

A New Class of Aromatic Poly(1,3,4-oxadiazole)s and Poly(amide-1,3,4-oxadiazole)s Containing (Naphthalenedioxy)diphenylene Groups

Sheng-Huei HSIAO[†] and Guey-Sheng LIOU*

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan, Republic of China

*Department of Applied Chemistry, National Chi Nan University, 1 University Road Puli, Nantou Hsien 545, Taiwan, Republic of China

(Received August 12, 2002; Accepted October 29, 2002)

ABSTRACT: Polyhydrazides and poly(amide-hydrazide)s having inherent viscosities of 0.31–1.17 dL g⁻¹ were prepared from two ether-naphthalene-dicarboxylic acids, 4,4'-(1,5-naphthalenedioxy)dibenzoic acid (1,5-NDA) and 4,4'-(2,3-naphthalenedioxy)dibenzoic acid (2,3-NDA) with terephthalic dihydrazide, isophthalic dihydrazide, and *p*-aminobenzhydrazide *via* the phosphorylation polycondensation reaction. Except for one example, the hydrazide polymers were essentially amorphous and readily soluble in polar organic solvents such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc). They could be cast into transparent, flexible, and tough films with good mechanical strengths from solution in DMAc. These hydrazide polymers exhibited glass-transition temperatures (T_g s) in the range 179–190 °C and could be thermally cyclodehydrated into the corresponding poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s in the solid state at elevated temperatures. The oxadiazole polymers had T_g s of 228–242 °C (by differential scanning calorimetry) and 10% weight loss temperatures above 500 °C, as revealed by thermogravimetric analysis in nitrogen or in air.

KEY WORDS Naphthalenedioxy / Polyhydrazide / Poly(amide-hydrazide) / Poly(1,3,4-oxadiazole) / Poly(amide-1,3,4-oxadiazole) /

Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.^{1,2} They are considered to be interesting alternatives for the development of high temperature and flame resistant fibers,^{3,4} or thermally stable membranes for gas separation.⁵ In addition, oxadiazole-based polymers have been widely investigated in the field of polymer light-emitting diodes as well as other fields of polymer electronics.^{6–11} Unfortunately, aromatic polyoxadiazoles are difficult to process owing to their infusible and insoluble properties and their tendency to be brittle. Many efforts have been made to improve the solubility and lower the T_g , hence to make such polymers more easily processable, for example by incorporating flexible linkages in the backbone or bulky pendant group on the aromatic rings.^{12–18}

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 heating in a dehydrating solvent such as sulfuric acid, polyphosphoric acid, or phospho-

ryl chloride.^{19–21} A different synthetic procedure produces polyoxadiazoles in one step by the solution polymerization of a dicarboxylic acid or the corresponding nitrile, amide, or ester with hydrazine or its salt in polyphosphoric or sulfuric acid or a phosphorus pentoxide/methanesulfonic acid mixture.^{16,22,23} In addition, aromatic polyether synthesis through aromatic nucleophilic displacement reaction has been used for the preparation of aryl ether-containing poly(1,3,4-oxadiazole)s or 1,3,4-oxadiazole-containing polyethers.^{15,24}

We have demonstrated that (1,5- or 2,3-naphthalenedioxy)diphenylene-unit-containing dicarboxylic acids and dianhydrides are able to give aromatic polyamides and polyimides with a good combination of properties and processability.²⁵ These monomers are also able to restrict regular chain packing into an ordered structure. In order 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-naphthalene-dicarboxylic acids 1,5-NDA and 2,3-NDA with commercially available dihydrazide or aminohydrazide monomers. It was hoped that incor-

[†]To whom correspondence should be addressed (E-mail: shhsiao@ttu.edu.tw).

poration of both ether and 1,5- or 2,3-naphthalenediyl units would result in amorphous oxadiazole polymers with enhanced processing characteristics.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP) and pyridine were stirred over powdered calcium hydride overnight and then distilled under reduced pressure and stored over 4 Å molecular sieves. Terephthalic dihydrazide (TPH), isophthalic dihydrazide (IPH), and *p*-aminobenzhydrazide (*p*-ABH) were purchased from TCI and used without further purification. As described in previous publications,²⁵ the ether-naphthalenedicarboxylic acids, 4,4'-(1,5-naphthalenedioxy)dibenzoic acid (1,5-NDA) (mp 336–337 °C, by DSC) and 4,4'-(2,3-naphthalenedioxy)dibenzoic acid (2,3-NDA) (mp 281–282 °C, by DSC), were prepared by the fluorodisplacement of *p*-fluorobenzonitrile with the potassium naphthoxide of 1,5-dihydroxynaphthalene and 2,3-dihydroxynaphthalene, respectively, and subsequent alkaline hydrolysis of the intermediate dinitriles. Commercially obtained anhydrous calcium chloride (CaCl₂) was dried under vacuum at 180 °C for 8 h. Other reagents and solvents were obtained commercially and used as received.

General Polymer Synthesis

The phosphorylation polycondensation method was used to prepare the polyhydrazides and poly(amide-hydrazide)s presented in this study. A typical synthetic procedure for polyhydrazide **2** is described as follows. A dried 50-mL flask was charged with 1,5-NDA (0.6006 g; 1.5 mmol), IPH (0.2913 g; 1.5 mmol), NMP (6 mL), CaCl₂ (0.6 g), diphenyl phosphite (DPP) (1.2 mL), and pyridine (1.5 mL). The mixture was heated with stirring at 120 °C for 3 h. As polycondensation proceeded, the solution became viscous gradually. The resulting highly viscous polymer solution was poured slowly into 300 mL of methanol with stirring, giving a fibrous pale-brown precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried. The yield was quantitative, and the inherent viscosity of the polymer **2** was 0.71 dL g⁻¹, measured in DMSO at a concentration of 0.5 g dL⁻¹ at 30 °C. IR (film): 3252 (N–H), 1653 (C=O), 1251 cm⁻¹ (Ar–O–Ar).

Film Preparation and Cyclodehydration of the Hydrazide Polymers

A solution of the hydrazide polymer of approximate 10 wt% was made by dissolving about 0.8 g of the poly-

mer in 8 mL of DMAc. The clear solution was poured into a 9-cm diameter glass culture dish, which was placed in an oven at 90 °C overnight in order to slowly release the cast solvent. The obtained semidried polymer film was lifted off the glass substrate and further dried in vacuum at 160 °C for 8 h. The thickness of these films was controlled between 60–70 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 by heating the above fabricated polymer films at 200 °C for 30 min, 250 °C for 1 h, 300 °C for 1 h, and 350 °C for 1 h under a nitrogen atmosphere.

Measurements

Inherent viscosities (η_{inh}) were measured for a polymer solution of 0.5 g dL⁻¹ concentration at 30 °C using a Cannon–Fenske viscometer. Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer on solution cast films or films cast on potassium bromide (KBr) windows. Elemental analyses were performed by a Heraeus VarioEL-III analyzer. Wide-angle X-Ray diffraction (WAXD) measurements were performed at room temperature on a Siemens Kristalloflex D5000 X-Ray diffractometer, operating in the 2 θ range of 5–45° at the scan rate of 3° min⁻¹ using nickel-filtered Cu-K α radiation (λ = 1.5418 Å, operating at 40 kV and 20 mA). An Instron universal tester model 1130 with a load cell of 5 kg was used to study the stress–strain behavior of the polymer films. A gauge length of 2 cm and a crosshead speed of 5 mm min⁻¹ were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and 60–70 μm thick), and an average of at least three replicas was used. Differential scanning calorimetry (DSC) was performed on a PerkinElmer DSC 7 differential scanning calorimeter in flowing nitrogen with a heating rate of 20 °C min⁻¹. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. 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 cm³ min⁻¹) at a scan rate of 20 °C min⁻¹. The measurements were taken after a 350 °C/30 min drying step for all the polyoxadiazole and poly(amide-oxadiazole) 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 from various combinations of the monomers listed in Figure 1. The reaction proceeds through an intermediate polyhydrazide or poly(amide-hydrazide) whose hydrazide groups undergo thermal cyclodehydration to form the 1,3,4-oxadiazole rings. Structures and codes of all the polymers are shown in Figure 2. The Yamazaki–Higashi phosphorylation technique²⁶ was used for the synthesis 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 clear and viscous polymer solutions. The inherent viscosity values of the resulting hydrazide polymers were in the range 0.31–1.17 dL g⁻¹, indicative of a modest degree of polymerization. Except polymers **1** and **4**, which were derived from rigid and symmetrical TPH, all of the other polyhydrazides and poly(amide-hydrazide)s formed transparent and creasable films from DMAc. The cast films of the hydrazide polymers (**4–6**) derived from 2,3-NDA exhibited a high optical transparency and were essentially colorless, and those of polymers **1–3** from 1,5-NDA were light yellow in color.

The hydrazide polymers were cyclodehydrated through heating in the solid state. Probably due to the increased length of conjugated chain and/or the formation of charge-transfer complex between the oxadiazole ring and the aromatic unit, the films or the bulks turned into darkened and deep brown after cyclodehydration. The films of thermally cured poly(amide-1,3,4-oxadiazole)s **9** and **12** were still good and non-brittle. However, in other cases, conversion resulted in shrunken and embrittled poly(1,3,4-oxadiazole) films. The observed brittleness is similar to that reported in literature²⁰ and is likely to be caused by chain shrinkage upon conversion, a low molecular weight, a lack of orientation, or a combination of these phenomena.

Thermal conversion of the hydrazide group to the

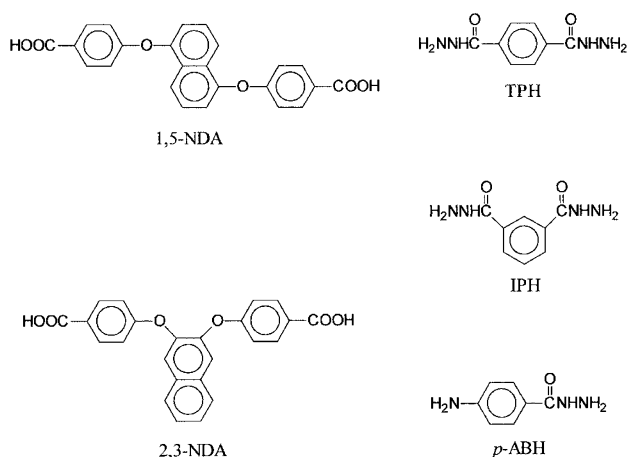


Figure 1. Structures and codes of monomers.

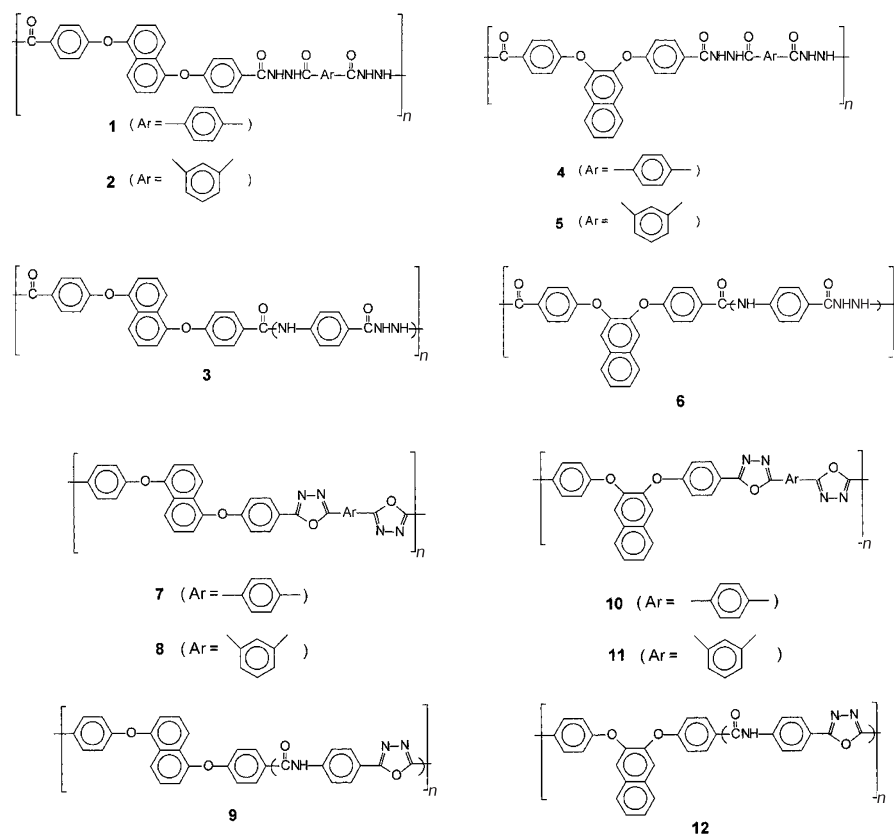


Figure 2. Structures and codes of polymers.

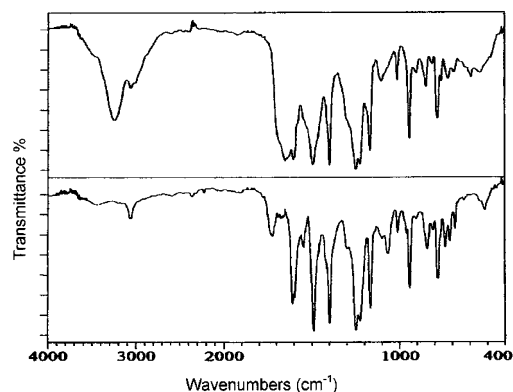
Table I. Synthetic conditions, inherent viscosities, and film quality of polyhydrazides and poly(amide-hydrazide)s

| Polymer code | Combination of monomers | Amount of reagents used ^a | | | | η_{inh} (dL g ⁻¹) ^b | Film quality ^c |
|--------------|-------------------------|--------------------------------------|------------|-------------|--------------------------|--|---------------------------|
| | | NMP (mL) | Py (mL) | DPP (mL) | CaCl ₂ (g) | | |
| 1 | 1,5-NDA + TPH | 8 | 2.0 | 1.2 | 0.8 | 0.65 | Highly brittle |
| 2 | 1,5-NDA + IPH | 6 | 1.5 | 1.2 | 0.6 | 0.71 | Flexible |
| 3 | 1,5-NDA + <i>p</i> -ABH | 6 | 1.5 | 1.2 | 0.6 | 1.17 | Flexible |
| 4 | 2,3-NDA + TPH | 3 | 0.8 | 1.2 | 0.3 | 0.31 | Slightly brittle |
| 5 | 2,3-NDA + IPH | 3 | 0.8 | 1.2 | 0.3 | 0.32 | Flexible |
| 6 | 2,3-NDA + <i>p</i> -ABH | 3 | 0.8 | 1.2 | 0.3 | 0.50 | Flexible |

^a1.5 mmol each of the diacid and dihydrazide or *p*-ABH were used. Reaction temperature = 120 °C; time = 3 h; NMP = *N*-methyl-2-pyrrolidone; Py = pyridine; DPP = diphenyl phosphite. ^bMeasured in dimethyl sulfoxide at 30 °C on 0.5 g dL⁻¹. ^cFilms were cast from slow evaporation of the polymer solutions in *N,N*-dimethylacetamide.

Table II. Elemental analysis of poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s

| Polymer code | Formula (Formula weight) | Elemental analysis | | | | | |
|--------------|--|--------------------|------|-------|-----------|------|-------|
| | | Calcd (%) | | | Found (%) | | |
| | | C | H | N | C | H | N |
| 7 | (C ₃₂ H ₁₈ N ₄ O ₄) _n (522.52) _n | 73.56 | 3.47 | 10.72 | 71.93 | 3.38 | 10.42 |
| 8 | (C ₃₂ H ₁₈ N ₄ O ₄) _n (522.52) _n | 73.56 | 3.47 | 10.72 | 71.21 | 3.46 | 10.08 |
| 9 | (C ₃₁ H ₁₉ N ₃ O ₄) _n (497.51) _n | 74.84 | 3.85 | 8.45 | 72.87 | 3.92 | 8.15 |
| 10 | (C ₃₂ H ₁₈ N ₄ O ₄) _n (522.52) _n | 73.56 | 3.47 | 10.72 | 71.46 | 3.64 | 10.55 |
| 11 | (C ₃₂ H ₁₈ N ₄ O ₄) _n (522.52) _n | 73.56 | 3.47 | 10.72 | 72.01 | 3.46 | 10.25 |
| 12 | (C ₃₁ H ₁₉ N ₃ O ₄) _n (497.51) _n | 74.84 | 3.85 | 8.45 | 73.14 | 3.92 | 8.24 |

**Figure 3.** FT-IR spectra of polyhydrazide **2** (top) and poly(1,3,4-oxadiazole) **8** (bottom).

1,3,4-oxadiazole ring could be monitored by FT-IR. Figure 3 shows IR spectra of a typical set of polyhydrazide **2** and its corresponding poly(1,3,4-oxadiazole) **8**. Conversion of the acyl hydrazide group to the 1,3,4-oxadiazole unit can be confirmed by the disappearance of the N–H stretching absorption at 3252 cm⁻¹ and the carbonyl peak at 1653 cm⁻¹, together with the appearance of the oxadiazole characteristic bands at 1550 and 1070 cm⁻¹. Other characteristic vibrations include the stretching of the aryl ether groups at 1251

and 1160 cm⁻¹, and the aromatic skeletal stretching at 1610 and 1480 cm⁻¹. TGA and DSC, as discussed subsequently, were also used to investigate cyclization to the oxadiazole structure. Elemental analyses of the poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s are in a good agreement with the proposed structures, missing only the values found for the C-percentages that are always lower than the theoretical ones (Table II). That certainly can be attributed to the very aromatic nature of these polymers, which commonly leave a small coal residue in the standard conditions of microanalysis.

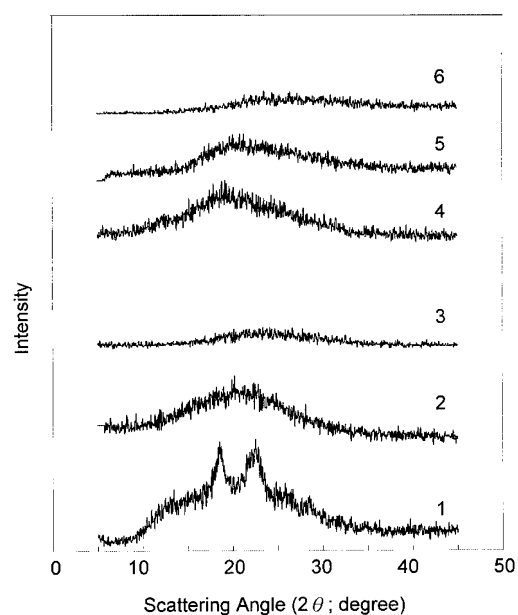
Polymer Properties

As shown in Table III, all of the polyhydrazides and poly(amide-hydrazide)s were readily soluble in polar solvents such as NMP, DMAc, and DMSO at room temperature. Except for polymer **1**, all of the polymers also dissolved in DMF and less polar *m*-cresol. The incorporation of ether linkages provides an increased chain flexibility, and introduction of the 2,3-naphthalenediyl unit into polymer backbone leads to increased chain packing distances and decreased interchain interactions such as hydrogen bonding; thus, polymers **4–6** are more

Table III. Solubility behavior of polyhydrazides and poly(amide-hydrazide)s^a

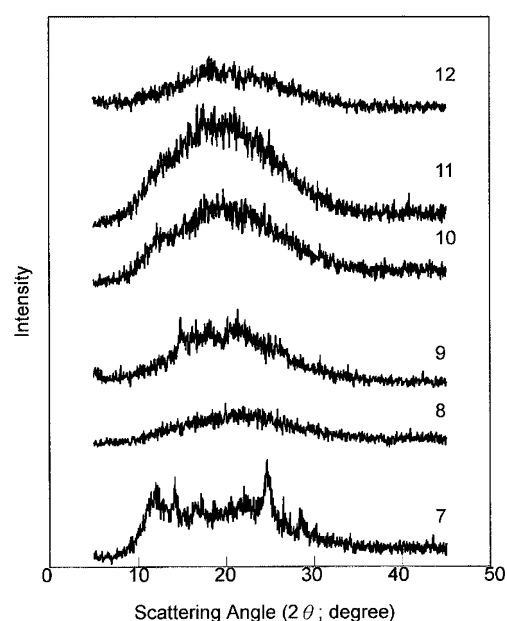
| Polymer | Solvent ^b | | | | | | | |
|----------|----------------------|------|-----|------|------------------|-----------|-----|------------|
| | NMP | DMAc | DMF | DMSO | <i>m</i> -Cresol | Sulfolane | THF | Chloroform |
| 1 | + | + | – | + | – | – | – | – |
| 2 | + | + | + | + | + | – | – | – |
| 3 | + | + | + | + | + | – | – | – |
| 4 | + | + | + | + | + | +h | – | – |
| 5 | + | + | + | + | + | +h | – | – |
| 6 | + | + | + | + | + | +h | – | – |

^aQualitative solubility was tested by using 10 mg of sample in 1 mL of solvent. +: soluble at room temperature; +h: soluble on heating at 100 °C; –: insoluble even on heating. ^bNMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; sulfolane: tetrahydrothiophene-1,1-dioxide; THF: tetrahydrofuran.

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

soluble than the corresponding polymers **1–3** containing the 1,5-naphthalenediyl units. Due to the increased chain rigidity, the oxadiazole polymers showed a dramatically decreased solubility as compared to the corresponding hydrazide prepolymers. The oxadiazole-based polymers **7–12** were insoluble in all the organic solvents tested. This also indicates that these oxadiazole polymers exhibit good chemical stability.

Wide-angle X-Ray diffraction patterns of all the polyhydrazides and poly(amide-hydrazide)s are shown in Figure 4. These diffractograms indicate that except polymer **1** all the hydrazide polymers are amorphous. The amorphous nature of these polymers was also reflected on their excellent solubility in organic solvents. Polyhydrazide **1** showed a semicrystalline pattern because of the more symmetrical 1,5-naphthalenediyl unit and rigid TPH moiety. By contrast, its structurally similar polyhydrazide **4** revealed an amorphous diffractogram due to the lateral arrangement of the 2,3-naphthalenediyl groups that will hinder interchain

**Figure 5.** Wide angle X-Ray diffractograms of poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s.

packing and help to reduce crystallinity. The X-Ray diffraction patterns of all oxadiazole polymers are given in Figure 5. All the oxadiazole polymers showed no dramatic increase in crystallinity, despite the presence of the rigid oxadiazole ring.

Most 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 64–83 MPa and elongations to break of 8–16%, indicating a moderate degree of toughness. The mechanical properties of the oxadiazole polymers were not evaluated, because most of them were too brittle that they cracked upon “fingernail” creasing.

DSC and TGA were employed to evaluate the thermal properties of all the hydrazide and oxadiazole polymers. In order to eliminate the effect of absorbed moisture and residual solvent on the thermal transitions,

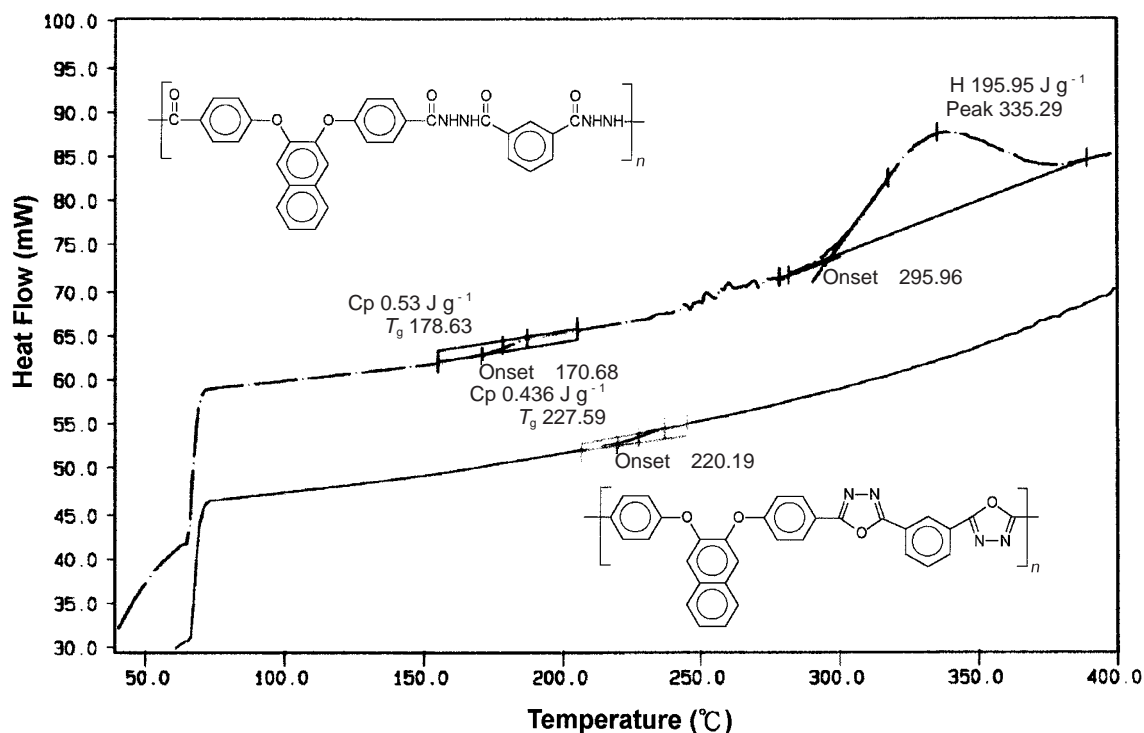


Figure 6. DSC traces of polyhydrazide **5** and poly(1,3,4-oxadiazole) **11** with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen.

Table IV. Tensile properties of polyhydrazide and poly(amide-hydrazide) films

| Polymer | Strength to break (MPa) | Elongation to break (%) | Initial modulus (GPa) |
|---------|-------------------------|-------------------------|-----------------------|
| 2 | 83 | 12 | 2.0 |
| 3 | 78 | 16 | 2.2 |
| 5 | 64 | 8 | 2.0 |
| 6 | 69 | 12 | 2.4 |

all the hydrazide polymers were heated from $30\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ at $20\text{ }^{\circ}\text{C min}^{-1}$ followed by rapid cooling to $30\text{ }^{\circ}\text{C}$ at $-100\text{ }^{\circ}\text{C min}^{-1}$. The subsequent DSC scan yields the baseline shift due to glass transition and endothermic peak due to cyclodehydration of the polyhydrazide samples. After quenching from $400\text{ }^{\circ}\text{C}$ with a programmed cooling rate of $100\text{ }^{\circ}\text{C min}^{-1}$, 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 **5** and poly(1,3,4-oxadiazole) **11** are illustrated in Figure 6. All the other polymers displayed similar DSC traces, and some of the DSC data are given in Tables V and VI. For the hydrazide precursor polymers, polymers **1** and **3** did not reveal discernible T_g , and the other polymers showed a distinct T_g centered in the range of $179\text{--}190\text{ }^{\circ}\text{C}$. As can be seen from the DSC thermograms, all the hydrazide polymers were almost completely converted to the corresponding oxadiazole polymers when heated to $350\text{--}400\text{ }^{\circ}\text{C}$ at a scan rate of $20\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen. Poly(1,3,4-oxadiazole) **7** did

Table V. Thermal behavior data of polyhydrazides and poly(amide-hydrazide)s^a

| Polymer | T_g ($^{\circ}\text{C}$) | T_o ($^{\circ}\text{C}$) | T_p ($^{\circ}\text{C}$) |
|---------|------------------------------|------------------------------|------------------------------|
| 1 | — ^b | 346 | 369 |
| 2 | 190 | 269 | 322 |
| 3 | — ^b | 336 | 356 |
| 4 | 181 | 293 | 326 |
| 5 | 179 | 296 | 335 |
| 6 | 185 | 293 | 350 |

^aDSC data obtained from the second DSC heating traces with a heating rate $20\text{ }^{\circ}\text{C min}^{-1}$. The samples were first heated to $250\text{ }^{\circ}\text{C}$ and then cooling down to $30\text{ }^{\circ}\text{C}$ at $-100\text{ }^{\circ}\text{C min}^{-1}$. T_g : the midpoint of baseline shift on the DSC curve; T_o : extrapolated onset temperature of the endotherm peak; T_p : endotherm peak temperature. ^bNo discernible T_g was observed.

not show a well-defined T_g by DSC because of high level of crystallinity. The other amorphous oxadiazole polymers displayed an obvious T_g on the DSC trace. As expected, all the oxadiazole polymers showed higher T_g values in comparison with the corresponding hydrazide prepolymers due to the increased chain rigidity; their T_g s stayed between 228 and $242\text{ }^{\circ}\text{C}$ (Table VI). The introduction of ether linkage in the chain increases the conformational freedom of the polymer chain and tends to decrease the T_g . Slightly higher T_g s for the **7–9** series in comparison to the **10–12** series might be a result of strong interactions and better packing due to the symmetrical nature of the 1,5-naphthalenediyl unit.

The TGA thermograms of all hydrazide polymers revealed an initial weight loss in the region of 300--

Table VI. Thermal behavior data of poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s

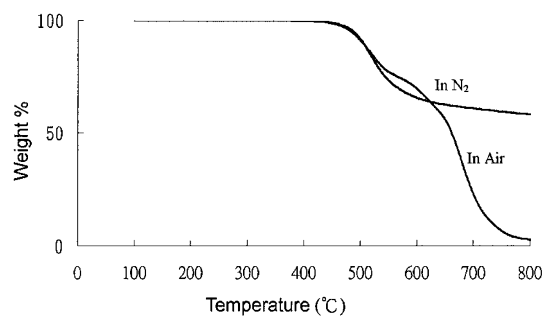
| Polymer | $T_g^a/^\circ\text{C}$ | $T_d^{b/f}/^\circ\text{C}$ | | Char yield (%) ^c |
|---------|------------------------|----------------------------|--------|-----------------------------|
| | | In N ₂ | In air | |
| 7 | — ^d | 505 | 504 | 59 |
| 8 | 237 | 503 | 503 | 59 |
| 9 | 242 | 521 | 519 | 63 |
| 10 | 233 | 504 | 504 | 56 |
| 11 | 228 | 503 | 506 | 56 |
| 12 | 233 | 501 | 509 | 61 |

^aMidpoint temperature of baseline shift on the second DSC heating trace (scan rate = 20 °C min⁻¹) of the sample after quenching from 400 °C. ^bDecomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C min⁻¹. ^cResidual weight % at 800 °C in nitrogen. ^dNo discernible T_g was observed.

400 °C. The weight loss is due to thermal cyclodehydration, which also agrees well with the strong endothermic peak on the DSC trace. Dynamic TGA implies that all the polyoxadiazoles and poly(amide-oxadiazole)s exhibit good thermal stability, because no significant weight losses were observed up to 450 °C in air or nitrogen atmosphere. Typical TGA curves are shown in Figure 7. Decomposition temperatures (T_d) corresponding to a weight loss of 10% were recorded in the range of 503–519 °C in air and 501–521 °C in nitrogen. There is no clear dependence between the thermal stability and the chemical structure of the polymer. It is also noted that there is a large window between T_g and the decomposition temperature of most oxadiazole polymers, which could be advantageous in the processing of these polymers by the thermoforming technique.

CONCLUSIONS

Moderate to high molecular weight polyhydrazides and poly(amide-hydrazide)s, as the poly(1,3,4-oxadiazole) and poly(amide-1,3,4-oxadiazole) precursors, were successfully synthesized from ether-naphthalene-dicarboxylic acids such as 1,5-NDA and 2,3-NDA with TPH, IPH or *p*-ABH via the phosphorylation solution polycondensation. The polyhydrazide derived from 1,5-NDA and TPH was semicrystalline and showed less solubility. The other hydrazide polymers were amorphous and readily soluble in a variety of organic solvents, and most of them could afford tough, good quality, and creasable films by solution casting. They had T_g s between 179–190 °C and could be converted into the respective polyoxadiazoles and poly(amide-oxadiazole)s at elevated temperatures. The thermally cured oxadiazole polymers showed significantly decreased solubility and mechanical strengths and increased T_g s (228–242 °C) as compared to the

**Figure 7.** TGA thermograms of poly(1,3,4-oxadiazole) 7 with a heating rate of 20 °C min⁻¹.

corresponding hydrazide precursors. The oxadiazole polymers derived from 2,3-NDA showed slightly lower T_g s compared to the corresponding ones based on 1,5-NDA. Incorporation of ether linkages and naphthalene units does not seem to influence the thermal stability of the oxadiazole polymers.

Acknowledgments. The authors are grateful to the National Science Council of the Republic of China for financial support of this work.

REFERENCES

- P. E. Cassidy, "Thermally Stable Polymers Synthesis and Properties", Marcel Dekker, New York, N.Y., 1980, p 179.
- M. J. Nanjan, in "Encyclopedia of Polymer Science and Engineering", H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwitz, Ed., John Wiley & Sons, Inc., New York, N.Y., 1988, vol. 12.
- A. H. Frazer and F. T. Wallenberger, *J. Polym. Sci., A*, **2**, 1171 (1964).
- H. H. Yang, "Aromatic High-Strength Fibers," John Wiley & Sons, Inc., New York, N.Y., 1989, pp 315–348.
- B. M. H. Gebben, M. H. V. Mulder, and C. A. Smolders, *J. Membr. Sci.*, **46**, 29 (1989).
- B. Schulz, L. Brehmer, B. Dietzel, and Th. Zetzsche, *React. Funct. Polym.*, **30**, 353 (1996).
- W.-L. Yu, H. Meng, J. Pei, W. Huang, Y. Li, and A. J. Heeger, *Macromolecules*, **31**, 4838 (1998).
- W. Huang, H. Meng, W.-L. Yu, J. Pei, Z.-K. Chen, and Y.-H. Lai, *Macromolecules*, **32**, 118 (1999).
- S.-Y. Song, M. S. Jang, M.-K. Shim, D.-H. Hwang, and T. Zyung, *Macromolecules*, **32**, 1482 (1999).
- Y.-Z. Lee and S.-A. Chen, *Synth. Met.*, **105**, 185 (1999).
- S. Janietz, S. Analau, and A. Wedel, *Macromol. Chem. Phys.*, **203**, 433 (2002).
- J. L. Hedrich, *Polymer*, **33**, 3375 (1992).
- C. J. Thaeplitz, W. J. Weikeil, and P. E. Cassidy, *Polymer*, **33**, 3278 (1992).
- E. R. Hensema, M. E. R. Sena, M. H. V. Mulder, and C. A. Smolders, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 527 (1994).
- Y. Saegusa, T. Iwasaki, and S. Nakamura, *Macromol. Chem. Phys.*, **198**, 1799 (1997).

16. G. Maglio, R. Palumbo, M. Tortora, M. Trifuoggi, and G. Varicchio, *Polymer*, **25**, 6407 (1998).
17. S.-H. Hsiao and C.-H. Yu, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 1847 (1998).
18. S.-H. Hsiao, L.-R. Dai, and M.-S. He, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 1169 (1999).
19. A. H. Frazer, W. Sweeny, and F. T. Wallenberger, *J. Polym. Sci., A*, **2**, 1157 (1964).
20. E. R. Hensema, J. P. Boom, M. H. V. Mulder, and C. A. Smolders, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 513 (1994).
21. S. Janietz and S. Anlauf, *Macromol. Chem. Phys.*, **203**, 427 (2002).
22. Y. Iwakura, K. Uno, and S. Hara, *J. Polym. Sci., A*, **3**, 45 (1965).
23. D. Gomes, C. P. Borges, and J. C. Pinto, *Polymer*, **42**, 851 (2001).
24. J. W. Connell, P. M. Hergenrother, and P. Wolf, U. S. Patent 5 118 781 (June 2, 1992).
25. a) S.-H. Hsiao and K.-Y. Chu, *Macromol. Chem. Phys.*, **198**, 819 (1997).
b) S.-H. Hsiao and K.-Y. Chu, *J. Polym. Sci., Part A: Polym. Chem.*, **35**, 3385 (1997).
c) S.-H. Hsiao, C.-P. Yang, and K.-Y. Chu, *Macromol. Chem. Phys.*, **198**, 2153 (1997).
d) S.-H. Hsiao, C.-P. Yang, and K.-Y. Chu, *Macromolecules*, **30**, 165 (1997).
26. a) J. Preston and W. L. Hofferbert, Jr., *J. Polym. Sci., Polym. Symp.*, **65**, 13 (1978).
b) F. Higashi and N. Kokubo, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1639 (1980).
c) F. Higashi and M. Ishikawa, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 2905 (1980).