

# Synthesis and Properties of Novel Aromatic Polyhydrazides and Poly(amide–hydrazide)s Based on the Bis(ether benzoic acid)s from Hydroquinone and Substituted Hydroquinones

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**ABSTRACT:** 4,4'-(1,4-Phenylenedioxy)dibenzoic acid as well as the 2-methyl-, 2-*tert*-butyl-, or 2-phenyl-substituted derivatives of this dicarboxylic acid were synthesized in two main steps from *p*-fluorobenzonitrile and hydroquinone or its methyl-, *tert*-butyl-, or phenyl-substituted derivatives. Polyhydrazides and poly(amide–hydrazide)s were prepared from these bis(ether benzoic acid)s or their diacyl chlorides with terephthalic dihydrazide, isophthalic dihydrazide, or *p*-aminobenzoyl hydrazide by means of the phosphorylation reaction or low-temperature solution polycondensation. Most of the hydrazide polymers and copolymers are amorphous and readily soluble in various polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide. They could be solution-cast into transparent, flexible, and tough films. These polyhydrazides and poly(amide–hydrazide)s had  $T_g$ s in the range of 167–237°C and could be thermally cyclodehydrated into the corresponding poly(1,3,4-oxadiazole)s and poly(amide–1,3,4-oxadiazole)s approximately in the region of 250–350°C, as evidenced by the DSC thermograms. All the *tert*-butyl-substituted oxadiazole polymers and those derived from isophthalic dihydrazide were organic soluble. The thermally converted oxadiazole polymers exhibited  $T_g$ s in the range of 208–243°C and did not show significant weight loss before 450°C either in nitrogen or in air. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 1169–1181, 1999

**Keywords:** hydroquinone; bis(ether benzoic acid)s; polyhydrazides; poly(amide–hydrazide)s; poly(1,3,4-oxadiazole)s; poly(amide–1,3,4-oxadiazole)s

## INTRODUCTION

Aromatic polyhydrazides are well-known from the work of DuPont scientists<sup>1–3</sup> in the early 1960s. They also demonstrated that these polymers could be thermally cyclodehydrated into the poly(1,3,4-oxadiazole)s. Aromatic poly(amide–hydrazide)s were developed extensively by Monsanto scientists in the early 1970s. Details of poly(amide–hydrazide) synthesis have been reported by Culbertson and Murphy<sup>4</sup> and by Black, Pres-

ton, and co-workers.<sup>5,6</sup> High-strength, high-modulus fibers have been made from poly(terephthalic hydrazide) and poly(amide–hydrazide)s with ordered structures.<sup>6–9</sup> Yang<sup>10</sup> has made an excellent review on hydrazide polymers and copolymers.

Aromatic polyhydrazides are generally prepared by the low-temperature solution polycondensation of an aromatic dihydrazide with an aromatic diacid chloride in amide solvents such as NMP and *N,N*-dimethylacetamide (DMAc) in the presence of an inorganic salt like lithium chloride.<sup>1–9</sup> High molecular weight polyhydrazides and poly(amide–hydrazide)s<sup>11,12</sup> also could be prepared by the direct polycondensation from a

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dihydrazide or aminohydrazide monomer with an aromatic dicarboxylic acid using the Yamazaki–Higashi phosphorylation technique,<sup>13</sup> which was popularly used in the polyamide synthesis recently. In our previous papers,<sup>14,15</sup> we have described the preparation of bis(ether benzoic acid)s derived from hydroquinone and its derivatives as well as their derived aromatic polyamides. To more fully evaluate the preparation of other polymer systems on the basis of the prepared dicarboxylic acids, the present study extends their use in the preparation of polyhydrazides and poly-(amide–hydrazide)s. Basic characterization of these novel polymers and the thermal cyclodehydration to poly(1,3,4-oxadiazole)s and poly-(amide–1,3,4-oxadiazole)s are also investigated. Incorporation of ether linkages into the polymer backbone and attachment of pendent groups on the aromatic rings are expected to increase the solubility of the oxadiazole polymers.

## EXPERIMENTAL

### Materials

Hydroquinone (**1**) (from Acros), methylhydroquinone (Me-**1**) (from Tokyo Chemical Industry; TCI), *tert*-butylhydroquinone (*t*-Bu-**1**) (from Acros), phenylhydroquinone (Ph-**1**) (from Aldrich), *p*-fluorobenzonitrile (from Wako), diphenyl phosphite (DPP) (from TCI), terephthalic dihydrazide (TPH) (from TCI), isophthalic dihydrazide (IPH) (from TCI), and *p*-aminobenzoyl hydrazide (*p*-ABH) (from TCI) were used without previous purification. Commercially obtained anhydrous calcium chloride was 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

#### Syntheses of Bis(ether benzonitrile)s

The bis(ether nitrile)s were prepared from the nucleophilic fluorodisplacement reaction of *p*-fluorobenzonitrile with the corresponding hydroquinones in a polar solvent such as DMF in the presence of a base such as potassium carbonate. A representative procedure for the preparation of bis(ether nitrile) *t*-Bu-**2** is as follows.

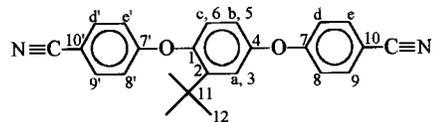
In a 1000-mL round-bottomed flask, 16.6 g (0.1 mol) of *tert*-butylhydroquinone (*t*-Bu-**1**) and 27.6 g (0.2 mol) of potassium carbonate were suspended in a mixture of 100 mL of DMF and 30 mL of toluene. The suspension solution was heated at a reflux temperature using a Dean–Stark trap to remove the water by azeotropic distillation with toluene. After complete removal of water, the residual toluene was distilled off. Then, the reaction mixture was cooled to about 60°C, and 24.4 g (0.2 mol + 0.2 g) of *p*-fluorobenzonitrile was added and heating was continued at 150°C for 10 h. On cooling, the reaction solution was poured into 700 mL of water, and the precipitated solid was collected and washed thoroughly with water. The yield of the crude product was quantitative. Recrystallization from acetonitrile–methanol (120/30 mL) yields a brown granular crystal of pure 4,4'-(2-*tert*-butyl-1,4-phenylenedioxy)dibenzonitrile (*t*-Bu-**2**). The yield of the purified product was 31.7 g (86%); mp 112–113°C.

IR (KBr): 2222 (C≡N str.), 1603–1481 (arom. C=C str.), 1236 cm<sup>-1</sup> (C—O—C str.).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.60 (two overlapped AB doublets, 4H, H<sub>e</sub> + H<sub>e'</sub>), 7.13 (s, 1H, H<sub>a</sub>), 7.00 (two overlapped AB doublets, 4H, H<sub>d</sub> + H<sub>d'</sub>), 6.87 (s, 2H, H<sub>b</sub> + H<sub>c</sub>), 1.32 ppm (s, 9H, —CH<sub>3</sub>).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 161.49 (C<sup>1</sup>), 161.45 (C<sup>4</sup>), 150.06 (C<sup>7</sup>), 150.44 (C<sup>7'</sup>), 144.33 (C<sup>2</sup>), 134.16 (C<sup>9</sup>), 134.10 (C<sup>9'</sup>), 122.82 (C<sup>3</sup>), 119.98 (C<sup>6</sup>), 118.88 (C<sup>5</sup>), 118.67 (—C≡N), 117.92 (C<sup>8</sup>), 117.55 (C<sup>8'</sup>), 105.74 (C<sup>10</sup>, C<sup>10'</sup>), 34.87 (C<sup>11</sup>), 29.88 ppm (C<sup>12</sup>).

Anal. Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (368.43): C, 78.24%; H, 5.47%; N, 7.6%. Found: C, 77.92%; H, 5.66%; N, 7.59%.



The other three bis(ether benzonitrile)s, 4,4'-(1,4-phenylenedioxy)dibenzonitrile (**2**) (mp 212–213°C), 4,4'-(2,5-tolylenedioxy)dibenzonitrile (Me-**2**) (mp 162–163°C), and 4,4'-(2,5-biphenylenedioxy)dibenzonitrile (Ph-**2**) (mp 191–192°C), were prepared by an analogous procedure using hydroquinone, methylhydroquinone, and phenylhydroquinone, respectively, instead of *tert*-butylhydroquinone. The characterization data for these three bis(ether benzonitrile)s have been reported in a previous publication.<sup>15</sup>

### Syntheses of Bis(ether benzoic acid)s

The bis(ether benzoic acid)s were prepared from alkaline hydrolysis of the corresponding bis(ether benzonitrile)s. A representative synthetic procedure for bis(ether benzoic acid) *t*-Bu-**3** is described as follows.

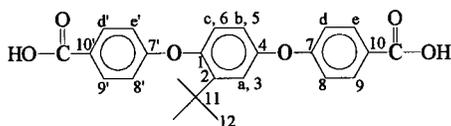
Bis(ether benzonitrile) *t*-Bu-**2** (30 g, 0.0814 mol) was suspended in a mixed ethanol/water solution (150 mL/150 mL) containing dissolved 46 g (0.814 mol) of potassium hydroxide. The suspension turned into a clear solution when heated to reflux, and reflux was continued for about 30 h until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and acidified by concentrated HCl to pH = 2–3 to precipitate a white solid which was filtered out, thoroughly washed with water, and dried *in vacuo* to afford 32.62 g (98.6%) of 4,4'-(2-*tert*-butyl-1,4-phenylenedioxy)dibenzoic acid (*t*-Bu-**3**); mp 292–295°C.

IR (KBr): 2960–2546 (O—H str.), 1689 (C=O str.), 1605–1425 (arom. C=C str.), 1231 cm<sup>-1</sup> (C—O—C str.).

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 12.5 (broad, 2H, —COOH), 7.95 (two overlapped AB doublets, 4H, H<sub>e</sub> + H<sub>e'</sub>), 7.13 (s, 1H, H<sub>a</sub>), 7.03 (two overlapped AB doublets, 4H, H<sub>d</sub> + H<sub>d'</sub>), 6.96 (s, 2H, H<sub>b</sub> + H<sub>b'</sub>), 1.28 ppm (s, 9H, —CH<sub>3</sub>).

<sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 166.82 (C=O), 161.43 (C<sup>4</sup>), 161.14 (C<sup>1</sup>), 151.30 (C<sup>7</sup>), 150.15 (C<sup>7'</sup>), 143.27 (C<sup>2</sup>), 131.78 (C<sup>9</sup>), 131.75 (C<sup>9'</sup>), 125.23 (C<sup>10</sup>), 124.98 (C<sup>10'</sup>), 123.18 (C<sup>3</sup>), 119.21 (C<sup>6</sup>), 118.82 (C<sup>5</sup>), 117.08 (C<sup>8</sup>), 116.94 (C<sup>8'</sup>), 34.59 (C<sup>11</sup>), 29.80 (C<sup>12</sup>).

Anal. Calcd for C<sub>24</sub>H<sub>22</sub>O<sub>6</sub> (406.43): C, 70.93%; H, 4.96%. Found: C, 70.18%; H, 5.55%.



The other three bis(ether benzoic acid)s, 4,4'-(1,4-phenylenedioxy)dibenzoic acid (**3**) (mp 322–324°C), 4,4'-(2,5-tolylenedioxy)dibenzoic acid (Me-**3**) (mp 302–304°C), and 4,4'-(2,5-biphenylenedioxy)dibenzoic acid (Ph-**3**) (mp 261–263°C), were synthesized in an analogous procedure from alkaline hydrolysis of the corresponding bis(ether benzonitrile)s. Their characterization data have been reported previously.<sup>15</sup>

### Syntheses of Bis(ether benzoyl chloride)s

The diacyl chloride monomers were prepared by chlorination with thionyl chloride of the corresponding bis(ether benzoic acid)s. A representative synthetic procedure for 4,4'-(2-*tert*-butyl-1,4-phenylenedioxy)dibenzoyl chloride (*t*-Bu-**4**) is as follows. 4,4'-(2-*tert*-Butyl-1,4-phenylenedioxy)dibenzoic acid (*t*-Bu-**3**) (19.73 g, 0.0485 mol) was suspended in 60 mL of thionyl chloride and 50 mL of dichloromethane in the presence of one drop of DMF. The mixture was heated with stirring at 60°C. After about 4 h, the suspension solution turned into a clear solution. Dichloromethane and excess thionyl chloride were removed by distillation. The resulting white solid was dried at 100°C in a vacuum to give 21.3 g (99%) of diacyl chloride *t*-Bu-**4**; mp 126–128°C. IR (KBr): 2962 (C—H str.), 1768 (C=O str.), 1599–1416 (arom. C=C str.), 1234 cm<sup>-1</sup> (C—O—C).

The other diacyl chlorides, 4,4'-(1,4-phenylenedioxy)dibenzoyl chloride (**4**) (mp 207–209°C), 4,4'-(2,5-tolylenedioxy)dibenzoyl chloride (Me-**4**) (mp 165–167°C), and 4,4'-(2,5-biphenylenedioxy)dibenzoyl chloride (Ph-**4**) (mp 118–121°C), were synthesized in an analogous procedure from the corresponding bis(ether benzoic acid)s. Diacyl chlorides **4** and Me-**4** were purified by sublimation prior to use for polymerization, whereas Ph-**4** was used without further purification.

### General Polymer Synthesis

Typical procedures for the synthesis of poly-(amide–hydrazide) *t*-Bu-**7** are as follows.

#### Direct Polycondensation via the Phosphorylation Reaction

In a 50 mL flask, a mixture of equimolar amounts (1 mmol) of bis(ether benzoic acid) *t*-Bu-**3** (0.4060 g) and *p*-aminobenzoyl hydrazide (0.1512 g), 0.2 g of lithium chloride, 1 mL of NMP, 1.2 mL of DPP, and 0.5 mL of pyridine was heated with stirring at 120°C. The reaction solution turned into an opaque paste after 1 h. Then, an additional 2 mL of NMP and 0.2 g of calcium chloride were added, and the reaction was maintained at 120°C for another 2 h. The milky solution became gradually homogeneously transparent, leading to a clear, highly viscous polymer solution. After cooling, the viscous solution was poured slowly with stirring into 300 mL of methanol. The white fiberlike precipitate formed was washed repeatedly with methanol and hot water, collected by filtration,

and dried to give a quantitative yield of poly-(amide-hydrazide) *t*-Bu-7. The inherent viscosity of the polymer was 1.09 dL/g, measured in DMSO at a concentration of 0.5 g/dL at 30°C.

#### Low-Temperature Solution Polycondensation

In a 50 mL flask, a solution of 5 mL of NMP containing dissolved 0.2 g of lithium chloride and 1 mmol of *p*-aminobenzoyl hydrazide (0.1512 g) was prepared and cooled by an external ice-acetone bath. The solution was stirred, and to it were added 1 mmol of diacyl chloride *t*-Bu-4 (0.4433 g). The reaction was continued overnight. The resulting polymer solution was treated by a similar procedure as described above. The obtained poly(amide-hydrazide) *t*-Bu-7 had an inherent viscosity of 0.53 dL/g (0.5 g/dL, 30°C, DMSO). IR (film): 3276 (N—H str.), 2960 (aliphatic C—H str.), 1650 (C=O str.), 1230 cm<sup>-1</sup> (C—O str.).

#### Film Preparation and Cyclodehydration of the Hydrazide Polymers

A polymer solution was made by dissolving about 0.6 g of the polyhydrazide or poly(amide-hydrazide) samples in 6 mL of *N,N*-dimethylacetamide (DMAc). The solution was poured 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 lifted off the glass substrate and further dried *in vacuo* at 150°C for 8 h. The obtained films had about 0.05 mm in thickness.

The conversion of polyhydrazides or poly(amide-hydrazide)s to poly(1,3,4-oxadiazole)s or poly(amide-1,3,4-oxadiazole)s was carried out by heating the above fabricated polymer films at 200°C for 30 min, 250°C for 30 min, and 300°C for 3 h under a nitrogen atmosphere. The inherent viscosities of the oxadiazole polymers were measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30°C.

#### Measurements

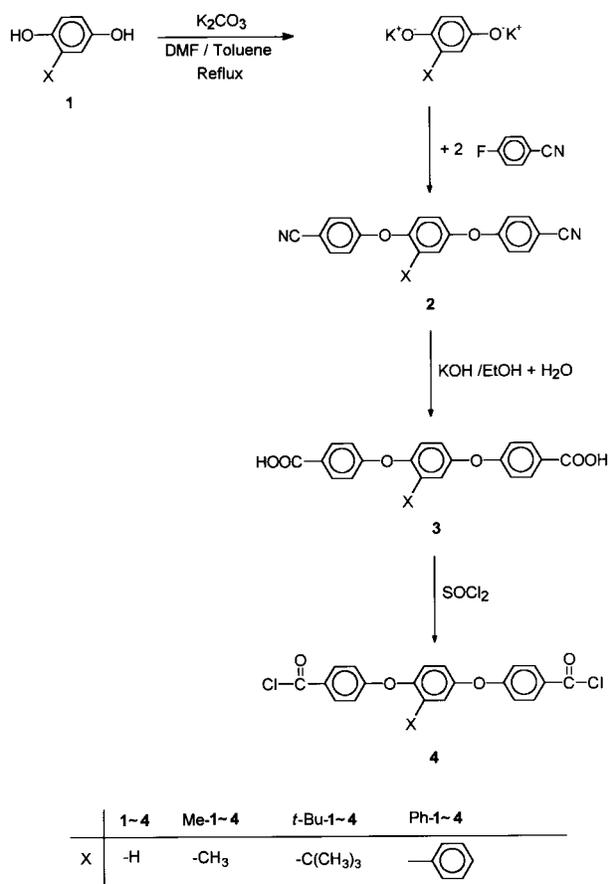
The melting points were measured with a MEL-TEMP II apparatus or a differential scanning calorimeter (heating rate: 10°C/min). Elemental analyses were carried out on a Perkin-Elmer model 2400 C, H, N analyzer at the National Taiwan University (Taipei). IR spectra were recorded on a Jasco FT/IR-7000 Fourier trans-

form infrared spectrometer. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were determined at 30°C on a Jeol EX-400 NMR spectrometer with deuteriochloroform (CDCl<sub>3</sub>) or perdeuteriodimethyl sulfoxide (DMSO-*d*<sub>6</sub>) as an internal reference. The inherent viscosities were measured with an Ubbelohde viscometer at 30°C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 thermal analyzer was used to determine the thermal transitions. Scans were run at 20°C/min. Glass transition temperatures (*T*<sub>g,s</sub>) were read at the middle of the change in the heat capacity. Dynamic thermogravimetry (TG) was performed using a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 thermal analyst. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm<sup>3</sup>/min) at a heating rate of 20°C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered CuKα radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of 2θ = 5–40°. 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 an elongation rate of 5 cm/min 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 mm thick). An average of at least five individual determinations was used.

## RESULTS AND DISCUSSION

### Monomer Synthesis

Bis(ether benzoic acid)s **3**, Me-**3**, *t*-Bu-**3**, and Ph-**3** were prepared starting from the fluoro displacement of *p*-fluorobenzonitrile with hydroquinone or its derivatives via a two-step reaction sequence. These bis(ether benzoyl chloride)s were converted to the corresponding diacyl chlorides by treatment with thionyl chloride in the presence of a trace amount of DMF. The synthetic route is outlined in Scheme 1. The structures of the intermediate bis(ether benzonitrile)s and the bis(ether benzoic acid)s were confirmed by elemental analysis and infrared, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy, whereas the structures of the diacyl chlorides were ascertained by IR spectroscopy only.



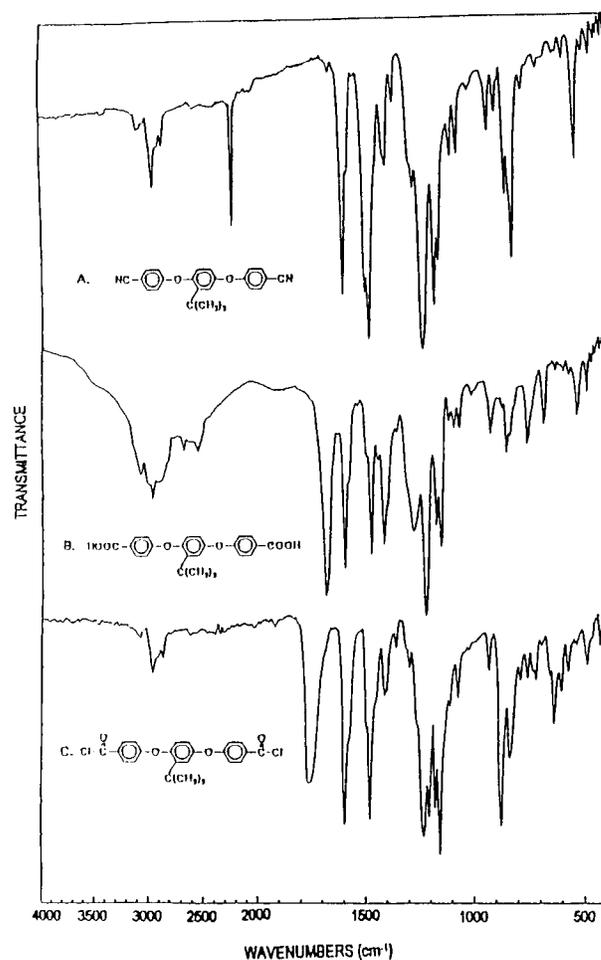
**Scheme 1.** Synthesis of bis(ether benzoic acids) and diacyl chlorides.

Figure 1 summarizes the IR spectra of bis(ether benzonitrile) *t*-Bu-2, bis(ether benzoic acid) *t*-Bu-3, and bis(ether benzoyl chloride) *t*-Bu-4. After the cyano group was hydrolyzed to the carboxyl group, the sharp absorption near  $2220\text{ cm}^{-1}$  peculiar to the cyano group disappeared, and there appeared the carbonyl stretching absorption around  $1690\text{ cm}^{-1}$  and the broad O—H absorption in the region between  $2550$  and  $1960\text{ cm}^{-1}$ . After the bis(ether benzoic acid) was chlorinated to the diacyl chloride, the broad O—H absorption disappeared, and the C=O absorption appeared at a higher frequency ( $1768\text{ cm}^{-1}$ ). The  $^{13}\text{C}$ -NMR spectra of *t*-Bu-2 and *t*-Bu-3 are illustrated in Figure 2. The most obvious features of the spectra are the shifts of the resonance signals for the carbons of the cyano group and its adjacent carbons  $\text{C}_{10}$  and  $\text{C}_{10'}$ . The  $\text{C}_{10}$  and  $\text{C}_{10'}$  of *t*-Bu-2 are shielded by the anisotropic field induced by the  $\pi$  electrons of the cyano group, and hence  $\text{C}_{10}$  and  $\text{C}_{10'}$  resonate at higher fields than the other aromatic carbons. After the cyano group

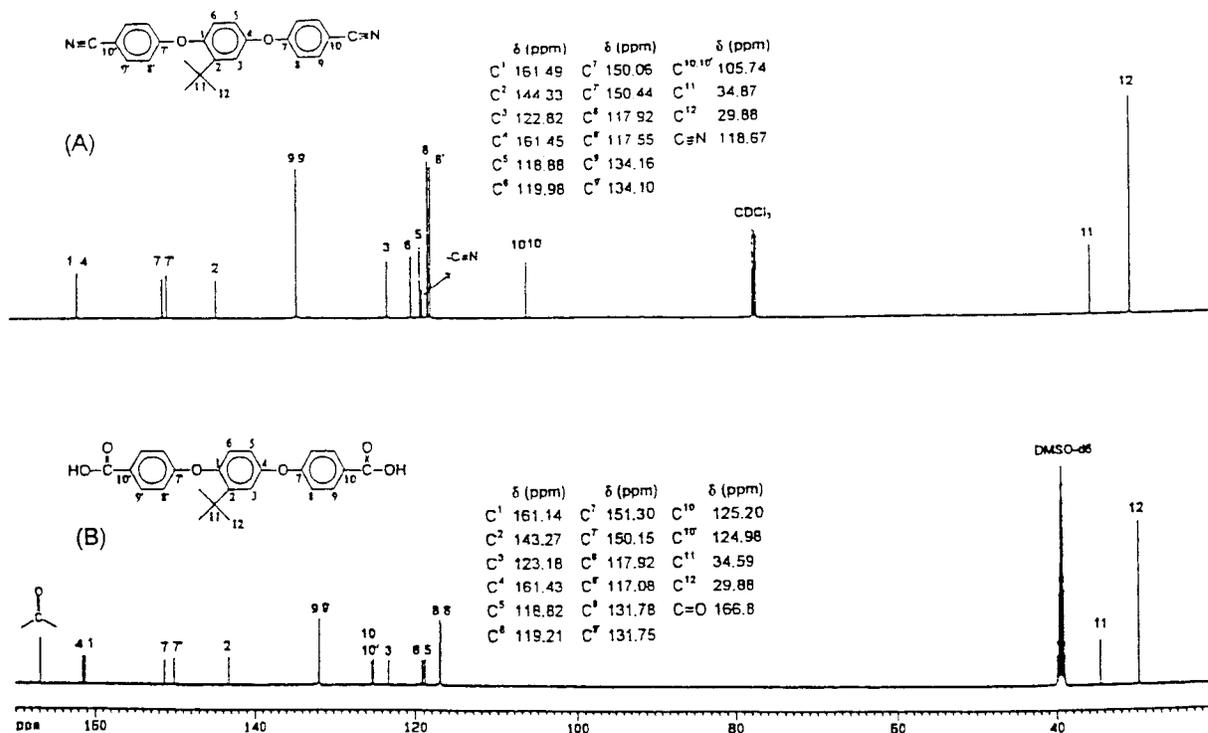
was converted to the carboxyl group, the resonance signals of  $\text{C}_{10}$  and  $\text{C}_{10'}$  moved to lower fields (from  $105.72$  to  $124.98$  and  $125.23$  ppm) due to the lack of anisotropic shielding, the original signal at  $118.67$  ppm assigned to cyano carbon disappeared, and the resonance of carbonyl carbon occurred at the farthest downfield ( $166.83$  ppm).

### Polymer Synthesis

Both the direct polycondensation technique and the low-temperature solution polycondensation technique 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 5-7 indicate that the unsymmetrical dicarboxylic acid or aminobenzoyl hydrazide moi-



**Figure 1.** IR spectra of (A) bis(ether benzonitrile) *t*-Bu-2, (B) bis(ether benzoic acid) *t*-Bu-3, and (C) bis(ether benzoyl chloride) *t*-Bu-4.



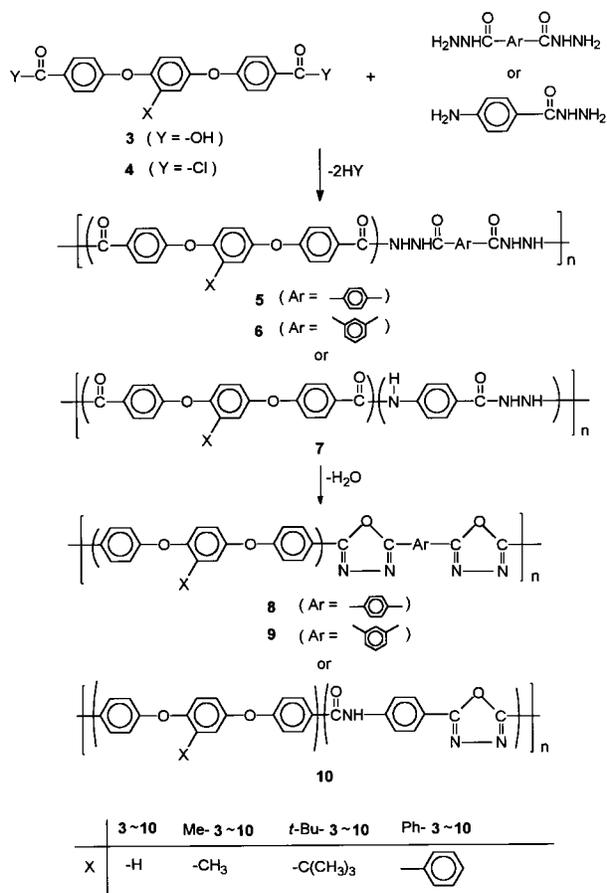
**Figure 2.**  $^{13}\text{C}$ -NMR spectra of (A) 4,4'-(2-*tert*-butyl-1,4-phenylenedioxy)dibenzonitrile (*t*-Bu-2) and (B) 4,4'-(2-*tert*-butyl-1,4-phenylenedioxy)dibenzoic acid (*t*-Bu-3).

ety may appear in the polymer chain as shown or in the reverse order. This convention is needed since the simple order of diacid or aminobenzoyl hydrazide repeating units cannot be assumed.

In the direct polycondensation, serial polyhydrazides **5** and **6** and poly(amide-hydrazide)s **7** were prepared by the Yamazaki-Higashi phosphorylation polycondensation reaction directly from bis(ether benzoic acid)s **3** with terephthalic dihydrazide (TPH), isophthalic dihydrazide (IPH), and *p*-aminobenzoyl hydrazide (*p*-ABH) using diphenyl phosphite (DPP) and pyridine as condensing agents. Homogeneity of the reaction medium favors the polycondensation reaction. A sufficient amount of metal salts, such as calcium chloride or lithium chloride, dissolved in the reaction solvent is necessary to prevent an early precipitation or the formation of swollen gel that may hinder the polycondensation reaction. In general, using a higher initial reactant concentration and adding a supplemental solvent before a swollen gel formed or precipitation occurred usually could produce polymers with a higher inherent viscosity. Synthesis conditions for the polyhydrazides and poly(amide-hydrazide)s by means of phosphorylation reaction are summarized in Table I.

With the exception of polyhydrazides **5** and Me-**5**, all the polycondensations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. Most of the polymers precipitated into a tough string form when slowly pouring the resulting polymer solutions into stirring methanol. An early precipitation occurred during the syntheses of polymers **5** and Me-**5**, and increasing the amount of metal salts or solvent in order to carry out the reaction in a homogeneous phase has met with failure in obtaining clear, viscous polymer solutions. The unsatisfactory results may be attributed to their poor solubility, possibly due to the presence of more symmetric TPH moieties in the polymer backbones which give a higher crystallinity. As shown in Table II, the polyhydrazides and poly(amide-hydrazide)s prepared by the phosphorylation reaction exhibited inherent viscosities between 0.41 and 1.09 dL/g, indicative of moderate to high molecular weights.

In the low-temperature polycondensation, the polyhydrazides and poly(amide-hydrazide)s were prepared by reacting diacyl chlorides **4** with TPH, IPH, and *p*-ABH in a NMP solution containing dissolved LiCl cooled by an external ice-acetone



**Scheme 2.** Synthesis of hydrazide and oxadiazole polymers and copolymers.

bath. The reaction temperature was maintained at  $-10$  to  $0^\circ\text{C}$  in the initial 2 h. In order to obtain maximum molecular weight, the reaction was then allowed to proceed overnight at room temperature. As summarized in Table II, the inherent viscosities of the polymers produced via the acyl chloride route stayed in the range of 0.47–1.02 dL/g. As can be seen from Table II, in the cases of nonsubstituted and methyl-substituted polymers, the polymer sample with a higher inherent viscosity was attained via the low-temperature polycondensation technique, possibly due to less side reaction. However, for the *tert*-butyl- and phenyl-substituted polymers, a lower inherent viscosity was attained by this route. This may be attributed to the purity of the monomers. The diacyl chlorides **4** and Me-**4** were readily sublimed, while purification of the *t*-Bu-**4** and Ph-**4** acid chlorides proved to be difficult, owing to their greater molecular weight and less symmetric structure, which do not sublime as easily.

### Cyclodehydration of the Polyhydrazides and Poly(amide–hydrazide)s

As shown in Table II, except for polymers **5**, **7**, and Me-**5**, the other polymers could be solution-cast into flexible and tough films, and most of them were transparent and colorless. These polyhydrazides and poly(amide–hydrazide)s were subjected to thermal cyclodehydration. The conversion to poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s was carried out in the form of films at  $200^\circ\text{C}$  for 30 min,  $250^\circ\text{C}$  for 30 min, and  $300^\circ\text{C}$  for 3 h in nitrogen. Due to the conjugation between the oxadiazole ring and aromatic unit, the films turned from colorless into pale yellow or brownish after heat treatment. Structures and codes of poly(oxadiazole)s and poly(amide–oxadiazole)s are also shown in Scheme 2. As shown in Table III, the oxadiazole polymers exhibited inherent viscosities between 0.13 and 0.98 dL/g when measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at  $30^\circ\text{C}$ .

Thin films cast from DMAc of the polyhydrazides and poly(amide–hydrazide)s were studied by IR spectroscopy to monitor their cyclodehydration. Figure 3 is representative of the series and comprises the IR spectrum of a thin film of poly(amide–hydrazide) **7** that was cast from DMAc and dried under vacuum at  $150^\circ\text{C}$  for 24 h. The film sample was then cyclodehydrated at  $300^\circ\text{C}$  for 3 h before its IR spectrum was taken again. Figure 3 shows the decrease of the poly(amide–hydrazide)'s N–H stretching absorbance around  $3300\text{ cm}^{-1}$  after cyclodehydration. The decrease of the amide carbonyl peak at  $1650\text{--}1660\text{ cm}^{-1}$  during the cyclodehydration of poly(amide–hydrazide) **7** is also shown. Cyclization to the oxadiazole structure was also studied by thermogravimetry and differential scanning calorimetry, as discussed subsequently.

### Polymer Characterization

The polyhydrazide and poly(amide–hydrazide) samples obtained by the direct polycondensation technique were characterized.

### Solubility

Solubility of the polyhydrazides and poly(amide–hydrazide)s synthesized in this study was determined for the film samples in excess solvents, and the results are listed in Table IV. Most of the polyhydrazides and poly(amide–hydrazide)s were readily soluble in polar aprotic solvents such as

**Table I.** Reaction Conditions for the Preparation of Polyhydrazides and Poly(amide–hydrazide)s by Means of the Phosphorylation Reaction<sup>a</sup>

Polymer Code	Combination of Monomers <sup>b</sup>	Initial Amounts of Reagents Used <sup>c</sup>				Supplemental <sup>d</sup>	
		NMP (mL)	Py (mL)	LiCl (g)	CaCl <sub>2</sub> (g)	NMP (mL)	CaCl <sub>2</sub> (g)
<b>5</b> <sup>e</sup>	<b>3</b> + TPH	4.0	1.0	0.2	0.2	7.0	0.2
<b>6</b>	<b>3</b> + IPH	2.5	0.5	0.2	0.2	2.0	
<b>7</b>	<b>3</b> + <i>p</i> -ABH	2.5	0.5	0.2	0.1	1.0	0.1
Me- <b>5</b> <sup>e</sup>	Me- <b>3</b> + TPH	3.0	0.5	0.2	0.2	4.0	0.1
Me- <b>6</b>	Me- <b>3</b> + IPH	4.0	0.5	0.2	0.2		
Me- <b>7</b>	Me- <b>3</b> + <i>p</i> -ABH	3.0	0.5	0.3		0.5	0.1
<i>t</i> -Bu- <b>5</b>	<i>t</i> -Bu- <b>3</b> + TPH	3.0	0.5	0.2	0.2		
<i>t</i> -Bu- <b>6</b>	<i>t</i> -Bu- <b>3</b> + IPH	2.0	0.5	0.2	0.1	2.0	0.1
<i>t</i> -Bu- <b>7</b>	<i>t</i> -Bu- <b>3</b> + <i>p</i> -ABH	2.0	0.5	0.2		2.0	0.2
Ph- <b>5</b>	Ph- <b>3</b> + TPH	2.5	0.5	0.2	0.1	1.0	
Ph- <b>6</b>	Ph- <b>3</b> + IPH	2.5	0.5	0.2	0.1	1.0	0.1
Ph- <b>7</b>	Ph- <b>3</b> + <i>p</i> -ABH	2.0	0.5	0.2		1.0	0.2

<sup>a</sup> Reaction temperature = 120°C; reaction time = 3 h.

<sup>b</sup> Monomer scale = 1 mmol. TPH: terephthalic hydrazide, IPH: isophthalic hydrazide, *p*-ABH: *p*-aminobenzoyl hydrazide.

<sup>c</sup> DPP = 1.2 mL (2 mmol). Py: pyridine.

<sup>d</sup> Additional amounts of the solvent and metal salt were added after the reaction was carried out for about 1 h.

<sup>e</sup> Precipitation occurred during the polycondensation reaction, and further addition of solvent failed to redissolve the precipitated polymers.

NMP, DMAc, DMF, and DMSO at room temperature. Polymers **5**, **7**, and Me-**5** showed a lower solubility; e.g., they were insoluble in DMF. The introduction of bulky *tert*-butyl and phenyl groups resulted in an increased solubility. In addition to highly polar solvents, the *tert*-butyl- and phenyl-substituted polymers were also soluble in hot *m*-cresol. Moreover, they showed good resistance to common organic solvents such as THF, chloroform, acetone, and ethanol.

Solubility of the polyoxadiazoles and poly(amide–oxadiazole)s were determined in three dipolar solvents NMP, DMAc, and DMSO. The results are shown in Table III. Due to the increased chain stiffness, the oxadiazole polymers showed less solubility as compared to the corresponding hydrazide polymers. When the solubilities of polymers that differ only by *meta* and *para* linkages are compared, the *meta* structure (**9** series) shows a higher solubility. The *tert*-butyl-substituted oxadiazole polymers showed the highest solubility of the polymer series, which may be attributed to the presence of the packing-disruptive *tert*-butyl group.

### Tensile Properties

The polymers except **5**, **7**, and Me-**5** could be solution-cast into flexible films. These flexible films

were subjected to tensile testing, and the results are included in Table IV. Their tensile strengths, elongations at break, and initial moduli were in the range of 89–119 MPa, 4–37%, and 2.62–4.16 GPa, respectively. Most of the thermally converted oxadiazole polymer films are flexible and tough. However, most of them shrank or bubbled during the cyclization process; therefore, their mechanical properties were not evaluated. Good-quality and smooth oxadiazole polymer films may be obtained if a carefully designed heating program is employed.

### Crystallinity

The wide-angle X-ray diffraction patterns of some polyhydrazides and poly(amide–hydrazide)s over the  $2\theta$  range of 5–40° are shown in Figures 4 and 5. As shown in Figure 4, the polyhydrazide (**5**) derived from terephthalic dihydrazide (TPH) showed a relatively higher crystalline pattern. Changing the TPH moiety to isophthalic dihydrazide (IPH) moiety reduced the polymer crystallinity drastically. Polyhydrazide **6** reveals an almost completely amorphous pattern. Poly(amide–hydrazide) **7** also reveals a nearly amorphous pattern, although it exhibits all *para*-linked phenylene rings along the polymer backbone. This may be attributed to the fact that the regularity of

**Table II.** Inherent Viscosities and Film Quality of Polyhydrazides and Poly(amide-hydrazide)s

Polymer Code	Method of Preparation <sup>a</sup>	$\eta_{inh}^b$ (dL/g)	Film <sup>c</sup> Quality
<b>5</b>	A	0.45	Brittle, opaque
	B	0.84	Highly brittle, opaque
<b>6</b>	A	0.55	Flexible, opaque
	B	0.75	Highly brittle, opaque
<b>7</b>	A	0.55	Brittle, semitransparent
	B	1.02	Highly brittle, opaque
Me-5	A	0.57	Brittle, opaque
	B	0.72	Brittle, opaque
Me-6	A	0.41	Flexible, semitransparent
	B	0.79	Flexible, semitransparent
Me-7	A	0.63	Flexible, transparent
	B	0.98	Flexible, transparent
<i>t</i> -Bu-5	A	0.55	Flexible, transparent
	B	0.55	Flexible, transparent
<i>t</i> -Bu-6	A	0.53	Flexible, transparent
	B	0.51	Flexible, transparent
<i>t</i> -Bu-7	A	1.09	Flexible, transparent
	B	0.53	Flexible, transparent
Ph-5	A	0.55	Flexible, transparent
	B	0.47	Flexible, transparent
Ph-6	A	0.57	Flexible, transparent
	B	0.47	Flexible, transparent
Ph-7	A	1.07	Flexible, transparent
	B	0.59	Flexible, transparent

<sup>a</sup> A: Direct polycondensation; the reaction conditions are listed in Table I. B: Low-temperature polycondensation; monomer scale = 1 mmol, NMP = 5 mL, LiCl = 0.2 g.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMSO at 30°C.

<sup>c</sup> Films were cast from slow evaporation of the polymer solutions in DMAc.

the repeating units in polymer **7** is disrupted by the different appearing orders of the amide and hydrazide groups, thus leading to a decreased crystallinity. The effect of introducing pendent groups on the polymer crystallinity can be seen from Figure 5. Methyl substitution seems to result in little influence. The introduction of bulky pendent *tert*-butyl or phenyl group destroys the backbone symmetry and regularity and interferes with the intermolecular hydrogen bonding and the tight packing of the polymer chains, thus resulting in a significant decrease in crystallinity.

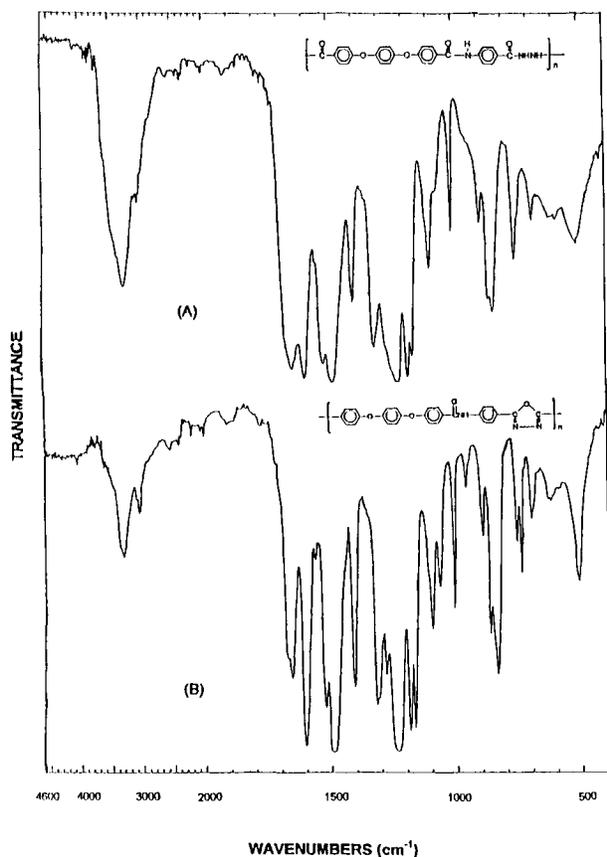
All the poly(oxadiazole)s and poly(amide-oxadiazole)s were also subjected to wide-angle X-ray diffraction measurements. Generally, all the oxadiazole polymers displayed amorphous nature and showed a stronger reflection hump around  $2\theta = 20^\circ$  as compared to the corresponding hydrazide polymers. Figure 6 shows the X-ray diffraction patterns of a pair of hydrazide and oxadiazole polymers. After cyclodehydration, poly(amide-

**Table III.** Inherent Viscosities and Solubility Behavior of Poly(oxadiazole)s and Poly(amide-oxadiazole)s

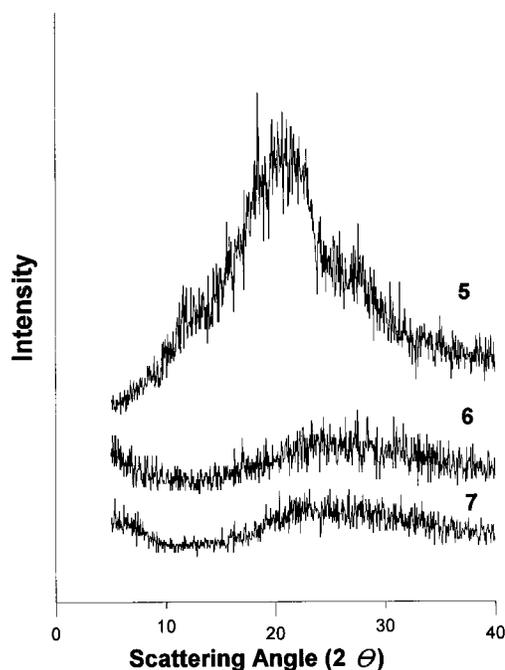
Polymer Code	$\eta_{inh}^a$ (dL/g)	Solubility <sup>b</sup>		
		NMP	DMAc	DMSO
<b>8</b>	0.20	–	–	–
<b>9</b>	0.13	+	+	+
<b>10</b>	0.32	–	–	–
Me-8	0.30	–	–	–
Me-9	0.35	+	+	–
Me-10	0.27	–	–	–
<i>t</i> -Bu-8	0.41	+	+	–
<i>t</i> -Bu-9	0.30	+	+	–
<i>t</i> -Bu-10	0.98	+	+	–
Ph-8	0.44	–	–	–
Ph-9	0.21	+	+	–
Ph-10	0.85	–	–	–

<sup>a</sup> Measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30°C.

<sup>b</sup> +, soluble; –, insoluble at room temperature.



**Figure 3.** IR spectra of (A) poly(amide-hydrizide) **7** and (B) poly(amide-1,3,4-oxadiazole) **10**.



**Figure 4.** Wide-angle X-ray diffractograms of polyhydrazides and poly(amide-hydrizide)s.

oxadiazole)s **10** showed a strong reflection hump around  $2\theta = 20^\circ$ , indicating a higher packing density.

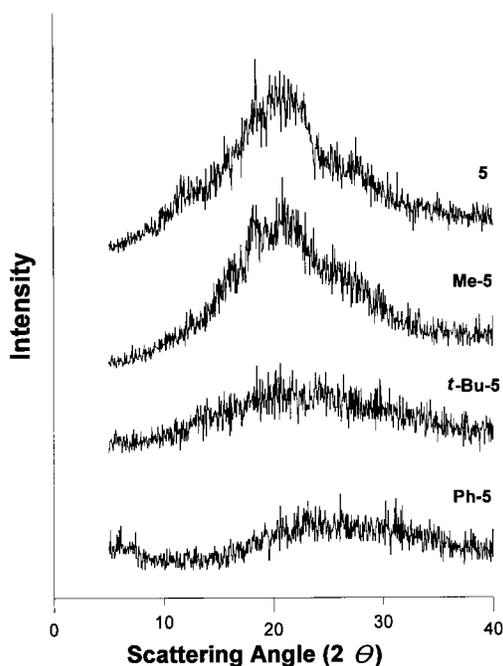
**Table IV.** Solubility Behavior<sup>a</sup> and Tensile Properties of Polyhydrazides and Poly(amide-hydrizide)s

Polymer	Solvent <sup>b</sup>					Tensile Properties of Polymer Films <sup>c</sup>		
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
<b>5</b>	+h	+	-	+	-			
<b>6</b>	+	+	+	+	-	89	35	3.32
<b>7</b>	+	+	-	+	-			
Me- <b>5</b>	-	+	-	+h	-			
Me- <b>6</b>	+	+	+	+	+h	92	4	2.85
Me- <b>7</b>	+	+	+	+	+h	113	27	2.72
<i>t</i> -Bu- <b>5</b>	+	+	+	+	+h	112	8	2.74
<i>t</i> -Bu- <b>6</b>	+	+	+	+	+h	106	7	2.62
<i>t</i> -Bu- <b>7</b>	+	+	+	+	+h	110	37	4.16
Ph- <b>5</b>	+	+	+	+	+h	99	8	2.79
Ph- <b>6</b>	+	+	+	+	+h	100	18	3.10
Ph- <b>7</b>	+	+	+	+	+h	119	8	3.82

<sup>a</sup> +, soluble at room temperature; +h, soluble on heating; -, insoluble even on heating.

<sup>b</sup> NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide. All the polymers were insoluble in tetrahydrofuran, chloroform, acetone, and ethanol.

<sup>c</sup> Films were cast from slow evaporation of the polymers in DMAc and further dried *in vacuo* at 150°C for about 6 h.



**Figure 5.** Wide-angle X-ray diffractograms of polyhydrazides.

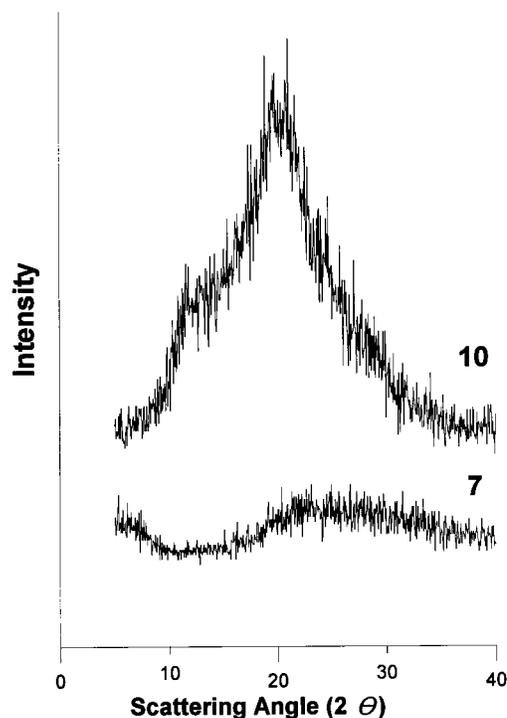
### Thermal Properties

The thermal properties of all polyhydrazides and poly(amide-hydrazide)s were evaluated by differential scanning calorimetry (DSC) and thermogravimetry (TG). Some thermal behavior data for all the polymers are summarized in Table V. Except for polyhydrazide **5**, all the hydrazide polymers showed a distinct glass transition centered in the range of 167–237°C on their DSC heating traces. Among these three series of hydrazide polymers, the poly(amide-hydrazide)s of **7** series had higher  $T_g$  values, possibly due to the presence of amide segment which is more rigid than the hydrazide segment. Moreover, on the DSC heating traces, all the hydrazide polymers gave strong endothermic peaks approximately in the range from 237 to 400°C, which are attributable to loss of water during the conversion of hydrazide group to the 1,3,4-oxadiazole ring.

As can be seen from the DSC diagrams, all the hydrazide polymers were almost completely converted to the corresponding oxadiazole polymers when heated to 350–400°C at a scan rate of 20°C/min in nitrogen. Rapid cooling from elevated temperatures of approximately 450°C to room temperature to form predominantly amorphous materials, and thus, all the oxadiazole polymers displayed distinct glass transitions on the subse-

quent heating DSC traces. Typical DSC curves of polyhydrazide of **6** and poly(1,3,4-oxadiazole) **9** are illustrated in Figure 7. These oxadiazole polymers had  $T_g$ s in the range of 208–243°C. Due to the increased chain rigidity, all the oxadiazole polymers showed higher  $T_g$  values than the corresponding hydrazide polymers. Furthermore, all the poly(amide-1,3,4-oxadiazole)s of **10** series displayed higher  $T_g$  than their corresponding poly(1,3,4-oxadiazole)s of **8** and **9** series. This is probably the result of the presence of the amide group, which may lead to increased interchain interaction due to hydrogen bonding. The role of the pendent group is not very clear, but it is possible to recognize some trends. In most cases, the introduction of methyl or *tert*-butyl group led to a slight increase in  $T_g$  due to the increased steric hindrance of chain mobility. However, the attachment of a phenyl group caused a  $T_g$  decrease. Thus, the effect of chain separation, asymmetry, and irregularity introduced with the bulky phenyl group, which should decrease  $T_g$ , may outweigh the steric effect.

Figure 8 shows a typical pair of TG curves for the representative polyhydrazide **5** and poly(1,3,4-oxadiazole) **8**. Weight loss corresponding to conversion



**Figure 6.** Wide-angle X-ray diffractograms of poly(amide-hydrazide) **7** and its corresponding poly(amide-1,3,4-oxadiazole) **10**.

**Table V.** Thermal Behavior Data for Polyhydrazides and Poly(1,3,4-oxadiazole)s

Polyhydrazide <sup>a</sup>			Poly(1,3,4-oxadiazole)			Char Yield <sup>d</sup> (%)	
Code	$T_g$ (°C)	$T_o$ (°C)	$T_p$ (°C)	Code	$T_g$ <sup>b</sup>		$T_d$ <sup>c</sup> (°C)
<b>5</b>		270	345	<b>8</b>	222	496 (504)	57
Me-5	200	290	340	Me-8	228	489	61
<i>t</i> -Bu-5	197	247	303	<i>t</i> -Bu-8	222	496	50
Ph-5	206	258	287	Ph-8	208	506	54
<b>6</b>	176	237	295	<b>9</b>	220	502	60
Me-6	175	252	303	Me-9	225	486	63
<i>t</i> -Bu-6	192	263	305	<i>t</i> -Bu-9	220	500	54
Ph-6	167	248	302	Ph-9	215	504	58
<b>7</b>	202	288	325	<b>10</b>	240 (407)	505	54
Me-7	223	274	300	Me-10	237	500	69
<i>t</i> -Bu-7	237	283	320	<i>t</i> -Bu-10	243	500	51
Ph-7	217	290	317	Ph-10	230	502	58

<sup>a</sup> DSC data obtained from the first DSC heating trace with a heating rate of 20°C/min.  $T_g$ : midpoint of baseline shift on the DSC curve.  $T_o$ : extrapolated onset temperature of the endotherm peak.  $T_p$ : endotherm peak temperature.

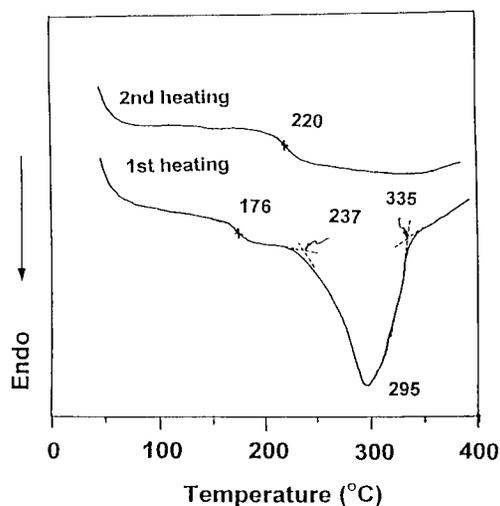
<sup>b</sup> Midpoint temperature of baseline shift on the second DSC heating trace of the sample after quenching from 450°C.

<sup>c</sup> The temperature at which 10% weight loss was recorded by TG at a heating rate of 20°C/min in nitrogen. The value indicated in parentheses was that observed in air.

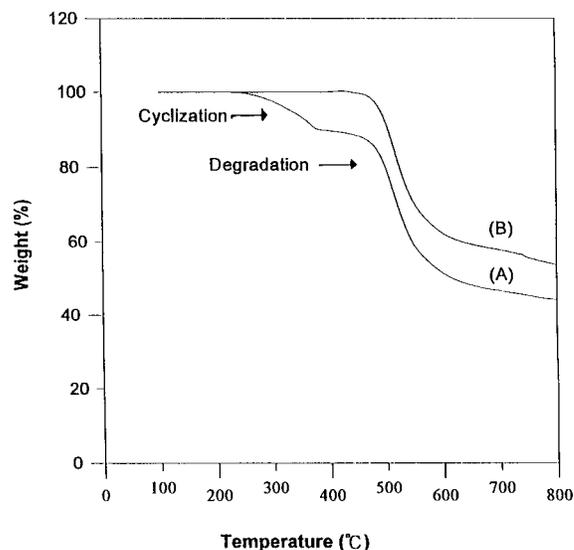
<sup>d</sup> Residual weight % when heated to 800°C in nitrogen.

of the polyhydrazide **5** to the poly(1,3,4-oxadiazole) **8** started at temperatures in the vicinity of 270°C and continued for another 100°C. This also agreed quite well with the strong endothermic peak between 270 and 370°C in the DSC trace. The second break in the TG curve occurred at approximately between 500 and 600°C and corresponded to decom-

position of the poly(1,3,4-oxadiazole) formed *in situ*. At 800°C in nitrogen, the polymer left 57% char (based on the poly(1,3,4-oxadiazole)). The other polymers showed a similar TG behavior, and the TG data of all polymers are listed in Table V. The poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s showed good thermal stability, with 10%



**Figure 7.** DSC curves of polyhydrazide **6** (the first heating trace) and the corresponding poly(1,3,4-oxadiazole) **9** (the second heating trace) with a heating rate of 20°C/min in nitrogen.



**Figure 8.** TG curves of polyhydrazide **5** (A) and poly(1,3,4-oxadiazole) **8** (B) with a heating rate of 20°C/min in nitrogen.

weight loss temperature being recorded in the 486–506°C range in nitrogen. They left 50–69% char residue when heated to 800°C in nitrogen.

## CONCLUSIONS

The fluoro displacement reactions between *p*-fluorobenzonitrile and the potassium phenolates of hydroquinone, methylhydroquinone, *tert*-butylhydroquinone, and phenylhydroquinone were successfully carried out to form the corresponding bis(ether benzonitrile)s, which were subsequently hydrolyzed and acidified to the desired bis(ether benzoic acid)s in high purity and high yields. High-molecular-weight polyhydrazides and poly(amide–hydrazide)s were directly prepared from the bis(ether benzoic acid)s with terephthalic dihydrazide, isophthalic dihydrazide, and *p*-aminobenzoyl hydrazide by the phosphorylation reaction by means of diphenyl phosphite and pyridine in NMP in the presence of metal salts or prepared from the bis(ether benzoyl chloride)s with the hydrazide monomers by the low-temperature solution polycondensation in NMP/LiCl. The inherent viscosities of the polymers were in the range of 0.41–1.09 dL/g, and most of the polymers could be solution-cast into colorless, flexible, and tough films. The polyhydrazides and poly(amide–hydrazide)s had  $T_g$ s in the range of 167–237°C and could be thermally cyclodehydrated into the corresponding poly(oxadiazole)s and poly(amide–oxadiazole)s approximately in the region of 250–400°C. Some of the thermally converted oxadiazole polymers are organic soluble. The  $T_g$ s of these thermally converted poly(1,3,4-oxadiazole)s and poly(amide–1,3,4-oxadiazole)s were recorded

in the range of 208–240°C. The poly(oxadiazole)s and poly(amide–oxadiazole)s showed good thermal stability, with 10% weight loss temperature being recorded above 486°C in air or nitrogen atmosphere.

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