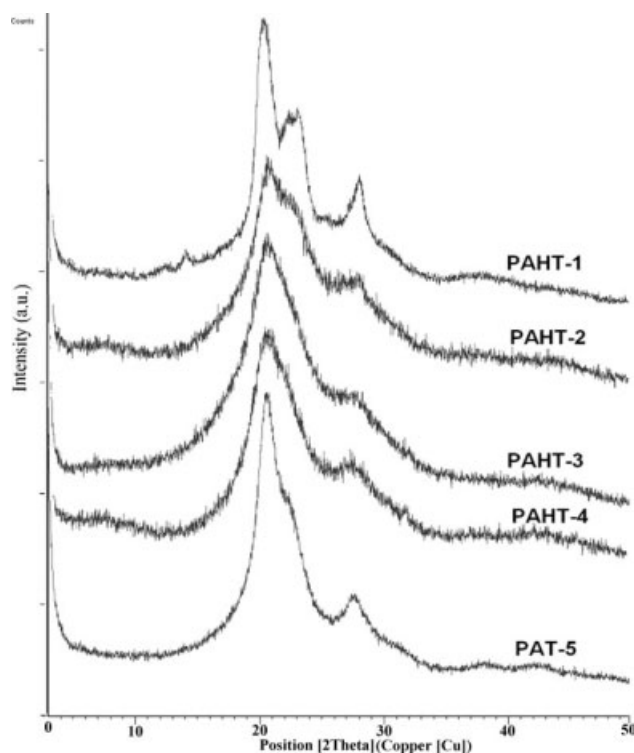

Figure 6 IR spectra of polymers PAHT-1 to PAT-5.

Figure 8 X-ray diffractograms of polymers PAHT-1 to PAT-5.

TABLE II
Solubility Data of Polymers in Different Solvents

Solvent	Polymer									
	PAHI 1	PAHI 2	PAHI 3	PAHI 4	PAI 5	PAHT 1	PAHT 2	PAHT 3	PAHT 4	PAT 5
NMP[a]	+ −	+ −	+	+ −	+	+ −	+ −	+	+ −	+
DMSO[a]	−	+ −	+ −	+	+	−	+ −	+ −	+ −	+ −
DMAC[a]	+ −	+ −	+	+	+	+ −	+	+	+ −	+
DMF[a]	−	+ −	+ −	−	−	−	−	+ −	−	−
m-Cresol	−	−	+ −	+ −	+	−	−	−	+ −	+ −
Conc. H_2SO_4	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +

Soluble = + +, soluble on heating = +, partly soluble = + −, insoluble = −.
[a] [Most of the poly(amide-hydrazide)s are soluble in polar aprotic solvent in the presence of LiCl].

sizes for polymers were determined by the Scherrer equation. The crystal size for PAHI-1 and PAHT-1 were 16.9 and 18.9 Å respectively. The copoly (amide-hydrazide)s showed the crystal sizes in the range 14.4–16.9 Å, whereas for the crystal sizes for polyamides (PAI-5 and PAT-5) were 18.3 and 22.5 Å, respectively.

XRD data could be correlated to solubility behavior of these polymers. Poly(amide-hydrazide)s PAHI-1 and PAHT-1 were neither soluble in common organic solvents nor in polar aprotic solvents; where as the copolymers had moderate solubility in many solvents (when LiCl was added to the solvent). The polymers based on terephthaloyl chloride possessed limited solubility, as incorporation of 1,4-linkages generally leads to higher crystallinity due to efficient packing. The 1,3-catenation in isophthaloyl chloride based polymers, favored the improved solubility (Table II). The 1,4-catenated rigid macromolecules (PAHI-1, PAHT-1) were insoluble where as copolymers obtained from ODA, IPC, and BABH dissolved in some aprotic polar solvents containing LiCl. The enhanced solubility of such polymers can be assigned to combined effect of (i) 1, 3-catenation, (ii) copolymerization leading to random structure and (iii) decreased hydrogen bonding as bis-(4-aminophenyl) ether mol % increased.[22,27,28] However, the presence of only methylene groups in main chain of poly(amide-hydrazide)s and copoly(amide-hydrazide)s improved the solubility marginally as compared to the solubility improved in corresponding polyamides when both phenylated moiety and methylene linkages[27] were introduced in the main polymer chain.

Thermal behavior of poly(amide-hydrazide)s, copoly(amide-hydrazide)s was studied by thermogravimetry and the data is presented in Table III. All these poly(amide-hydrazide) and copoly(amide-hydrazide) polymers showed similar two step pattern of decomposition (Fig. 9). In the first step initial weight loss for these poly(amide-hydrazide) and copoly(amide-hydrazide) polymers began around 160°C, and continued up-to 250–280 °C due to cyclo-dehydration of hydrazide unit, leading to the *in situ* formation of poly(amide-oxadiazole)s.[9,22,29] The second step of decomposition is nothing but thermal behavior of the poly(amide-oxadiazole)s in TG analysis. The temperatures of maximum rate of decomposition for second step were in the range of 398–542°C and the char yields at 900°C were about 35–45%. T_{max} values can be correlated to the mol % of BABH in the polymer. As the mol % of BABH is decreased along the PAHI-1 to PAHI-4 and PAI-5; the T_{max} values increased from 398 to 533°C. This trend is reasonable since decreased moiety of BABH means increased moiety of ODA and ODA derived polyamide units are thermally more stable than BABH derived hydrazide-amide structures. Similar trend is observed for the T_{max} values of PAHT-3, PAHT-4 and PAT-5; wherein T_{max} increased from 509 to 542°C along the series with increase in ODA content.

Glass transition temperature values for polyhydrazides and copoly(amide-hydrazide)s; could not be determined. On providing heat energy in DSC experiment, polyhydrazides and poly(amide-hydrazide)s start loosing molecule of water at about 160–175°C, due to dehydration of hydrazide units in

TABLE III
Thermal Properties[a] of Poly(amide-hydrazide)s

Polymer code	[b]T_i (°C)	[c]T_{max} (°C)	Residual mass (%) at 900°C
PAHI-1	165	398	35
PAHI-2	160	399	35
PAHI-3	169	401	39
PAHI-4	173	524	36
PAI-5	375	533	45
PAHT-3	166	509	40
PAHT-4	172	518	36
PAT-5	380	542	40

[a] Thermogravimetric analyzes were conducted at a heating rate of 10°C/min under nitrogen.
[b] Temperature at which weight loss initiated.
[c] Temperature at which maximum rate of weight loss was observed; determined from DTG curve.
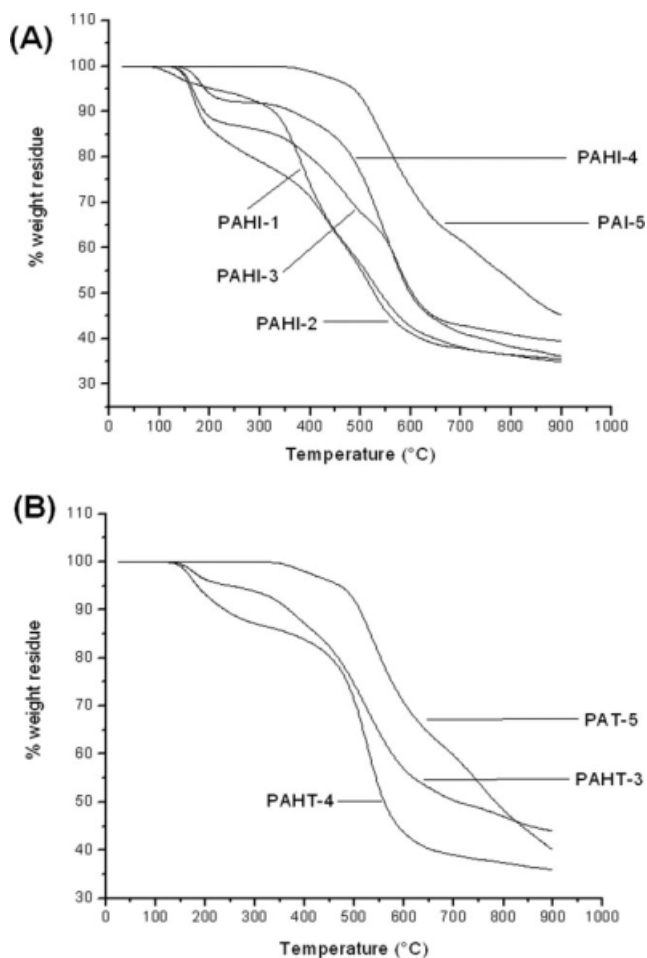
Figure 9 TG curves of poly(amide-hydrazide)s, polyamides and copoly(amide-hydrazide)s.

these polymers. Thus before actual T_g was detected in polyhydrazides and copoly(amide-hydrazide)s; conversion of these polymers to poly(amide-1,3,4-oxadiazole) polymers occurred *in situ* with simultaneous loss of water. Cyclo-dehydration of polyhydrazides to poly(1,3,4-oxadiazole)s is popular method to prepare oxadiazoles.[9,29–31]

Polyamides, PAI-5 and PAT-5; had initial decomposition temperature (IDT; T_i) of 375–380°C; as these polymers do-not contain hydrazide groups and hence there is no cyclodehydration around 160°C. DSC analysis of PAI-5 and PAT-5 showed the glass transition temperatures of these polyamides at 266 and 280°C respectively. Thus polyamide based on terephthaloyl moiety (1,4-catenation) had higher T_g than the corresponding polyamide derived from isophthaloyl units (1,3-catenation).

CONCLUSIONS

Preformed hydrazide and methylene linkage containing novel aromatic diamine, viz., bis-(4-amino-benzyl) hydrazide (BABH), was successfully synthesized. Two series of new poly(amide-hydrazide)s and copoly(amide-hydrazide)s and the related polyamides were synthesized from BABH and/or ODA with IPC/TPC by low temperature solution polymerization method. Polymers had inherent viscosities in the range of 0.18–0.93 dL/g indicating formation of medium to high molecular weight polymers. XRD analysis of polymers showed partially crystalline nature possibly due to high level of hydrogen bonding in hydrazide units incorporated. The polymers having higher mol % of BABH and terephthaloyl units were less soluble than its corresponding polymers containing bis-(4-aminophenyl) ether and isophthaloyl moieties. TGA showed that poly(amide-hydrazide)s initially undergo cyclodehydration leading to the *in situ* formation of poly(amide-oxadiazole)s.

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