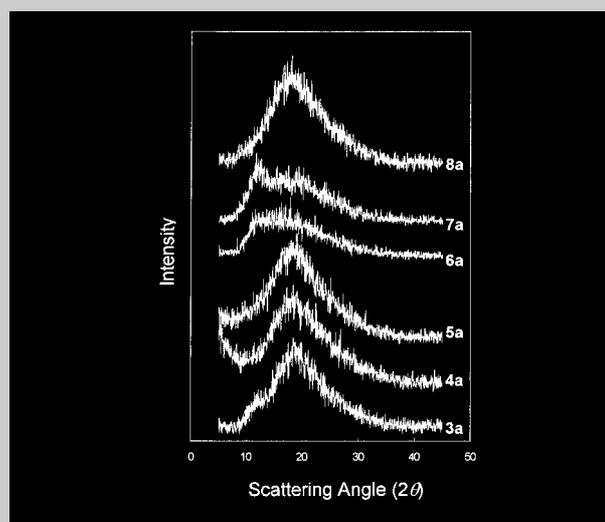


Full Paper: A series of polyhydrazides and poly(amide hydrazide)s bearing ether and cardo groups were prepared from three bis(ether carboxylic acid)s, 1,1-bis[4-(4-carboxyphenoxy)phenyl]cyclohexane, 5,5-bis[4-(4-carboxyphenoxy)phenyl]-4,7-methanohexahydroindan and 9,9-bis[4-(4-carboxyphenoxy)phenyl]fluorene, or their diacyl chlorides with terephthalic dihydrazide, isophthalic dihydrazide and *p*-aminobenzoyl hydrazide via the phosphorylation reaction or the low-temperature solution polycondensation. The resulting hydrazide-containing polymers exhibited inherent viscosities in the range of 0.35–0.71 dL · g⁻¹. All the hydrazide polymers were found to be amorphous as determined by X-ray diffraction analysis and soluble in many organic polar solvents, and most of them afforded flexible and tough films by solvent casting. The hydrazide polymers had glass transition temperatures (T_g) between 157 and 197 °C. All hydrazide polymers could be thermally converted into the corresponding oxadiazole polymers approximately in the region of 270–370 °C, as evidenced by the DSC thermograms. The oxadiazole polymers showed a slightly enhanced crystallinity and an increase of T_g and a dramatically decreased solubility compared to their hydrazide prepolymers. They exhibited T_g 's of 218–259 °C and showed insignificant weight loss up to 450 °C.



Wide-angle X-ray diffractograms of the hydrazide and oxadiazole polymers.

Synthesis and Properties of Novel Cardo Aromatic Poly(ether oxadiazole)s and Poly(ether-amide oxadiazole)s

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Introduction

Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.^[1,2] These polymers were studied as high temperature and flame resistant fibers^[3,4] or thermally stable films.^[5] Recently, oxadiazole-based polymers have been widely investigated in the fields of polymer light-emitting diodes as well as other fields of polymer electronics.^[6–11] Although poly(arylene-1,3,4-oxadiazole)s have a combination of excellent properties, their application is rather

limited due to their poor solubility in organic solvents and their high transition temperatures. For example, poly(1,4-phenylene)-1,3,4-oxadiazole is only soluble in sulfuric acid, a solvent which is very difficult to handle in practice.

Many efforts have been devoted to develop processable polyoxadiazoles by preparing copolymers^[12–15] containing amide, imide or ether groups, by incorporating flexible linkages or hinges into the polymer main chain^[16–18] and by attaching bulky pendant groups onto the polymer

backbone.^[14,16,18] An impressive series of high T_g soluble polymers, referred as cardo polymers, was pioneered in the early 1960s and was reviewed by Korshak et al.^[19] Such polymers contain at least one element in the repeating unit that includes a cyclic side group which imparts a combination of enhanced thermal stability, high T_g , and excellent solubility. We have recently demonstrated that multi-ring dicarboxylic acids and diamines containing both flexible ether linkage and cardo group are able to restrict close chain packing and to attain aromatic polyamides with excellent solubility and modest T_g 's.^[20–22] The present study deals with the synthesis and basic characterization of related aromatic polyoxadiazoles prepared from some of the above mentioned flexible diacids or their acyl chloride derivatives with a view to obtain amorphous polyoxadiazoles which are soluble in solvents other than strong acids and have acceptable T_g which allow melt processability.

Experimental Part

Materials

Diphenyl phosphite (DPP) (from Fluka), terephthalic dihydrazide (TPH) (from TCI), isophthalic dihydrazide (IPH) (from TCI) and *p*-aminobenzoyl hydrazide (*p*-ABH) (from TCI) were used without previous purification. Calcium chloride and lithium chloride were dried under vacuum at 180 °C for 10 h. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Monomer Synthesis

According to a reported procedure,^[23] the bis(ether carboxylic acid) monomers that included 1,1-bis[4-(4-carboxyphenoxy)phenyl]cyclohexane (**1a**) (m.p. 251 °C; peak top temperature of the DSC melting endotherm), 5,5-bis[4-(4-carboxyphenoxy)phenyl]-4,7-methanohexahydroindan (**1b**) (m.p. 278 °C; determined by DSC) and 9,9-bis[4-(4-carboxyphenoxy)phenyl]fluorene (**1c**) (m.p. 293 °C; determined by DSC) were prepared by the fluorodisplacement reaction of *p*-fluorobenzonitrile with the potassium salts of the corresponding bisphenols, i.e., 1,1-bis(4-hydroxyphenyl)cyclohexane, 5,5-bis(4-hydroxyphenyl)-4,7-methanohexahydroindan, and 9,9-bis(4-hydroxyphenyl)fluorene, followed by alkaline hydrolysis of the intermediate bis(ether nitrile)s. Details of the synthesis and characterization data of diacids **1a–c** have been reported in the preceding papers.^[20–22]

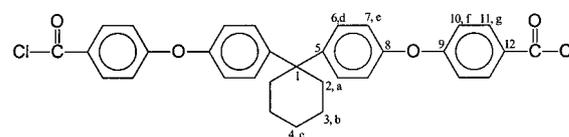
The diacyl chloride monomers were prepared by chlorination of the corresponding bis(ether carboxylic acid)s with thionyl chloride. A typical synthetic procedure for 1,1-bis[4-(4-chloroformylphenoxy)phenyl]cyclohexane (**2a**) is as follows: The bis(ether carboxylic acid) **1a** (10.2 g, 0.02 mol) was suspended in a mixture of 30 mL of thionyl chloride and 30 mL of dichloromethane in the presence of one drop of DMF as the catalyst. After heating the mixture at 60 °C for about 2 h, the suspension solution turned into a clear solu-

tion. The solution was kept at 60 °C for another 2 h to ensure a complete reaction. Dichloromethane and excess of thionyl chloride were removed by distillation. Recrystallization of the crude product from hexane/toluene (130/20 mL) yielded white crystals of pure 1,1-bis[4-(4-chloroformylphenoxy)phenyl]cyclohexane (**2a**). The product was collected by filtration and dried in vacuum to give 10.9 g (76.2%) of **2a**; m.p.: 85.5–87.0 °C.

IR (KBr): 2933 (C–H str.), 1758 (C=O str.), 1593, 1496 (arom. C=C str.), 1257 (C–O), 1171, 883 cm^{-1} (C–Cl).

¹H NMR (400 MHz, in CDCl_3): δ = 8.06 (d, 4H, H_d), 7.34 (d, 4H, H_d), 7.0 (two overlapped AB doublets, 8H, $H_e + H_f$), 2.31 (s, 4H, H_a), 1.58 (m, 6H, $H_b + H_c$).

¹³C NMR (100 MHz, in CDCl_3): δ = 168.16 (C=O), 165.19 (C^9), 153.18 (C^8), 146.27 (C^5), 134.59 (C^{11}), 129.50 (C^6), 127.50 (C^{12}), 120.73 (C^7), 117.59 (C^{10}), 45.28 (C^1), 36.78 (C^2), 25.55 (C^4), 22.11 (C^3).



$\text{C}_{32}\text{H}_{26}\text{O}_4\text{Cl}_2$ (545.46): Calcd. C 70.46 H 4.80; Found C 70.20 H 4.89.

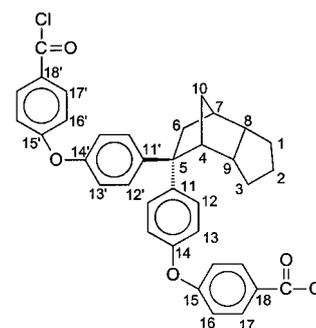
The other two bis(ether acyl chloride)s, 5,5-bis[4-(4-chloroformylphenoxy)phenyl]-4,7-methanohexahydroindan (**2b**) (m.p. 70–72 °C), and 9,9-bis[4-(4-chloroformylphenoxy)phenyl]fluorene (**2c**) (m.p. 256–258 °C), were synthesized in a similar procedure from diacids **1b** and **1c**. The spectroscopic data are shown below.

Bis(ether acyl chloride) **2b**

IR (KBr): 2943 (C–H str.), 1770 (C=O str.), 1591, 1496 (arom. C=C str.), 1252 (C–O), 1159, 885 cm^{-1} (C–Cl).

¹H NMR (400 MHz, CDCl_3): δ = 8.07, 8.05 (2d, 4H, $H_{17,17'}$), 7.37, 7.32 (2d, 4H, $H_{12,12'}$), 6.94–7.00 (m, 8H, $H_{13,13'}$ + $H_{17,17'}$), 2.94 (s, 1H, H_4), 2.32 (2d, 2H, H_{10}), 2.18 (s, 1H, H_9), 1.84 (lump, 4H, $H_{1a,3a,7,8}$), 1.66 (lump, 1H, H_{2a}), 1.56, 1.47 (2d, 2H, $H_{6a,6b}$), 1.08 (lump, 3H, $H_{1b,2b,3b}$).

¹³C NMR (100 MHz, CDCl_3): δ = 169.26 (C=O), 166.24, 166.19 (C^{15} , $C^{15'}$), 153.65, 153.59 (C^{14} , $C^{14'}$), 151.33, 147.11 (C^{11} , $C^{11'}$), 135.63 (C^{17} , $C^{17'}$), 134.06, 131.16 (C^{12} , $C^{12'}$), 130.27 (C^{18} , $C^{18'}$), 121.52 (C^{16} , $C^{16'}$), 118.67, 118.58 (C^{13} , $C^{13'}$), 55.79 (C^4), 50.10 (C^5), 48.52 (C^8), 44.11 (C^{10}), 42.98 (C^7 , C^9), 32.84, 32.52, 32.41 (C^1 , C^3 , C^6), 27.60 (C^2).



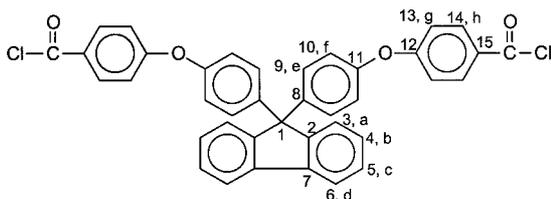
$\text{C}_{36}\text{H}_{30}\text{O}_4\text{Cl}_2$ (597.54): Calcd. C 72.36 H 4.80; Found C 72.20 H 4.89.

Bis(ether acyl chloride) **2c**

IR (KBr): 3 056 (C—H str.), 1 760 (C=O str.), 1 589, 1 493 (arom. C=C str.), 1 254 (C—O), 1 159, 883 cm^{-1} (C—Cl).

^1H NMR (400 MHz, CDCl_3): δ = 8.03 (d, 4H, H_h), 7.79 (d, 2H, H_d), 7.32–7.43 (m, 6H, $\text{H}_a + \text{H}_b + \text{H}_c$), 7.26 (d, 2H, H_e), 6.95, 6.97 (2d, 4H, $\text{H}_f + \text{H}_g$).

^{13}C NMR (100 MHz, CDCl_3): δ = 168.15 (C=O), 164.93 (C^{12}), 154.43 (C^{11}), 151.61 (C^2), 143.49 (C^7), 140.81 (C^8), 134.58 (C^{14}), 130.48 (C^9), 128.58, 128.50 (C^4 , C^5), 127.66 (C^{15}), 126.59 (C^3), 120.95 (C^{10}), 120.74 (C^6), 117.70 (C^{13}), 64.33 (C^1).



$\text{C}_{39}\text{H}_{24}\text{O}_4\text{Cl}_2$ (627.52): Calcd. C 74.65 H 3.85; Found C 74.23 H 3.92.

Preparation of Polyhydrazides and Poly(amide hydrazide)s

Typical procedures for the synthesis of poly(amide hydrazide) **5a** are as follows.

Direct polycondensation via the phosphorylation reaction: In a 50 mL flask, a mixture of equimolar (2 mmol) of diacid **1a** (1.0172 g) and *p*-ABH (0.3025 g) with 0.5 g of CaCl_2 , 4 mL of NMP, 1.2 mL of DPP and 1 mL of pyridine was heated under stirring at 120 °C. After 3 h, the reaction solution became gradually homogeneously transparent, leading to a clear, highly viscous polymer solution. After cooling, the viscous solution was poured slowly under stirring into methanol, giving rise to a tough white fiber-like precipitate. The product was washed repeatedly with methanol and hot water, collected by filtration and then dried at 90 °C to obtain a quantitative yield of poly(amide hydrazide) **5a**. The inherent viscosity of the polymer was 0.71 $\text{dL} \cdot \text{g}^{-1}$, measured in DMSO at a concentration of 0.5 $\text{g} \cdot \text{dL}^{-1}$ at 30 °C.

Low-temperature solution polycondensation: In a 50-mL flask, 1 mmol of *p*-ABH (0.1517 g) was dissolved at room temperature in 5 mL of NMP solution containing 0.2 g of LiCl. After complete dissolution of the solid, the solution was cooled by an external ice-acetone bath, and 1 mmol of diacyl chloride **2a** (0.5455 g) was added into the solution. The reaction was carried out at –10 to 0 °C for 2 h and stirred overnight at room temperature. The resulting viscous solution was poured slowly under stirring into methanol. The white fiber-like precipitate was washed repeatedly with methanol and hot water, collected by filtration and dried to obtain a quantitative yield of poly(amide hydrazide) **5a**. The inherent viscosity of the polymer was 0.64 $\text{dL} \cdot \text{g}^{-1}$, measured in DMSO at a concentration of 0.5 $\text{g} \cdot \text{dL}^{-1}$ at 30 °C.

Film Preparation and Cyclodehydration of the Hydrazide Polymers

A polymer solution was prepared by dissolving about 0.6 g of the polyhydrazides or poly(amide hydrazide)s in 20 mL of

N,N-dimethylacetamide (DMAc). The solutions were filtered over a paper filter to remove any insoluble substances into a flat glass culture dish of 9 cm diameter, which was placed in a 90 °C oven for 12 h to remove the solvent. Then, the obtained semidried polymer film was removed from the glass plates and further dried at 150 °C for 8 h under vacuum. The thickness of the polymer films was controlled to be in the range of 50–60 μm .

The conversion of polyhydrazides and poly(amide hydrazide)s to poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s was carried out by heating the above fabricated polymer films under nitrogen for 30 min at 250 °C, for 30 min at 300 °C, and for 1 h at 320 °C.

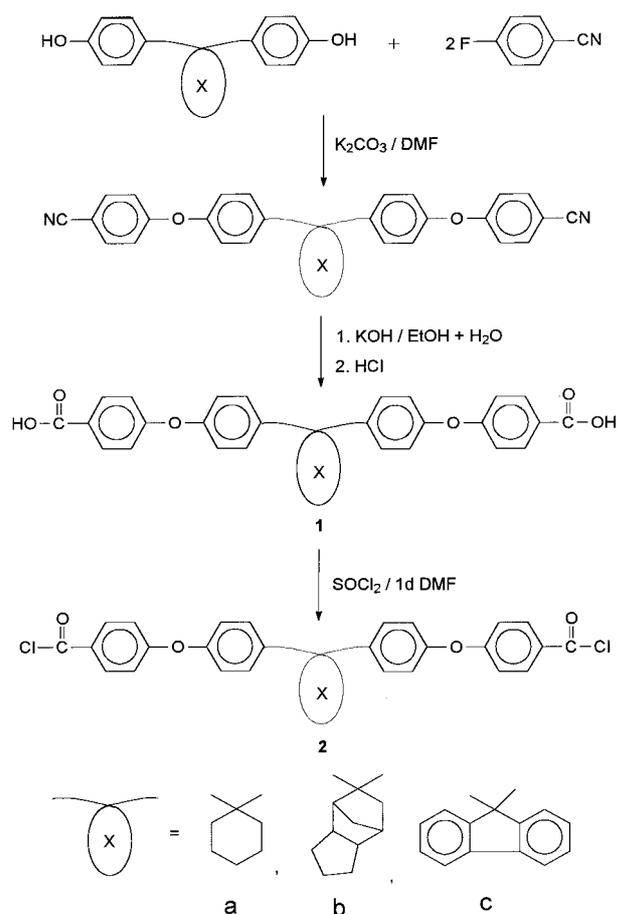
Measurements

The melting points were measured with a MEL-TEMP II apparatus or a differential scanning calorimeter (DSC, heating rate: 10 °C \cdot min $^{-1}$). Elemental analyses were run in a Perkin-Elmer Model 2400 CHN analyzer. IR spectra were recorded on a Horiba FT-720 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained using a Jeol EX-400 spectrometer operating at 399.65 and 100.40 MHz, respectively. The inherent viscosities of polymer solutions were measured with a Cannon-Fenske viscometer at a concentration of 0.5 $\text{g} \cdot \text{dL}^{-1}$ at 30 °C. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC 7 differential scanning calorimeter equipped with a thermal analysis controller TAC 7/DX. Amounts of about 6–8 mg of the polymer samples were placed in aluminum sample pans, and the experiments were carried out with a heating rate of 20 °C \cdot min $^{-1}$ under a nitrogen purge gas stream. Glass transition temperatures (T_g 's) were read at the middle of the change in the heat capacity. Thermogravimetric analysis (TGA) was performed using a DuPont 951 Thermogravimetric Analyzer coupled to a DuPont 2000 Thermal Analyst. Experiments were carried out on 9–11 mg of the samples under nitrogen or air purge gas (50 mL \cdot min $^{-1}$) from 100 to 800 °C at a heating rate of 20 °C \cdot min $^{-1}$. Wide-angle X-ray diffraction measurements were performed at room temperature on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered Cu K_α radiation operating at 40 kV and 15 mA. The scanning rate was 2 deg \cdot min $^{-1}$ over a range of $2\theta = 5$ –45°. An Instron universal tester model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm \cdot min $^{-1}$ were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.05–0.06 mm thick). An average of at least five individual determinations was used.

Results and Discussion

Monomer Synthesis

Bis(ether carboxylic acid)s **1a–c** were prepared via a two-step reaction sequence starting from the aromatic nucleophilic substitution reaction of *p*-fluorobenzonitrile with the potassium phenolates of the corresponding



Scheme 1.

bisphenol precursors. These bis(ether carboxylic acid)s were converted to their corresponding diacyl chlorides by the treatment with thionyl chloride in the presence of a trace amount of DMF. The synthetic route is outlined in Scheme 1. Elemental, infrared, ^1H NMR and ^{13}C NMR analysis confirmed the structures of these diacyl chloride monomers.

Polymer Synthesis

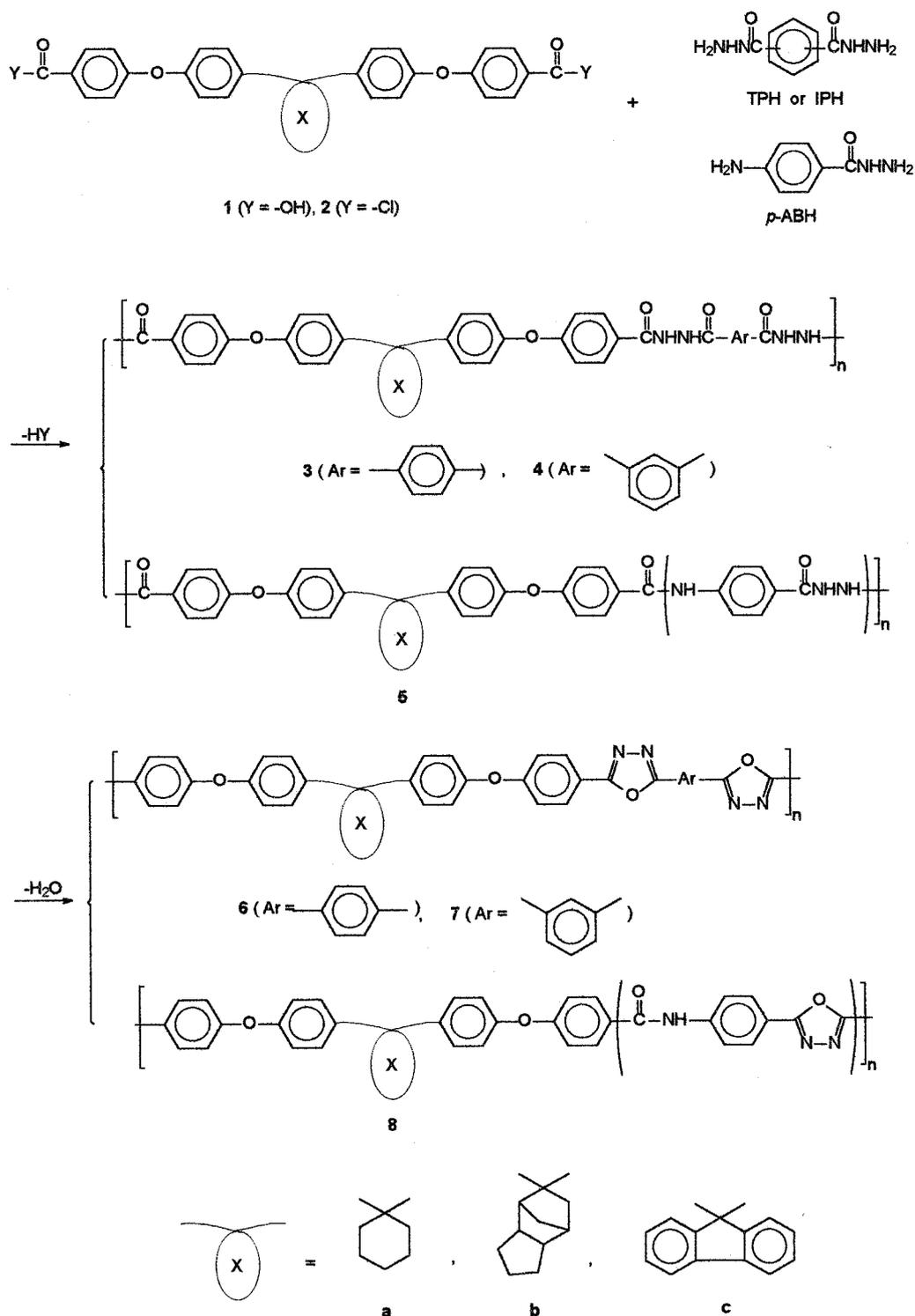
Several different reaction pathways have been developed to prepare poly(1,3,4-oxadiazole)s. The most popular synthesis involves the preparation of a precursor polyhydrazide by the reaction of a diacyl chloride or derivative with hydrazine or a dihydrazide compound. This precursor polyhydrazide is cyclized to the polyoxadiazole by heating to 200–300 °C under vacuum or by heating in a high boiling dehydrating solvent such as sulfuric or polyphosphoric acid.^[24, 25] A different synthetic procedure produces polyoxadiazoles in one step by solution polymerization of a dicarboxylic acid or the corresponding nitrile, amide, or ester with hydrazine or its salt in polyphosphoric, sulfuric acid or a phosphorus pentoxide/methanesulfonic acid mixture.^[25, 26] Because the diacids or diacyl

chlorides used in this study are acid-sensitive monomers which may decompose in a high polar and strong acidic medium, the two-step procedure was employed to prepare polyoxadiazoles. The first stage consists of the synthesis of a polyhydrazide or a poly(amide hydrazide) precursor which is converted to the corresponding poly(1,3,4-oxadiazole) or poly(amide-1,3,4-oxadiazole) by the thermal cyclodehydration of the hydrazide group into the 1,3,4-oxadiazole ring. Both the direct polycondensation and low-temperature solution polycondensation techniques were used for the synthesis of the polyhydrazides and poly(amide hydrazide)s as shown in Scheme 2 from various combinations of monomers. The parentheses in the formulas of polymers **5** and **8** indicate that the unsymmetrical aminobenzoyl hydrazide moiety may appear in the polymer chain as shown or in the reverse order.

First, serial new polyhydrazides **3a–c** and **4a–c** and poly(amide hydrazide)s **5a–c** were prepared by high temperature direct polycondensation of bis(ether carboxylic acid)s **1a–c** with TPH, IPH, and *p*-ABH using diphenyl phosphite (DPP) and pyridine as condensing agents, according to a modification of Yamazaki's and Higashi's phosphorylation method^[27] developed by Higashi and Ishikawa^[28] for the synthesis of poly(amide-hydrazide)s. By using the synthetic conditions listed in Table 1, all the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. Most of the polymers precipitated in a tough fiber-like form when slowly pouring the resulting polymer solutions under stirring into methanol. As shown in Table 1, the polyhydrazides and poly(amide hydrazide)s prepared by this method had inherent viscosities between 0.35 and 0.71 dL · g⁻¹. All polymers except polyhydrazide **3a** could be cast into colorless, flexible and tough films, indicative of moderate to high molecular weight polymers.

In addition, the polyhydrazides and poly(amide hydrazide)s were also prepared by the low-temperature solution polycondensation from bis(ether acyl chloride)s **2a–c** with TPH, IPH and *p*-ABH in the NMP solution containing dissolved LiCl cooled by an ice-acetone bath. The reaction temperature was maintained at –10 to 0 °C in the initial 2 h. In order to obtain maximum molecular weight, the reaction was then carried out overnight at room temperature. As summarized in Table 1, the inherent viscosities of the polymers produced via the acid chloride route stayed in the range of 0.43–0.64 dL · g⁻¹. In general, the inherent viscosities and film properties of the polymers obtained via the low-temperature solution polycondensation technique are comparable to those of the polymers produced via the phosphorylation technique.

The polyhydrazides and poly(amide hydrazide)s were converted to the corresponding poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s by thermal cyclodehydration in bulk. The experiment conditions for the cycli-



Scheme 2.

zation were selected on the basis of the weight loss behavior observed by dynamic TGA and the cyclodehydration endotherm on the DSC thermogram. A typical TGA profile of polyhydrazide **4b** is shown in Figure 1, and the corresponding DSC thermogram is shown in Figure 2. The main endothermal cyclodehydration reaction of the

hydrazide group occurs with water evolution in the range 250–350°C. Thermal conversion of the hydrazide group into 1,3,4-oxadiazole ring was also monitored by FTIR. A thin-film sample of polyhydrazide **4b** cast on a KBr window was heated under nitrogen atmosphere sequentially for 30 min at 250°C, 300°C and 320°C. The IR

Table 1. Synthetic conditions, inherent viscosities and film quality of polyhydrazides and poly(amide hydrazide)s.

Polymer code	Method of preparation ^{a)}	Combination of monomers ^{b)}	Amounts of reagents used ^{c)}					$\eta_{inh}^d)$ dL · g ⁻¹	Film quality ^{e)}
			Monomer scale mmol	NMP mL	Py mL	DPP mL	CaCl ₂ g		
3a	A	1a + TPH	2	5	1.25	2	0.5	0.47	Brittle
	B	2a + TPH	1	5				0.58	Brittle
4a	A	1a + IPH	2	4	1	2	0.4	0.49	Flexible
	B	2a + IPH	1	5				0.64	Flexible
5a	A	1a + <i>p</i> -ABH	2	5	1.25	2	0.5	0.71	Flexible
	B	2a + <i>p</i> -ABH	1	5				0.64	Flexible
3b	A	1b + TPH	1.5	3	1	1.5	0.3	0.35	Flexible
	B	2b + TPH	1	5				0.55	Flexible
4b	A	1b + IPH	1.5	2.5	1	1.5	0.3	0.51	Flexible
	B	2b + IPH	1	5				0.48	Flexible
5b	A	1b + <i>p</i> -ABH	1.5	3	1	1.5	0.3	0.60	Flexible
	B	2b + <i>p</i> -ABH	1	5				0.43	Flexible
3c	A	1c + TPH	1.25	5	1	1.5	0.3	0.43	Flexible
	B	2c + TPH	1	8				0.52	Flexible
4c	A	1c + IPH	1.25	3	1	1.5	0.3	0.53	Flexible
	B	2c + IPH	1	8				0.65	Flexible
5c	A	1c + <i>p</i> -ABH	1.25	4	1	1.5	0.3	0.60	Flexible
	B	2c + <i>p</i> -ABH	1	8				0.44	Flexible

a) A: direct polycondensation; B: low-temperature polycondensation.

b) TPH: terephthalic hydrazide; IPH: isophthalic hydrazide; *p*-ABH: *p*-aminobenzoyl hydrazide.

c) Py: pyridine; DPP: diphenyl phosphite. The reaction was carried out at 120 °C for 3 h.

d) Measured at a concentration of 0.5 g · dL⁻¹ in DMSO at 30 °C.

e) Films were cast from slow evaporation of polymer solutions in DMAc. All the films are optically transparent, almost colorless.

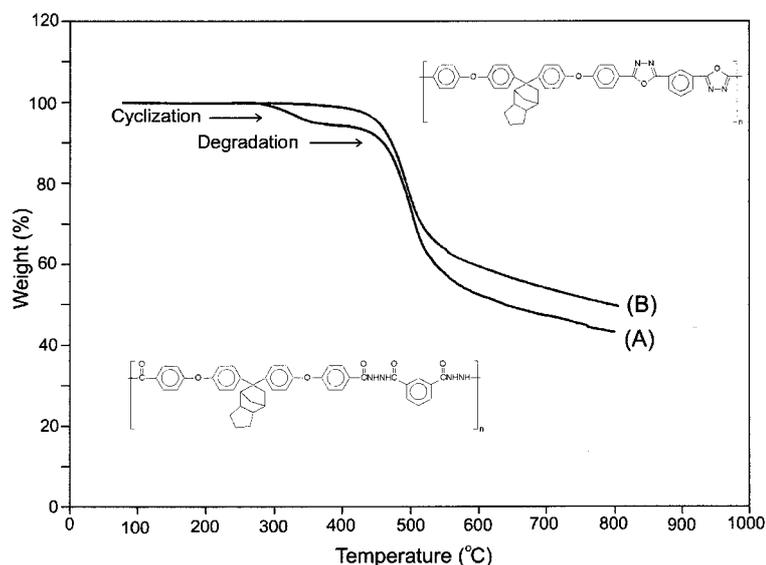


Figure 1. TGA curves of polyhydrazide **4b** (A) and poly(1,3,4-oxadiazole) **7b** (B) with a heating rate of 20 °C · min⁻¹ in nitrogen.

spectra of these samples are illustrated in Figure 3. Cyclization of polyhydrazide **4b** to poly(1,3,4-oxadiazole) **7b** clearly occurred at 300 °C as seen by the disappearance of characteristic hydrazide N-H peak at 3263 cm⁻¹ and only a small carbonyl absorbance remaining at 1647 cm⁻¹. Almost complete conversion to the polyoxadiazole was

observed at 320 °C, with disappearance of the carbonyl stretch at 1647 cm⁻¹. The characteristic band due to the oxadiazole ring vibration, usually reported^[29] in the region between 1500 and 1600 cm⁻¹, were probably buried in the strong absorption bands at 1500 and 1600 cm⁻¹ peculiar to the phenylene skeletal vibrations.

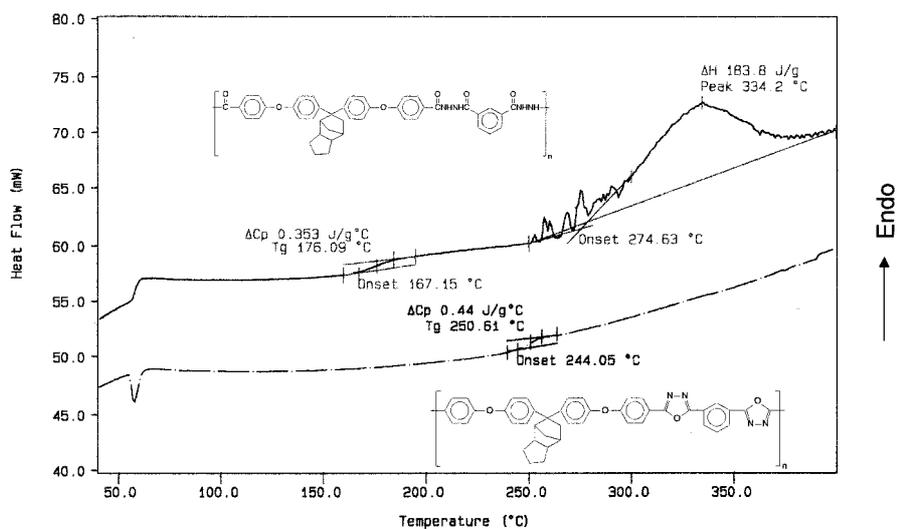


Figure 2. DSC curves of polyhydrazide **4b** and the corresponding poly(1,3,4-oxadiazole) **7b** with a heating rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$ in nitrogen.

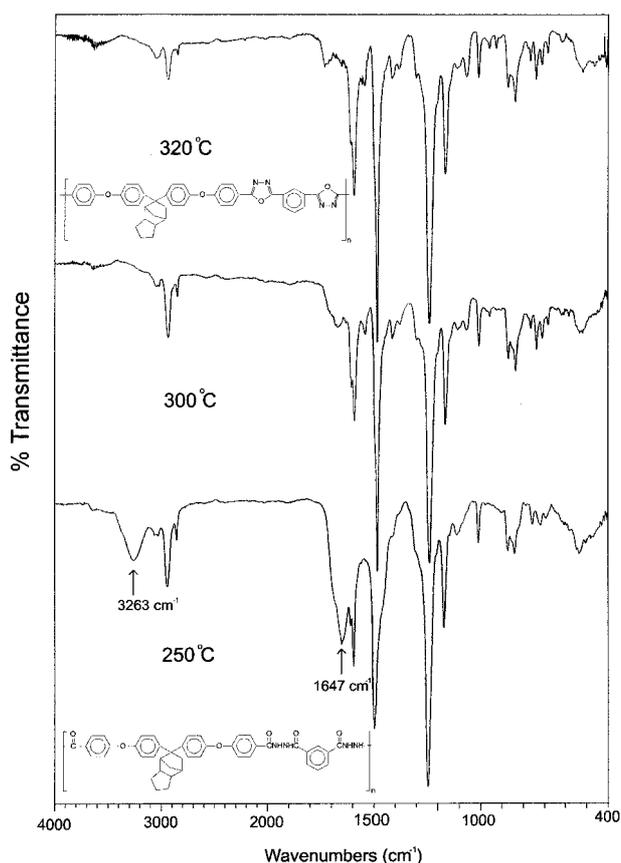


Figure 3. IR spectra of polyhydrazide **4b** after sequential heating 30 min at the indicated temperatures.

Polymer Properties

The samples of the polyhydrazides and poly(amide hydrazide)s obtained by the direct polycondensation technique were characterized.

The results of solubility tests of the hydrazide and oxadiazole polymers are listed in Table 2. As expected, all of the polyhydrazides and poly(amide hydrazide)s showed excellent solubility and were readily soluble in polar solvents such as NMP, DMAc, DMF, and DMSO at room temperature, and in hot *m*-cresol. However, the oxadiazole polymers showed less solubility than the corresponding hydrazide prepolymers, because of the increased chain rigidity. As can be seen from Table 2, the oxadiazole polymers of the **6–8a** and **6–8b** series were insoluble in all the test organic solvents. They dissolved in concentrated sulfuric acid but not in methanesulfuric acid. However, the **6–8c** series polymers were soluble at least in NMP at room temperature and in *m*-cresol upon heating. The relatively higher solubility associated with these polymers are believed to be related to the presence of rigid, bulky, and aromatic fluorene units, which hamper the close packing of chains and decrease inter-chain interactions. Good solubility behavior of poly(amide-1,3,4-oxadiazole) **8c** in organic solvents can be explained by the additional effects of molecular irregularity and a lower density of oxadiazole ring per repeat unit. The slight solubility differences between the **6–8a** or **6–8b** and **6–8c** series may be attributable to the fact that the pendant segment of the former is nonaromatic and has motional flexibility involving boat-chair-twisted boat or *exo-endo* conformational transformations, which possibly results in a better chain packing. Moreover, it was found that most of the oxadiazole polymers were also soluble in the solvent system consisting of a nitroalkane and a Lewis acid, such as nitromethane containing 10 wt.-% AlCl_3 , similar to the results reported in literature.^[30] This is an indication that interactions may exist between the nitrogen atoms of the oxadiazole ring and the Lewis acid.

Table 2. Solubility behavior of hydrazide and oxadiazole polymers. +: soluble at room temperature, +h: soluble on heating at 100 °C, ±: partially soluble, -: insoluble even on heating.

Polymer code	Solvent ^{a)}							
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	CH ₃ NO ₂ / 10 wt.-% AlCl ₃	H ₂ SO ₄	CH ₃ SO ₃ H
3a	+	+	+	+	+h			
4a	+	+	+	+	+h			
5a	+	+	+	+	+h			
3b	+	+	+	+	+h			
4b	+	+	+	+	+h			
5b	+	+	+	+	+h			
3c	+	+	+	+	+h			
4c	+	+	+	+	+h			
5c	+	+	+	+	+h			
6a	-	-	-	-	-	+	+	-
7a	-	-	-	-	-	±	+	-
8a	-	-	-	-	-	+	+	-
6b	-	-	-	-	-	+	+	-
7b	-	-	-	-	-	±	+	-
8b	-	-	-	-	-	-	+	-
6c	+	-	-	-	+h	+	+	-
7c	+	-	-	-	+h	+	+	-
8c	+	+	+	+h	+h	+	+	-

^{a)} NMP: *N*-methyl-2-pyrrolidone, DMAc: *N,N*-dimethylacetamide, DMF: *N,N*-dimethylformamide, DMSO: dimethyl sulfoxide.

Table 3. Tensile properties of polyhydrazides and poly(amide hydrazide)s. Films were cast from slow evaporation of polymer solutions in DMAc. The cast films were dried under vacuum at 150 °C for 6 h prior to tensile test.

Polymer code	Tensile strength	Elongation to break	Tensile modulus
	MPa	%	GPa
4a	77	12	1.8
5a	71	13	2.1
3b	72	12	2.0
4b	71	10	1.6
5b	72	9	1.8
3c	75	12	2.5
4c	73	11	1.8
5c	90	9	2.6

As described in Table 1, all the hydrazide polymers except **3a** could be solution-cast into flexible and creasable films. These flexible films were subjected to tensile testing, and the results are summarized in Table 3. Their tensile strengths, elongations to break, and tensile moduli were in the range 71–90 MPa, 9–13% and 1.6–2.6 GPa, respectively. Various polyhydrazide and poly(amide hydrazide) films were thermally converted into poly(1,3,4-oxadiazole) and poly(amide-1,3,4-oxadiazole) films under a nitrogen atmosphere in a furnace with a heating program: 250 °C for 30 min, 300 °C for 30 min, and 320 °C for 1 h. However, conversion resulted in almost all cases (except for poly(amide-1,3,4-oxadiazole) **8c**) in embrittled oxadiazole films. Due to the conjugation between the oxadiazole ring and the phenylene unit and/or the increased charge transfer complex formation

between chains, the films turned from colorless into pale yellow or brownish after heat treatment. The films were so brittle that they cracked upon creasing. No mechanical properties could be measured. The observed brittleness may be explained in terms of stress build-up caused by chain shrinkage upon conversion.

The wide-angle X-ray diffraction patterns of all the hydrazide and oxadiazole polymers over the 2θ range of 5–45° are shown in Figure 4. All of the hydrazide polymers revealed an essentially amorphous pattern. Obviously, the bulky cardo groups hindered chain packing and reduced the level of crystallinity. The amorphous nature of these polymers was also reflected in their good solubility. After the conversion of hydrazide polymers into the corresponding oxadiazole polymers, the **6a–c** and **7a–c** series poly(1,3,4-oxadiazole)s displayed slightly enhanced crystallinity because of their rigid molecular structure due to the presence of oxadiazole ring. The common feature of their diffraction patterns is the presence of a medium to strong reflection hump around $2\theta = 12^\circ$, indicating a higher packing density. However, poly(amide-1,3,4-oxadiazole)s **8a–c**, despite the presence of the rigid oxadiazole ring, showed no increased ordering as indicated by the X-ray diffractograms. This may be attributed to the fact that the regularity of the repeating units in polymer **8a–c** is disrupted by the different appearing orders of the amide and oxadiazole groups, thus leading to a decreased crystallinity. The almost completely amorphous nature of poly(amide-1,3,4-oxadiazole) **8c** was also reflected in its good solubility in organic solvents.

Table 4. Thermal behavior data of hydrazide and oxadiazole polymers.

Polyhydrazides and poly(amide hydrazide)s ^{a)}			Poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s					
Code	T_g °C	T_o °C	T_p °C	Code	$\eta_{inh}^{b)}$ dL · g ⁻¹	$T_g^{c)}$ °C	$T_d^{d)}$ °C	Char yield ^{e)} %
							in N ₂	in air
3a	178	275	353	6a		218	478	478
4a	157	286	352	7a		219	484	480
5a	185	299	347	8a		221	482	489
3b	190	277	331	6b		254	473	491
4b	176	265	334	7b		251	475	489
5b	197	290	344	8b		252	475	482
3c	194	270	352	6c	0.40	254	513	504
4c	187	287	354	7c	0.41	250	511	507
5c	190	291	348	8c	0.53	259	502	511

^{a)} DSC data from the first DSC heating trace at 20 °C · min⁻¹, T_g : midpoint of baseline shift on the DSC curve, T_o : extrapolated onset temperature of the endotherm peak, T_p : endotherm peak temperature.

^{b)} Measured in NMP at a concentration of 0.5 g · dL⁻¹ at 30 °C.

^{c)} Midpoint temperature of baseline shift on the second DSC heating trace of the sample after quenching from 400 °C.

^{d)} The temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C · min⁻¹ in nitrogen and in air.

^{e)} Residual wt.-% when heated to 800 °C in nitrogen.

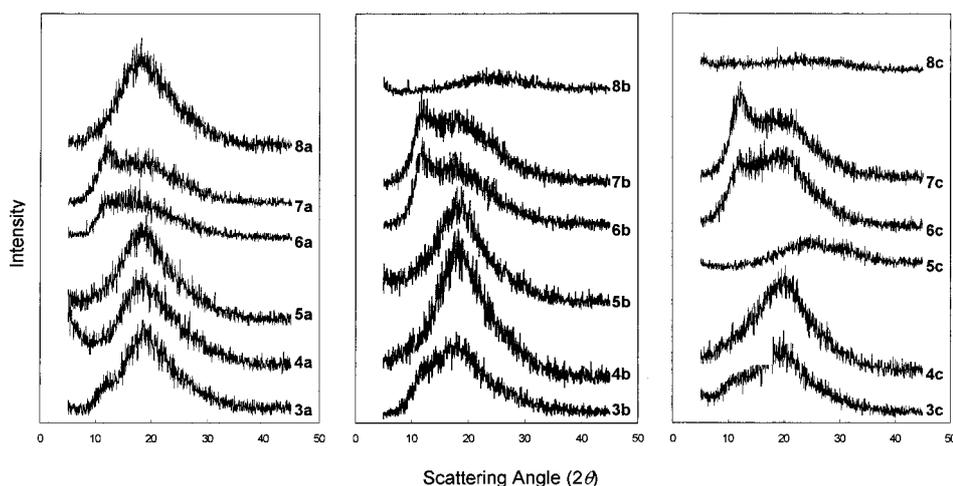


Figure 4. Wide-angle X-ray diffractograms of the hydrazide and oxadiazole polymers.

The thermal behavior of all the hydrazide and oxadiazole polymers was investigated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in nitrogen. The relevant results are reported in Table 4.

Each sample was subjected to three subsequent DSC heating runs, the first run from 30 to 250 °C, after which the sample was cooled down with 100 °C · min⁻¹ to 30 °C, followed by a second run from 30 to 400 °C, after which the sample was cooled down again with 100 °C · min⁻¹ to 30 °C, followed by a third run with an end temperature of 400 °C. All scans were recorded with a programmed rate of 20 °C · min⁻¹ under nitrogen atmosphere. The first run was aimed to eliminate any possible volatiles such as the absorbed moisture and the residual solvent in the samples. The second run yields the glass-transition temperature (T_g) and endothermic peak due to cyclodehydration of the polyhydrazide or poly(amide hydrazide) sample.

After rapid cooling from the elevated temperature, the poly(1,3,4-oxadiazole)s or poly(amide-1,3,4-oxadiazole)s formed *in situ* in the DSC cell were predominantly amorphous. Thus, in the third run, all the oxadiazole polymers exhibited a clear heat capacity jump. A typical pair of DSC curves for polyhydrazide **4b** and poly(1,3,4-oxadiazole) **7b** are shown in Figure 2 (only the second and third heating runs are shown). During the second run to 400 °C, polyhydrazide **4b** showed a clear T_g around 176 °C and a strong endotherm between 275 and 400 °C due to the conversion of the hydrazide group into the 1,3,4-oxadiazole ring. After quenching from 400 °C, in the subsequent scan of the poly(1,3,4-oxadiazole) **7b** which is formed *in situ* during the second heating scan reveals an obvious T_g at 251 °C. All the other polymers displayed similar DSC traces, and some of the DSC data are given in Table 4. All the hydrazide precursor polymers showed a distinct T_g centered in the range of 157–194 °C depending on the

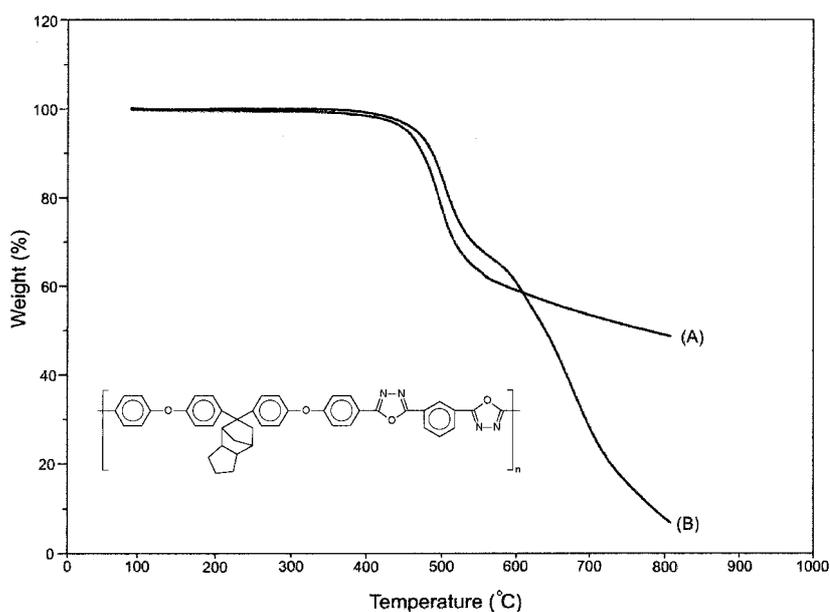


Figure 5. TGA curves of poly(1,3,4-oxadiazole) **7b** in nitrogen (A) and in air (B) with a heating rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$.

chemical structure. The T_g values are influenced by several factors, e.g. chain symmetry and inter-chain interactions, but they primarily depend on chain flexibility. Thus, the polyhydrazides (**4a–c**) derived from *m*-oriented aromatic dihydrazide component (IPH) showed relatively lower T_g 's as compared with their *p*-oriented counterparts (**3a–c**). As can be seen from the DSC thermograms, all the hydrazide polymers were almost completely converted to the corresponding oxadiazole polymers when heated to $350\text{--}400^{\circ}\text{C}$ at a scan rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$ in nitrogen. The thermally converted oxadiazole polymers had T_g 's in the range $218\text{--}259^{\circ}\text{C}$. Due to the increased chain stiffness, all the oxadiazole polymers exhibited higher T_g values than the corresponding hydrazide polymers by $36\text{--}69^{\circ}\text{C}$. It is interesting to note that the poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s derived from the same bis(ether carboxylic acid) showed similar T_g values. This indicates that the catenation position on the phenylene unit does not play an important role in determining the T_g 's of the rigid oxadiazole-based polymers. Another interesting point is that in most cases the polymers, either hydrazide or oxadiazole polymers, derived from diacid **1b** exhibited similar T_g values comparable to those based on diacid **1c**. The result may indicate that the methanohexahydroindan and fluorene cardo groups have a similar effect on chain flexibility. On the other hand, the **3–5a** series hydrazide polymers and the **6–8a** series oxadiazole polymers exhibited lower T_g 's if compared with the corresponding analogs of the **b** and **c** series polymers. This is reasonable because the cyclohexane structure has a smaller effect of steric hindrance in comparison with the other two bulkier cardo groups.

Figure 1 shows a typical pair of TGA curves measured in nitrogen for the representative polyhydrazide **4b** and poly(1,3,4-oxadiazole) **7b**. Weight loss corresponding to conversion of the polyhydrazide **4b** to the poly(1,3,4-oxadiazole) **7b** started at temperature in the vicinity of 270°C and continued for another 100°C . This is also in good agreement with the strong endothermic peak between 270 and 370°C in the DSC trace. The initial weight loss amount to 5 wt.-% corresponded well to the calculated amount (4.7%) of the water released from cyclization. The second break in the TGA curve occurred at around 450°C and corresponded to decomposition of the poly(1,3,4-oxadiazole) formed in situ. A comparison of TGA behavior in air and in nitrogen for the representative poly(1,3,4-oxadiazole) **7b** is shown in Figure 5. At earlier stages the decomposition rate in air is slower than in nitrogen, possibly due to oxidative crosslinking or an early weight-gained oxidation of the aliphatic cardo groups when thermally degraded in air. The other polymers showed a similar TGA behavior, and the TGA data of all oxadiazole polymers are listed in Table 4. The polymers **6–8c** with fluorene cardo groups showed good thermal stability, with 10% weight loss temperatures being recorded above 500°C in air or nitrogen atmosphere. As expected, the polymers containing aliphatic cardo group revealed a lower thermal stability and char residue.

Conclusions

A series of novel polyhydrazides and poly(amide hydrazide)s bearing ether and cardo groups were successfully prepared from 1,1-bis[4-(4-carboxyphenoxy)phenyl]cyclohexane (**1a**), 5,5-bis[4-(4-carboxyphenoxy)-phenyl]-

4,7-methanohexahydroindan (**1b**) and 9,9-bis[4-(4-carboxyphenoxy)phenyl]fluorene (**1c**) or their diacyl chlorides (**2a–c**) with TPH, IPH and *p*-ABH via the phosphorylation reaction or the low-temperature solution polycondensation. All the hydrazide polymers were amorphous and soluble in various polar solvents such as NMP, DMAc, DMF, DMSO and *m*-cresol. Most of them could be solution-cast into flexible, transparent (almost colorless) and tough films. The polyhydrazides and poly-(amide hydrazide)s had T_g 's in the range of 157–197 °C and could be thermally cyclodehydrated into the corresponding oxadiazole polymers in the region of 270–370 °C. The oxadiazole polymers showed a slightly enhanced crystallinity and a slight increase in T_g and a dramatically decreased solubility compared to their hydrazide prepolymers. The polymers with bulkier cardo groups such as the 4,7-methanohexahydroindan and fluorene units had higher T_g values. The oxadiazole polymers exhibited T_g 's in the range of 218–259 °C and did not show significant weight loss before 470 °C. The wholly aromatic poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole) showed good thermal stability, with 10% weight loss temperatures being recorded higher than 500 °C. The large window between the T_g and the decomposition temperature could be advantageous in the processing of these polymers.

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