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ORIGINAL PAPER

Synthesis and characterization of some new aromatic polyoxadiazoles through cyclodehydration of polyhydrazides

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Abstract A series of new polyhydrazides containing pyridine heterocyclic ring, bearing bulky aromatic pendent groups, were synthesized from the reaction of diacid chlorides with dihydrazides via low-temperature solution polycondensation. All the polymers were readily soluble in polar solvents such as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), and 1-methyl-2-pyrrolidone (NMP) and showed inherent viscosities equal to 0.38–0.68 dL/g. They indicated glass transition temperatures (T_g) ranging from 190 to 220 °C. Polyhydrazides were subjected to cyclodehydration to prepare poly(1,3,4-oxadiazole)s either by thermally or chemically cyclodehydration approximately in the region of 150–320 °C. The poly(1,3,4-oxadiazole)s, made by chemically cyclodehydration exhibited T_gs of 220–250 °C and inherent viscosities equal to 0.38–0.62 dL/g, while the PODs made via thermally cyclodehydration of polyhydrazides did not show any glass transition and exhibited inherent viscosities equal to 0.39–0.66 dL/g. The former polymers were soluble in conc. H_2SO_4 and partially soluble in hot DMF, NMP, DMSO, and DMAc, and the latter were only soluble in conc. H_2SO_4. They had useful

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levels of thermal stability and were stable up to 450 °C in nitrogen. The structure of polymers was fully characterized by IR and NMR spectroscopies.

Keywords Poly(1,3,4-oxadiazole) · Polyhydrazide · Pyridine ring · Thermal stability

Introduction

Aromatic poly(1,3,4-oxadiazole)s (PODs) are known by their high chemical and thermal resistance, hydrolytic stability, low dielectric constants, tough mechanical properties, and relatively low density [1, 2]. They can be used in light-emitting diodes [3], acid sensors [4], electron and proton conducting materials [5], membranes for gas separation [6], flame resistant fibers [7], and solar cells [8]. One of the early most important methods for the preparation of PODs is thermal treatment of polyhydrazides (PHs) [9–20], which leads to cyclodehydration of the hydrazide groups and, consequently, the formation of oxadiazole ring.

Despite having the usual characteristics, aromatic PODs are rigid and insoluble in organic solvents and do not melt and do not show a glass transition temperature. They degrade before melting, which makes their processing quite difficult [21]. One of the most promising solutions to improve solubility and lowering glass transition temperature, while maintaining thermal stability, is introducing bulky moieties into the main chain or on the aromatic rings [22]. The incorporation of bulky pendent groups can provide beneficial effects for solubility because this approach produces a separation of chains, a weakening of hydrogen bonding and lowering of chain packing with a gain of free volume [23].

In a continuation of our interest on the synthesis of thermally stable polymers [23, 24], herein we report the synthesis and characterization of some new PHs which were converted to the corresponding PODs by thermal or chemical cyclodehydration.

Experimental

Materials

Chemicals were either prepared in our laboratory or purchased from Merck and Fluka chemical companies. *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), and 1-methyl-2-pyrrolidone (NMP) were dried by distillation under reduced pressure over CaH_2 and then stored over molecular sieve 4A. Commercially obtained anhydrous lithium chloride was dried under vacuum at 170 °C for 6 h. Other reagents were used as received.

Techniques

IR spectra were run on a Shimadzu FT–IR-8300 spectrophotometer. The ^{1}H NMR spectra was recorded in dimethyl sulfoxide (DMSO-d_6) or chloroform ($CDCl_3$)

using a Bruker Advance DPX instrument (250 MHz). Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed by a Stanton Redcraft STA-780 with 20 °C/min heating rate in N_2. Melting points were determined in open capillaries with Galen Kamp melting point apparatus and are not corrected. Inherent viscosities of polymers were determined for a solution of 0.5 g/dL in DMSO at 30 °C or concentrated H_2SO_4 using an Ubbelohde viscometer.

Synthesis of monomers

Synthesis of 4-aryl-2,6-bis(4-methylphenyl)pyridines ($DM_{a–c}$), 4-aryl-2,6-bis(4-carboxyphenyl)pyridines ($DAC_{a–c}$), and 4-aryl-2,6-bis(4-chlorocarbonylphenyl)pyridines ($DACL_{a–c}$)

The detailed synthesis and characterization of these monomers can be found in our previous report [23].

Synthesis of dihydrazides (DHs)

A mixture of diethyl (or dimethyl) ester of a dibasic acid (0.1 mol) and hydrazine hydrate (0.3 mol, 20.55 g) was refluxed in dry methanol (50 mL) for 24 h. The solid dihydrazide, which precipitates during the reaction, was collected and recrystallized from water or ethanol.

Synthesis of polymers

Synthesis of PHs

A solution of 1 mmol dihydrazide ($DH_{1–6}$) and 5–10 mL NMP containing 5% LiCl was placed in an ice-cooled reaction flask equipped with stirrer, nitrogen inlet and drying tube. To this 1 mmol of a diacid chloride ($DACL_{a–c}$) was added portion wise over a period of 15 min. The reaction mixture was stirred overnight and poured into 100 mL water. The precipitated polymer was washed with ethanol and dried in a vacuum oven at 80 °C overnight. Representative examples of spectroscopic data and elemental analysis are given below.

PH_{1a}: Yield: 94%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.6$ (NH, 4H), 7.1–8.3 (C–H arom, 19H) ppm; FT–IR (KBr) $\nu = 3260$ (NH), 1660 (C=O) cm^{-1}; Anal. Calcd. for $C_{33}H_{23}N_5O_4$: C, 71.60; H, 4.19; N, 12.65. Found: C, 71.70; H, 4.24; N, 12.74.

PH_{1b}: Yield: 92%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.6$ (NH, 4H), 7.0–8.1 (C–H arom, 18H), 3.7 (OCH_3, 3H) ppm; FT–IR (KBr) $\nu = 3270$ (NH), 1650 (C=O) cm^{-1}; Anal. Calcd. for $C_{34}H_{25}N_5O_5$: C, 69.97; H, 4.32; N, 12.00. Found: C, 69.99; H, 4.39; N, 12.09.

PH_{1c}: Yield: 92%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.6$ (NH, 4H), 7.1–8.1 (C–H arom, 18H) ppm; FT–IR (KBr) $\nu = 3270$ (NH), 1650 (C=O) cm^{-1}; Anal. Calcd. for $C_{33}H_{22}ClN_5O_4$: C, 67.41; H, 3.77; N, 11.91. Found: C, 67.49; H, 3.86; N, 11.99.

PH_{2a}: Yield: 92%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.6$ (NH, 4H), 7.5–8.5 (C–H arom, 19H) ppm; FT–IR (KBr) $v = 3270$ (NH), 1650 (C=O) cm^{-1}; Anal. Calcd. for $C_{33}H_{23}N_5O_4$: C, 71.60; H, 4.19; N, 12.65. Found: C, 71.69; H, 4.22; N, 12.71.

PH_{2b}: Yield: 91%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.7$ (NH, 4H), 7.3–8.2 (C–H arom, 18H), 3.6 (OCH_3, 3H) ppm; FT–IR (KBr) $v = 3260$ (NH), 1660 (C=O) cm^{-1}; Anal. Calcd. for $C_{34}H_{25}N_5O_5$: C, 69.97; H, 4.32; N, 12.00. Found: C, 69.99; H, 4.34; N, 12.09.

PH_{3c}: Yield: 90%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.8$ (NH, 4H), 7.1–8.1 (C–H arom, 18H) ppm; FT–IR (KBr) $v = 3260$ (NH), 1660 (C=O) cm^{-1}; Anal. Calcd. for $C_{33}H_{22}ClN_5O_4$: C, 67.41; H, 3.77; N, 11.91. Found: C, 67.49; H, 3.82; N, 11.99.

PH_{4a}: Yield: 94%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.7$ (NH, 4H), 7.3–8.5 (C–H arom, 23H) ppm; FT–IR (KBr) $v = 3260$ (NH), 1650 (C=O) cm^{-1}; Anal. Calcd. for $C_{39}H_{27}N_5O_4$: C, 74.39; H, 4.32; N, 11.12. Found: C, 74.42; H, 4.40; N, 11.19.

PH_{4c}: Yield: 90%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.5$ (NH, 4H), 7.5–8.5 (C–H arom, 22H) ppm; FT–IR (KBr) $v = 3260$ (NH), 1650 (C=O) cm^{-1}; Anal. Calcd. for $C_{39}H_{26}ClN_5O_4$: C, 70.53; H, 3.95; N, 10.55. Found: C, 70.63; H, 3.99; N, 10.62.

PH_{5a}: Yield: 90%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.4$ (NH, 4H), 7.2–8.5 (C–H arom, 15H), 3.1 (CH_2, 2H) ppm; FT–IR (KBr) $v = 3270$ (NH), 1650 (C=O) cm^{-1}; Anal. Calcd. for $C_{28}H_{21}N_5O_4$: C, 68.42; H, 4.31; N, 14.25. Found: C, 68.52; H, 4.41; N, 14.31.

PH_{6a}: Yield: 92%; ^{1}H NMR (250 MHz, DMSO-d_6): $\delta = 10.4$ (NH, 4H), 7.2–8.5 (C–H arom, 15H), 1.4–1.5 (P, 1H); FT–IR (KBr) $v = 3230$ (NH), 1650 (C=O), 1260, 820 (HOP=O) cm^{-1}; Anal. Calcd. for $C_{25}H_{20}N_5O_3P$: C, 63.96; H, 4.29; N, 14.92. Found: C, 64.01; H, 4.31; N, 14.99.

PH_{6b}: Yield: 89%; ^{1}H NMR (250 MHz, DMSO-d_6): 10.5 (NH, 4H), 7–8.1 (C–H arom, 14H), 3.5 (OCH_3, 3H), 1.4–1.5 (P, 1H). FT–IR (KBr) $v = 3240$ (NH), 1650 (C=O), 1260, 820 (HOP=O) cm^{-1}; Anal. Calcd. for $C_{26}H_{22}N_5O_4P$: C, 62.52; H, 4.44; N, 14.02. Found: C, 62.59; H, 4.49; N, 14.10.

Synthesis of PODs

Thermally cyclodehydration of PHs PODs were prepared by heating solid PHs, in a vacuum oven with stepwise temperature rise: to 160 °C for 3 h, 250 °C for 3 h, and finally 320 °C for 2 h.

Chemically cyclodehydration of PHs A mixture of PH and polyphosphoric acid (PPA) in a molar ratio of 1/25 (PH/PPA) was added to a three-necked flask, equipped with a mechanical stirrer, nitrogen inlet and a reflux condenser. The solution was continuously stirred and kept at 150 °C for 3 h. Then, the temperature was raised to 190 °C in 4–5 h. The viscous solution was poured into ice water and washed with ethanol and water. The polymer is dried at 100 °C in a vacuum oven for 2 days. Representative examples of analytical data are given below.

POD_{1a}: Anal. Calcd. for $C_{33}H_{19}N_5O_2$: C, 76.58; H, 3.70; N, 13.53. Found: C, 76.62; H, 3.78; N, 13.61.

POD_{2b}: Anal. Calcd. for $C_{34}H_{21}N_5O_3$: C, 74.58; H, 3.87; N, 12.79. Found: C, 74.65; H, 3.96; N, 12.84.

POD_{3c}: Anal. Calcd. for $C_{33}H_{18}N_5O_2Cl$: C, 71.81; H, 3.29; N, 12.69. Found: C, 71.87; H, 3.33; N, 12.73.

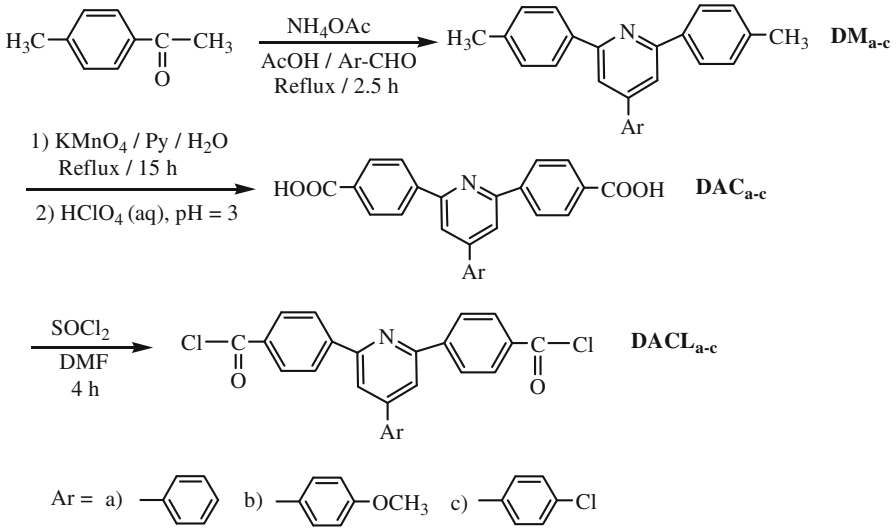
POD_{4a}: Anal. Calcd. for $C_{39}H_{23}N_5O_2$: C, 78.91; H, 3.91; N, 11.80. Found: C, 78.99; H, 3.99; N, 11.88.

POD_{5a}: Anal. Calcd. for $C_{28}H_{17}N_5O_2$: C, 73.84; H, 3.76; N, 15.38. Found: C, 73.91; H, 3.83; N, 15.42.

Results and discussion

Synthesis and characterization of PHs

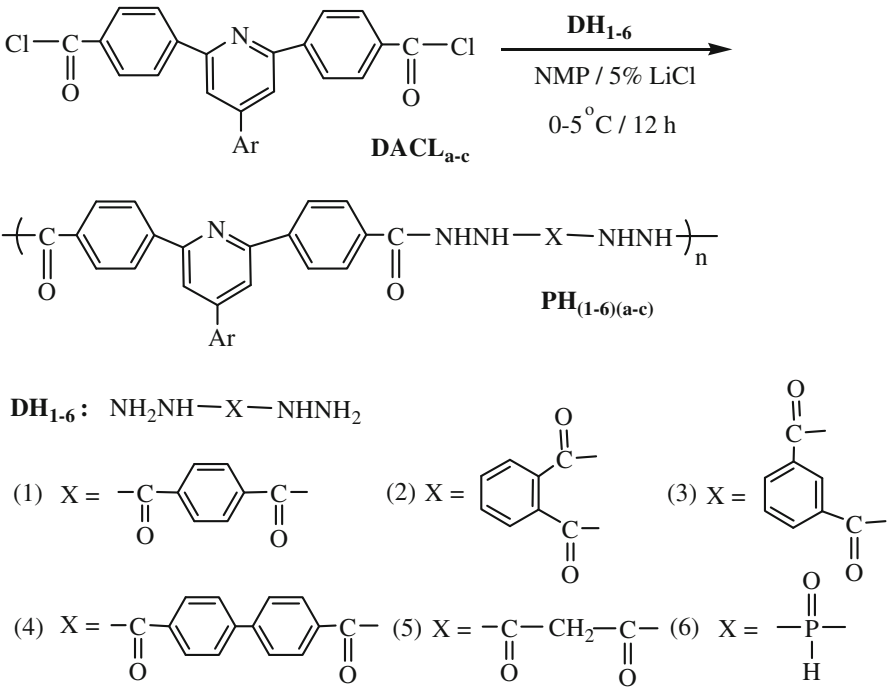
The synthetic routes for the dimethyl, diacid, and diacid chloride monomers are shown in Scheme 1. Dimethyl monomers ($DM_{a–c}$) were prepared by the reaction of 4-methylacetophenone and different aryl aldehydes in the presence of ammonium acetate and glacial acetic acid under reflux conditions according to modified Chichibabin method [25]. Diacid monomers ($DAC_{a–c}$) were prepared via an oxidation of the corresponding $DM_{a–c}$ using potassium permanganate in pyridine/water (80/20 ratio) which were then treated with excess thionyl chloride in the presence of a few drops of DMF as catalyst to obtain diacid chloride monomers ($DACL_{a–c}$). The structure of $DM_{a–c}$, $DAC_{a–c}$, and $DACL_{a–c}$ have been established [23].



Scheme 1 Synthesis of monomers ($DM_{a–c}$, $DAC_{a–c}$, and $DACL_{a–c}$)

Different types of dihydrazides ($DH_{1–6}$) were synthesized by the reaction of diethyl (or dimethyl) ester of a dibasic acid with hydrazine hydrate under reflux conditions in dry methanol. In this manner terephthalic dihydrrazide, phthalic dihydrazide, isophthalic dihydrazide, biphenyl 4,4′-dicarboxilic dihydrazide, malonic dihydrazide, and phosphoric dihydrazide were prepared and characterized by comparison of their physical and spectral data with those reported in the literature [26–28]. FT–IR spectra of DHs showed an amidic carbonyl band and an amidic N–H band at 1600–1700 and 3200–3300 cm^{-1}, respectively.

PHs were synthesized by low-temperature solution polycondensation reaction of an equimolar mixture of six different $DH_{1–6}$ with $DACL_{a–c}$ in NMP containing 5% LiCl (LiCl increases the solvating power of NMP and hence LiCl–NMP solution is powerful enough to keep the growing polymer chain in solution as its molecular weight builds up) in an ice-cooled reaction flask equipped with stirrer, nitrogen inlet and drying tube (Scheme 2). All PHs were white or pale-yellow which were characterized by IR and ^1H NMR spectroscopy. IR spectra of the polymers showed N–H bands in the region of 3230–3270 and 1650–1660 cm^{-1} for carbonyl groups. ^1H NMR spectra of polymers showed two peaks in the region about δ(ppm): 10.4–10.8 and 7.0–8.5 assigned to the hydrogen of (NH) and aromatic hydrogens, respectively. Figures 1 and 2 show the ^1H NMR and IR spectra of PH_{1a}, as a typical. Solubility of PHs was examined in different solvents. As expected, all polymers showed excellent solubility and were readily soluble in conc. H_2SO_4 and polar



Scheme 2 Synthesis of polyhydrazides ($PH_{(1–6)(a–c)}$)

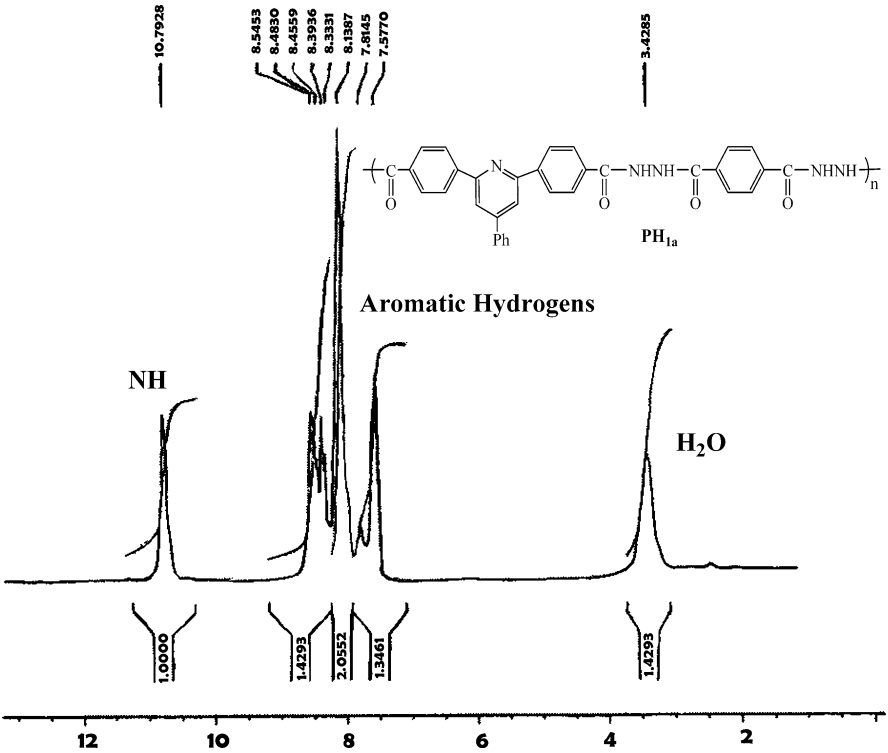


Fig. 1 ^{1}H NMR (in DMSO-d_6) spectrum of PH_{1a}

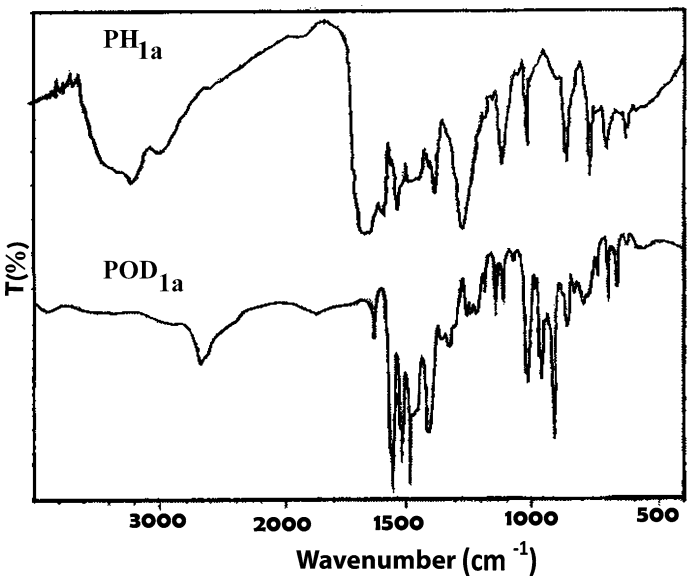


Fig. 2 FT–IR (KBr pellet) spectrum of PH_{1a} and POD_{1a}

Table 1 Characterization of PHs

PH	η_{inh}^{a} (dL/g)	T_g (°C)	$T_{10\%}^{b}$ (°C)	Char yield (%)[c]	Solubility			
					DMAc	NMP	DMSO	DMF
PH_{1a}	0.65	215	480	49	+h	+h	+h	+h
PH_{1b}	0.63	208	470	47	+h	+h	+h	+h
PH_{1c}	0.62	206	470	47	+h	+h	+h	+h
PH_{2a}	0.57	200	440	45	+	+	+	+
PH_{2b}	0.55	200	430	45	+	+	+	+
PH_{3a}	0.53	200	430	45	+	+	+	+
PH_{3c}	0.51	195	430	45	+	+	+	+
PH_{4a}	0.68	220	485	55	+h	+h	+h	+h
PH_{4c}	0.66	220	485	53	+h	+h	+h	+h
PH_{5a}	0.38	190	400	42	+	+	+	+
PH_{6a}	0.56	210	420	52	+	+	+	+
PH_{6b}	0.53	205	430	53	+	+	+	+

+ indicates soluble at room temperature, +h indicates soluble on heating

[a] Determined at a concentration of 0.5 g/dL in DMSO at 30 °C

[b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 20 °C/min in nitrogen

[c] Residual wt% when heated to 600 °C in nitrogen

aprotic solvents such as DMAc, NMP, DMF, and DMSO (Table 1). They were insoluble in solvents such as ethanol, methanol, benzene, acetonitrile, and acetone. The relatively higher solubility associated with these polymers is believed to be related to the presence of the pendent bulky groups, which prevent the close packing of chains and decrease interchain interaction.

To get estimation about the relative molecular weights of polyhydraizdes, inherent viscosities (η_{inh}) of polymers were measured in 0.5 g/dL concentration in DMSO at 30 °C. The η_{inh} of polymers were in the range of 0.38–0.68 dL/g which showed relatively high molecular weight of polymers (Table 1).

TGA and DSC were employed to investigate the thermal behaviors of the polymers. A typical DSC curve of PH_{1a} is illustrated in Fig. 3. PH_{1a} showed a discernible glass transition temperature at 215 °C and a strong endothermic peak between 330 and 360 °C that was attributed to loss of water during the conversion of the hydrazide group to the polyoxadiazole ring. The POD_{1a} formed in situ during the first heating scan under rapid condition (20 °C/min) of DSC technique revealed a T_g at 232 °C in the subsequent scan. Figure 4 shows a typical TGA curve for PH_{1a}. In TGA curves two breaks are observed in all cases. The first break is due to the conversion of the PH to POD (cyclodehydration) which is started in the vicinity of 300–400 °C and the second break occurred about 480–600 °C is due to the decomposition of the corresponding POD formed in situ. The PH_{1a} showed a 10% weight loss near 480 °C in nitrogen and the char residue remaining at 600 °C in a nitrogen atmosphere was 49%. Other polymers showed a similar DSC and TGA behaviors. DSC and TGA data of some of the polymers are listed in Table 1.

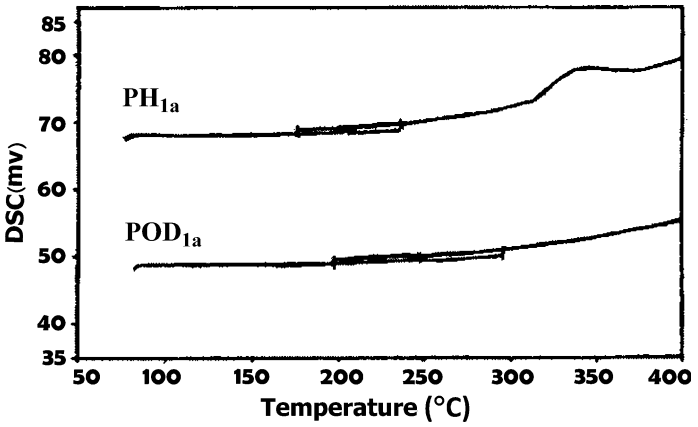


Fig. 3 DSC curves of PH_{1a} and POD_{1a} (obtained from chemically cyclodehydration reaction) with a heating rate of 20 °C/min in nitrogen

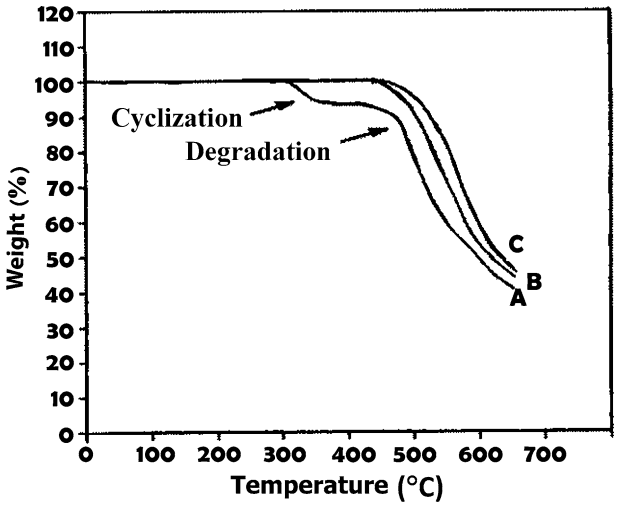
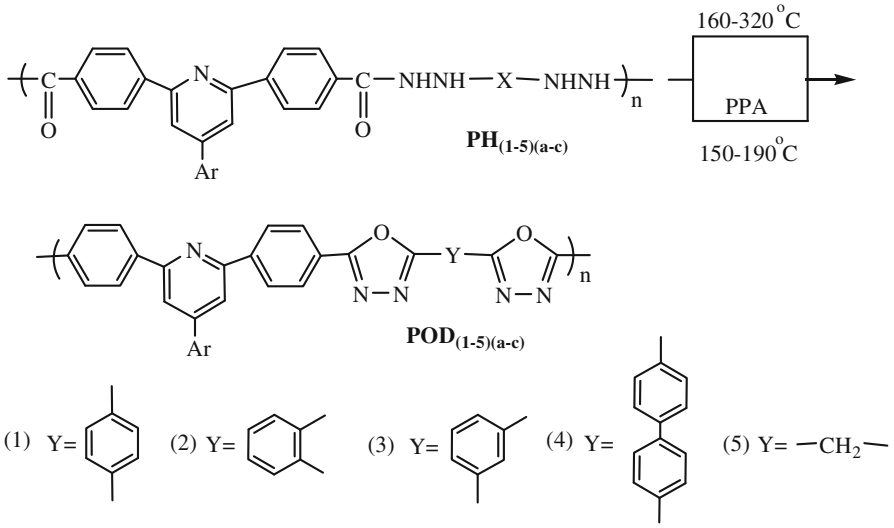


Fig. 4 TGA curves of PH_{1a} (*A*), POD_{1a} made via chemically cyclodehydration reaction (*B*), and POD_{1a} made via thermally cyclodehydration reaction (*C*) with a heating rate of 20 °C/min in nitrogen

Synthesis and characterization of PODs

PODs were prepared by thermally or chemically cyclodehydration of the corresponding PHs (Scheme 3). In the first method, the conversion of PHs to PODs was carried out in vacuo on various heating cycles (160–320 °C over approximately 8 h). In the second method, PHs were heated at 150–190 °C in nitrogen atmosphere in PPA, which function both as solvent and dehydrating agent. The PODs, made via the former method became completely insoluble in any organic solvent and were only soluble in conc. H_2SO_4. It is believed that some



Scheme 3 Synthesis of poly(1,3,4-oxadiazole)s ($POD_{(1–5)(a–c)}$)

branching and crosslinking might have taken place during heating in bulk state which may be responsible for solubility problems. The PODs obtained from chemically cyclodehydration of PHs were soluble in conc. H_2SO_4 and partially soluble in hot DMF, NMP, DMSO, and DMAC, and insoluble in common organic solvents, such as chloroform, butanol and tetrahydrofurane (Table 2). The PODs obtained from chemically and thermally cyclodehydration of PHs exhibited inherent viscosities equal to 0.38–0.62 and 0.39–0.66 dL/g, respectively. The successful

Table 2 Characterization of representative PODs made via chemically cyclodehydration of PHs

POD from	η_{inh}[a] (dL/g)	T_g (°C)	$T^b_{10\%}$ (°C)	Char yield (%)[c]	Solubility			
					DMAc	NMP	DMSO	DMF
PH_{1a}	0.62	250	500	54	+h	–	+h	–
PH_{1b}	0.60	245	500	55	+h	–	+h	–
PH_{1c}	0.60	245	500	55	+h	–	+h	–
PH_{2a}	0.48	234	480	55	+h	+h	+h	+h
PH_{2b}	0.46	230	480	53	+h	+h	+h	+h
PH_{3c}	0.41	230	465	53	+h	+h	+h	+h
PH_{4a}	0.62	250	525	55	+h	–	+h	–
PH_{4c}	0.60	250	520	55	+h	–	+h	–
PH_{5a}	0.38	220	460	50	+h	+h	+h	+h

+h partially soluble on heating, – insoluble

[a] Determined at a concentration of 0.5 g/dL in conc. H_2SO_4

[b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 20 °C/min in nitrogen

[c] Residual wt% when heated to 600 °C in nitrogen

conversion of polyhydrazide into polyoxadiazole was confirmed by FT–IR spectra. The stretching bands of C=O and N–H groups in PHs around 1650–1660 and 3230–3270 cm^{-1}, respectively, disappear in the IR spectra of the corresponding PODs, where as the band corresponding to >C=N– stretching in an oxadiazole ring around 1550–1580 cm^{-1}, was newly generated. In addition, oxadiazole =C–O–C= stretching was observed around 960–1000 cm^{-1} for these polymers. The PODs are tan and light-tan in color.

The thermal stability of all PODs was studied by TGA and DSC thermograms. The PODs, made by chemically cyclodehydration of PHs, showed 10% weight loss in N_2 in the range of 460–525 °C, while the PODs, made via thermally cyclodehydration of PHs, exhibit the same percentage of 10% weight loss about 465–535 °C. Figure 4 shows a typical TGA curve for POD_{1a}. The T_gs of PODs obtained from chemically cyclization were recorded in the 220–250 °C. POD_{1a} revealed a clean T_g at 250 °C (Fig. 3). PODs, made by thermal cyclization, do not show any glass transition. These observations indicated that the PODs made by thermal cyclization, show higher thermal stability than their analogs made by chemical cyclization. All the PODs did not lose weight, up to 450 °C in N_2. The representative TGA and DSC data are summarized in Table 2.

Conclusion

PHs containing pyridine heterocyclic ring, bearing bulky aromatic pendent groups, with reasonably high molecular weights were prepared in good yields by reaction of diacid chlorides with dihydrazides via low-temperature solution polycondensation. The introduction of pyridine heterocyclic ring units together with bulky aromatic pendent groups into the chain of PHs led to polymers with good solubility. PHs showed good thermal stability and could be converted into corresponding poly(1,3,4-oxadiazole)s thermally or chemically. All polyoxadiazoles have well defined structure and displayed good thermal stability with decomposing temperature being above 450 °C. They exhibited lower solubility and higher T_gs in comparison with the corresponding hydrazide precursors.

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