New Poly(1,3,4-oxadiazole)s Bearing Pentadecyl Side Chains: Synthesis and Characterization

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ABSTRACT: The 4-[4′-(Hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide was polycondensed with aromatic diacid chlorides *viz.*, terephthalic acid chloride (TPC), isophthalic acid chloride (IPC), and a mixture of TPC : IPC (50 : 50 mol %) to obtain polyhydrazides which on subsequent cyclodehydration reaction in the presence of phosphoryl chloride yielded new poly(1,3,4-oxadiazole)s bearing flexibilizing ether linkages and pentadecyl side chains. Inherent viscosities of polyhydrazides and poly(1,3,4-oxadiazole)s were in the range 0.53–0.66 dL g^{-1} and 0.49–0.53 dL g^{-1}, respectively, indicating formation of medium to reasonably high molecular weight polymers. The number average molecular weights (M_n) and polydispersities (M_w/M_n) of poly(1,3,4-oxadiazole)s were in the range 14,660–21,370 and 2.2–2.5, respectively. Polyhydrazides and poly(1,3,4-oxadiazole)s were soluble in polar aprotic solvents such as *N,N*-dimethylacetamide, 1-methyl-2-pyrrolidinone, and *N,N*-dimethylformamide. Furthermore, poly(1,3,4-oxadiazole)s were also found to be soluble in solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine, and *m*-cresol. Transparent, flexible, and tough films of polyhydrazides and poly(1,3,4-oxadiazole)s could be cast from *N,N*-dimethylacetamide and chloroform solutions, respectively. Both polyhydrazides and poly(1,3,4-oxadiazole)s were amorphous in nature and formation of layered structure was observed due to packing of pentadecyl chains. A decrease in glass transition temperature was observed both in polyhydrazides (143–166°C) and poly(1,3,4-oxadiazole)s (90–102°C) which could be ascribed to "internal plasticization" effect of pentadecyl chains. The T_{10} values, obtained from TG curves, for poly(1,3,4-oxadiazole)s were in the range of 433–449°C indicating their good thermal stability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1281–1289, 2012

Key words: polyhydrazides; poly(1,3,4-oxadiazole)s; pentadecyl; cashew nut shell liquid; thermal stability

INTRODUCTION

Poly(1,3,4-oxadiazole)s have been the focus of considerable interest particularly owing to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring which from the spectral and electronic point of view is similar to a *p*-phenylene structure.[1–6] The exploration of poly(1,3,4-oxadiazole)s has led to the host of new materials favorable for opto-electronics by offering not only improved balance of charge mobility but enhanced thermal and photostability as well.[7–16] The conventional aromatic poly(1,3,4-oxadiazole)s are difficult to process due to their infusible and insoluble nature and their tendency to be brittle. Many efforts have been made to improve the solubility, *viz*, by incorporation of flexible linkages in the polymer backbone or by incorporation of bulky pendant groups on the aromatic rings.[16–30] Among various strategies adopted to improve processability of poly(1,3,4-oxadiazole)s, the incorporation of long and flexible side chains has proven satisfactory.[14,31,32] In general, such long alkyl chains not only bring about improved solubility but also help lower the melting and/or glass transition temperatures.

Cashew nut shell liquid (CNSL) – a by-product of cashew processing industries – is a source of alkenyl phenols whose structural features permit chemists to transform them into a variety of useful products. Recently, we have reported a series of soluble and processable high performance polymers containing pendant pentadecyl chains starting from (CNSL). It was demonstrated that, the pentadecyl chains acts as an internal plasticizers and hence aids in improved processability and simultaneously imparts the solubility characteristics to the resulting polymer.[33–38] In continuation with our ongoing efforts to obtain polymers with improved solubility, we wish to report herein synthesis of a series of new poly(1,3,4-oxadiazole)s containing flexibilizing ether linkages and pentadecyl side chains. The 4-[4′-(Hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide was polycondensed with aromatic diacid chlorides *viz.*, terephthalic acid chloride (TPC), isophthalic acid

chloride (IPC), and a mixture of TPC : IPC (50 : 50 mol %), to obtain new polyhydrazides. Polyhydrazides on subsequent cyclodehydration reaction in the presence of phosphoryl chloride yielded poly(1,3,4-oxadiazole)s containing flexibilizing ether linkages and pentadecyl side chains. Polyhydrazides and poly(1,3,4-oxadiazole)s were characterized by inherent viscosity measurements, solubility tests, FTIR, ^{1}H NMR spectroscopy, gel permeation chromatography (GPC), X-ray diffraction (WAXD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The effects of pentadecyl side chains and flexibilizing ether linkages on polymer properties such as solubility and thermal behavior were investigated.

EXPERIMENTAL

Materials

The 4-[4'-(hydrazinocarbonyl)phenoxy]-2-pentadecylbenzohydrazide (HPPB) was synthesized starting from cashewnut shell liquid (CNSL) using procedure described in our previous work.[33] Terephthalic acid chloride (TPC) and isophthalic acid chloride (IPC) were synthesized from terephthalic acid and isophthalic acid (Aldrich, USA), respectively, using excess thionyl chloride in the presence of N,N-dimethylformamide (DMF) as a catalyst and were purified by distillation under reduced pressure. Anhydrous lithium chloride (Aldrich, USA) was dried at 180°C for 8 h under reduced pressure. N,N-dimethylacetamide (DMAc), (Merck, India) was dried over calcium hydride and distilled under reduced pressure. Phosphoryl chloride (Merck, India) was distilled under reduced pressure. Sodium hydroxide, sodium chloride, sodium bicarbonate and sodium sulfate, (Merck, India and E-Merck, Germany) were used as received. The solvents were of reagent grade quality and were purified prior to use according to the reported procedures.[39]

Measurements

Inherent viscosities of polyhydrazides and poly(1,3,4-oxadiazole)s were measured with 0.5% (w/v) solution of polymer in DMAc and CHCl₃, respectively, at 30°C ± 0.1°C using an Ubbelohde suspended level viscometer. Solubility of polymers was determined at 3 wt % concentration in various solvents at room temperature or upon heating. FTIR spectra were recorded using polymer films on a Perkin–Elmer Spectrum GX spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker 200 MHz spectrometer using CDCl₃ or DMSO-d_6 as a solvent. Molecular weights of poly(1,3,4-oxadiazole)s were measured on ThermoFinnigan make gel permeation
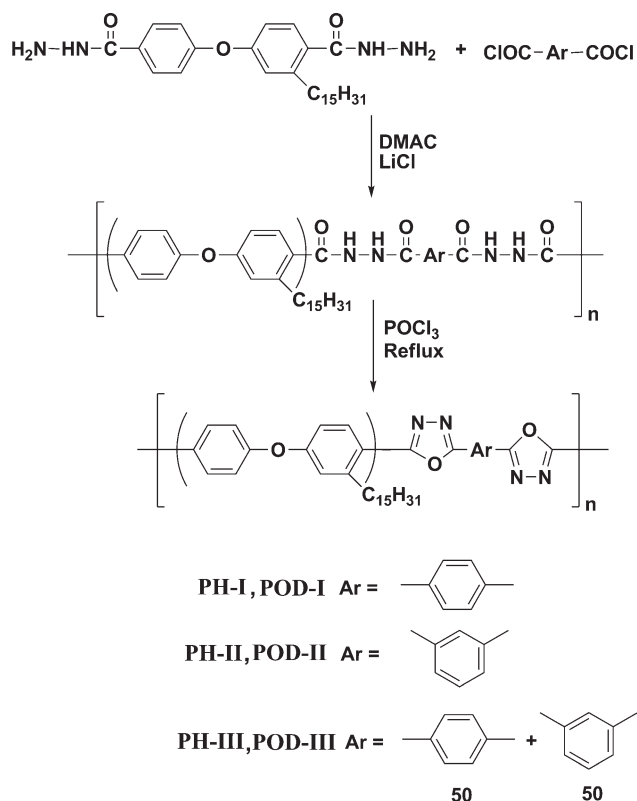
Scheme 1 Synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s bearing pentadecyl side chains.

chromatograph (GPC), using the following conditions: Column—polystyrene-divinylbenzene (10^5 Å to 50 Å), Detector—RI, room temperature. Polystyrene was used as the calibration standard. Polymer sample (5 mg) was dissolved in 5 mL chloroform and filtered through 0.2-µ PTFE syringe filter. X-ray diffraction patterns of polymers were obtained on a RigakuDmax 2500 X-ray diffractometer at a tilting rate of 2° min⁻¹. Thermogravimetric analysis was performed on Perkin–Elmer TGA-7 system at a heating rate of 15°C min⁻¹ under nitrogen atmosphere. Sample weight taken was ∼ 5 mg. DSC analysis was carried out on TA Instruments DSC Q10 at a heating rate of 10°C min⁻¹ in nitrogen atmosphere.

Synthesis of poly(1,3,4-oxadiazole)s

Synthesis of precursor polyhydrazides

A representative procedure for the synthesis of polyhydrazides is given below:

Into a 50-mL two necked round bottom flask equipped with a calcium chloride guard tube, a nitrogen inlet tube and a magnetic stirring bar were placed HPPB (600 mg, 1.21 mmol) and DMAc (10 mL) containing LiCl (5 wt % based on solvent). The reaction mixture was cooled to 0°C. Thereafter, TPC (240 mg, 1.21 mmol) was added in portions to

TABLE I
Synthesis and Properties of Polyhydrazides and Poly(1,3,4-oxadiazole)s Bearing Pentadecyl Side Chains

Polymer	Polymer[a]	Diacid chloride (mol %)		Yield (%)	η_{inh} (dL g^{-1})	GPC[b]		
		TPC	IPC			M_n	M_w	M_w/M_n
PH-I		100	0	96	0.64[c]	_[d]	_[d]	_[d]
PH-II		0	100	93	0.53[c]	_[d]	_[d]	_[d]
PH-III		50	50	95	0.66[c]	_[d]	_[d]	_[d]
POD-I		100	0	96	0.49[e]	14,660	36,860	2.5
POD-II		0	100	94	0.50[e]	15,210	34,230	2.2
POD-III		50	50	93	0.53[e]	21,370	47,390	2.2

[a] R is HPPB.
[b] Measured by GPC in chloroform, polystyrene was used as the calibration standard.
[c] η_{inh} was measured with 0.5% (w/v) solution of polyhydrazide in DMAc at 30°C ± 0.1°C.
[d] Insoluble in CHCl$_3$.
[e] η_{inh} was measured with 0.5 (w/v) solution of poly(1,3,4-oxadiazole) in CHCl$_3$ at 30°C ± 0.1°C.

the reaction mixture. The reaction was carried out at 0°C for 2 h and at room temperature for 12 h. At the end of the reaction time, the viscous solution formed was poured into aqueous methanol and the precipitated polymer was filtered and washed several times with water and then with methanol. The polymer was dried at 60°C under reduced pressure.

A similar procedure was followed for the synthesis of other polyhydrazides.

Synthesis of poly(1,3,4-oxadiazole)s

Poly(1,3,4-oxadiazole)s were synthesized by chemical cyclodehydration of polyhydrazides in phosphoryl chloride.

Into a 50 mL two necked round bottom flask equipped with a reflux condenser, a nitrogen inlet and a magnetic stirring bar were placed polyhydrazide (derived from HPPB and TPC; 500 g) and phosphoryl chloride (25 mL). The reaction mixture was refluxed for 12 h under nitrogen atmosphere. The clear solution obtained was slowly poured into aqueous methanol. The precipitated polymer was filtered, washed several times with water and then with methanol. Finally, the polymer was dried under reduced pressure at 50°C for 3 h.

A similar procedure was followed for the synthesis of other poly(1,3,4-oxadiazole)s.

RESULTS AND DISCUSSION

Polymer synthesis

Scheme 1 illustrates the route for the synthesis of poly(1,3,4-oxadiazole)s bearing pentadecyl side chains. HPPB was polycondensed with equimolar quantities of aromatic diacid chlorides in DMAc containing anhydrous lithium chloride to obtain polyhydrazides as white fibrous materials. The polyhydrazides were further subjected to cyclodehydration reaction in the presence of phosphoryl chlorideto obtain corresponding poly(1,3,4-oxadiazole)s. The results of synthesis of polyhydrazides and poly(1,3,4-oxadiazole)s are summarized in Table I. Inherent viscosities of polyhydrazides were in the range 0.53–0.66 dL g^{-1} indicating formation of medium to reasonably high molecular weight polymers.[13,40] Inherent viscosities of corresponding poly(1,3,4-oxadiazole)s determined in chloroform were in the range 0.49–0.53 dL g^{-1} and were found to be reduced in comparison with the parent polyhydrazides. This could be attributed partly to the different solvent used for inherent viscosity measurements and partly
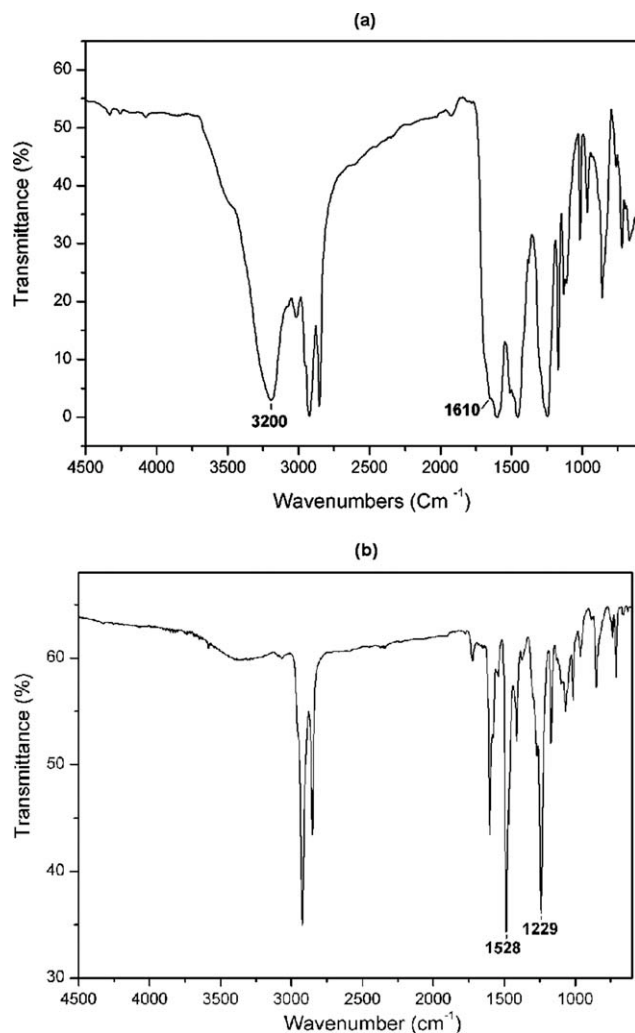
Figure 1 FTIR spectra of (a) polyhydrazide (PH-I) and (b) poly(1,3,4-oxadiazole), (POD-I) bearing pentadecyl side chains.

to the compactness of the chain structure while going from polyhydrazides to poly(1,3,4-oxadiazole)s.[4,31,40] Transparent, flexible, and tough films of polyhydrazides and poly(1,3,4-oxadiazole)s could be cast from DMAc and CHCl$_3$ solutions, respectively.

Poly(1,3,4-oxadiazole)s bearing pentadecyl side chains were soluble in CHCl$_3$, permitting their molecular weight determination by GPC. The results of GPC measurements of poly(1,3,4-oxadiazole)s are presented in Table I. The number average molecular weights (M_n) and polydispersities (M_w/M_n) of poly(1,3,4-oxadiazole)s were in the range 14,660–21,370 and 2.2–2.5, respectively. Inherent viscosity and GPC data indicated the formation of medium to reasonably high molecular weight polymers. However, the molecular weight values provided by GPC should not be taken as absolute as the calibration of GPC was carried out using polystyrene standards.

Polymer characterization

The structures of polyhydrazides and poly(1,3,4-oxadiazole)s were confirmed by FTIR and ^{1}H NMR spectroscopy. In Figures 1(a,b), a comparison of FTIR spectra of PH-I and POD-I is shown as an example. After the chemical cyclodehydration of polyhydrazide in the presence phosphoryl chloride, the intense strong absorption band at around 1610 arising from carbonyl groups of polyhydrazide and bands in the region 3200–3300 cm^{-1} due to N—H stretching disappeared. Meanwhile, the band corresponding to the stretching of the 1,3,4-oxadiazole ring at 1528 cm^{-1} appeared, which confirmed the complete cyclization of polyhydrazide into poly(1,3,4-oxadiazole). ^{1}H NMR spectra of PH-I and POD-I derived from HPPB and TPC are shown in Figures 2(a,b) as an example. In ^{1}H NMR spectrum of PH-I, [Fig. 2(a)], the four protons on terephthalic acid ring and two protons "d" *ortho* to carbonyl appeared as a multiplet in the range 7.97–8.08 δ ppm. The proton *ortho* to carbonyl group on pentadecyl-substituted aromatic ring appeared as a doublet at 7.55 δ ppm, while four protons *ortho* to ether linkage of diacylhydrazide component exhibited a multiplet in the range 6.98–7.19 δ ppm. The benzylic —CH$_2$ appeared as a triplet at 2.79 δ ppm. The methylene protons β to aromatic ring exhibited a multiplet centered at 1.60 δ ppm. The other methylene protons displayed a multiplet over the range 1.18–1.26 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.83 δ ppm.

The hydrazide protons, flanked by two carbonyl groups (—CO—NH—NH—CO—), appeared as three distinct singlets of unequal intensity at 10.31, 10.57, and 10.69 δ ppm. The presence of pentadecyl chain on only one aromatic ring in HPPB disturbed the symmetry of the molecule, while making the protons of hydrazide linkages magnetically nonequivalent. Additionally, there is a possibility of formation of constitutional isomers due to the use of unsymmetrical diacylhydrazide monomer. It is well reported in the literature that when an asymmetric monomer reacts with a symmetric monomer, constitutional isomerism would arise.[41,42] The probable structural orientations are four *viz,* (a) head-to-head, (b) tail-to-tail, (c) head-to-tail and (d) tail-to-head. Thus, the presence of three distinct singlets in 200 MHz NMR spectrum of polyhydrazide could be ascribed to the combined effect of constitutional isomerism and asymmetric nature of HPPB monomer.

In ^{1}H NMR spectrum of POD-I, [Fig. 2(b)] the absence of signals corresponding to hydrazide protons in the range 10.29–10.71 δ ppm confirmed the complete cyclodehydration of polyhydrazide into poly(1,3,4-oxadiazole). The four protons of terephthalic acid unit appeared as a singlet at 8.31 δ ppm.
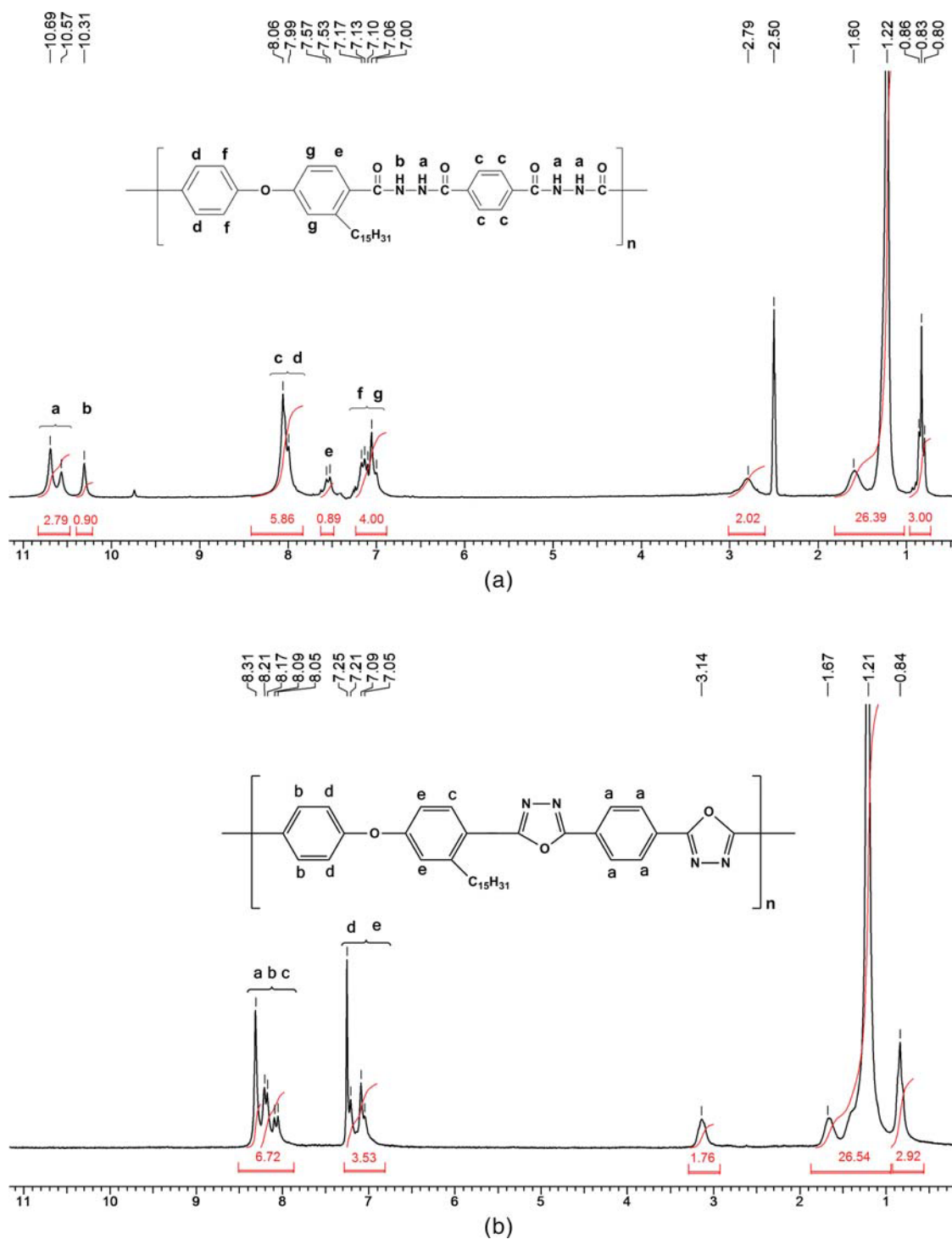
Figure 2 (a) ^{1}H NMR spectrum of polyhydrazide (PH-I) in DMSO-d_6. (b) ^{1}H NMR spectrum of poly(1,3,4-oxadiazole), (POD-I) CDCl$_3$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Aromatic protons "*b*" *meta* to ether linkage and aromatic proton "*c*" *ortho* to oxadiazole ring appeared as a multiplet in the region 8.03–8.23 δ ppm. The four aromatic protons *ortho* to ether linkage exhibited a multiplet in the range 7.03–7.27 δ ppm. The benzylic —CH$_2$ appeared as a triplet at 3.14 δ ppm. The methylene protons β to aromatic ring exhibited a multiplet centered at 1.67 δ ppm. The other meth-

ylene protons displayed a multiplet over the range 1.19–1.24 δ ppm. Methyl protons of the aliphatic chain appeared as a triplet at 0.83 δ ppm.

Solubility measurements

The solubility of polyhydrazides and poly(1,3,4-oxadiazole)s bearing pentadecyl side chains was tested

TABLE II
Solubility Data of Polyhydrazides and Poly(1,3,4-oxadiazole)s Bearing Pentadecyl Side Chains

Polymer	CHCl$_3$	DCM	THF	DMF	DMAc	NMP	Pyridine	m-Cresol	DMSO
PH-I	--	--	--	+-	++	++	--	+-	+-
PH-II	--	--	--	++	++	++	++	++	++
PH-III	--	--	--	++	++	++	+-	+-	+-
POD-I	+-	+-	+-	--	--	--	+-	++	--
POD-II	++	++	++	+-	+-	+-	++	++	+-
POD-III	++	++	+-	--	+-	+-	+-	++	--

++ : soluble at room temperature; +− : soluble upon heating; −− : insoluble even on heating.

in various organic solvents at 3 wt % concentration and data is summarized in Table II. Polyhydrazides exhibited excellent solubility in polar aprotic solvents such as DMAc, NMP, DMF, and were also found to be soluble in m-cresol at room temperature or upon heating. The improved solubility of polyhydrazides could be attributed to the flexible pentadecyl side chains in the repeat unit which restricted the close packing of polymer chains and therefore allowed solvent molecules to penetrate into the polymer chains. In spite of having rigid 1,3,4-oxadiazole moiety in the polymer backbone, poly(1,3,4-oxadiazole)s dissolved in solvents such as chloroform, dichloromethane, tetrahydrofuran, pyridine, and m-cresol at room temperature or upon heating. Except for POD-I, rest of the poly(1,3,4-oxadiazole)s were also soluble in polar aprotic solvents such as DMAc and NMP upon heating. Because of the presence of planar and symmetrical 1,4-linkage of terephthaloyl moiety in POD-I it results into more dense chain packing of polymer chains which in turn results into lesser solubility. The enhanced solubility behavior of poly(1,3,4-oxadiazole)s is due to the presence of pentadecyl side chains. The presence of pentadecyl side chains in poly(1,3,4-oxadiazole)s disrupted the packing of polymer chains as well as provided an additional "handle" for interaction with solvents.

X-ray diffraction studies

X-ray diffractograms of polyhydrazides (a) and poly(1,3,4-oxadiazole)s (b) bearing pentadecyl side chains are shown in Figure 3. Polyhydrazides and poly(1,3,4-oxadiazole)s exhibited broad halo at around $2\theta = \sim 20°$ revealing an essentially amorphous nature. The presence of pentadecyl side chain in the polymer backbone hindered chain packing and decreased the crystallinity.

It is generally known that polymers having long flexible side chains crystallize into layered structures in which the main chains come together to form backbone layers and the side chains to form a separate crystal region.[31–35,38,43–45] X-ray diffractograms of polyhydrazides and poly(1,3,4-oxadiazole)s displayed presence of sharp reflection peak in the small-angle region at around $2\theta = \sim 3°$. The observed reflections are characteristics of a typical layered structure resulting from the packing of the pentadecyl side chains.

Thermal properties

In the present study, thermal stability of the polyhydrazides and poly(1,3,4-oxadiazole)s was determined by thermogravimetric analysis (TGA) at a heating rate of 15°C min^{-1} under nitrogen. Thermogravimetric (TG) curves of polyhydrazides and poly(1,3,4-
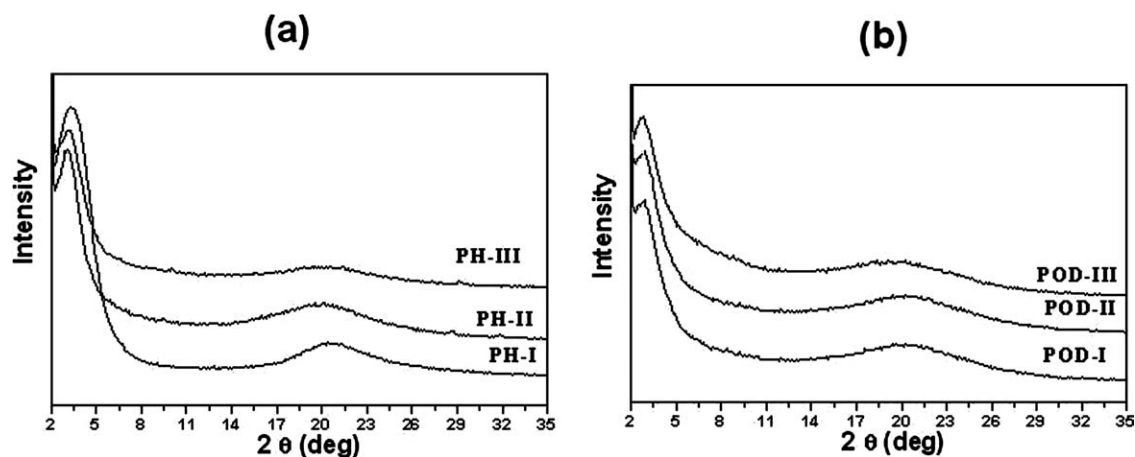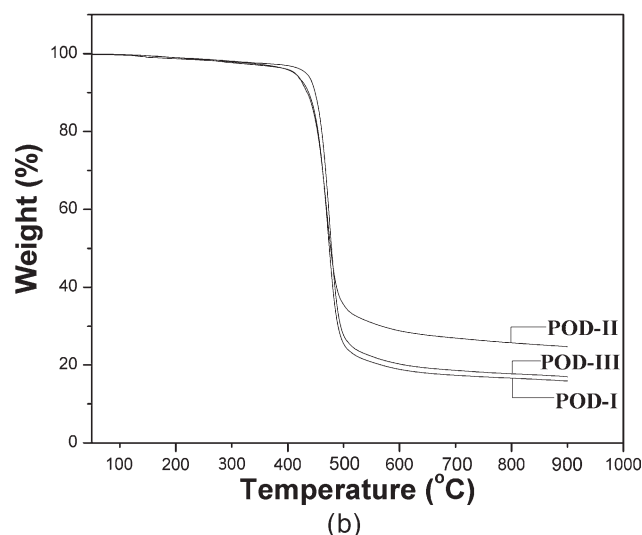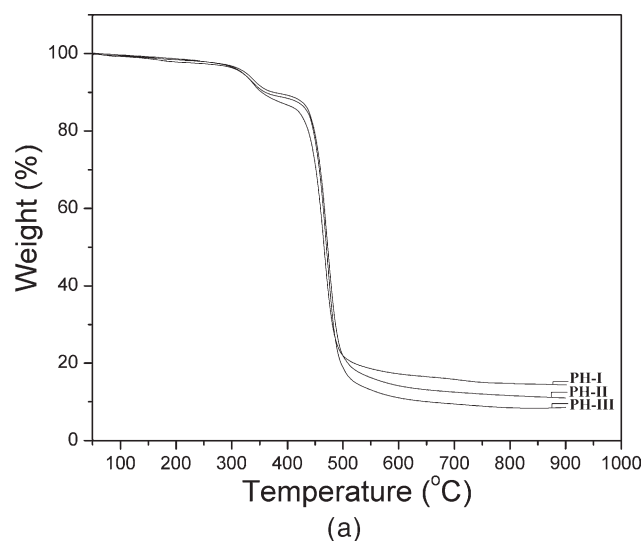

Figure 3 X-ray diffractograms of (a) polyhydrazides and (b) poly(1,3,4-oxadiazole)s bearing pentadecyl side chains.

oxadiazole)s are shown in Figures 4(a,b), respectively. The initial decomposition temperature (T_0), the temperature at 10% weight loss (T_{10}) and the weight residues at 900°C for polymers are given in Table III. The T_0 and the T_{10} value are some of the main criteria to determine the thermal stability of polymers. Polyhydrazides showed a sudden weight loss at around 300°C [Fig. 4(a)] which may be attributed to the loss of water due to the thermally activated cyclodehydration reaction leading to the *in situ* formation of corresponding poly(1,3,4-oxadiazole).[29–32] Poly(1,3,4-oxadiazole)s [Fig. 4(b)] showed degradation temperatures higher than corresponding polyhydrazides owing to the better thermal stability of 1,3,4-oxadiazole ring. The T_{10} values, obtained from TG curves for poly(1,3,4-oxadiazole)s, were in the range 433–449°C indicating their good thermal stability.

TABLE III
Thermal Properties of Polyhydrazides and Poly(1,3,4-oxadiazole)s Bearing Pentadecyl Side Chains

Polymer	T_0 (°C)[a]	T_{10} (°C)[b]	Weight residue at 900°C (%)	T_g (°C)
PH-I	300	–	15	166
PH-II	298	–	09	143
PH-III	303	–	11	148
POD-I	395	435	16	102
POD-II	383	433	25	90
POD-III	404	449	17	100

[a] Initial decomposition temperature.
[b] Temperature at which 10% weight loss was observed.

Glass transition temperature (T_g) of the polyhydrazides and poly(1,3,4-oxadiazole)s was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polymer samples at a heating rate of 10°C min^{-1}. DSC curves for polyhydrazides and poly(1,3,4-oxadiazole)s are reproduced in Figures 5(a,b), respectively. The T_g

Figure 4 (a) TG curves of polyhydrazides bearing pentadecyl side chains. (b) TG curves of poly(1,3,4-oxadiazole)s bearing pentadecyl side chains.
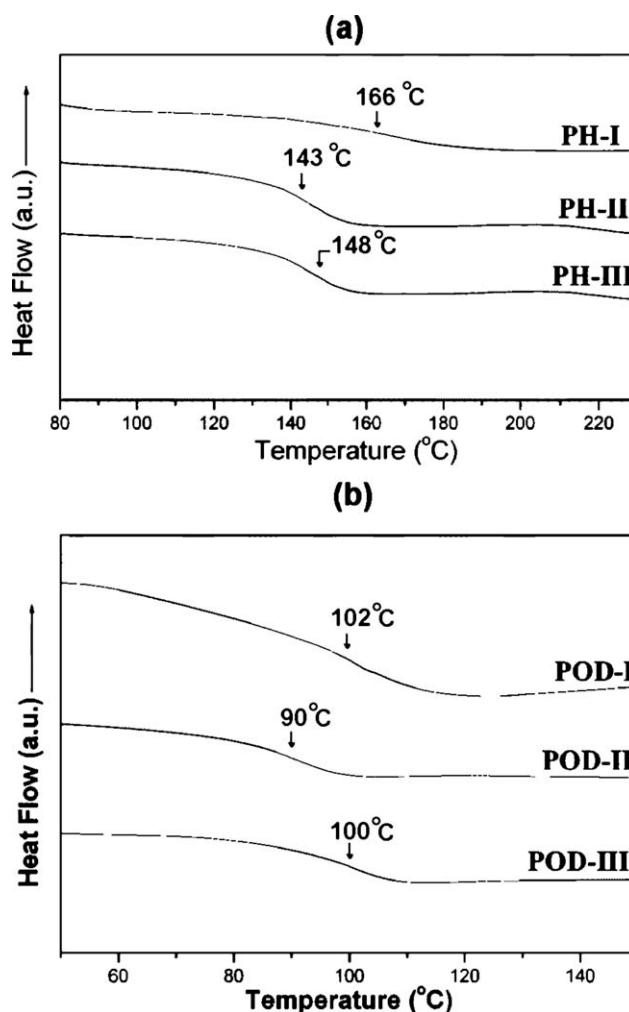

Figure 5 DSC curves of (a) polyhydrazides and (b) poly(1,3,4-oxadiazole)s bearing pentadecyl side chains.

values are given in Table III. The T_g values of PH-I, PH-II, and PH-III were 166, 143, and 148°C, respectively. It is well known that T_g depends on the rigidity of the polymer main chain; the increase of the rigidity of the polymer increases the energy barriers for segmental motion, and hence T_g increases. PH-I showed highest T_g among three PHs. This could be attributed to the rigid 1,4-phenylene unit in the polymer chain which imparts rigidity to the polymer chain. A comparison of the T_g data with analogues polyhydrazides reported in the literature showed that, the polyhydrazide derived from 4,4′-oxybisbenzohydrazide and TPC showed a T_g at 196°C.[46] A drop in T_g values of polyhydrazides synthesized in the present study could be attributed to the "internal plasticization" effect of flexible pentadecyl side chains. The influence of the presence of 1,3,4-oxadiazole unit in the polymer backbone on thermal transitions was evaluated [Fig. 5(b)]. It was observed that, the T_g values of derived poly(1,3,4-oxadiazole)s were lower than that of parent polyhydrazides. Inspite of having rigid 1,3,4-oxadiazole repeat unit in the polymer chain, T_g values observed were in the range 90–102°C. This could be explained in terms of presence of hydrogen bonding in polyhydrazides. The ability of polyhydrazides to form hydrogen bonding overpowered the internal plasticization effect of pentadecyl chains substantially, whereas in polyoxadiazoles, the glass transition temperatures are governed by flexible pentadecyl chains. Similar observations have been reported in the literature for polyhydrazides and their corresponding poly(1,3,4-oxadiazole)s with alkyl chains.[31] A large difference between glass transition (90–102°C) and initial decomposition temperature (383–404°C) was observed for poly(1,3,4-oxadiazole)s, which offers them a wide processing window.

CONCLUSIONS

A series of new poly(1,3,4-oxadiazole)s bearing pentadecyl side chains and ether linkages was synthesized starting from 4-[4′-(hydrazinocarbonyl)-phenoxy]-2-pentadecyl benzohydrazide via cyclodehydration reaction of polyhydrazides in the presence of phosphoryl chloride. Medium to reasonably high molecular weight polyhydrazides and poly(1,3,4-oxadiazole)s were obtained. Polyhydrazides and poly(1,3,4-oxadiazole)s were found to be soluble in common organic solvents either at room temperature or upon heating and could be solution-cast into transparent, flexible and tough films. X-ray diffractograms showed that polyhydrazides and poly(1,3,4-oxadiazole)s bearing pentadecyl side chains were amorphous in nature. In the small-angle region, a reflection was observed for both polyhydrazides and poly(1,3,4-oxadiazole)s indicating formation of layered structure due to ordered packing of pentadecyl chains. Both in the case of polyhydrazides and poly(1,3,4-oxadiazole)s, a decrease in T_g values was observed due to "internal plasticization" effect of pentadecyl side chains. The T_{10} values for poly(1,3,4-oxadiazole)s were in the range 433–449°C indicating their good thermal stability.

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