

Synthesis and Properties of Poly(imide-hydrazide)s and Poly(amide-imide-hydrazide)s from *N*-[*p*-(or *m*-)Carboxyphenyl]trimellitimide and Aromatic Dihydrazides or *p*-Aminobenzhydrazide via the Phosphorylation Reaction

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ABSTRACT: A series of new poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s were obtained by the direct polycondensation of *N*-[*p*-(or *m*-)carboxyphenyl]trimellitimide (*p*- or *m*-CPTMI) with terephthalic dihydrazide (TPH), isophthalic dihydrazide (IPH), and *p*-aminobenzhydrazide (*p*-ABH) by means of diphenyl phosphite and pyridine in the *N*-methyl-2-pyrrolidone (NMP) solutions containing dissolved CaCl₂. The resulting hydrazide-containing polymers exhibited inherent viscosities in the 0.15–0.96 dL/g range. Except for that derived from *p*-CPTMI with TPH or *p*-ABH, the other hydrazide copolymers were readily soluble in polar solvents such as NMP and dimethyl sulfoxide (DMSO). As evidenced by X-ray diffraction patterns, the hydrazide copolymer obtained from TPH showed a moderate level of crystallinity, whereas the others were amorphous in nature. Most of the amorphous hydrazide copolymers formed flexible and tough films by solvent casting. The amorphous hydrazide copolymers had glass-transition temperatures (T_g) between 187 and 233 °C. All hydrazide copolymers could be thermally converted into the corresponding oxadiazole copolymers approximately in the region of 250–400 °C, as evidenced by the DSC thermograms. The oxadiazole copolymers showed a significantly decreased solubility when compared to their respective hydrazide precursors. They exhibited T_g 's of 264–302 °C and did not show dramatic weight loss before 400 °C in air or nitrogen. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 1599–1608, 2000

Keywords: poly(imide-hydrazide); poly(amide-imide-hydrazide); polyoxadiazole; diphenyl phosphite; direct polycondensation

INTRODUCTION

Aromatic polyimides are important classes of high-performance polymers due to their high thermo-oxidative stability, mechanical strength, and resistance to environmental degradation.^{1,2}

However, rigidity of the backbone and charge transfer complex formation result in insolubility in most organic solvents and high softening temperatures. These properties make them generally difficult or too expensive to process, thus restricting their applications. Therefore, much work has been done to improve the processability of aromatic polyimides while maintaining desirable properties. It is well known that the synthesis of poly(amide-imide)s and poly(ether-imide)s can of-

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fer a compromise between excellent thermal stability and processability.³⁻⁶

Incorporation of hydrazide or amide plus hydrazide linkages into the polyimide backbone is another alternative to improve the processability of polyimides. In addition, the hydrazide groups in the main chain can also be further converted into the more chemically resistant and thermally stable oxadiazole structure by heating the polymer in the bulk or fiber form at elevated temperatures.⁷ Poly(imide-1,3,4-oxadiazole)s with good solubility as well as desirable mechanical properties and thermal properties might be attained by incorporating varied aromatic structure with flexible linkages such as hexafluoroisopropylidene, ether, sulfone, and isopropylidene into the polymer backbones.⁸⁻¹⁰ Poly(imide-1,3,4-oxadiazole)s can be readily prepared from oxadiazole-containing diamines with dianhydrides via the general two-step method used to prepare aromatic polyimides.¹¹ Another approach for the synthesis of poly(imide-oxadiazole)s is the cyclodehydration of the poly(imide-hydrazide)s,⁸⁻¹⁰ in which the intermediate poly(imide-hydrazide)s are prepared from imide-preformed diacid chlorides and an aromatic dihydrazide by the low-temperature polycondensation method. Recently, we found that high molecular weight poly(imide-hydrazide)s or poly(amide-imide-hydrazide)s could be readily prepared from the direct polycondensation of imide-containing dicarboxylic acids with an aromatic dihydrazide or amino hydrazide monomer using the Yamazaki-Higashi phosphorylation technique¹²⁻¹⁴ that has been successfully applied in the poly(amide-imide) synthesis in this laboratory.¹⁵⁻¹⁷ This report summarizes our recent findings. Basic characterization of the poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s, and the thermally cyclodehydrated poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s are also investigated.

EXPERIMENTAL

Materials

N-(*p*-Carboxyphenyl)trimellitimide (*p*-CPTMI) (mp 377 °C; peak temperature of the DSC endotherm) and *N*-(*m*-carboxyphenyl)trimellitimide (*m*-CPTMI) (mp 420 °C; peak temperature of the DSC endotherm) were prepared by condensation of trimellitic anhydride with *p*-aminobenzoic acid and *m*-aminobenzoic acid, respectively, according

to the reported method.¹⁶ Commercially obtained anhydrous calcium chloride was dried under vacuum at 180 °C for 10 h. *N*-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Terephthalic dihydrazide (TPH) (TCI), isophthalic dihydrazide (IPH) (TCI), *p*-aminobenzhydrazide (*p*-ABH) (TCI), and diphenyl phosphite (DPP) (Fluka) were used as received.

Preparation of Poly(imide-hydrazide)s and Poly(amide-imide-hydrazide)s

A typical procedure for the synthesis of poly(amide-imide-hydrazide) **6** is as follows. In a 50-mL flask, a mixture of *m*-CPTMI (0.6225 g, 2 mmol) and *p*-ABH (0.3023 g, 2 mmol), 0.4 g of calcium chloride, 4 mL of NMP, 2 mL of DPP, and 1 mL of pyridine was heated with stirring at 120 °C. The reaction solution became too viscous to stir after about 1 h. Thus, additional 2 mL of NMP and 0.2 g of calcium chloride were added into the reaction mixture, and the reaction was continued at 120 °C for another 2 h. The resulting viscous polymer solution was poured slowly with stirring into 300 mL of methanol. The light yellow fiber-like precipitate formed was washed repeatedly with methanol and hot water, collected by filtration, and dried to give a quantitative yield of poly(amide-imide-hydrazide) **6**. The inherent viscosity of the polymer was 0.84 dL/g, measured in DMAc-5 wt % LiCl at a concentration of 0.5 g/dL at 30 °C.

All other poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s were synthesized from different monomer combinations by an analogous procedure.

Film Preparation and Cyclodehydration of the Poly(imide-hydrazide)s and Poly(amide-imide-hydrazide)s

A polymer solution was made by dissolving about 0.9 g of the poly(imide-hydrazide) or poly(amide-imide-hydrazide) samples in 10 mL of *N,N*-dimethylacetamide (DMAc). The solution was poured into a flat glass culture dish, 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 vacuum at 160 °C for 8 h. The obtained films had about 0.06 mm in thickness and were

used for tensile testing and X-ray diffraction measurements.

The conversion of poly(imide-hydrazide)s or poly-(amide-imide-hydrazide)s to poly(imide-1,3,4-oxadiazole)s or poly(amide-imide-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 1 h under a nitrogen atmosphere. The inherent viscosities of the oxadiazole polymers were determined in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30 °C.

Measurements

IR spectra were recorded on a Jasco FTIR-7000 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained using a JEOL EX-400 spectrometer operating at 399.65 and 100.40 MHz, respectively, on polymer solutions in dimethyl sulfoxide- d_6 (DMSO- d_6). The inherent viscosities were measured with a Cannon–Fenske viscometer thermostated at 30 °C. A Perkin–Elmer DSC 7 differential scanning calorimeter equipped with a Thermal Analysis Controller TAC 7/DX was used to determine the thermal transitions. Heating rate was 20 °C/min. Glass-transition temperatures (T_g 's) were read at the middle of the change in the heat capacity. Thermogravimetric analysis (TGA) was conducted with a DuPont 951 thermogravimetric analyzer. Experiments were carried out on 9–12 mg samples heated in flowing nitrogen or air (50 cm³/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 Cu K_α radiation (operating at 40 kV and 20 mA). The scanning rate was 3°/min over a range of $2\theta = 5\text{--}45^\circ$. 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 1 mm/min were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.06–0.08 mm thick). An average of at least six individual determinations was used.

RESULTS AND DISCUSSION

Polymer Synthesis

Poly(imide-hydrazide)s **1–4** and poly(amide-imide-hydrazide)s **5** and **6** were obtained by a direct

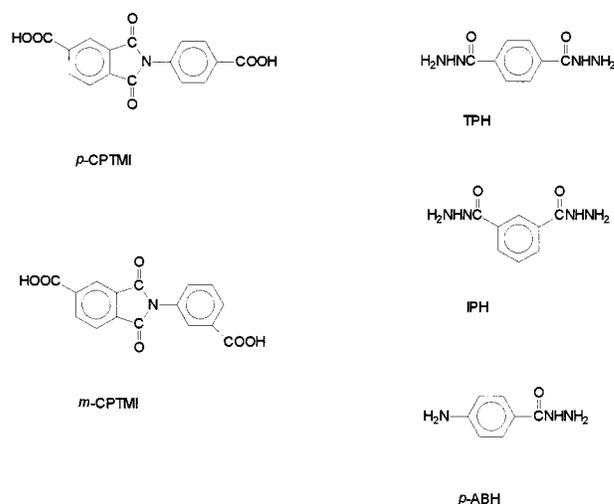


Figure 1. Structures and codes of monomers.

phosphorylation polycondensation from various combinations of the monomers listed in Figure 1, by means of diphenyl phosphite and pyridine, according to a modification of the Yamazaki–Higashi phosphorylation technique¹² developed by Preston and Hofferbert¹⁸ for the synthesis of poly-(amide-hydrazide)s. As described in one of our previous publications,¹⁹ more favorable results were obtained when using diphenyl phosphite (DPP) instead of triphenyl phosphite (TPP) in the phosphorylation polycondensation reactions between the dicarboxylic acid and dihydrazide or aminohydrazide monomers. A possible explanation proposed by Preston and Hofferbert¹⁸ is that the strongly basic acylhydrazine groups in monomers prevent the attainment of high molecular weight because such groups coordinate strongly with the phosphite complex than does the pyridine catalyst in the phosphorylation reaction. More favorable results from using DPP as the condensing agent possibly reflect that the acylhydrazine groups are less likely to complex with the phosphite intermediate derived from DPP than that derived from TPP. Therefore, DPP was employed as a condensing agent in this study. The structures and codes of these polymers are shown in Figure 2. The parentheses in the formulas of these polymers indicate that the asymmetric moieties may appear in the polymer chain as shown, or in the reverse orientation. 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. In general, using a higher

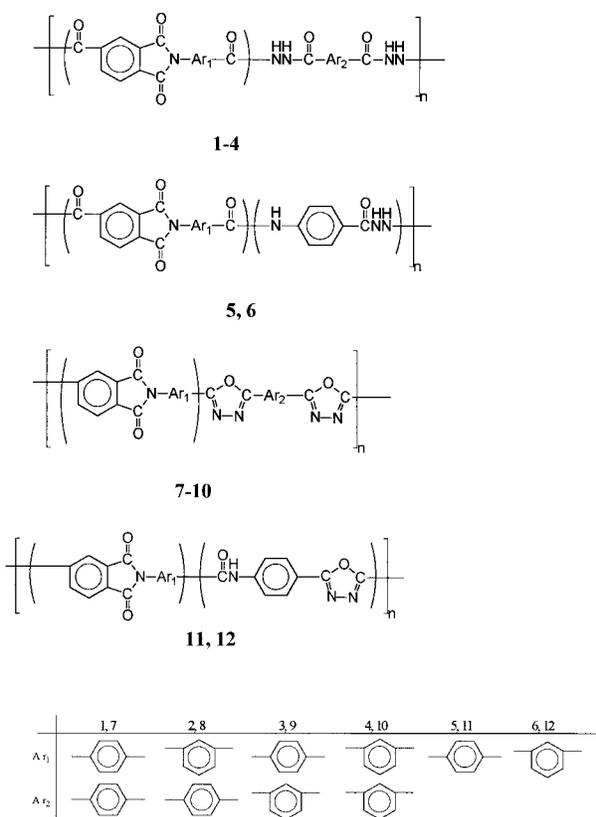


Figure 2. Structures and codes of polymers.

initial reaction concentration and adding a supplemental amount of the solvent and the metal salt before a swollen gel formed or precipitation occurred usually could produce polymers with a higher inherent viscosity. Synthesis conditions for the polycondensation reactions and the inherent viscosity values and film quality of the prepared poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s are summarized in Table I. Except for the reaction between *p*-CPTMI and TPH, all the polycondensation reactions proceeded homogeneously throughout the reaction and afforded clear, viscous polymer solutions. Most of the polymers were isolated as light yellow tough fibers upon precipitation in methanol. Although the reaction conditions were not optimized, using the conditions listed in Table I, polymers **2–6** having moderately high inherent viscosities of 0.30–0.96 dL/g were obtained, and most of them exhibited good film forming ability. These results indicate the formation of high molar mass polymers. The brittle nature of poly(imide-hydrazide) **2** may be due to its lower molecular weight or higher level of crystallinity. The cast film of poly(amide-imide-hydrazide) **5** cracked upon creasing, possibly due to the rigid nature of its backbone because of a high *para*-phenylene content. An early precipitation occurred during the synthesis of poly(imide-hydrazide) **1**, and increasing the amount of metal salts or solvent in order to carry out the reaction in a homogenous phase has met

Table I. Inherent Viscosities and Film Quality of Poly(imide-hydrazide)s and Poly(amide-imide-hydrazide)s

Polymer Code	Combination of Monomers	Amounts of Reagents Used ^a		Remark ^b	η_{inh}^c (dL/g)	Film Quality ^d
		NMP (mL)	CaCl ₂ (g)			
1	<i>p</i> -CPTMI + TPH	4 + 4	0.4 + 0.4	P	0.16 ^e	– ^g
2	<i>m</i> -CPTMI + TPH	4	0.4	H	0.30	Brittle
3	<i>p</i> -CPTMI + IPH	4 + 2	0.4 + 0.2	H	0.63	Flexible
4	<i>m</i> -CPTMI + IPH	4	0.4	H	0.52	Flexible
5	<i>p</i> -CPTMI + <i>p</i> -ABH	4 + 6	0.4 + 0.6	H	0.96 ^f	Slightly Brittle
6	<i>m</i> -CPTMI + <i>p</i> -ABH	4 + 2	0.4 + 0.2	H	0.84	Flexible

^a Reaction scale: 2 mmol of each monomer; pyridine = 1 mL; DPP = 2 mL; reaction temperature = 120 °C; reaction time = 3 h. “*x* + *y*” means that an initial amount of *x* mL NMP or *x* g CaCl₂ was used, and an additional *y* mL NMP or *y* g CaCl₂ was added when the reaction solution was too viscous to stir or precipitation occurred.

^b P: precipitation occurred during the reaction, H: homogeneously transparent throughout the reaction.

^c Measured at a concentration of 0.5 g/dL in DMAc–5 wt % LiCl at 30 °C.

^d Films were cast from slow evaporation of the polymer solutions in DMAc.

^e Measured in concentrated sulfuric acid.

^f Measured in dimethyl sulfoxide.

^g Insoluble in all available organic solvents.

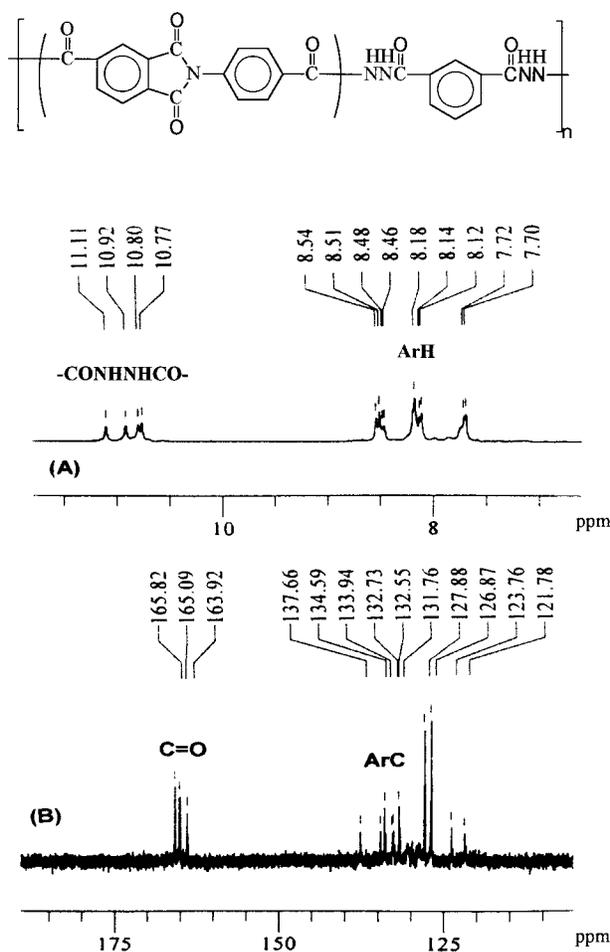


Figure 3. ^1H NMR (A) and ^{13}C NMR spectra (B) of poly(imide-hydrazide) **3** in $\text{DMSO-}d_6$.

with failure in obtaining a clear, viscous polymer solution. The unsatisfactory result may be attributable to its poor solubility because of the presence of more symmetric TPH moieties in the polymer chain, thus leading to a higher crystallinity.

The thermal cyclodehydration of all the hydrazide polymers was performed in bulk or film form by heating the polymers at 200 °C for 30 min, 250 °C for 30 min, and 300 °C for 1 h under nitrogen. The proposed structures and codes of the poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s are also shown in Figure 2.

The ^1H NMR and ^{13}C NMR analysis confirmed the molecular structure of the hydrazide polymers. Figure 3 shows the spectra of poly(imide-hydrazide) **3** as an example. In the ^1H NMR spectrum, the polymer showed its characteristic absorptions in the aromatic range of 7.70–8.54 δ . Multiple resonances for the hydrazide protons were observed between 10.7 and 11.1 δ . This may

be due to the constitutional disorder introduced by the asymmetric trimellitimide unit, which gives rise to a random enchainment of the repeat units. The same intensity of the NH resonances suggests a statistical random distribution of head-to-head and head-to-tail sequence in the polymer chain. In the ^{13}C NMR spectrum, the characteristic resonances of aromatic carbons were found in the range 121.8–137.7 δ , and the carbonyl carbons resonated at 163.9–165.8 δ . However, the NMR spectra of the corresponding oxadiazole polymer have not been determined because of its insolubility in common deuterated solvents. Thus, the cyclodehydration of the imide-hydrazide and amide-imide-hydrazide polymers was monitored by IR spectroscopy. Figure 4 shows the comparative IR spectra for poly(imide-hydrazide) **4** and its derived poly(imide-1,3,4-oxadiazole) **10**. The IR spectrum of **4** shows the NH stretching at around 3250 cm^{-1} and the carbonyl stretching at 1650–1680 cm^{-1} . These absorption bands disappeared in the IR spectrum of the poly(imide-1,3,4-oxadiazole) **10**. The characteristic band due to the oxadiazole ring vibration was observed at 1551 cm^{-1} , similar to that reported in literature.^{7, 20–22} The strong bands appearing in both spectra at 1781, 1725 (carbonyl stretching), 1371 (C–N stretching), 1100, and 727 cm^{-1} (imide ring deformation) were assigned to the imide rings. A small absorption appearing in both spectra at about 3480 cm^{-1} may be attributed to an overtone of the carbonyl stretching vibration (1725–1780 cm^{-1}). Moreover, cyclization of the hydrazide group to the oxadiazole structure has also been studied by DSC and TG, as discussed subsequently.

Polymer Properties

Solubility of the poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s was determined qualitatively, and the results are listed in Table II. Except for poly(imide-hydrazide) **1**, all the poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s were soluble at least in DMSO. Polymers **2–4** and **6** were also readily soluble in the amide-type polar solvents such as NMP, DMAc, and DMF. The relatively lower solubility associated with polymers **1** and **5** was believed to be related to their higher proportion of *p*-phenylene units, which allow relatively strong interchain interaction and the extended close packing of polymer chains. None of the polymers were soluble in sul-

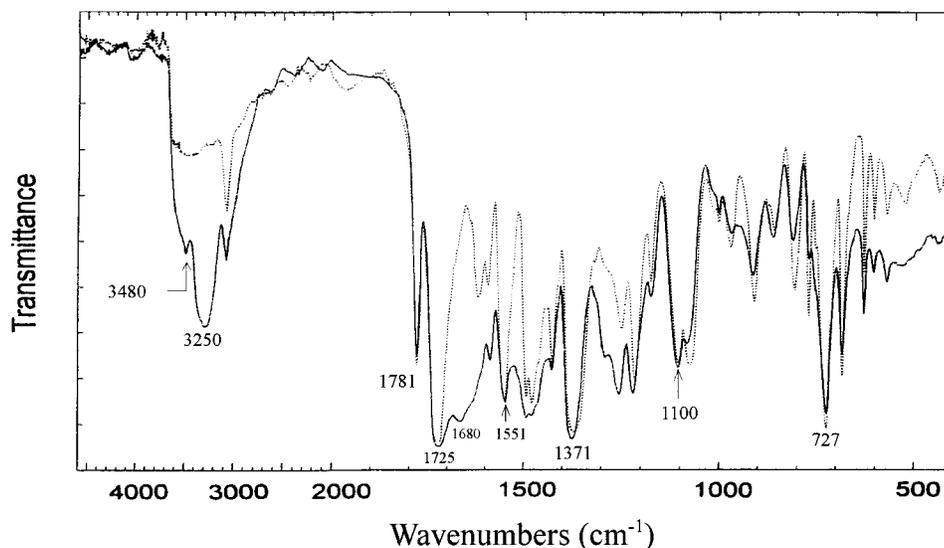


Figure 4. IR spectra of poly(imide-hydrazide) **4** (—) and poly(imide-1,3,4-oxadiazole) **10** (· · ·).

folane and common solvents like THF, chloroform, ethanol, and acetone.

The hydrazide polymers were cyclodehydrated by heating them in the solid state. Probably because of the conjugation between the oxadiazole ring and aromatic unit or the increased charge-transfer complexing, the films or the bulks turned from pale yellow into darkened, brownish after heat treatment. Thermal conversion in all cases resulted in shrunken and embrittled poly(imide-1,3,4-oxadiazole) and poly(amide-imide-1,3,4-oxa-

diazole) films. This effect has been previously reported by Henesema et al.,²⁰ and may be due to chain shrinkage upon conversion and/or insufficient molecular weight. There was also found a decrease in the inherent viscosity of the oxadiazole polymers when compared with the corresponding poly(imide-hydrazide) and poly(amide-imide-hydrazide) precursors. Similar results were obtained by Hamciuc et al.^{9, 10} and Maglio et al.²² for the syntheses of poly(imide-1,3,4-oxadiazole)s, poly(amide-imide-1,3,4-oxadiazole)s, and poly(1,3,4-oxadiazole)s. As shown in Table III, the inherent viscosities of our oxadiazole polymers ranged from 0.16 to 0.41 dL/g. As described above, poly(imide-hydrazide)s **2–4** and poly(amide-imide-hydrazide) **6** were readily soluble in polar solvents, whereas the corresponding oxadiazole polymers **8–10** and **12** were insoluble in the same solvents. Polymer **12** just swelled in hot NMP and DMAc, and all the oxadiazole polymers were soluble only in concentrated sulfuric acid. The significant decrease in solubility may be attributed to the increased chain stiffness and crystallinity caused by the formation of planar 1,3,4-oxadiazole ring.

Poly(imide-hydrazide)s **3** and **4** and poly(amide-imide-hydrazide) **6** could be solution-cast into good-quality, creasable films. These 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 107–110 MPa, 14–37 %, and 2.13–3.04 GPa, respectively. However, after thermal

Table II. Solubility Behavior of Poly(imide-hydrazide)s and Poly(amide-imide-hydrazide)s^a

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

^a Concentration: 1 mg/mL. Solubility: +, soluble at room temperature; –, insoluble even on heating.

^b NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

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

Polymer Code	η_{inh}^a (dL/g)	Solubility ^b			
		NMP	DMAc	DMSO	Conc. H ₂ SO ₄
7	0.16	—	—	—	+
8	0.21	—	—	—	+
9	0.25	—	—	—	+
10	0.19	—	—	—	+
11	0.35	—	—	—	+
12	0.41	s	s	—	+

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

^b —: insoluble even on heating; s: swelling. All the polymers were also insoluble in *N,N*-dimethylformamide, *m*-cresol, tetrahydrofuran, chloroform, sulfolane, and ethanol.

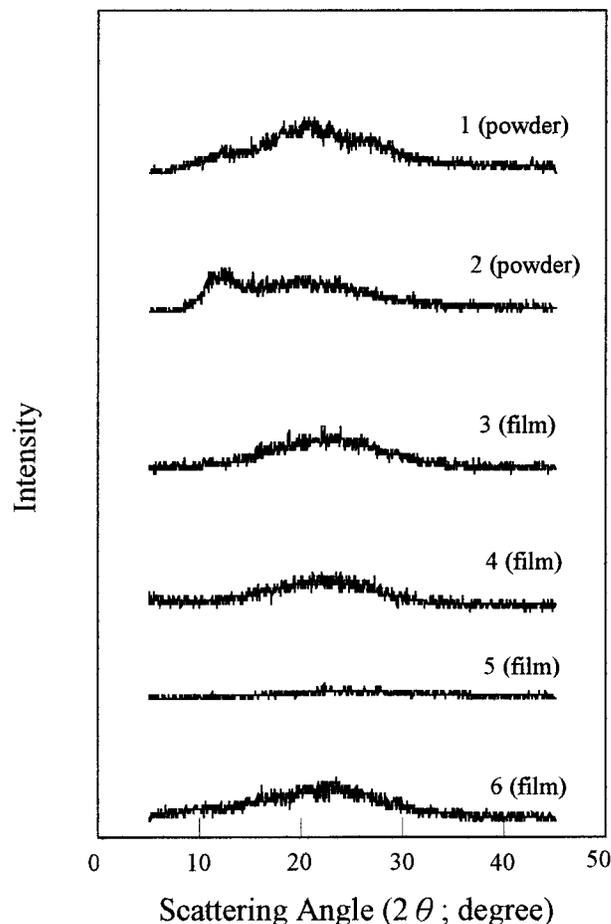
cyclization the films shrank or embrittled; therefore, the mechanical properties of the oxadiazole polymers were not evaluated.

The wide-angle X-ray diffraction patterns of the poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s over the 2θ range of 5–45° are shown in Figure 5. The poly(imide-hydrazide) (1) derived from *p*-CPTMI and TPH revealed a higher level of crystallinity, consistent with its poor solubility behavior. Changing the *p*-CPTMI moiety to *m*-CPTMI, TPH to IPH or *p*-ABH, or both all reduced the polymer crystallinity. Poly(amide-imide-hydrazide) 5 reveals a nearly amorphous pattern, although it exhibits high *p*-phenylene content along the polymer backbone. This may be attributable to the fact that the regularity of the repeat units in polymer 5 is disrupted by the different appearing orders of the amide and hydrazide groups, thus leading to a lower crystallinity.

All the poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s were also subjected to wide-angle X-ray diffraction measure-

Table IV. Tensile Properties of Poly(imide-hydrazide) and Poly(amide-imide-hydrazide) Films

Polymer Code	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
3	107	14	2.45
4	110	18	3.04
6	107	37	2.13

**Figure 5.** Wide-angle X-ray diffractograms of the poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s.

ments. The diffraction patterns shown in Figure 6 indicate that most oxadiazole polymers showed an increased crystallinity as compared to the corresponding hydrazide precursors, such as in the cases of 7, 9, and 11. This result may be ascribed to the fact that the 1,3,4-oxadiazole is similar to a *p*-phenylene structure, from the spectral and electronic points of view, which is known to be a planar, rigid unit.

The thermal properties of all polymers were evaluated by means of differential scanning calorimetry (DSC) and dynamic thermogravimetric analysis (TGA). Some thermal behavior data for all the polymers are summarized in Table V.

Each sample was subjected to three subsequent DSC heating runs, the first from 30 to 200 °C, after which the sample was cooled down with 100 °C/min to 30 °C, followed by a second run from 30 to 450 °C, after which the sample was

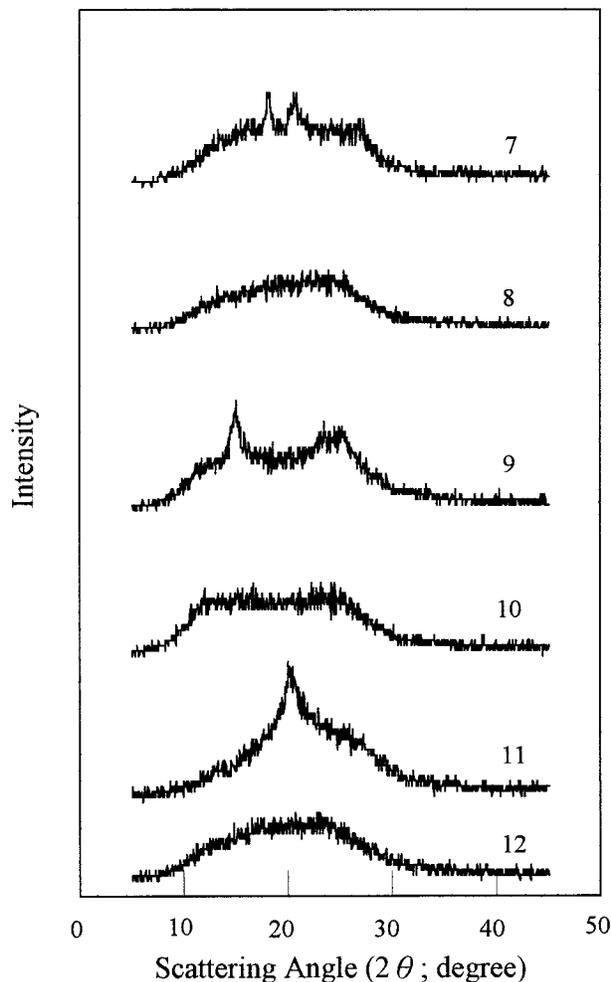


Figure 6. Wide-angle X-ray diffractograms of poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s.

Table V. Thermal Behavior Data for the Polymers

(Amide-)Imide-Hydrazide Polymers ^a					(Amide-)Imide-1,3,4-Oxadiazole Polymers					
Code	T_g (°C)	ΔC_p (J/g°C)	T_0 (°C)	T_p (°C)	ΔH (J/g)	Code	T_g^b (°C)	ΔC_p (J/g°C)	T_d^c (°C)	Char Yield ^d (%)
1			283	361	291.3	7	302	0.103	497 (498)	57
2			252	282	92.3	8	297	0.361	502 (506)	67
3	194	0.330	271	320	147.5	9	273	0.174	512 (486)	60
4	187	0.367	276	316	143.0	10	266	0.191	488 (473)	63
5	229	0.208	305	371	150.2	11	264	0.125	516 (505)	60
6	233	0.203	285	330	66.1	12	282	0.120	498 (507)	59

^a DSC data obtained from the second DSC heating trace at a heating rate of 20 °C/min after the first heating scan from 30 to 200 °C and cooling down to 30 °C with 100 °C/min. T_g : midpoint of baseline shift on the DSC curve. ΔC_p : heat capacity change at the glass transition. T_0 : extrapolated onset temperature of the endotherm peak. T_p : endotherm peak temperature. ΔH : specific heat of the cyclodehydration reaction.

^b Midpoint temperature of baseline shift on the third DSC heating trace of the sample after quenching from 450 °C.

^c Temperatures at which 10% weight loss was recorded by TGA at a heating rate of 20 °C/min in nitrogen. The values indicated in parentheses are those observed in air.

^d Residual wt % when heated to 800 °C in nitrogen.

cooled down again with 80 °C/min to 30 °C, followed by a third run with an end temperature of 400 °C. All scans were recorded with a heating rate of 20 °C/min under nitrogen. The first run was aimed to eliminate any possible volatiles such as the absorbed moisture and the residual solvent. The second run yields the glass-transition temperature (T_g) and the temperature range of cyclodehydration of the poly(imide-hydrazide) or poly(amide-imide-hydrazide) sample. After quenching from the elevated temperature, the poly(imide-1,3,4-oxadiazole)s or poly(amide-imide-1,3,4-oxadiazole)s formed *in situ* were predominantly amorphous. Thus, in the third run, all the oxadiazole polymers exhibited a clear heat capacity jump. Typical DSC curves of poly(imide-hydrazide) **3** and poly(imide-1,3,4-oxadiazole) **9** are reproduced in Figure 7 (only the second and third heating runs are shown). During the second run up to 450 °C, poly(imide-hydrazide) **3** showed a T_g around 194 °C and a strong endotherm between 282 and 371 °C due to the conversion of the hydrazide group into the 1,3,4-oxadiazole ring. After rapid cooling down, in the subsequent scan the poly(imide-1,3,4-oxadiazole) **9** formed *in situ* during the second heating scan reveals an obvious T_g at 264 °C. All the other polymers displayed similar DSC traces, and some of the DSC data are listed in Table V. For the hydrazide precursor polymers, polymers **1** and **2** did not reveal discernible T_g , and polymers **3–6** showed a distinct T_g centered in the range of 187–233 °C. As can be seen from the DSC thermograms, all the hydrazide poly-

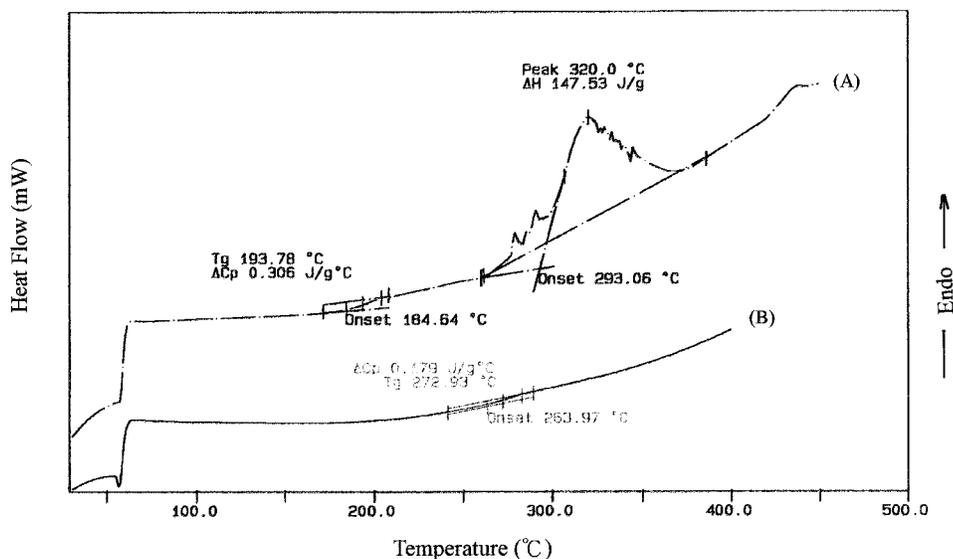


Figure 7. DSC curves of (A) poly(imide-hydrazide) **3** and (B) poly(imide-1,3,4-oxadiazole) **9** at heating rate of 20 °C/min in nitrogen.

mers 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. The poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s had T_g 's between 264 and 297 °C. Due to the increased chain rigidity, all the oxadiazole polymers showed higher T_g values than the corresponding hydrazide polymers by 35–79 °C. As expected, polymers derived from *m*-oriented aromatic dihydrazide components revealed relatively lower T_g 's.

The heat capacity jump (ΔC_p) at the glass transition and the specific heat (ΔH) of the endothermic peak are also shown in Table V. In the DSC thermogram, the magnitude of ΔC_p at the glass transition is proportional to the amorphous fraction of the polymer.²⁰ Increasing the ratio of *p*-phenylene units gives a more linear polymer, which obviously results in a polymer matrix with increased ordering and a decreased amorphous fraction. As shown in Table V, the ΔC_p values are generally increased if the *p*-phenylene group is replaced by the *m*-phenylene for the oxadiazole polymers. The difference in ΔC_p is small in the cases of hydrazide prepolymers. In addition, the ΔC_p values of the oxadiazole polymers are lower in comparison with the respective hydrazide precursors. This result indicates that the 1,3,4-oxadiazole ring results in a polymer matrix with increased ordering and an increased crystalline proportion after thermal dehydration from the hydrazide group. This result is also concordant

with that of wide-angle X-ray diffraction measurements. Furthermore, the cyclodehydration reaction of the poly(imide-hydrazide)s or poly(amide-imide-hydrazide)s may be accompanied with melting of the polymers. The specific heat of the endotherms was found to increase with increasing the ratio of *p*-phenylene groups in the main chain. For example, poly(imide-hydrazide) **1** had a particularly high specific heat due to its semicrystalline nature, as evidenced by its X-ray diffraction pattern described above.

Figure 8 shows a typical pair of TGA curves measured in nitrogen for the representative poly(imide-hydrazide) **2** and poly(imide-1,3,4-oxadia-

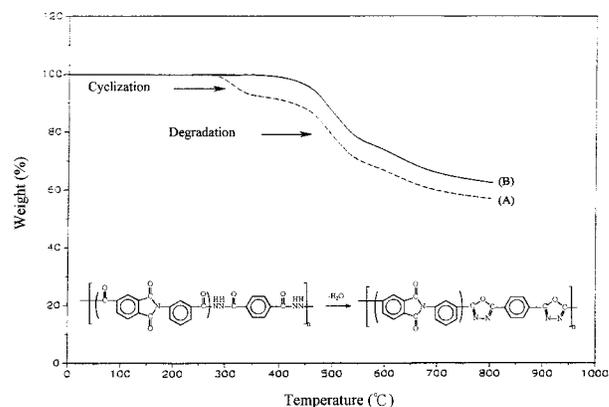


Figure 8. TG thermograms of (A) poly(imide-hydrazide) **2** and (B) poly(imide-1,3,4-oxadiazole) **8** at a heating rate of 20 °C/min in nitrogen.

zole) **8**. Weight loss corresponding to conversion of the poly(imide-hydrazide) **2** to the poly(imide-1,3,4-oxadiazole) **8** started at temperatures in the vicinity of 250 °C and continued for another 100 °C. This also agreed quite well with the strong endothermic peak between 282 and 371 °C in the DSC trace. The second break in the TGA curve occurred at around 450 °C and corresponded to decomposition of the poly(imide-1,3,4-oxadiazole) formed *in situ*. At 800 °C, the polymer left 67% char [based on the poly(imide-1,3,4-oxadiazole)]. The other polymers showed a similar TGA behavior, and the TGA data of all the oxadiazole polymers are also shown in Table V, in which all the oxadiazole polymers were heated at 350 °C for 10 min prior to analysis ensuring the complete cyclodehydration reactions of the unclosed rings. The poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s showed good thermal stability, with 10% weight loss temperature being recorded in the range of 488–516 °C in nitrogen and 473–507 °C in air. They left 57–67% char residue when heated to 800 °C in nitrogen, indicative of high intrinsic fire resistance.

CONCLUSIONS

This is the first time that moderate to high molecular weight poly(imide-hydrazide)s and poly(amide-imide-hydrazide)s were synthesized from the imide-preformed dicarboxylic acids with aromatic dihydrazides or aminohydrazide using a Yamazaki–Higashi phosphorylation technique. The imide-hydrazide and amide-imide-hydrazide polymers with less symmetric units were generally soluble in polar organic solvents and afforded light yellow, transparent, flexible, and tough films by solvent casting. The hydrazide polymers except for those from terephthalic dihydrazide showed T_g 's in the range of 187–233 °C and could be thermally cyclodehydrated in the solid state into the corresponding poly(imide-1,3,4-oxadiazole)s and poly(amide-imide-1,3,4-oxadiazole)s at elevated temperatures. The thermally converted 1,3,4-oxadiazole polymers had deep brown color and showed a significantly decreased solubility to organic solvents and higher T_g 's (264–302 °C) in comparison with the corresponding hydrazide prepolymers. The oxadiazole polymers showed good thermal stability, with 10% weight loss temperatures being recorded above 486 °C in nitrogen or air atmosphere.

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