Synthesis of Some New Polyhydrazides by Direct Polycondensation in Ionic Liquid and their Metallization Through Transition Metal Complexation

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ABSTRACT: A series of new polyhydrazides has been synthesized via direct polycondensation of benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid **(BBDA)** with dihydrazides in ionic liquids (ILs) as a new class of solvents, which have interesting properties, such as nonvolatility, high ionic concentration, good thermal stability, and nonflammability. Direct polycondensation is successfully proceeded in ILs and triphenyl phosphite (condensing agent) without any additional extra components, such as LiCl and pyridine, using in similar reactions in ordinary (IL can act as both solvent and catalyst). The polyhydrazides have been obtained in quantitative yield and their intrinsic viscosities ranged from 0.21 to 0.47 dL g^{-1}. The polyhydrazides were characterized by means of IR, ^{1}H-NMR, inherent viscosity (η_{inh}), solubility test, TGA, DSC, CHN analysis, and ultraviolet λ_{max}.

They could be thermally converted into the corresponding poly(1,3,4-oxadiazole)s approximately in the region of 210–330°C, as evidenced by the TGA thermograms.

The polymers were readily soluble in several organic polar solvents, such as DMAc, N,N-dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone and could be cast into flexible films. The polymer were metallized via complexation with various transition metal. The complexes were investigated by X-ray diffraction, IR, and UV spectrophotometry. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1935–1944, 2009

Key words: polyhydrazides; ionic liquid (IL); high-performance polymers; polycondensation; metal–polymer complexes

INTRODUCTION

A polyhydrazide is a condensation polymer with the hydrazide group in the main chain. In recent years, aromatic polyhydrazides have attracted considerable attention as one of the most important classes of special polymers. They have been extensively studied because they enhance dyeability of synthetic fibers; improve elasticity over other polymer types.[1] They provide a synthetic base for the chelate polymers,[2] because the hydrazide group —(—CO—NH—NH—CO)— can react with metal ions to form complexes. In the past few years, metallized plastics have received considerable academic and industrial attention for their desirable characteristics. They possess a good combination of properties of both the polymer and the metal. They can be widely applied in the electronics industry, such as for integrated circuits, packaging, printed circuits, and sensor applications.[3]

Polyhydrazide also are important intermediates in the preparation of poly(1,3,4-oxadiazole)s, through their cyclodehydration either by heating at elevated temperature or by use of dehydrating agents.[4–6] Poly(1,3,4-oxadiazole)s and copoly(1,3,4-oxadiazole)s are potentially interesting as materials for high-temperature applications owing to their high thermal stability and tough mechanical properties and have been investigated as high temperature and flame-resistant fibers,[7,8] thermally stable films[9] and in the fields of polymer light-emitting diodes and polymer electronics.[10–18]

Because of lots of benefits, such as thermal and chemical stability, negligible vapor pressure, capability to dissolve different compounds, ionic liquids are receiving considerable attention as novel, environment-friendly solvents[12,13] to replace traditional organic solvents (that evaporate into the atmosphere with detrimental effects on the enviroment and human health) in a number of industrial processes. They also become used as activating reaction medium for a plenty of polymerization reactions.[19,14–26] Recently, various polycondensation processes were successfully accomplished in ionic medium as well.[27–29] The reaction of different diamines with diacid chlorides in ionic solvents resulted in the formation of high-molecular weight polyamides.[30] ILs also are attracting more attention because of their significant role in controlling the reaction as catalyst. It is important that ILs are the chemicals that can be

applied as solvent and catalyst in green chemistry processes.[29]

Vygodskii and coworkers[31] synthesized different polymers by direct polycondensation effectively in ILs under the influence of triphenyl phosphite as activating agent, and revealed that there is no need to use any extra components, for example, LiCl and pyridine.

They also used hydrazine's salt to synthesis poly-oxidazole from diacid in "one-pot" direct polycondensation technique, using IL/TPP mixtures.[30,32]

Metallized plastics have recently received great academic and industrial interest for their useful applications in electronic devices, such as for integrated circuits, packaging, printed circuits, and sensor applications. They represent a class of materials that possess a good combination of properties of both the polymer and the metal. There are several techniques for plastic metallization, like, metal blending process; metal deposition process; and also metal complexation process in which the polymer is chelated with a transition metal salt.[3,33–36]

Polymer–metal complexes have attracted significant attention. They are often prepared by reacting a solution of the polymer with transition metal salts, and exhibit good solubility and easy processability into films and fibers. However, these metal complex films exhibited poor electrical resistivities after treatment with reducing agents.

Because of mentioned particular characteristics, polyhydrazides became the object of our investigation. Herein, we demonstrate that IL method is an efficient and enviroment-freindly green route for the synthesize of polyhydrazides. The usage of dicarboxylic acids in direct polycondensation instead of their significantly more toxic analogs, such as acid chlorides, is one of the main and important advantage of polymer synthesis in ionic liquids in comparison with conventional methods.[37] We also metallized the polymers via their complexation with various transition metal salts.

EXPERIMENTAL

Solvents and chemical materials were either prepared in our laboratory or purchased from Fluka (Switzerland) and Merck (Germany) chemical companies. Melting points were determined in open capillaries with a Buchi 535 melting point apparatus. Proton NMR spectra were recorded on a 250 MHz Bruker Avance DPX-250 spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical schifts are given in the δ scale in parts per million (ppm) singlet(s), doublet (d), triplet (t), multiplet (m), and doublet of doublet (dd) recorded. UV–vis absorption spectra were obtained in DMSO (ca. $\times 10^{-5}$) on a JASCO-570 UV–visible spectrometer using a 10-cm quartz cuvette. IR spectra were obtained as KBr pellets with a 680 plus-JASCO. The X-ray diffraction patterns are recorded by using a Philips Xpert MPD diffractometer equipped with a Cu Kα anode ($\lambda = 1.51418$ Å).

The inherent viscosities ($\eta_{inh} = \ln \eta_{rel}/C$, where η_{rel} is the relative viscosity and C is the concentration) of the polymers were determined in 0.5 g/dL solutions of DMF at 30°C with a Cannon-Fenske viscometer. TGA and DSC analysis were performed on a stanton STA-625 or TGA-1500 with heating rate of 10°C/min under N_2 atmosphere. The Heraeus CHN analyzer (Germany) was used for elemental analysis.

Materials

The preparation of Benzofuro [2,3-b] benzofurane-2,9-dicarboxylic acid(DA$_1$) has been reported by Banihashemi and Abdolmaleki[37] and Banihashemi and Pourabbas.[38] The dihydrazides were prepared by the following method: diethyl(or dimethyl)ester (1 mol) was refluxed with 3–4 mol of 100% hydrazine hydrate in 500–1000 mL of dry ethanol (or dry methanol) for several hours. The crude dihydrazide that separated out was crystallized from water or alcohol. They have characteristic IR absorption (KBr) at 3250 cm^{-1} (NH stretching) and 1620 cm^{-1} (C=O). All ILs were prepared and purified in accordance with the procedure described previously by Vygodskii et al.[27]
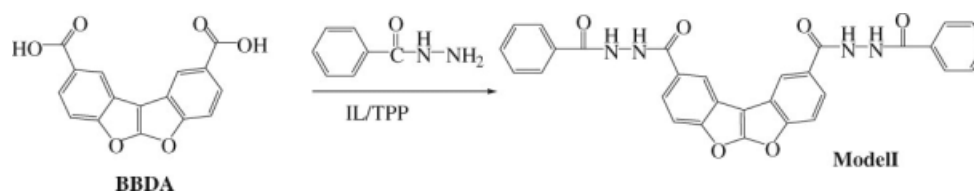
Model compound

From benzhydrazide and benzofuro[2,3-b] benzofuran-2,9-dicarboxylic (BBDA) acid

Model compound I were synthesized from benzhydrazide and benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid by direct polycondensation in IL. (0.001 mol) of benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid (BBDA) (0.001 mol) of benzhydrazide and (1-Me-3-Pr im)Br (3.20 g) were mixed at room temperature for 10 min. (0.52 mL, 0.00225 mol) of TPP was added. The mixture was heated under inert gas atmosphere up to 120°C for 2 h. The obtained dihydrazide was isolated by precipitation in excess methanol. Dihydrazide was thoroughly washed with methanol and dried in vacuo at 70°C; yield, 98% (overall) (Scheme 1); IR (KBr): $\nu = 3250$ (NH), 1650 (C=O) cm^{-1}; UV (DMF) λ_{max}: 297 nm; ^{1}H-NMR(250 MHz, DMSO-d_6) $\delta = 7.24$–7.52 (m, 8H, Ar), 7.94 (t, 6H, Ar), 8.44 (s, 2H, Ar), 10.55 (d, 4H, NH) (Fig. 1).

Preparation of polyhydrazides

All the polyhydrazides were synthesized by direct polycondensation in IL. 0.306 g, 0.001 mol of diacid (BBDA) (0.001 mol) of dihydrazides and 3.20 g (1-

Scheme 1 Preparation of model compound I from diacid (**BBDA**).

Me-3-Pr im)Br were mixed at room temperature for 10 min, then 0.52 mL, 0.00225 mol of TPP was added. The mixture was heated under inert atmosphere up to 140°C for 2–3 h. The obtained polyhydrazides were isolated by the precipitation in excess methanol. Polyhydrazides were thoroughly washed with methanol and dried in vacuo at 70°C (Scheme 2).

Polyhydrazide from BBDA and terephtalic dihydrazide (PH₁): Yield 97%. IR (KBr): $\nu = 3260$ (NH), 1660 (C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 7.28$ (t, 2H, Ar), 8.00 (t, 6H, Ar), 8.54 (t, 2H, Ar), 10.73 (s, 4H, NH).

Polyhydrazide from BBDA and isophtalic dihydrazide (PH2): Yield 97%. IR (KBr): $\nu = 3280$ (NH), 1660(C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 7.28$ (s, 2H, Ar), 7.43 (s, 2H, Ar), 8.00 (t, 4H, Ar), 8.50 (t, 2H, Ar), 10.72 (s, 4H, NH).

Polyhydrazide from BBDA and phthalic dihydrazide (PH3): Yield 90%. IR (KBr): $\nu = 3300$ (NH), 1660 (C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6)

$\delta = 7.31$ (s, 4H, Ar), 7.95 (s, 4H, Ar), 8.33 (t, 2H, Ar), 10.62 (s, 4H, NH).

Polyhydrazide from BBDA and biphenyl 4,4'-dicarboxilic dihydrazide (PH₄): Yield 98%. IR (KBr): $\nu = 3240$ (NH), 1660 (C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 7.26$ (t, 2H, Ar), 8.01 (t, 10H, Ar), 8.49 (t, 2H, Ar), 11.03 (s, 4H, NH).

Polyhydrazide from BBDA and oxalyl dihydrazide (PH5): Yield 95%. IR (KBr): $\nu = 3260$ (NH), 1650 (C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 7.32$ (d, 2H, Ar), 7.93 (s, 2H, Ar), 8.39 (t, 2H, Ar), 10.65 (d, 2H, NH), 10.77 (d, 2H, NH).

Polyhydrazide from BBDA and phosphonic hydrazide (PH6): Yield 96%. IR (KBr): $\nu = 3200$ (NH), 1640 (C=O), 1270, 830 (H-P=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 6.6$ (d, 1H, P), 7.24–8.78 (m, 8H, Ar, NH), 10.66 (d, 2H, NH).

Polyhydrazide from BBDA and malonic dihydrazide (PH₇): Yield 95% IR (KBr): $\nu = 3280$ (NH), 1650 (C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 3.1$
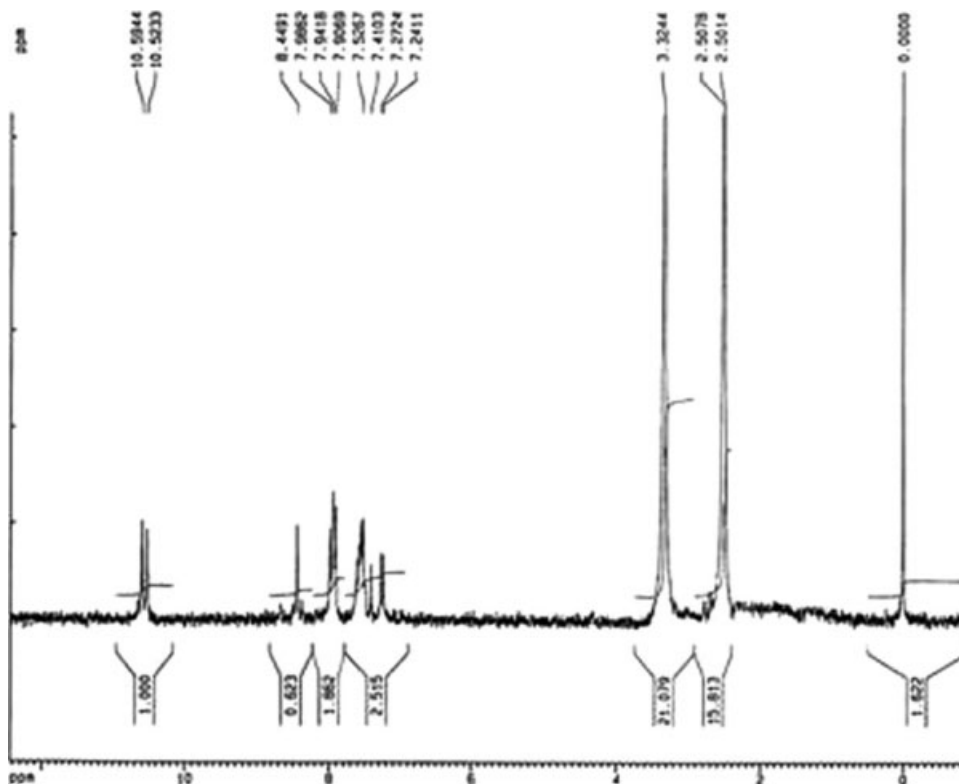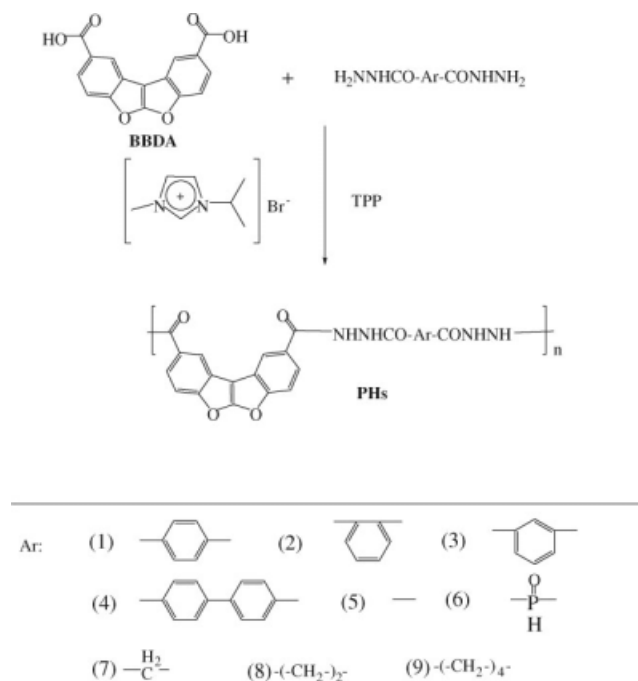

Figure 1 ^{1}H-NMR of model compound I.

Scheme 2 Polymer synthesis of polyhydrazides.

(s, 2H, CH_2), 7.23 (m, 2H, Ar), 7.90 (t, 2H, Ar), 8.47 (t, 2H, Ar), 10.18 (d, 2H, NH), 10.63 (d, 2H, NH).

Polyhydrazide from BBDA and succinic dihydrazide (PH8): Yield 98%. IR (KBr): $\nu = 3240$ (NH), 1650 (C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 2.69$ (t, 4H, CH_2), 7.25 (m, 2H, Ar), 7.90 (t, 2H, Ar), 8.38 (t, 2H, Ar), 9.98 (d, 2H, NH), 10.43 (d, 2H, NH).

Polyhydrazide from BBDA and adipic dihydrazide (PH9): Yield 97%. IR (KBr): $\nu = 3230$ (NH), 1670 (C=O) cm^{-1}; ^{1}H-NMR (250 MHz, DMSO-d_6) $\delta = 1.84$ (m, 4H, CH_2), 2.22 (t, 4H, CH_2), 7.28 (m, 2H, Ar), 7.88 (t, 2H, Ar), 8.40 (t, 2H, Ar), 9.97 (d, 2H, NH), 10.36 (d, 2H, NH).

Polyhydrazide–metal complexation

Polyhydrazide–metal complex has been prepared by dissolving predetermined molar ratios of polymer and metal salt separately in DMAc. After complete dissolution, the metal salt solution was mixed with the polymer solution and stirred well at room temperature overnight. The resulting highly viscous complex solution was cast on a dry clean Pyrex glass plate to a uniform thickness. The plate was introduced into an air circulating electrically heated oven at 60°C. Afterward, the plate was immersed into deionized water at 25°C to remove the residual solvent and unreacted metal salt from the obtained film. The later would normally separate from the glass plate surface after about 5 min in a water bath, after which about 24 h would usually be allowed for complete solvent and unreacted metal salt extraction. Finally, the film was dried at 100°C to constant

TABLE I
PH$_1$ Synthesized in Various Bromide ILs (140°C, 2.5 h, 2.25 mol of TPP/1 mol of Monomer, c = 0.4 mol/L)

| No	R_1	R_2	η_{inh} (dL/g)
1	CH_3	C_2H_5	0.41
2	CH_3	C_3H_7	0.42
3	CH_3	C_4H_9	0.39
4	CH_3	i-C_3H_7	0.44
5	C_3H_7	C_3H_7	0.28
6	C_4H_9	C_4H_9	0.37
7[a]	NMP		0.40

[a] In the presence of 4% wt. of LiCl.

weight. Metal salts used were silver nitrate, cupric chloride, nickel chloride, and cobaltous chloride. Their percent molar ratios were selected between 30 and 80%. All the films prepared by this way the thickness of the films was ≈ 0.2 mm, and appeared transparent and highly colored, and showed good mechanical strength with respect to handling.

RESULT AND DISCUSSION

A set of ILs bearing different alkyl groups and anions were synthesized (Tables I and II), and their applications as solvents and also catalysts were examined for the direct polycondensation of a dicarboxylic acid and dihydrazides ILs containing *n*-propyl or isopropyl alkyl chains seemed to be the best solvents for polymer synthesis (Table I). As far as anions are concerned, the best results were achieved in IL with Br$^-$ (Table II). After optimizing all the conditions reaction of dicarboxylic acids and dihydrazides in IL, namely, 1-Me-3-Pr-imidazolium bromide in the presence of TPP as an activating agent developed a simple technique and also good results. The best results were reached at 140°C. It is noteworthy that no polymer precipitation is observed during the polymer formation in this IL. A

TABLE II
PH$_1$ Synthesized in Various 1-methyl-3-Propylimidazolium Salts (140°C, 2.5 h, 2.25 mol of TPP/1 mol of monomer, c = 0.4 mol/L)

No	Y^-	η_{inh} (dL/g)
1	Br$^-$	0.44
2	Cl$^-$	0.39
3	BF$_4^-$	0.36
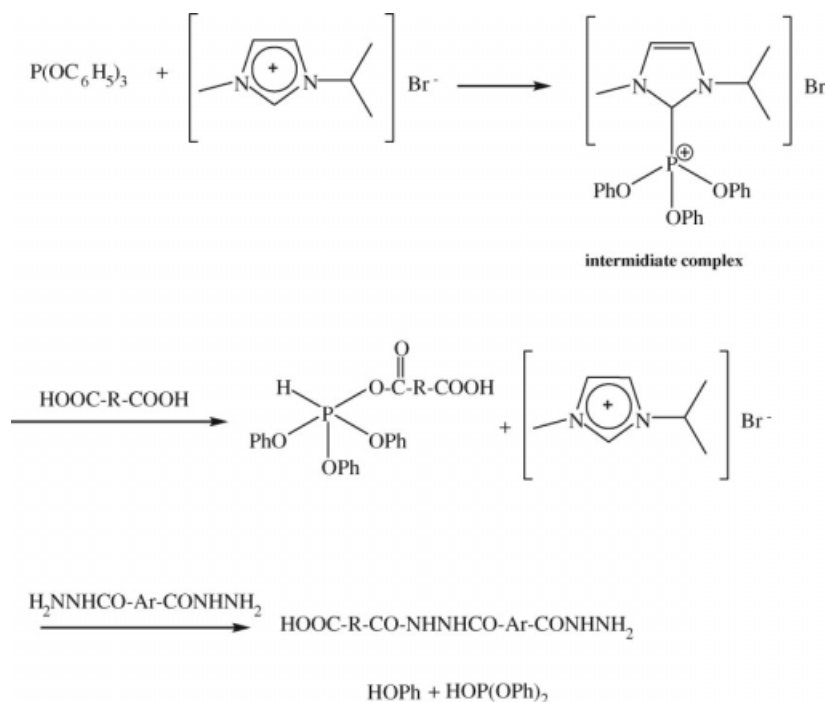
Scheme 3 Mechanism of activation of diacid by IL and TPP system.

reaction mechanism was proposed by Mallakpour and Kowsari (Scheme 3); initially an intermediate IL/triphenyl phosphate complex is formed. A subsequent attack of diacid by such a complex gives an active acyloxyphosphonium salt, and the interaction of this final salt and hydrazide (NH) group results in a hydrazide.[39]

Comparison of this new method of polymerization, direct polycondensation in ILs (method A) with classical method, direct polycondensation reaction in a NMP/TPP/Py/LiCl at the reflux temperature (method B) clearly shows the efficiency of method A.

The uses of nonvolatile solvent and possibility of the recovery and reuse of an IL/catalyst system and the ability to dissolve monomers are some advantages of using IL systems in method A. In method B, direct polycondensation commonly occurs in the presence of volatile organic solvents, NMP and Py, which has a notable effect on the formation and solubility of the resulting polymers. Also method A has higher viscosity and yield in comparison to method B (Table I).

All of these polymers are new and prepared for the first time in our laboratory. All the polymers were produced in a quantitative yield (Table III). The structure of polyhydrazides were ascertained by IR and ^{1}H-NMR spectroscopy. The IR spectra showed characteristic absorption near 3250 cm^{-1} ascribed to the stretching of N—H linkage with relatively low frequency to formation of hydrogen bonds, 1650–1660 cm^{-1} peculiar to carbonyl (C=O) stretching frequency, the C—N stretching frequency

was absorbed at 1260 $\pm$ 20 cm^{-1} for all polyhydrazides and ring stretching around 1480 with intensity. In the ^{1}H-NMR spectra, the absorption signals of aromatic protons appeared in the region of δ = 7.7–8.5 ppm. The peak corresponding to NH resonance from the hydrazide group was observed around 10.0–11.0 ppm (Fig. 2). For obtaining ^{13}C-NMR, it is necessary to have high concentration of polymers in duterated solvent; so because of limited solubility of our polyhydrazides in DMSO-d_6, we were not able to have suitable concentration of polymers, so the resulting spectrums were not good, and we do not rely on ^{13}C-NMR data.

TABLE III
Polymer's Structure and Properties

Polymer code	Yield (%)	M.p. (°C)	η^a_{inh} (dLg^{-1})	UV (nm)^c
PH$_1$	97	>300	0.44	273
PH$_2$	98	>300	0.37	273
PH$_3$	93	>300	0.38	296
PH$_4$	98	>300	0.47	282
PH$_5$	95	>300	0.33	295
PH$_6$	96	>300	0.27	274, 296
PH$_7$	95	>300	0.26	293
PH$_8$	98	$\cong$284^b	0.24	297
PH$_9$	97	$\cong$278^b	0.21	297

^{a} Inherent viscosity measured at concentration of 0.5 g dL^{-1} in DMF at 30°C.
^{b} Decomposed at this temperature.
^{c} In DMF.

Figure 2 ¹H-NMR of PH_1 and PH_2.

TABLE IV
Polyhydrazides Solubility's

Solvent/polyhydrazide	PH_1	PH_2	PH_3	PH_4	PH_5	PH_6	PH_7	PH_8	PH_9
Concentrated H_2SO_4	++	++	++	++	++	++	++	++	++
TFA	++	++	++	++	++	++	++	++	++
NMP	−+	−+	++	+	−+	++	++	++	++
NMP/LiCl	++	++	++	++	++	++	++	++	++
DMAc	−+	−+	−+	+	−+	−+	++	++	++
DMAc/LiCl	++	++	++	+	++	++	++	++	++
DMSO	++	++	++	++	++	++	++	++	++
DMF	+	+	+	++	++	++	++	++	++

++ Soluble at room temperature; −+ partially soluble; + soluble on heating.

To get a good estimation about the relative molecular weights of polyhydraizdes, inherent viscosity's of polymers were measured in 0.5 g/dL concentration in DMF at 30°C. The η_{inh} of polymers were in the range of 0.21–0.47 dL g^{-1}, which showed relatively high molecular weight of polymers.[40] It is clear from Table III that the wholly aromatic polyhydrazides have higher inherent viscosity. Also the para-substituted polyhydrazide has higher inherent viscosity in comparison to meta- and ortho-substituted polyhydrazides.

All the polyhydrazides that were referred are white or light yellow powders and entirely soluble in polar aprotic solvents, such as NMP, DMAc, and

TABLE V
Elemental Analysis of Model Compound and polyhydrazides

Compounds	Calculated			Found		
	%C	%H	%N	%C	%H	%N
Model I	67.66	3.78	10.52	66.64	3.55	10.42
PH_1	63.43	3.10	12.33	61.28	2.91	11.12
PH_2	63.43	3.10	12.33	61.12	2.81	11.21
PH_3	63.43	3.10	12.33	61.23	2.98	12.15
PH_4	67.92	3.42	10.56	65.61	3.22	9.86
PH_5	57.14	2.66	14.81	55.13	2.36	13.10
PH_6	51.90	2.99	15.13	49.68	2.76	14.85
PH_7	58.16	3.08	14.28	56.43	2.92	13.98
PH_8	59.11	3.47	13.78	56.86	3.29	13.21
PH_9	60.82	4.17	12.89	58.72	3.96	12.63

Figure 3 Thermogravimetric curves of polyhydrazide PH_2 with a heating rate of 10°C/min in nitrogen.

TABLE VI
Thermal Properties of Polyhydrazides

Polymer	T_g (°C)[a]	Char yield (%)[b]
PH_1	194	47
PH_2	179	43
PH_3	188	46
PH_4	210	49
PH_5	175	40
PH_6	185	43
PH_7	172	37
PH_8	168	34
PH_9	165	35

[a] From the second heating traces of DSC measurements conducted with a heating rate of 10°C/min in N_2.
[b] Weight percentage of material left undecomposed after TGA analysis at maximum temperature 600°C in N_2.

DMF at room temperature (Table IV). For the less polar solvents, some of the polyhydrazides were only soluble or swollen in hot *m*-cresol. Concentrated sulfuric acid is a solvent for these polymers, but it causes some breakdown as demonstrated by viscometric measurements. They also showed a good resistance to common organic solvents, such as THF, chloroform, acetone, and ethanol.

These polyhydrazides and model compound were also characterized by elemental analysis. The data obtained from elemental analysis were found to be in good agreement with the expected values. These results are summarized in Table V.

Thermal properties

Thermal resistivities of polyhydrozides are detected by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All the hydrazide polymers displayed discernible glass transitions between 184 and 210°C in the DSC traces. Two-step
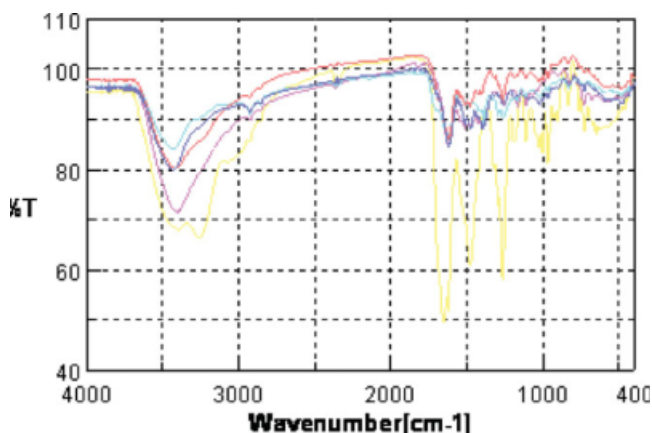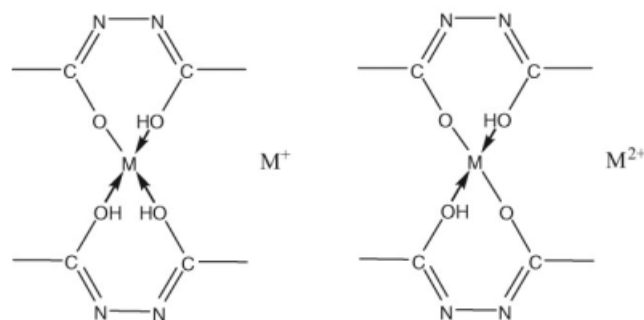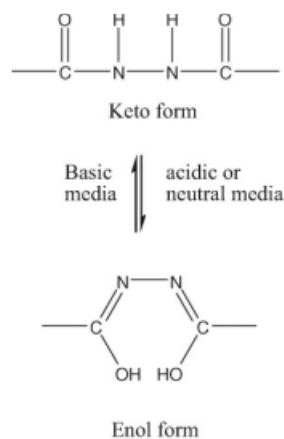

Figure 4 Fourier transform infrared spectroscopy of PH_4 and PH_4+ (Ni, Co, Cu, Ag). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scheme 4 Schematic hydrazide metal complexation.

weight loss is observed in most cases. First, a strong endothermic peak between 210 and 330°C that was attributed to loss of water during the conversion of the hydrazide group to the 1,3,4-oxadiazole ring (a relative weight loss between 6.6 and 9.2%).
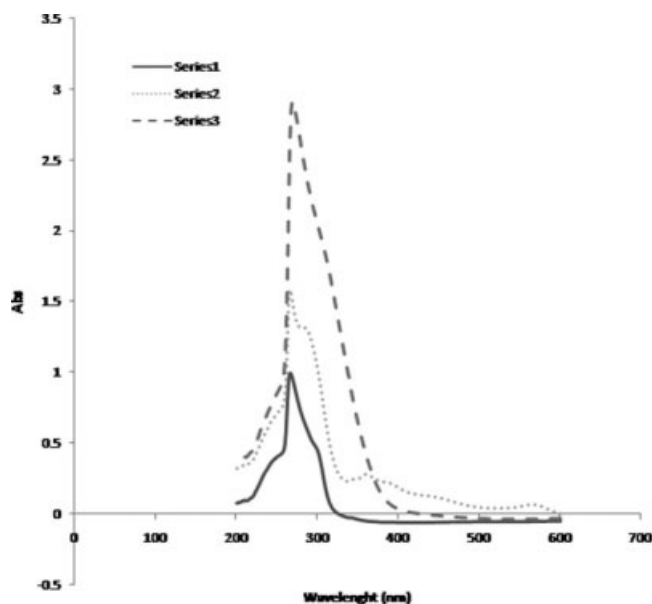

Figure 5 Uv spectrum of polymer PH_4 (——), PH_4+ Ag^+ (.....) and PH_4+ Cu^{2+} (----) complexes.

TABLE VII
Elemental Analysis of PH₄–Metal Complexes

Compounds	Found				Calculated			
	%C	%H	%N	%M	%C	%H	%N	%M
PH$_4$+ Ag(I)	56.41	2.72	8.38	—	56.53	2.69	8.79	16.92
PH$_4$+ Cu(II)	60.78	2.76	9.69	—	60.86	2.72	9.46	1073

The second break in the TGA curve occurred around 350 and 510°C and corresponded to decomposition of poly(1,3,4-oxadiazole)s, formed *in situ*. The char residue remaining at 600°C in nitrogen atmosphere is between 34 and 49% (Fig. 3). The thermal analysis data are summarized in Table VI.

Synthesis of polyhydrazide–metal complexes

Several polyhydrazide–metal complex films have readily been prepared by casting the stirred, mixed DMAc solutions of different molar ratios of several polymers with various metal salts at room temperature overnight.
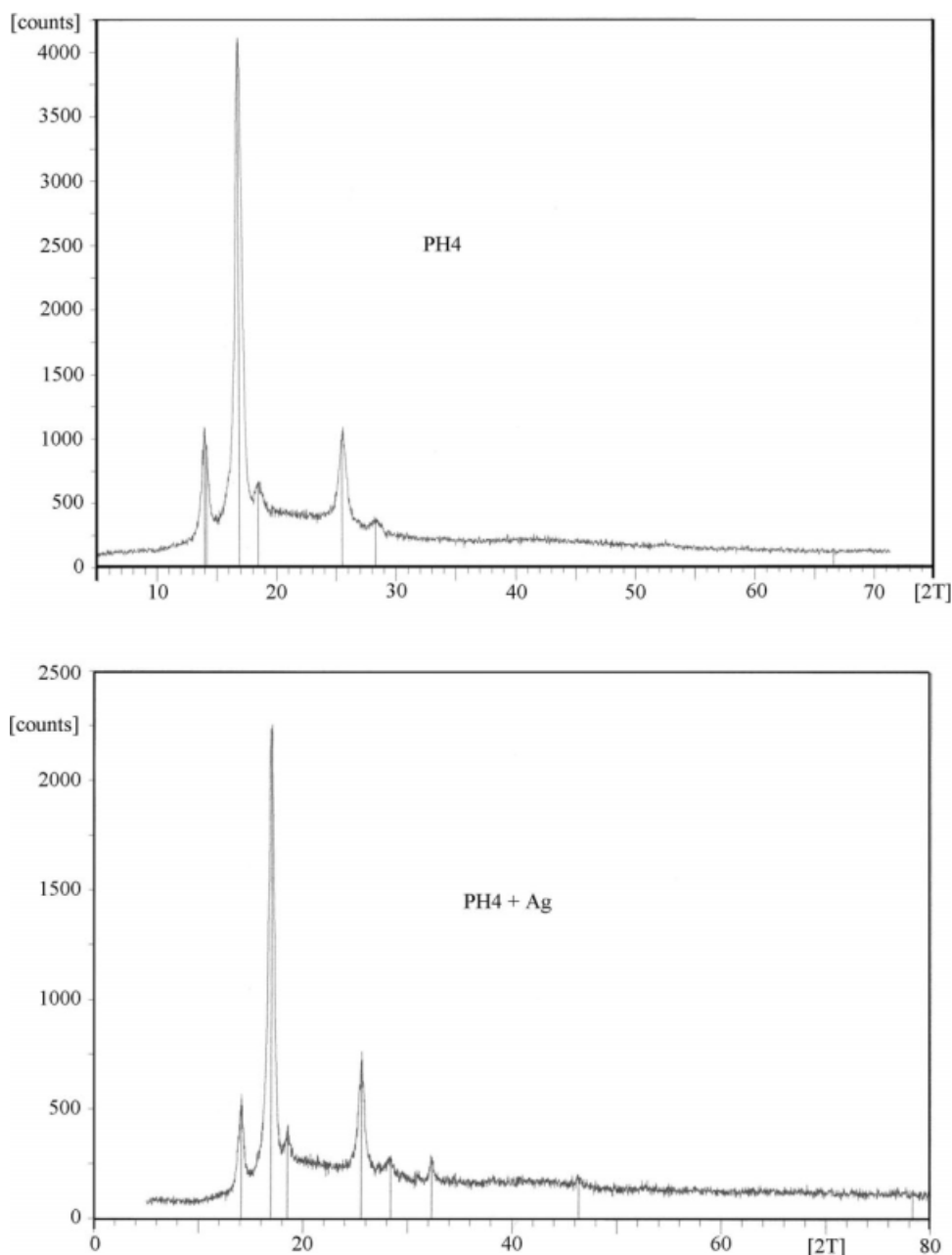

Figure 6 X-ray diffractograms of polymer PH$_4$ and polymer Ag$^+$ complex.

All the infrared spectra of the various polymer–metal complexes showed a common shift in the carbonyl absorption band to shorter frequency associated with a reduction of its intensity. This reflected that a chemical bond between the metal cation and carbonyl oxygen can be formed, resulting in a partial loss of carbonyl double bond character (Fig. 4). Moreover, the intensity of the bond corresponded to the enol configuration of the hydrazide linkages are increased, indicating participation of the enol form of the polymers in coordination. Thus, the complexation reaction may be preceded by a chemical interaction between the metal cation and the polymer enol form. On the basis of the elemental analyses for various bivalent metal complexes and according to their infrared spectra, the following possible structure can be deduced.

Similarly, for monovalent metal complex, structure can be proposed as follows (Scheme 4).

The complexation of polyhydrazides with various transition metal salts can additionally be proved from the color changes and UV–visible spectra of the polymer–metal complexes.

All the polymers used in this study appeared pale yellow color, absorbed strongly in the 200–400 nm region of the ultraviolet spectrum and do not show any absorption in the visible range (Fig. 5). On the other hand, all the polymer–metal complexes are highly colored.

Polymer–metal complex were also characterized by elemental analysis (Table VII). The data obtained from elemental analysis were found to be in good agreement with the expected values.

X-ray diffraction measurements

To give much more evidence for formation of poly-amide–hydrazide metal complex films, these surfaces were subjected to further characterization using X-ray diffraction. Figure 6 illustrates the X-ray diffractograms of polymer PH_4 complex films. As would be expected, these films showed sharp distinct diffraction compared with PH_4 film. The formed peaks show the metal polymer is collected together, thus, generate more crystalline surface. This result, leads us to believe that the metallized films consisting of a metallic complex layer could be easily obtained.

CONCLUSION

A series of PHs were synthesized by direct polycondensation of benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid with various dihydrazides in ILs under the influence of triphenyl phosphite as activating agent. Owing to ILs usage, there is no need to use any extra components, such as LiCl and pyridine. It is notable that these additives are used as a neces-sary participant in direct polycondensation of the same condensation monomers in ordinary molecular solvents, such as NMP. Also, the instability and toxicity of acid chlorides are the main drawbacks of low-temperature solution polycondensation method. The ILs used here are excellent media with a high solubilizing power for the polymerization reactions that increase chemical reactivity and, thus, lead to a decrease in reaction time and better results in comparision with conventional solvents. The resulting PHs are relatively thermally stable, and are readily soluble in common organic solvents.

In summary, we have used a facile methodology for the synthesis of polymers in ILs. The green solvent is harmless, economical, and environmentally friendly. The catalyst system can be used repeatedly. All polymers were metallized via coordination with various transition metal salts.

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