

# Aromatic Poly(1,3,4-oxadiazole)s and Poly(amide-1,3,4-oxadiazole)s Containing Ether Sulfone Linkages

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**ABSTRACT:** Polyhydrazides and poly(amide-hydrazide)s were prepared from two ether-sulfone-dicarboxylic acids, 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoic acid and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoic acid, or their diacyl chlorides with terephthalic dihydrazide, isophthalic dihydrazide, and *p*-aminobenzhydrazide via a phosphorylation reaction or a low-temperature solution polycondensation. All the hydrazide polymers were found to be amorphous according to X-ray diffraction analysis. They were readily soluble in polar organic solvents such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylacetamide and could afford colorless, flexible, and tough films with good mechanical strengths via solvent casting. These hydrazide polymers exhibited glass-transition temperatures of 149–207 °C and could be thermally cyclodehydrated into the corresponding oxadiazole polymers in the solid state at elevated temperatures. Although the oxadiazole polymers showed a significantly decreased solubility with respect to their hydrazide prepolymers, some oxadiazole polymers were still organosoluble. The thermally converted oxadiazole polymers had glass-transition temperatures of 217–255 °C and softening temperatures of 215–268 °C and did not show significant weight loss before 400 °C in nitrogen or air. For a comparative study, related sulfonyl polymers without the ether groups were also synthesized from 4,4'-sulfonyldibenzoic acid and the hydrazide monomers by the same synthetic routes. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 39: 2271–2286, 2001

**Keywords:** polyhydrazide; poly(amide-hydrazide); poly(1,3,4-oxadiazole); poly(amide-1,3,4-oxadiazole); poly(ether-sulfone-oxadiazole)

## INTRODUCTION

Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.<sup>1,2</sup> They are considered to be interesting alternatives for the development of high-temperature and flame-resistant fibers<sup>3,4</sup> and thermally stable membranes for gas separation.<sup>5</sup> In addition, oxadiazole-based polymers have been widely investigated in the field of poly-

mer light-emitting diodes as well as other fields of polymer electronics.<sup>6–11</sup> Unfortunately, aromatic polyoxadiazoles are difficult to process because of their infusible and insoluble properties and their tendency to be brittle. Many efforts have been made to improve the solubility and lower the glass-transition temperature ( $T_g$ ) to make such polymers more easily processable, such as by the incorporation of flexible linkages in the backbone or bulky pendant group on the aromatic rings.<sup>12–18</sup>

We have demonstrated that multiring dianhydrides, dicarboxylic acids, and diamines containing both ether and sulfone groups are able to give aromatic polyimides and polyamides with en-

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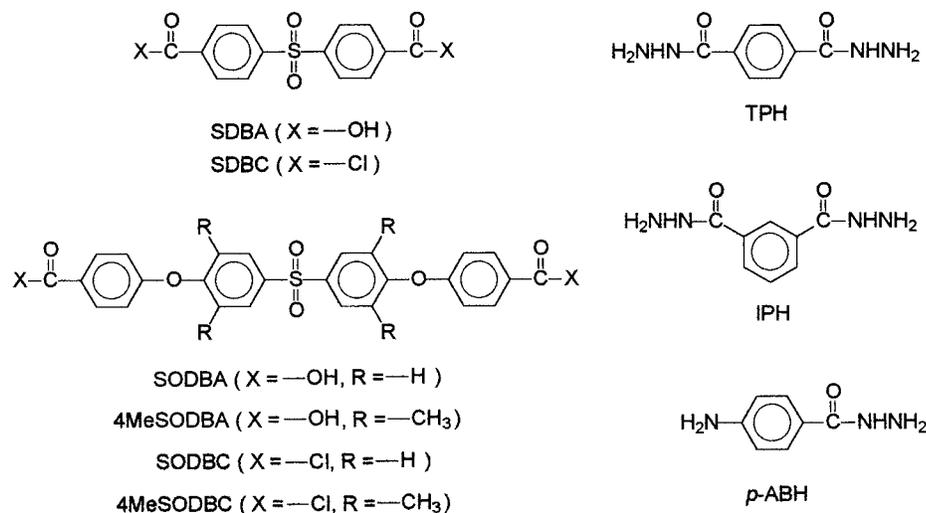


Figure 1. Structures and codes of monomers.

hanced solubility while maintaining moderately high  $T_g$ 's.<sup>19</sup> These monomers are also able to restrict regular chain packing into an ordered structure. To develop novel high-performance polymers and exploit their properties, herein we report our efforts in synthesizing aromatic polyoxadiazoles and poly(amide-oxadiazole)s via precursor polyhydrazides and poly(amide-hydrazide)s by the condensation of the ether-sulfone-dicarboxylic acids 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoic acid (SODBA) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoic acid (4MeSODBA) or their diacyl chlorides with commercially available dihydrazide or aminohydrazide monomers (Figs. 1–3). We hoped that the incorporation of both ether and sulfone groups would result in amorphous oxadiazole polymers with enhanced solubility in organic solvents and acceptable  $T_g$ 's and thermal stability. The effect of methyl substituents on the properties of the polymers was also investigated. For comparison, related sulfonyl polymers without ether linkages were also prepared from 4,4'-sulfonyldibenzoic acid (SDBA) or its diacyl chloride derivative according to the same synthetic routes.

## EXPERIMENTAL

### Materials

*N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and pyridine were stirred over powdered calcium hydride overnight and were then distilled under reduced pressure and stored over 4-Å molecular sieves. Terephthalic dihydra-

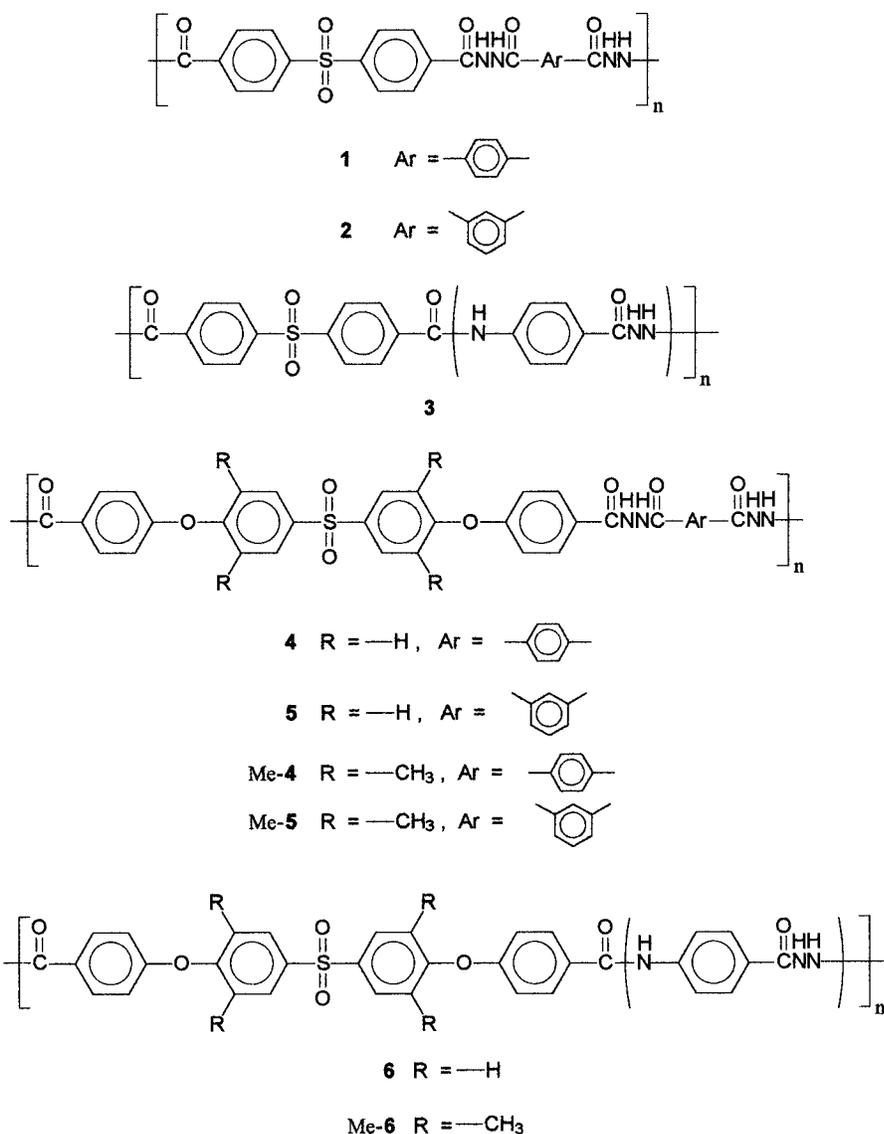
zide (TPH; TCI), isophthalic dihydrazide (IPH; TCI), and *p*-aminobenzhydrazide (*p*-ABH; TCI) were used without further purification. SDBA was kindly donated by New Japan Chemicals Co. Ltd. and was used without further purification. As described in a previous article,<sup>19(b)</sup> the ether-sulfone-dicarboxylic acids SODBA [mp = 291–292 °C by differential scanning calorimetry (DSC)] and 4MeSODBA (mp = 312–315 °C by DSC) were prepared by the fluorodisplacement of *p*-fluorobenzonitrile with the potassium salts of 4,4'-sulfonyldiphenol and 4,4'-sulfonylbis(2,6-dimethylphenol) and the subsequent alkaline hydrolysis of the intermediate dinitriles. Commercially obtained anhydrous calcium chloride (CaCl<sub>2</sub>) and lithium chloride (LiCl) were dried *in vacuo* at 180 °C for 8 h. Other reagents and solvents were obtained commercially and used as received.

### Synthesis of Diacid Chloride Monomers

According to a well-established procedure,<sup>17,18</sup> the diacyl chloride monomers 4,4'-sulfonyldibenzoyl chloride (SDBC), 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoyl chloride (SODBC), and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoyl chloride (4MeSODBC) were prepared by the reaction of SDBA, SODBA, and 4MeSODBA with thionyl chloride in the presence of a catalytic amount of DMF and were purified by crystallization from toluene/*n*-hexane.

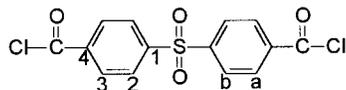
### SDBC

Yield: 77% (after recrystallization). mp: 160–161 °C (by DSC; lit.<sup>20</sup> 164 °C). IR (KBr): 1783 (C=O),



**Figure 2.** Structures and codes of sulfonyl polyhydrazides and poly(amide-hydrazide)s.

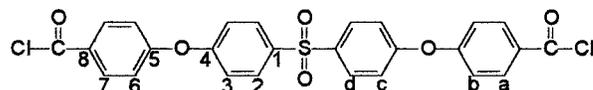
1327, 1300 [asymmetric S(=O)<sub>2</sub> stretching], 1194, 1155 [symmetric S(=O)<sub>2</sub> stretching], 881 cm<sup>-1</sup> (C—Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 8.27 (d, 4H, H<sub>a</sub>), 8.11 (d, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 168.31 (C=O), 147.05 (C<sup>1</sup>), 138.31 (C<sup>4</sup>), 132.81 (C<sup>3</sup>), 129.15 (C<sup>2</sup>).

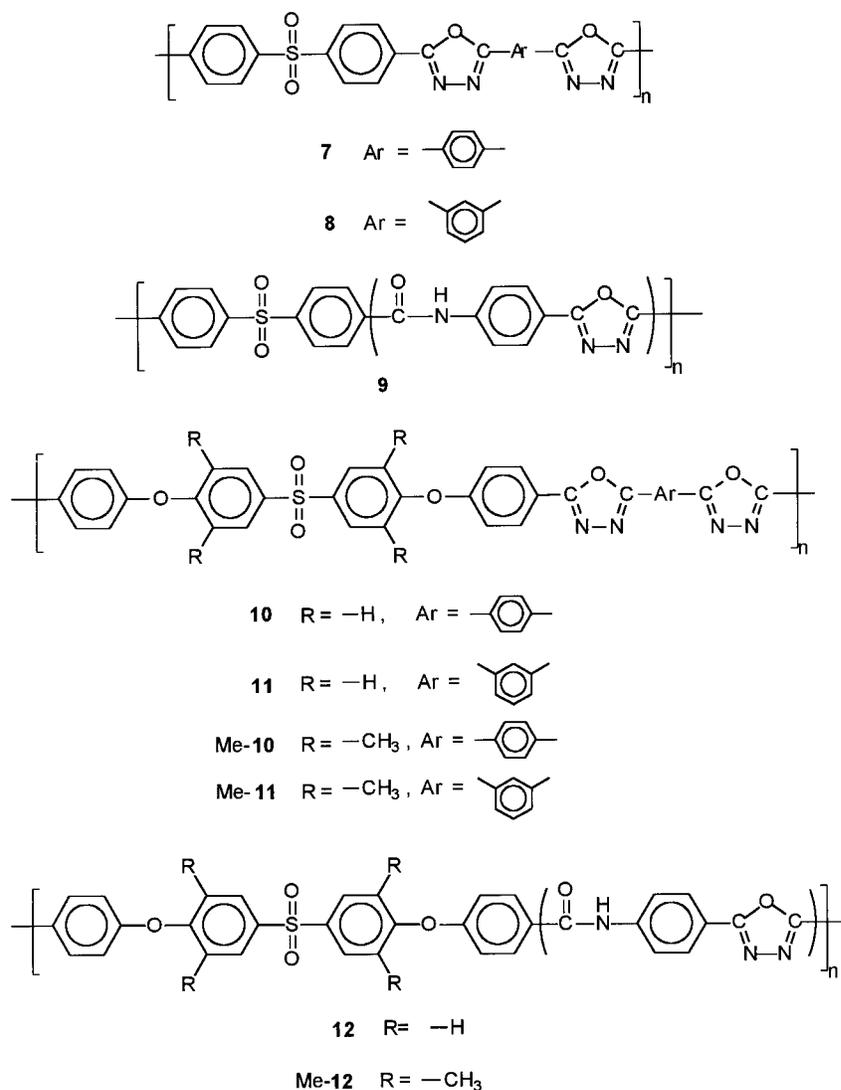


#### SODBC

Yield: 82% (after recrystallization). mp: 183–184 °C (by DSC; lit.<sup>21</sup> 183–185 °C). IR (KBr): 1759

(C=O), 1323, 1300 [asymmetric S(=O)<sub>2</sub> stretching], 1248, 1207 (C—O), 1157, 1103 [symmetric S(=O)<sub>2</sub> stretching], 883 cm<sup>-1</sup> (C—Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 8.14 (d, 4H, H<sub>a</sub>), 8.00 (d, 4H, H<sub>d</sub>), 7.18 (d, 4H, H<sub>c</sub>), 7.10 (d, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 168.14 (C=O), 162.75 (C<sup>5</sup>), 160.52 (C<sup>4</sup>), 138.11 (C<sup>1</sup>), 134.73 (C<sup>7</sup>), 130.88 (C<sup>2</sup>), 129.50 (C<sup>8</sup>), 120.46 (C<sup>3</sup>), 119.35 (C<sup>6</sup>).

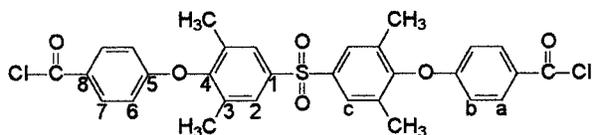




**Figure 3.** Structures and codes of sulfonyl poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s.

#### 4MeSODBC

Yield: 85% (after recrystallization). mp: 190–191 °C (by DSC). IR (KBr): 1770 (C=O), 1371, 1282 [asymmetric S(=O)<sub>2</sub> stretching], 1241, 1213 (C—O), 1161, 1138 [symmetric S(=O)<sub>2</sub> stretching], 881 cm<sup>-1</sup> (C—Cl). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 8.08 (d, 4H, H<sub>a</sub>), 7.79 (s, 4H, H<sub>c</sub>), 6.85 (d, 4H, H<sub>b</sub>), 2.20 (s, 12H, —CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 167.97 (C=O), 163.33 (C<sup>5</sup>), 155.01 (C<sup>4</sup>), 139.41 (C<sup>1</sup>), 134.96 (C<sup>7</sup>), 133.67 (C<sup>3</sup>), 129.37 (C<sup>2</sup>), 127.77 (C<sup>8</sup>), 115.42 (C<sup>6</sup>), 15.68 (—CH<sub>3</sub>).



#### General Polymer Synthesis

Both the phosphorylation polycondensation method and the low-temperature solution polycondensation technique were used to prepare the polyhydrazides and poly(amide-hydrazide)s presented in this study. Typical synthetic procedures for polyhydrazide **4** are illustrated as follows.

#### Direct Polycondensation via the Phosphorylation Reaction

A dried 50-mL flask was charged with SODBA (0.4905 g, 1 mmol), TPH (0.1942 g, 1 mmol), NMP (3 mL), CaCl<sub>2</sub> (0.3 g), diphenyl phosphite (1.2 mL), and pyridine (1 mL). The mixture was heated with stirring at 120 °C. The reaction solu-

tion became highly viscous after about 1 h. Then, an additional 1 mL of NMP was added, with the reaction proceeding 2 h more. The resulting polymer solution was precipitated in 300 mL of methanol and washed thoroughly with hot water and methanol. The white fiberlike precipitate was collected and dried to give a quantitative yield of polyhydrazide **4**. The inherent viscosity of the polymer was 0.47 dL/g, measured in *N,N*-dimethylacetamide (DMAc) 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 0.2 g of LiCl and 1 mmol of TPH (0.1942 g) was prepared and cooled with an external ice–acetone bath. To the stirred solution, 1 mmol of diacyl chloride SODBC (0.5273 g) was added all at once. The reaction was carried out at –10 to 0 °C for the initial 2 h and continued at room temperature overnight. The resulting polymer solution was treated with a procedure similar to that described previously. The obtained polyhydrazide **4** had an inherent viscosity of 0.44 dL/g (0.5 g/dL, 30 °C, DMAc).

IR (film): 3268 (N–H), 1654 (C=O), 1276 [asymmetric S(=O)<sub>2</sub> stretching], 1230 (C–O stretching), 1135, 1103 cm<sup>-1</sup> [symmetric S(=O)<sub>2</sub> stretching].

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

Solutions of the hydrazide polymers in DMAc (approximately 10 wt %) were filtered through a paper filter. Films were made by solution casting in clean glass culture dishes. Wet films were placed in an oven at 90 °C to slowly release the solvent. After 12 h, the obtained semidried polymer film was lifted off the glass substrate and further dried *in vacuo* at 160 °C for 8 h. The thickness of these films was controlled between 60 and 70 μm.

The cyclodehydration of the polyhydrazides or poly(amide-hydrazide)s to the corresponding poly(1,3,4-oxadiazole)s or poly(amide-1,3,4-oxadiazole)s was carried out via the heating of these fabricated polymer films at 200 °C for 30 min, 250 °C for 1 h, and 350 °C for 1 h under a nitrogen atmosphere.

#### Measurements

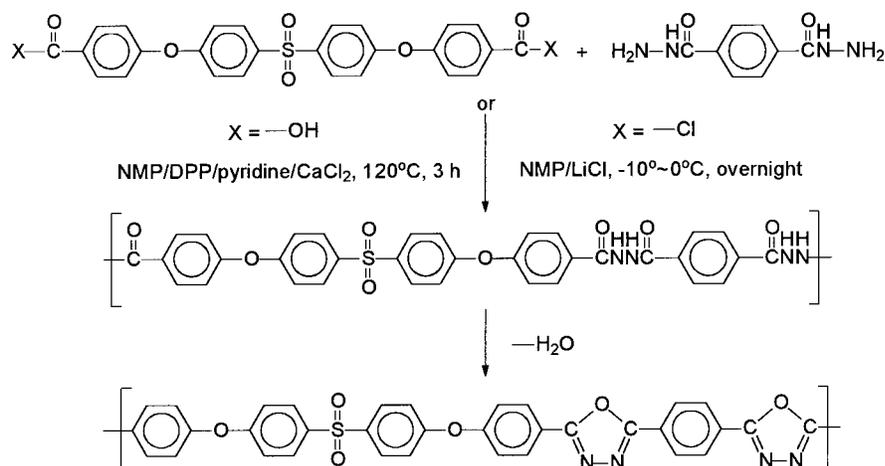
Inherent viscosities were measured for a polymer solution with a 0.5 g/dL concentration at 30 °C

with a Cannon-Fenske viscometer. IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer on solution-cast films or KBr pellets. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature on a Siemens Kristalloflex D5000 X-ray diffractometer operating in the 2θ range of 5–45° at a scan rate of 3°/min with nickel-filtered Cu Kα radiation (λ = 1.5418 Å, operating at 40 kV and 20 mA). DSC was performed on a PerkinElmer DSC 7 differential scanning calorimeter in flowing nitrogen with a heating rate of 20 °C/min. *T<sub>g</sub>*'s were read at the middle of the change in the heat capacity. Thermomechanical analysis (TMA) experiments were performed on a PerkinElmer TMA 7 instrument at a heating rate of 10 °C/min with a loaded penetration probe under an applied constant load of 10 mN. The experiments were carried out in duplicate from 40 to 300 °C. The softening temperatures (*T<sub>g</sub>*'s) were taken as the intersection of the extrapolation of the baseline with the extrapolation of the intersection from the second TMA traces. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050 thermogravimetric analyzer. Experiments were carried out on 9–11-mg samples heated in flowing nitrogen or air (100 cm<sup>3</sup>/min) at a scan rate of 20 °C/min. The measurements were taken after a 350 °C/30 min drying step for the polyoxadiazole samples.

## RESULTS AND DISCUSSION

### Polymer Synthesis

A two-step procedure was employed to obtain the poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s shown in Figure 3 from various combinations of the monomers listed in Figure 1. The reaction proceeds through an intermediate polyhydrazide or poly(amide-hydrazide) (see Fig. 2) whose hydrazide groups undergo thermal cyclodehydration to form the 1,3,4-oxadiazole rings. A typical synthetic scheme for polyhydrazide **4** and the corresponding poly(1,3,4-oxadiazole) **10** is shown in Scheme 1. The parentheses in the formulas of poly(amide-hydrazide)s and poly(amide-1,3,4-oxadiazole)s indicate that the unsymmetrical aminobenzoyl hydrazide moieties may appear in the polymer chain as shown or in the reverse order. Both the high-temperature Higashi phosphorylation technique<sup>22</sup> and the low-temperature solution polycondensation technique were used



**Scheme 1.** Typical synthetic scheme for polyhydrazide **4** and the corresponding polyoxadiazole **10**.

for the syntheses of the polyhydrazides and poly-(amide-hydrazide)s. The reaction conditions and results of these polymerizations are summarized in Table I. All polymerizations proceeded in homogeneous and transparent solutions and led to highly viscous polymer solutions. The inherent viscosity values of the resulting hydrazide polymers were in the range 0.41–0.59 dL/g, indicative

of a modest degree of polymerization. In most cases, the two synthetic methods produced polymer products with similar inherent viscosity values. All of the polyhydrazides and poly(amide-hydrazide)s formed tough, transparent (essentially colorless), and creasable films from DMAc.

The hydrazide polymers were cyclodehydrated through heating in the solid state. Probably be-

**Table I.** Synthesis Conditions, Inherent Viscosity ( $\eta_{inh}$ ), and Film Quality of Polyhydrazides and Poly(amide-hydrazide)s

Polymer Code	Combination of Monomers	Monomer Scale (mmol)	Amount of Reagents Used					$\eta_{inh}$ (dL/g) <sup>a</sup>
			NMP (mL)	DPP (mL)	Py (mL)	CaCl <sub>2</sub> (g)	LiCl (g)	
<b>1</b>	SDBA + TPH	2	7	2.0	2.0	0.50		0.56
	SDBC + TPH	2	10				0.4	0.43
<b>2</b>	SDBA + IPH	2	3	2.0	0.8	0.30		0.43
	SDBC + IPH	2	10				0.4	0.41
<b>3</b>	SDBA + <i>p</i> -ABH	1	2.5	1.0	0.6	0.25		0.59
	SDBC + <i>p</i> -ABH	1	10				0.4	0.57
<b>4</b>	SODBA + TPH	1	4	1.0	1.0	0.40		0.47
	SODBC + TPH	1	5				0.2	0.44
<b>5</b>	SODBA + IPH	1	2.5	1.0	0.6	0.25		0.43
	SODBC + IPH	1	5				0.2	0.40
<b>6</b>	SODBA + <i>p</i> -ABH	2	4	2.0	1.0	0.40		0.56
	SODBC + <i>p</i> -ABH	1	6				0.2	0.49
Me-4	4MeSODBA + TPH	1	3	1.0	0.8	0.30		0.46
	4MeSODBC + TPH	1	6				0.2	0.50
Me-5	4MeSODBA + IPH	1	3	1.0	0.8	0.30		0.55
	4MeSODBC + IPH	1	5				0.2	0.56
Me-6	4MeSODBA + <i>p</i> -ABH	2	6	2.0	1.5	0.60		0.54
	4MeSODBC + <i>p</i> -ABH	1	5				0.2	0.52

<sup>a</sup> Determined at a concentration of 0.5 g/dL in DMAc at 30 °C.

**Table II.** Inherent Viscosity ( $\eta_{inh}$ ) and Solubility Behavior of Polyoxadiazoles and Poly(amide-oxadiazole)s

Polymer Code	$\eta_{inh}$ (dL/g) <sup>a</sup>	Solubility <sup>c</sup>					CH <sub>3</sub> NO <sub>2</sub> /10 wt % AlCl <sub>3</sub>
		NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	
<b>7</b>	0.19	—	—	—	—	—	+
<b>8</b>	0.18	—	—	—	—	—	+
<b>9</b>	0.22	—	—	—	—	—	—
<b>10</b>	0.34	—	—	—	—	—	+
<b>11</b>	0.36	+	+h	+h	+h	+	+
<b>12</b>	0.35	+	+h	—	—	+	±
Me- <b>10</b>	— <sup>b</sup>	+	±	—	—	±	—
Me- <b>11</b>	0.26	±	±	±	—	—	±
Me- <b>12</b>	0.27	±	±	±	—	—	—

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

<sup>b</sup> Swelling in concentrated sulfuric acid.

<sup>c</sup> + = soluble at room temperature; +h = soluble on heating at 100 °C; — = insoluble even on heating; ± = partially soluble.

cause of the conjugation and/or formation of charge-transfer complex between the oxadiazole ring and the aromatic unit, the films or the bulks changed from being colorless to being darkened and brownish after cyclodehydration. Conversion resulted in most cases in shrunken and embrittled poly(1,3,4-oxadiazole) and poly(amide-1,3,4-oxadiazole) films. As listed in Table II, the oxadiazole polymers showed lower inherent viscosities than those of the corresponding hydrazide polymers. These results are consistent with those reported by Hensema et al.<sup>23</sup> and may be due to decreased intermolecular interactions and/or stress buildup caused by chain shrinkage during the cyclization.

Thermal conversion of the hydrazide group to the 1,3,4-oxadiazole ring was monitored with FTIR. As a representative study, a thin-film sample of polyhydrazide **1** was heated sequentially under a nitrogen atmosphere for 30 min each at 200, 250, 300, and 350 °C. The IR spectra of this sample are shown in Figure 4. After curing at 350 °C for 30 min, polyhydrazide **1** was almost completely cyclized to the corresponding poly(1,3,4-oxadiazole) **7**, as seen by the disappearance of the N—H stretching absorption at 3263 cm<sup>-1</sup> and the carbonyl peak at 1655 cm<sup>-1</sup>. The characteristic bands of the oxadiazole ring vibration were observed at 1545 and 1072 cm<sup>-1</sup>, similar to what is reported in the literature.<sup>24</sup> Other characteristic vibrations include the asymmetric and symmetric S(=O)<sub>2</sub> stretching of the sulfonyl groups at 1288 and 1157 cm<sup>-1</sup> and the aromatic skeletal stretching at 1577 and 1483 cm<sup>-1</sup>. TGA and DSC, as

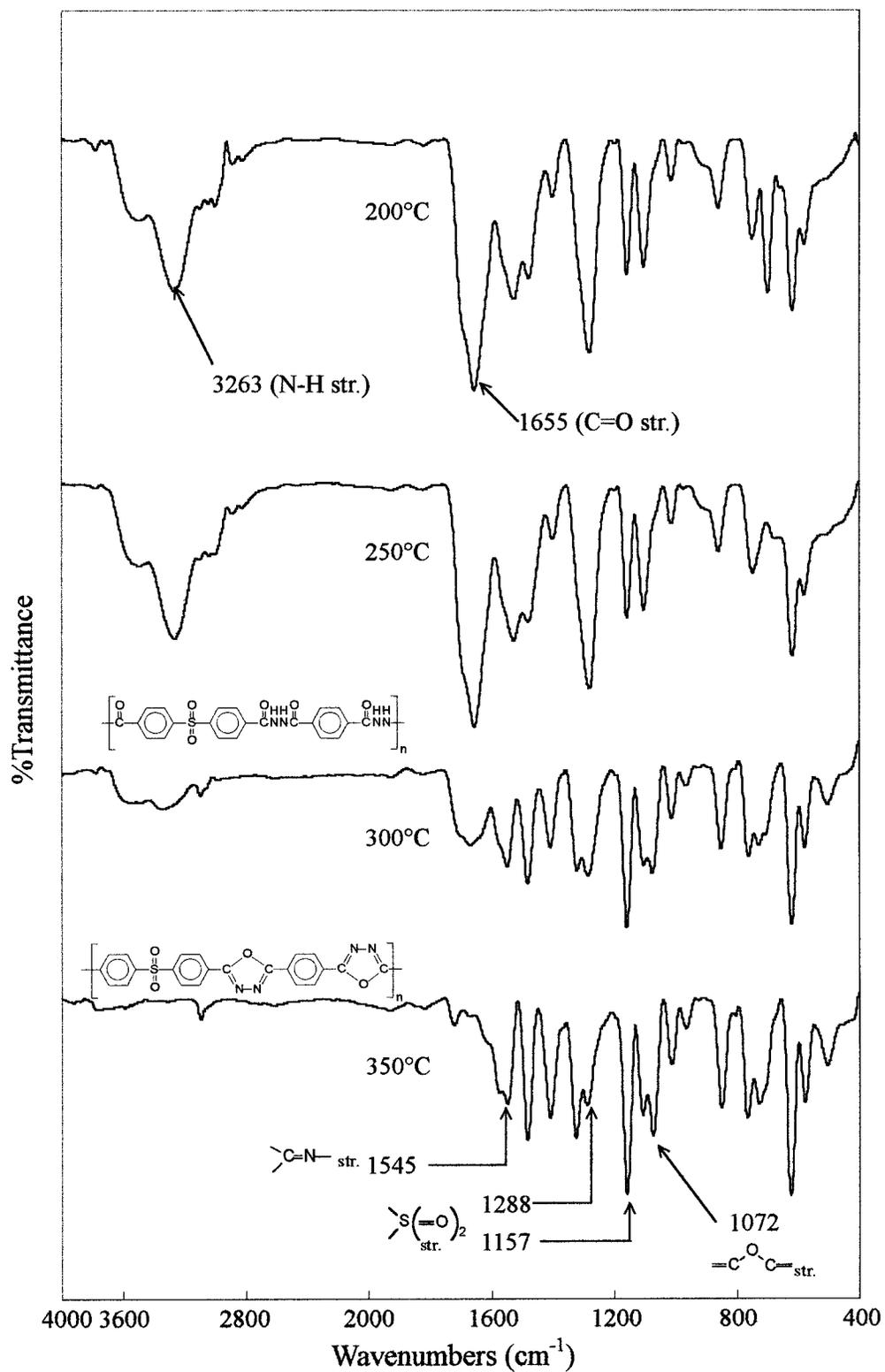
discussed later, also were used to investigate cyclization to the oxadiazole structure.

## Polymer Properties

### Solubility

As shown in Table III, all of the polyhydrazides and poly(amide-hydrazide)s were readily soluble in polar solvents such as NMP, DMAc, DMF, and dimethyl sulfoxide (DMSO) at room temperature. However, polymers **1–3** were insoluble in the less polar solvents such as *m*-cresol and tetrahydrofuran (THF). The incorporation of ether linkages provides increased chain flexibility, and the attachment of methyl substituents on the benzene rings leads to increased chain packing distances and decreased interchain interactions such as hydrogen bonding; thus, polymers Me-**4–6** were more soluble than the other polymers in *m*-cresol.

Because of the increased chain rigidity, the oxadiazole polymers showed a dramatically decreased solubility with respect to the corresponding hydrazide prepolymers. As can be seen in Table II, the oxadiazole-based polymers **7–10** were insoluble in all the organic solvents tested. The introduction of flexible ether linkages slightly increased the solubility of the oxadiazole polymers, as in **11** and **12**. However, for Me-**11** and Me-**12**, the methyl substituents attached to the chain restricted its internal rotation, thus increasing chain rigidity and decreasing solubility. Moreover, it was also found that most of the oxadiazole polymers were soluble in nitromethane



**Figure 4.** FTIR spectra (thin films) of polyhydrazide 1 after heating for 30 min under nitrogen at the indicated temperatures.

**Table III.** Solubility Behavior of Polyhydrazides and Poly(amide-hydrazide)s

Polymer Code	Solubility <sup>a</sup>					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
<b>1</b>	+	+	+	+	–	–
<b>2</b>	+	+	+	+	–	–
<b>3</b>	+	+	+	+	–	–
<b>4</b>	+	+	+	+	+h	–
<b>5</b>	+	+	+	+	+h	–
<b>6</b>	+	+	+	+	+h	–
Me- <b>4</b>	+	+	+	+	+	–
Me- <b>5</b>	+	+	+	+	+	–
Me- <b>6</b>	+	+	+	+	+	–

<sup>a</sup> Qualitative solubility was tested with a 10-mg sample in 1 mL of solvent. + = soluble at room temperature; +h = soluble on heating at 100 °C; – = insoluble even on heating.

containing 10 wt % AlCl<sub>3</sub>, a solvent system described for aromatic heterocyclic rigid polymers such as polybenzoxazoles, polybenzimidazoles, or polyoxadiazoles.<sup>25,26</sup>

### Crystallinity

WAXD patterns of all the polyhydrazides and poly(amide-hydrazide)s are shown in Figure 5. These diffractograms indicate that all the hydrazide polymers were amorphous. The amorphous nature of these polymers was also reflected in their excellent solubility in organic solvents.

The X-ray diffraction patterns of all the oxadiazole polymers are given in Figure 6. Polymers **7** and **9** showed a greatly increased crystallinity, and polymer **8** showed a slightly increased crystallinity with respect to the corresponding hydrazide precursors. This result may be attributed to the fact that, from spectral and electronic points of view, 1,3,4-oxadiazole is similar to a *p*-phenylene structure, which is known to be a planar, rigid unit. The higher level of crystallinity of the oxadiazole polymers **7–9** was consistent with their insolubility in organic solvents. Poly(1,3,4-oxadiazole)s **11** and Me-**11** also displayed slightly enhanced crystallinity. However, the other oxadiazole polymers containing both sulfonyl and ether groups in the backbones had almost no increased ordering, as indicated by the X-ray diffractograms.

### Tensile Properties

All of the polyhydrazides and poly(amide-hydrazide)s gave good-quality creasable films

suitable for the tensile testing. Tensile properties of these thin films are presented in Table IV. These films had strengths to break of 60–91 MPa and elongations to break of 6–21%, indicating a moderate degree of toughness. However, the thermally converted oxadiazole polymer films were so brittle that they cracked upon fingernail creasing. Their mechanical properties were not evaluated.

### Thermal Properties

DSC, TMA, and TGA were used to evaluate the thermal properties of all the hydrazide and oxadiazole polymers, and the results are summarized in Table V. To eliminate the effects of absorbed moisture and residual solvent on the thermal transitions, all the hydrazide polymers were heated from 30 to 250 °C at 20 °C/min, and this was followed by rapid cooling to 30 °C at –100 °C/min. The subsequent DSC scan yields the baseline shift due to the glass transition and the endothermic peak due to cyclodehydration of the polyhydrazide samples. After quenching from 400 °C with a programmed cooling rate of 100 °C/min, the oxadiazole polymers formed *in situ* in the DSC cell were predominantly amorphous. Thus, in the second run most of the oxadiazole polymers exhibited a clear baseline shift. A typical pair of DSC curves for polyhydrazide **4** and poly(1,3,4-oxadiazole) **10** are illustrated in Figure 7. All the other polymers displayed similar DSC traces, and some of the DSC data are given in Table V. For the hydrazide precursor polymers, polymers **1** and **3** did not reveal discernible  $T_g$ 's, and the other polymers showed a distinct  $T_g$  centered in the range 149–207 °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 350–400 °C at a scan rate of 20 °C/min in nitrogen. Because of the increased chain rigidity, all the oxadiazole polymers showed higher  $T_g$  values in comparison with the corresponding hydrazide polymers; their  $T_g$ 's stayed between 218 and 260 °C. Polymers **7** and **9** showed no discernible glass transitions in their DSC traces, probably because of high crystallinity.

The  $T_s$  values of the oxadiazole polymers in the form of thin films were determined by TMA experiments via a penetration method. In most cases, the  $T_s$  values measured by TMA are comparable to the  $T_g$  values determined by DSC. The introduction of ether linkage in the chain in-

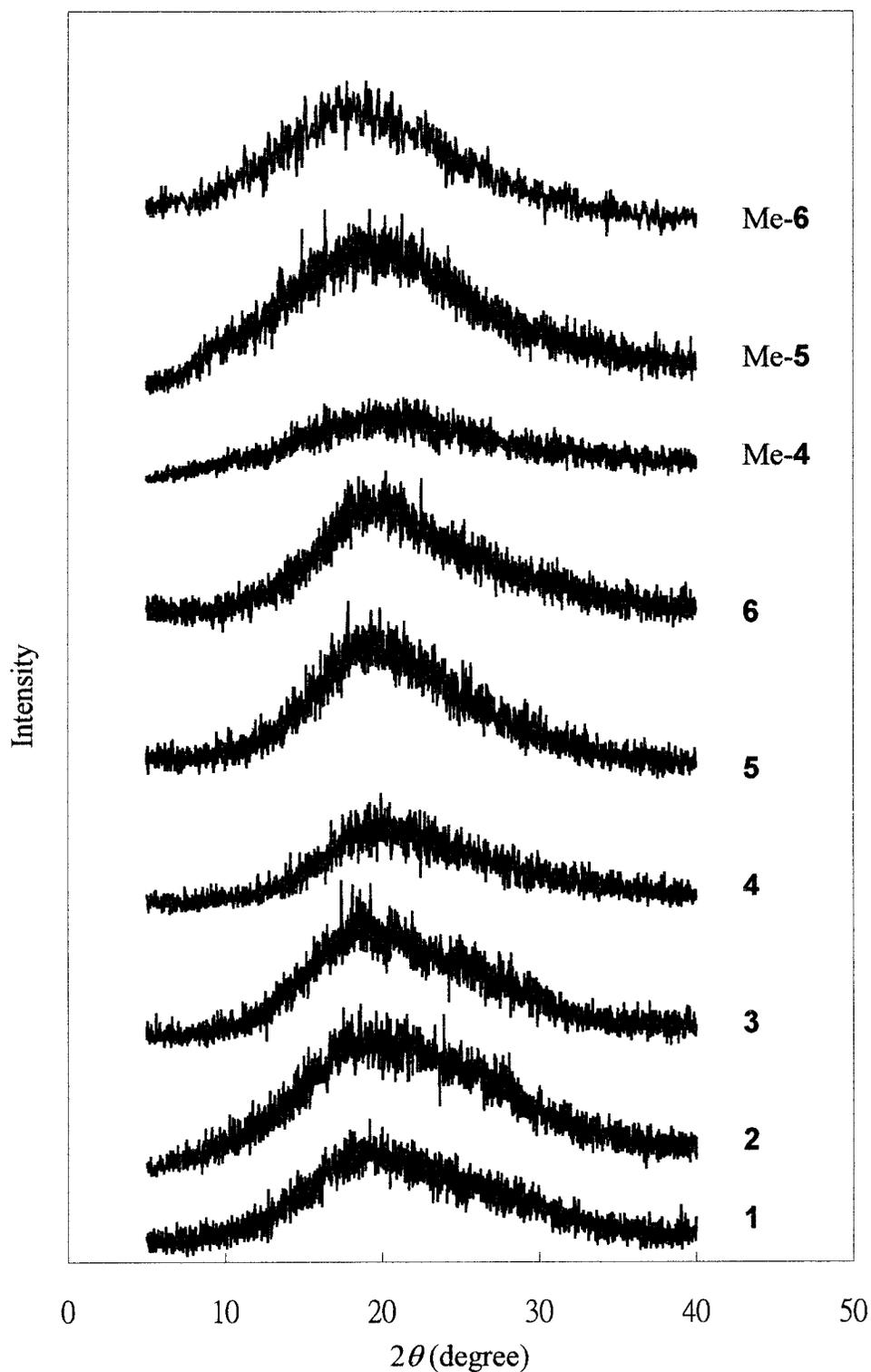


Figure 5. WAXD patterns of hydrazide polymers.

creases the conformational freedom of the polymer chain and tends to decrease  $T_g$  or  $T_s$ . However, the attachment of methyl substituents to

the backbone restricts the internal rotation, thus generally increasing,  $T_g$  or  $T_s$  of the hydrazide and oxadiazole polymers.<sup>27</sup>

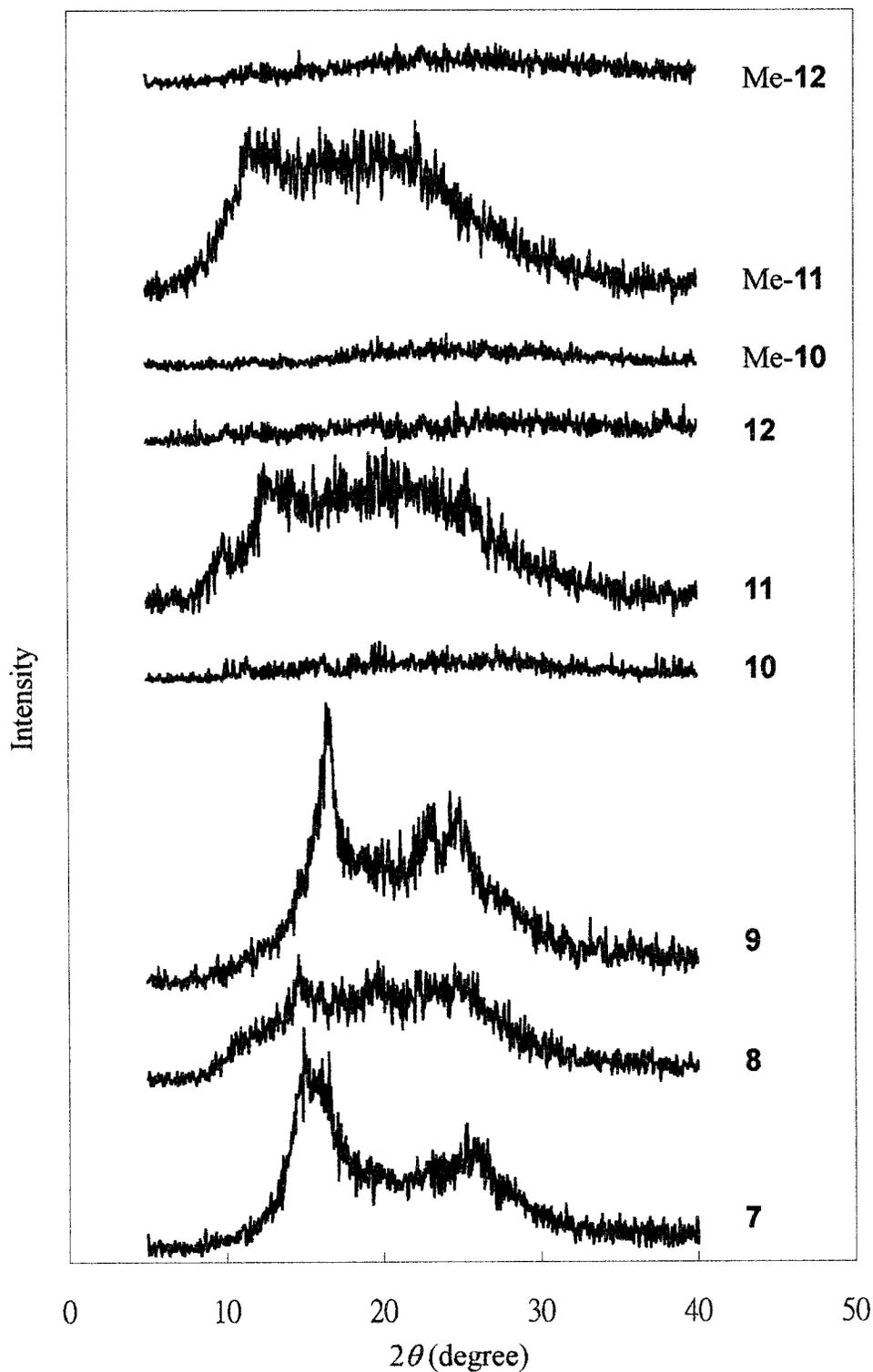


Figure 6. WAXD patterns of oxadiazole polymers.

Dynamic TGA implied that all the polyoxadiazoles and poly(amide-oxadiazole)s exhibited good thermal stability because no significant weight

losses were observed up to 400–450 °C in air or nitrogen atmospheres. Typical TGA curves are shown in Figure 8. Decomposition temperatures

**Table IV.** Tensile Properties of Polyhydrazide and Poly(amide-hydrazide) Films<sup>a</sup>

Polymer Code	Yield Strength (MPa)	Strength to Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
<b>1</b>	71	62	17	2.34
<b>2</b>	75	60	8	2.52
<b>3</b>	72	71	21	2.75
<b>4</b>	92	91	10	2.55
<b>5</b>	90	88	9	2.36
<b>6</b>	84	81	8	2.69
Me-4	85	82	10	2.46
Me-5	88	83	12	2.17
Me-6	70	69	6	2.22

<sup>a</sup> Films were cast from a slow evaporation of DMAc solutions and further dried *in vacuo* at 160 °C for about 6 h.

( $T_d$ 's) corresponding to a weight loss of 10% were recorded in a range of 477–501 °C in air and 476–502 °C in nitrogen. There is no clear dependence between the thermal stability and chemical structure of the polymer. The degradation seems to start by breaking the sulfonyl groups, and so the structure of diacid or hydrazide monomers does not seem to influence the thermal stability.

Finally, the methyl substituent in the Me-10–12 polyoxadiazoles may be thermally oxidized to form a pendant carboxyl group followed by decarboxylation at elevated temperatures. Figure 9 shows IR spectra of a thin film of poly(1,3,4-oxadiazole) Me-10 after being heated sequentially in air for 30 min each at 350, 400, 425, 450, and 475 °C. After heating at 350 °C for 30 min, a decrease in relative intensities around 2800–2900  $\text{cm}^{-1}$  ( $-\text{CH}_3$  stretching) indicates some loss of methyl groups. The intense bands at 1680 and 1740  $\text{cm}^{-1}$  are characteristic of carbonyl stretching. After further heating at 400 °C for 30 min, the disappearance of the methyl stretching at 2800–2900  $\text{cm}^{-1}$  and an increase in intensities at 1680 and 3000–3500  $\text{cm}^{-1}$  are suggestive of complete oxidation of the methyl substituents and the appearance of carboxyl groups instead. Upon further heating to higher temperatures such as 450 °C, decomposition of the carboxyl groups is confirmed by the decrease in intensities of the carboxyl absorption bands. At a higher degree of decomposition (heated to 475 °C), the residual solid shows a typical spectrum of highly carbonized materials. A broad absorption around 1500–1600  $\text{cm}^{-1}$  demonstrates the presence of individual aromatic rings and small polynuclear aromatic systems. The ab-

**Table V.** Thermal Properties of Hydrazide and Oxadiazole Polymers

Hydrazide Polymers				Oxadiazole Polymers					
Polymer Code	$T_g$ (°C) <sup>a</sup>	$T_o$ (°C) <sup>b</sup>	$T_p$ (°C) <sup>c</sup>	Code	$T_g$ (°C) <sup>d</sup>	$T_g$ (°C) <sup>e</sup>	$T_d$ (°C) <sup>f</sup>		Char Yield (%) <sup>g</sup>
							In Air	In N <sub>2</sub>	
<b>1</b>	— <sup>h</sup>	278	308	<b>7</b>	315	— <sup>h</sup>	491	488	45
<b>2</b>	181	264	324	<b>8</b>	257	260	477	476	45
<b>3</b>	—	285	302	<b>9</b>	320	—	490	484	46
<b>4</b>	156	267	309	<b>10</b>	215	217	501	502	55
<b>5</b>	178	251	304	<b>11</b>	251	255	496	499	52
<b>6</b>	149	236	274	<b>12</b>	238	224	497	500	45
Me-4	207	277	307	Me-10	268	251	495	491	60
Me-5	202	269	301	Me-11	245	243	487	488	62
Me-6	203	268	282	Me-12	238	236	484	489	55

<sup>a</sup> Temperature at the middle point of the baseline shift on the first DSC heating trace with a heating rate of 20 °C/min in nitrogen.

<sup>b</sup> Extrapolated onset temperature of the endothermic peak.

<sup>c</sup> Endothermic peak temperature.

<sup>d</sup> Onset temperature of probe displacement on the TMA trace, in which the TMA experiments were conducted with a penetration probe 1.0 mm in diameter, an applied constant load of 10 mN, and a heating rate of 10 °C/min.

<sup>e</sup> Midpoint temperature of the baseline shift on the second DSC heating trace of the sample after rapid cooling from 400 °C in nitrogen.

<sup>f</sup> Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

<sup>g</sup> Residual weight percentage when heated to 800 °C in nitrogen.

<sup>h</sup> No discernible transitions were observed.

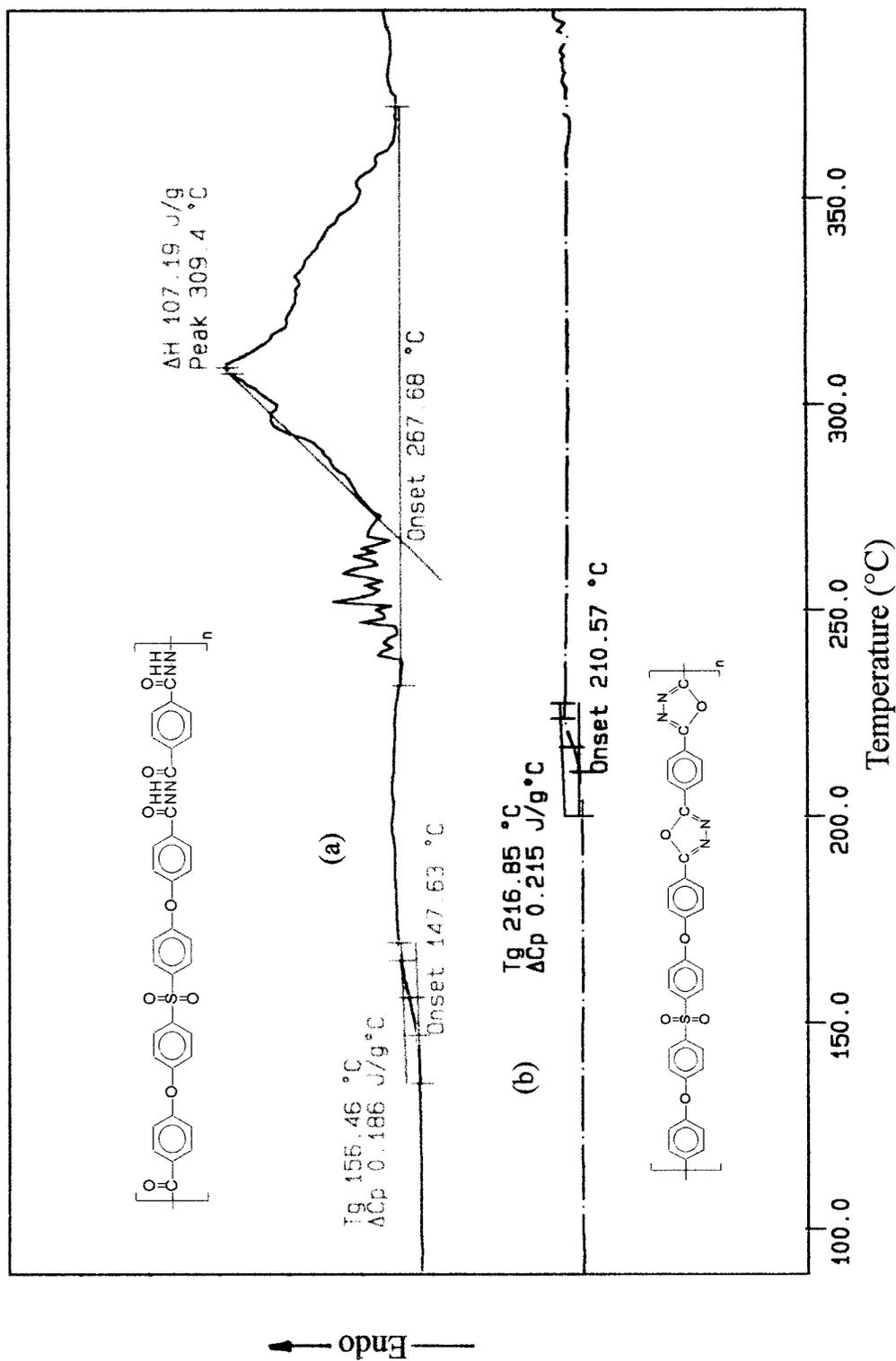
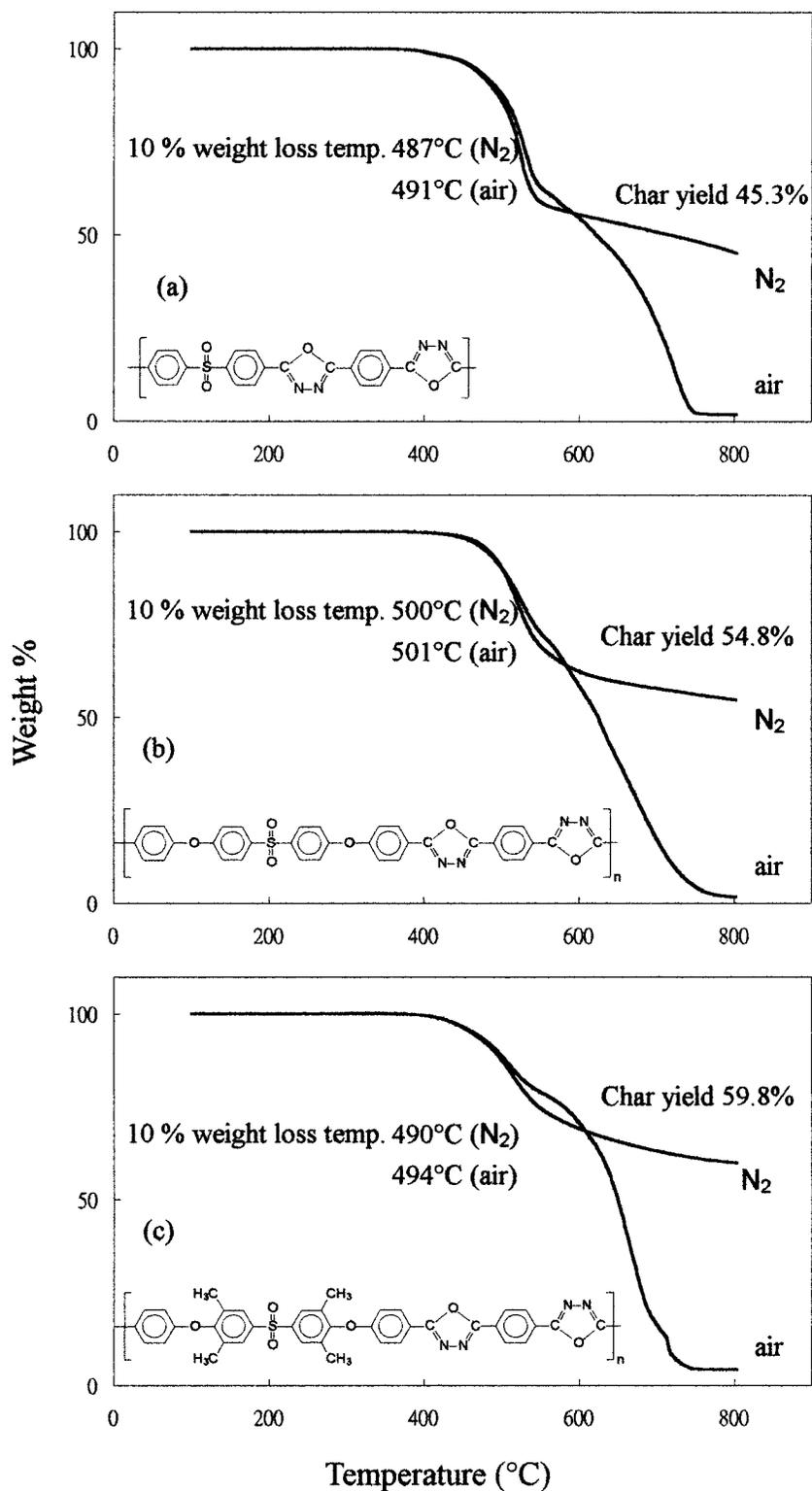
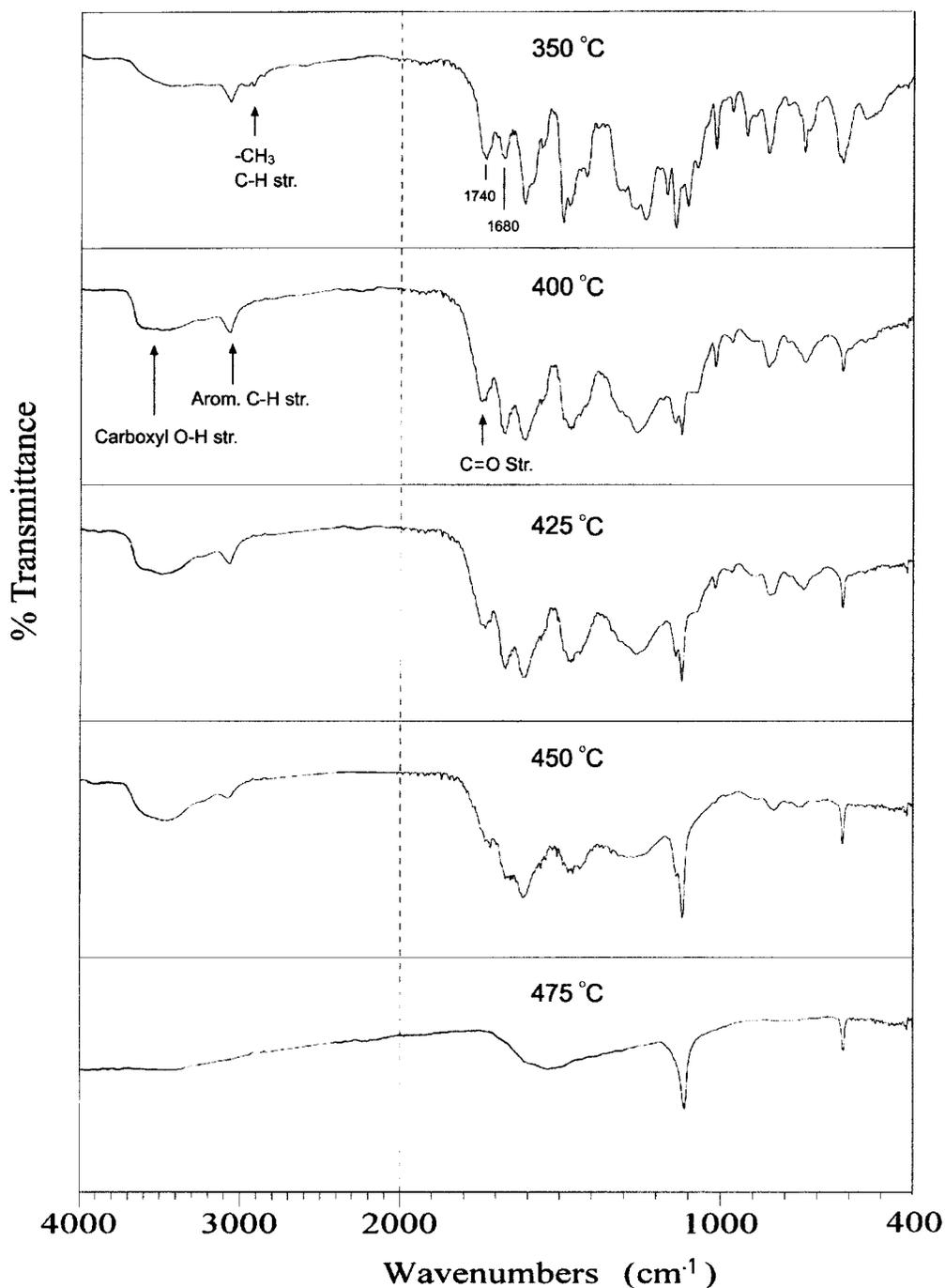


Figure 7. DSC curves of (a) polyhydrazide 4 and (b) poly(1,3,4-oxadiazole) 10 at a heating rate of 20 °C/min under nitrogen.



**Figure 8.** TGA curves of poly(1,3,4-oxadiazole)s (a) **7**, (b) **10**, and (c) **Me-10** at a heating rate of 20 °C/min.



**Figure 9.** FTIR spectra (thin films) of poly(1,3,4-oxadiazole) Me-10 after sequential heating in air at the indicated temperatures, each for 30 min.

sorption band that appeared at  $1100\text{ cm}^{-1}$  likely belongs remaining ether groups.

## CONCLUSIONS

Moderate to high molecular weight polyhydrazides and poly(amide-hydrazide)s as poly(1,3,4-

oxadiazole) and poly(amide-1,3,4-oxadiazole) precursors were successfully synthesized from sulfonyl dicarboxylic acids such as SDBA, SODBA, and 4MeSODBA or their diacyl chlorides with TPH, IPH, or *p*-ABH via the phosphorylation technique or low-temperature solution polycondensation. All the hydrazide polymers were amor-

phous and readily soluble in a variety of organic solvents and afforded colorless, good quality, and creasable films by solution casting. They had  $T_g$ 's between 149 and 207 °C and could be converted into the respective polyoxadiazoles and poly-(amide-oxadiazole)s at elevated temperatures. The oxadiazole polymers had a deep brown color. They showed significantly decreased solubility and mechanical strengths and increased  $T_g$ 's (218–260 °C) with respect to the corresponding hydrazide precursors. The polymers derived from SODBA and 4MeSODBA showed lower  $T_g$ 's and less crystallinity with respect to the corresponding ones based on SDBA. It was also demonstrated that tetramethyl substitution at the ortho positions to the flexible ether linkages increased rotational barriers and formed more rigid segments that enhanced  $T_g$  and  $T_s$  values. The incorporation of ether linkages and methyl substituents did not seem to significantly influence the thermal stability of the oxadiazole polymers.

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