

Novel Aromatic Polyhydrazides and Poly(amide-hydrazide)s Based on "Multiring" Flexible Dicarboxylic Acids

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ABSTRACT: Two flexible dicarboxylic acid monomers, 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**1**) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**3**), were synthesized from readily available compounds in two steps in high yields. High molecular-weight polyhydrazides and poly(amide-hydrazide)s were directly prepared from dicarboxylic acids **1** and **3** with terephthalic dihydrazide (**5**), isophthalic dihydrazide (**6**), and *p*-aminobenzhydrazide (**7**) by the phosphorylation reaction by means of diphenyl phosphite (DPP) and pyridine in *N*-methyl-2-pyrrolidone (NMP)/LiCl, or prepared from the diacyl chlorides of **1** and **3** with the hydrazide monomers **5–7** by the low-temperature solution polycondensation in NMP/LiCl. Less favorable results were obtained when using triphenyl phosphite (TPP) instead of DPP in the direct polycondensation reactions. Except for those derived from terephthalic dihydrazide, the resulting polyhydrazides and poly(amide-hydrazide)s could be cast into colorless, flexible, and tough films with good tensile strengths. All the hydrazide polymers and copolymers are amorphous in nature and are readily soluble in various polar solvents such as NMP and dimethyl sulfoxide (DMSO). Their T_g s were recorded in the range of 162–198°C and could be thermally cyclodehydrated into the corresponding polyoxadiazoles and poly(amide-oxadiazole)s approximately in the region of 300–380°C, as evidenced by the DSC thermograms. The oxadiazole polymers and copolymers showed a dramatically decreased solubility and higher T_g when compared to their respective hydrazide prepolymers. They exhibited T_g s of 190–216°C and were stable up to 450°C in air or nitrogen. © 1998 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 36: 1847–1854, 1998

Keywords: polyhydrazides; poly-1,3,4-oxadiazoles; thermal behavior

INTRODUCTION

Aromatic polyhydrazides are well known from the work of Frazer et al.^{1–3} as precursors to poly-1,3,4-oxadiazoles. Aromatic poly(amide-hydrazide)s were developed extensively by Monsanto scientists in the early 1970s. Details of poly(amide-hydraz-

ide) synthesis have been reported by Black, Preston, and co-workers,^{4,5} and by Culbertson and Murphy.⁶ High-strength, high-modulus fibers have been made from poly(terephthalic hydrazide) and poly(amide-hydrazide)s with ordered structures.^{5,7,8} Yang⁹ has made an excellent review on hydrazide polymers and copolymers.

Aromatic polyhydrazides are generally synthesized by the low-temperature solution polycondensation of an aromatic dihydrazide with an aromatic diacid chloride in amide solvents such as NMP in the presence of an inorganic salt like lith-

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ium chloride.^{1–9} Higashi and co-workers^{10,11} demonstrated that high-molecular-weight polyhydrazides and poly(amide-hydrazide)s could be synthesized by the direct polycondensation reaction of an aromatic dihydrazide or an aminohydrazide with an aromatic dicarboxylic acid by means of di- or triphenyl phosphite. In the previous publication,¹² two multiring, flexible dicarboxylic acids of 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**1**) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**3**) were synthesized and were used for the preparation of easily processable aromatic polyamides with high molecular weights. To more fully evaluate other polymer systems based on these dicarboxylic acids, the present study extends their use in the preparation of polyhydrazides and poly(amide-hydrazide)s. Basic characterization of these novel polymers and the thermal cyclodehydration to poly-1,3,4-oxadiazoles are also investigated.

EXPERIMENTAL

Materials

Terephthalic dihydrazide (**5**) (TCI), isophthalic dihydrazide (**6**) (TCI), and 4-aminobenzhydrazide (**7**) (TCI) were used as received. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) (TCI) and diphenyl phosphite (DPP) (TCI) were purified by distillation under reduced pressure. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180°C for 8 h. Other reagent-grade reagents and solvents were used as received.

Preparation of Monomers

4,4'-[Isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**1**) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**3**) were prepared according to reported procedures.^{13–16} Details of the synthesis and characterization data of diacid **1** and **3** have been described in the preceding article.¹²

Preparation of 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**2**): 60 mL of thionyl chloride and one drop of *N,N*-dimethylformamide (DMF) were added to a suspension of 15.5

g (33 mmol) of diacid **1** in 40 mL of dichloromethane, and the mixture was heated with stirring at 60°C for 10 h. Dichloromethane and excess thionyl chloride were removed by distillation using a rotary evaporator. The resulting white solid was dried at 100°C in a vacuum to give 15.5 g of diacyl chloride **2** (quantitative yield); m.p. 140°C. The IR spectrum (KBr) exhibited absorptions at 1757 (C=O), 1247 (C—O—C), 1209 cm⁻¹ (C—Cl).

4,4'-[Hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**4**) was prepared in a similar procedure in a quantitative yield with a melting point at 160–161°C.

General Polymerization Procedures

Direct Polycondensation via Phosphorylation Reaction

A mixture of equimolar amounts (1 mmol) of dicarboxylic acids (**1** or **3**) and dihydrazides (**5** or **6**) or aminohydrazide (**7**), 2 mmol of TPP or DPP, 0.2 g of lithium chloride, 0.5 mL of pyridine, and 2–3 mL of NMP was heated with stirring at 120°C for 3 h. The viscosity of the solution remarkably increased during the reaction. After cooling, the viscous solution was poured slowly into 300 mL of methanol, and the white fiber-like or powdery precipitate was washed repeatedly with methanol and hot water, collected by filtration, and dried to give quantitative yields of polyhydrazides or poly(amide-hydrazide)s.

Low-Temperature Solution Polycondensation

A solution of 5 mL of NMP containing dissolved 0.2 g of lithium chloride and 1 mmol of terephthalic dihydrazide (0.1942 g), isophthalic dihydrazide (0.1942 g), or *p*-aminobenzhydrazide (0.1512 g) was prepared and cooled by an external ice–acetone bath. The solution was stirred and to it was added 1 mmol of diacyl chloride **2** (0.5054 g) or **4** (0.6133 g). The reaction was continued overnight. The resulting polymer solutions were treated by a similar procedure as described above.

Preparation of Polyhydrazide and Poly(amide-hydrazide) Films and Their Conversion to Corresponding Poly-1,3,4-oxadiazoles

A polymer solution was made by dissolving about 0.6 g of the polyhydrazide or poly(amide-hydrazide) samples in 6 mL of *N,N*-dimethylacetamide (DMAc). The solution was poured into a glass

culture dish of 9 cm diameter, which was placed in a 90°C oven for 12 h to remove the solvent. Then, the obtained semidried polymer film was stripped from the glass substrate and further dried *in vacuo* at 150°C for 8 h. The obtained films had about 0.05 mm in thickness.

The conversion of polyhydrazides or poly(amide-hydrazide)s to polyoxadiazoles or poly(amide-oxadiazole)s was carried out by heating the polymer strips cut from the above fabricated films at 300°C for 8 h *in vacuo*. Their inherent viscosities were measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30°C.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. The ¹H-NMR spectrum was determined at 30°C on a JEOL JNM-PMX 60 NMR spectrometer with tetramethylsilane as an internal reference. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer at the National Taiwan University (Taipei). The inherent viscosities were measured with a Cannon-Fenske viscometer thermostated at 30°C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 analyzer 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, and were taken from the second heating scan after quick cooling. Thermogravimetry (TG) was conducted with a DuPont 951 thermogravimetric analyzer coupled to a DuPont Thermal analyst 2000. Experiments were carried out on 9–11-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 CuK_α radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. An Instron universal tester Model HT-9102 (Hung Ta Instrument Co., Taiwan) with a load cell 100 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a crosshead speed of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.05 mm thick). An average of at least five individual determinations was reported.

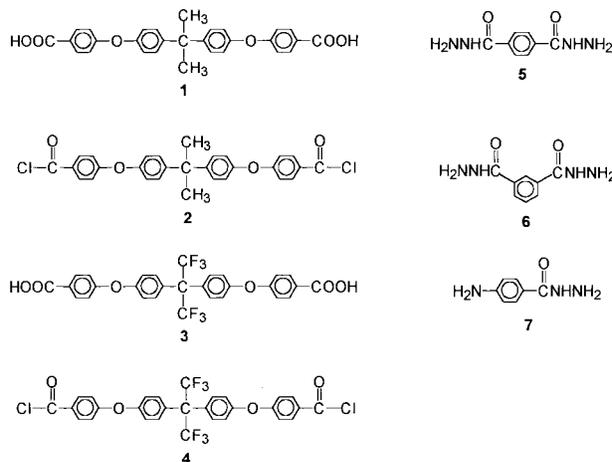


Figure 1. Structures and codes of monomers.

RESULTS AND DISCUSSION

Monomer Synthesis

As described in the preceding article,¹² 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**1**) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**3**) were prepared in high purity and high yields through the nucleophilic fluorodisplacement of *p*-fluorobenzonitrile by the bisphenoxide ions of the corresponding bisphenol precursors followed by alkaline hydrolysis of the intermediate dicyano compounds. Dicarboxylic acids **1** and **3** were converted to diacyl chlorides **2** and **4** by treatment with thionyl chloride in the presence of a trace amount of DMF. The yields of the diacyl chlorides were quantitative and the purity was high enough for the preparation of polymers with high molecular weights. Their structures were ascertained by elemental analysis and IR spectroscopy.

Preparation of Polyhydrazides and Poly(amide-hydrazide)s

Both the direct phosphorylation polycondensation and the low-temperature solution polycondensation techniques were used for the synthesis of the polyhydrazides and poly(amide-hydrazide)s (as shown in Fig. 2) from various combinations of the monomers shown in Figure 1. The parentheses in the formulas of polymers **12** and **13** indicate that the unsymmetrical aminobenzhydrazide moiety may appear in the polymer chain as shown, or in the reverse orientation. This convention is needed

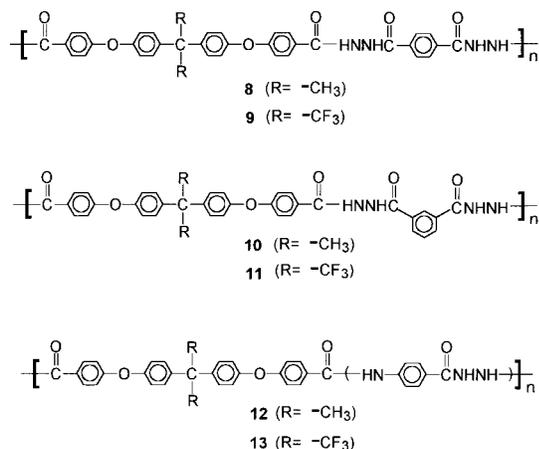


Figure 2. Structures and codes of polyhydrazides and poly(amide-hydrazide)s.

because the simple order of aminobenzhydrazide repeating units cannot be assumed. The inherent viscosity values and film quality of the prepared polyhydrazides and poly(amide-hydrazide)s are summarized in Table I.

In the direct polycondensation, diphenyl phosphite (DPP) and triphenyl phosphite (TPP) were individually used as a condensing agent. In each case, the inherent viscosity of the polymer prepared by using DPP was higher than that prepared by using TPP. The inherent viscosities of the polymers prepared by means of DPP stayed in the 0.39–0.73 dL/g range. Except for polymers **8** and **9** derived from terephthalic dihydrazide (**5**), the other polymers prepared by using DPP had adequate molecular weight to permit the casting of flexible and tough films. These films are transparent and colorless. For the polymers prepared by using TPP as the condensing agent, however, almost all the casting films are brittle and noncreasable, with the exception of that made from polymer **12**. The polymers obtained by means of TPP had relatively lower molecular weights, as indicated by inherent viscosities of 0.17–0.55 dL/g and did not provide flexible and strong films. A possible explanation proposed by Preston and Hofferbert¹⁷ is that the strongly basic hydrazide 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 hydrazide groups are less likely to

complex with the phosphite intermediate derived from DPP than that derived from TPP.

In almost all cases, except for that in the preparation of poly(amide-hydrazide) **12**, the polymer sample with the highest inherent viscosity was attained via the low-temperature polycondensation technique, possibly due to less side reaction. Polymers **10–13** produced via the acyl chloride route possessed an adequate molecular weight (inherent viscosity = 0.57–0.77 dL/g) and could be fabricated into colorless, flexible, and tough films. The films made from polyhydrazides **8** and **9** synthesized by this route were opaque and highly brittle, despite the fact that they exhibit a moderately higher inherent viscosity (0.55–0.59 dL/g). Thus, the brittle nature of their cast films is probably attributable to the high packing density of their polymer chains caused by the presence of the symmetrical terephthalic dihydrazide moiety,

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

Code	Combination of Monomers ^a	η_{inh}^b (dL/g)	Film Quality ^c
8	1 + 5 (by DPP)	0.46	Highly brittle, opaque
	1 + 5 (by TPP)	0.22	Highly brittle, opaque
	2 + 5	0.59	Highly brittle, opaque
9	3 + 5 (by DPP)	0.45	Highly brittle, opaque
	3 + 5 (by TPP)	0.17	Highly brittle, opaque
	4 + 5	0.55	Highly brittle, opaque
10	1 + 6 (by DPP)	0.39	Flexible, transparent
	1 + 6 (by TPP)	0.31	Slightly brittle, transparent
11	2 + 6	0.57	Flexible, transparent
	3 + 6 (by DPP)	0.51	Flexible, transparent
12	3 + 6 (by TPP)	0.33	Highly brittle, transparent
	4 + 6	0.77	Flexible, transparent
	1 + 7 (by DPP)	0.73	Flexible, transparent
13	1 + 7 (by TPP)	0.55	Flexible, transparent
	2 + 7	0.59	Flexible, transparent
	3 + 7 (by DPP)	0.55	Flexible, transparent
13	3 + 7 (by TPP)	0.24	Highly brittle, transparent
	4 + 7	0.68	Flexible, transparent

^a Initial synthesis conditions for the phosphorylation reaction: monomer = 1 mmol; TPP or DPP = 2 mmol; LiCl = 0.2 g; NMP = 2 mL (3 mL for polymers **8** and **9**); pyridine = 0.5 mL; temperature = 120°C; time = 3 h. Conditions for the low temperature polycondensation reaction: monomer = 1 mmol; LiCl = 0.2 g; NMP = 5 mL.

^b Determined at a concentration of 0.5 g/dL in DMSO at 30°C.

^c Cast from slow evaporation of DMAc solutions.

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

Polymer	Solvent ^b								
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF	Chloroform	Acetone	Ethanol
8	+	+	+	+	—	—	—	—	—
9	+	+	+	+	—	—	—	—	—
10	+	+	+	+	+h	—	—	—	—
11	+	+	+	+	s	—	—	—	—
12	+	+	+	+	+h	—	—	—	—
13	+	+	+	+	+h	—	—	—	—

^a +: soluble at room temperature; +h: soluble on heating; s: swollen on heating; —: insoluble even on heating.

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

although X-ray diffraction results revealed that polymers **8** and **9** exhibited a low level of crystallinity.

The structure of polyhydrazides and poly(amide-hydrazide)s was ascertained by IR and ¹H-NMR spectroscopy. Typical IR and ¹H-NMR spectra of a representative polyhydrazide **10** were determined. The IR spectrum showed characteristic absorptions near 3250 (N—H), 1650 (C=O), and 1245 cm⁻¹ (C—O—C). In the ¹H-NMR spectrum, the absorption signals of aromatic protons appeared in the region of δ 6.6–8.4 ppm. The peak corresponding to NH resonance from the hydrazide group was observed around 10.4 ppm. The resonance peak specific to the isopropylidene protons appeared at 1.6 ppm.

Properties of Polyhydrazides and Poly(amide-hydrazide)s

The polyhydrazide and poly(amide-hydrazide) samples obtained by the low-temperature polycondensation technique were characterized. As shown in Table II, all of the polyhydrazides and poly(amide-hydrazide)s were readily soluble in polar aprotic solvents such as NMP, DMAc, DMSO, and DMF at room temperature. For the less polar solvents, some of them were only soluble or swollen in hot *m*-cresol. They showed good resistance to common organic solvents such as THF, chloroform, acetone, and ethanol.

The polymers, except **8** and **9** from the rigid monomer **5**, possess good quality and are creasable. These flexible films were subjected to tensile testing, and the results are included in Table III. Their tensile strengths and elongations to break were in the range of 85–94 MPa and 8–13%, re-

spectively. They behaved as hard and strong materials. The crystallinity of the polyhydrazides and poly(amide-hydrazide)s was examined by wide-angle X-ray diffraction in film samples. All the polymers, even the brittle polyhydrazides **8** and **9**, showed amorphous patterns. The amorphous nature of these polymers can be mainly explained by the presence of flexible ether and isopropylidene or hexafluoroisopropylidene linkages in the polymer backbone.

The thermal properties of all the polyhydrazides and poly(amide-hydrazide)s were evaluated by differential scanning calorimetry (DSC) and thermogravimetry (TG). All these polymers showed a distinct glass transition centered in the

Table III. Tensile Properties and Thermal Behavior Data of Polyhydrazides and Poly(amide-hydrazide)s

Polymer ^a	Tensile Properties of Polymer Films		DSC Data		
	Strength-to-Break (MPa)	Elongation-to-Break (%)	T_g^b (°C)	T_o^c (°C)	T_p^d (°C)
8	—	—	192	296	340
9	—	—	197	302	338
10	91	8	162	240	325
11	94	9	171	300	337
12	85	9	172	227	327
13	90	13	198	290	338

^a Samples obtained from the low temperature polycondensation method.

^b Midpoint of baseline shift on the DSC heating trace. Heating rate = 20°C/min.

^c Extrapolated onset temperature of the endotherm peak.

^d Endotherm peak temperature.

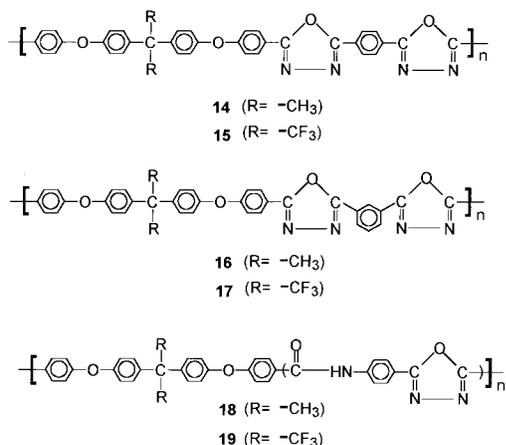


Figure 3. Structures and codes of poly(oxadiazole)s and poly(amide-oxadiazole)s.

range of 162–198°C on their DSC heating traces (Table III). As expected, polyhydrazides derived from *m*-oriented aromatic dihydrazide components revealed relatively lower T_g s. All the fluoropolymers exhibited higher glass transition temperatures than their respective nonfluorine-containing counterparts. This is reasonable because barrier of segment movement increased due to the presence of bulky trifluoromethyl group. In addition to a distinct glass transition, strong endothermic peaks are exhibited between 227 and 380°C, centered around 325–340°C, which are attributable to loss of water during the conversion of hydrazide group to the 1,3,4-oxadiazole ring.

Figure 4 shows a typical pair of TG and DSC curves for the representative polyhydrazide **9**. Weight loss corresponding to conversion of the polyhydrazide to the poly-1,3,4-oxadiazole started at temperatures in the vicinity of 300°C and continued for another 80°C. The initial weight loss amount to about 5% (based on dry polymer) and corresponded well to the calculated amount (4.9%) of water released from cyclization. This also agreed quite well with the strong endothermic peak between 302–375°C in the DSC trace. The second break in the TG curve occurred at approximately between 490–600°C and corresponded to decomposition of poly-1,3,4-oxadiazole (**15**) formed *in situ*. At 800°C in nitrogen, the polymer left 53.4% char (based on polyhydrazide).

Properties of Poly-1,3,4-oxadiazoles and Poly(amide-1,3,4-oxadiazole)s

The polyhydrazides and poly(amide-hydrazide)s were subjected to thermal cyclodehydration. The

conversion to poly-1,3,4-oxadiazoles and poly(amide-1,3,4-oxadiazole)s was carried out in the form of films at 300°C *in vacuo*. Due to the conjugation between the oxadiazole ring and aromatic group, the films turned from colorless into pale yellow or brownish after heat treatment. Structures and codes of polyoxadiazoles and poly(amide-oxadiazole)s are shown in Figure 3. The results of some basic characterization of these polymers are listed in Table IV. As described above, polyhydrazides and poly(amide-hydrazide)s showed excellent solubility in polar solvents such as NMP, DMAc, DMF, and DMSO. The corresponding oxadiazole polymers, on the other hand, dissolved only in concentrated sulfuric acid. The isopropylidene-containing polymers were decomposed in sulfuric acid, as evidenced by the relatively lower inherent viscosity. On the contrary, the hexafluoroisopropylidene polymers showed outstanding acid resistance. The fluorine-containing polyoxadiazoles and poly(amide-oxadiazole)s had inherent viscosities of 0.43–0.90 dL/g in concentrated sulfuric acid, pointing at that no thermal degradation leading to molecular chain scission took place during the conversion process.

The thermal behavior data of the oxadiazole polymers were obtained from their DSC and TG thermograms. The samples were prepared *in situ* under (rapid) dynamic conditions (20°C/min) of the DSC and TG techniques. The T_g s of these oxadiazole polymers were recorded in the 190–216°C range, which were 14–40°C higher than that of the corresponding hydrazide prepolymers. The increase in T_g is consistent because the formation of oxadiazole ring resulted in an increased chain stiffness. In all cases, the fluoropolyoxadiazoles exhibited higher T_g s than those of corresponding —CH₃ containing analogues. This effect can be attributable to the increase of structural hindrance due to the bulky —CF₃ units. All the polyoxadiazoles and poly(amide-oxadiazole)s did not lose weight up to 450°C in air or nitrogen, and the temperatures at which 10% weight was recorded were above 510°C.

CONCLUSIONS

Polyhydrazides and poly(amide-hydrazide)s with high molar masses have been prepared from 4,4'-[isopropylidenebis(1,4-phenylene)dioxy]-dibenzoic acid (**1**) and 4,4'-[hexafluoroisopropylidenebis(1,4-phenylene)-dioxy]dibenzoic acid (**3**) with

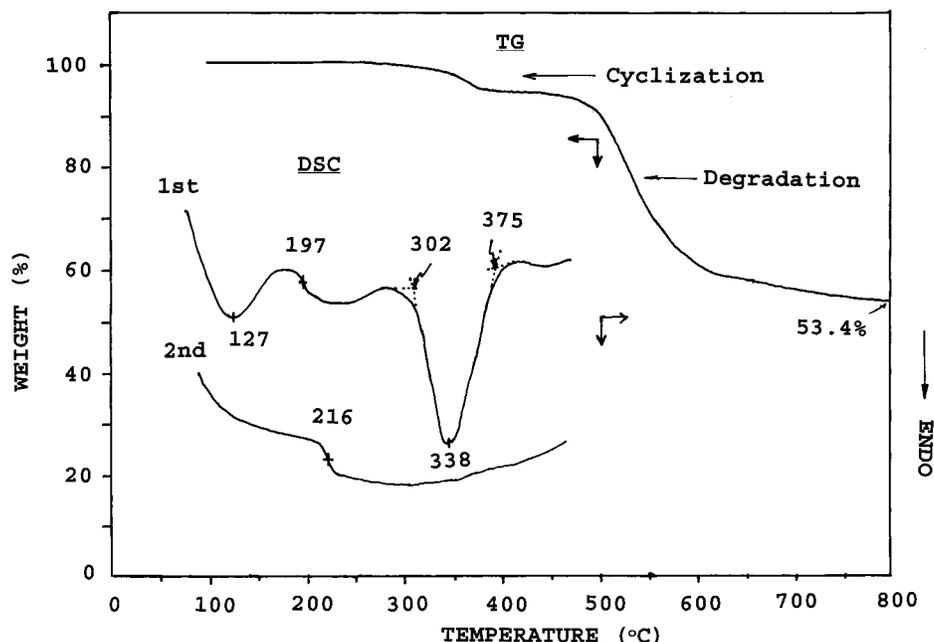


Figure 4. TG and DSC thermograms of polyhydrazone **9** with a heating rate of 20°C/min in nitrogen.

dihydrazides or aminohydrazone via the phosphorylation reaction using diphenyl phosphite (DPP) and pyridine as the condensing agent, or prepared by the low-temperature solution polycondensation of the diacyl chlorides of **1** and **3** with the hydrazone monomers. Using triphenyl phosphite (TPP) instead of DPP in the phosphorylation reactions resulted in less favorable results. In general, the obtained polyhydrazides and poly-

(amide-hydrazone)s that had inherent viscosity above 0.5 g/dL could afford colorless, good quality, and creasable films by solution casting. All the hydrazone polymers and copolymers are amorphous and readily soluble in a variety of organic solvents. They had T_g s between 162–198°C and could be converted into the respective polyoxadiazoles and poly(amide-oxadiazole)s at elevated temperatures. The oxadiazole polymers and copol-

Table IV. Characterization of Polyoxadiazoles and Poly(amide-1,3,4-oxadiazole)s^a

Polymer	η_{inh}^b (dL/g)	Solubility ^c		T_g^d (°C)	T_d^e (°C)	Char Yield ^f (%)
		NMP	Conc. H ₂ SO ₄			
14	0.05	—	Dec.	208	500	42.8
15	0.83	—	+	216	515	52.5
16	0.06	—	Dec.	190	498 (485)	49.9
17	0.90	—	+	211	516 (506)	53.1
18	0.06	—	Dec.	205	500	39.3
19	0.43	—	+	212	511	45.8

^a The conversion of the polyhydrazone to polyoxadiazole was carried out by heating at 300°C for 8 h *in vacuo*. The polyhydrazides were obtained by the low-temperature polycondensation technique.

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

^c +: soluble; -: insoluble; dec.: decomposed.

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

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

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

ymers had pale yellow or brownish color and showed a significantly decreased solubility to organic solvents and slightly higher T_g s (190–216°C) in comparison with the corresponding hydrazide precursors. The polyoxadiazoles and poly(amide-oxadiazole)s showed good thermal stability, with 10% weight loss temperature being recorded above 500°C in air or nitrogen atmosphere.

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