NOTES

Synthesis of Poly(1,3,4-oxadiazole)s by Direct Polycondensation of Bisamidrazones with Dicarboxylic Acids Using Phosphorus Pentoxide/Methanesulfonic Acid

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Our studies on the synthesis of condensation polymers by the direct polymerization in phosphorus pentoxide/methanesulfonic acid (PPMA) in a weight ratio of 1:10 have revealed that PPMA is a suitable condensing agent and solvent for the preparation of poly(ketone)s, poly(ether-sulfone)s and heterocyclic polymers.¹

In order to extend the preparative utility of this method, we examined the reaction of amidrazones with carboxylic acids in PPMA and found a new method for the synthesis of 1,3,4-oxadiazoles. Poly(1,3,4-oxadiazole)s have already been synthesized from poly(*N*-acylamidrazone)s, obtained from the polycondensation of bis(amidrazone)s and diacid chlorides.²

This article describes a successful synthesis of poly(1,3,4-oxadiazole)s by the direct polycondensation of dicarboxylic acids with isophthalamidrazone using PPMA.

EXPERIMENTAL

Materials

The reagent PPMA was prepared according to the reported procedure.³ Various substituted benzoic acids **2a**—**2d** of reagent grade were used as received. Benzamidrazone (**1**) and

isophthalamidrazone (**5**) were prepared from the corresponding nitrile compounds in two steps by the reported procedure.⁴ 4,4'-Oxybisbenzoic acid (**8a**), 3,3'-(*p*-phenylenedioxy)dibenzoic acid (**8b**), and 4,4'-(*p*-phenylenedioxy)dibenzoic acid (**8c**) were prepared through oxidation of the corresponding dimethyl compounds with potassium permanganate in pyridine–water. These dicarboxylic acids were purified by recrystallization. **8a**: mp 337°C (by DTA) (lit.⁵ 331—333°C, from acetic acid), **8b**: mp 312°C (by DTA) (lit.⁶ 305—313°C, from acetic acid), **8c**: mp 333°C (by DTA) (lit.⁶ 331—333°C, from dioxane).

Model Reaction

Typical example is as follows:

N-Benzoylbenzamidrazone (**3a**). A mixture of **1** (0.135 g, 1.0 mmol) and **2a** (0.122 g, 1.0 mmol) in PPMA (2 ml) was stirred at 60°C for 1 h. The solution was poured into ice-water (150 ml), and neutralized with sodium carbonate. The product was filtered, washed with water and dried. The yield was 0.216 g (90%). Recrystallization from ethanol produced white needles. mp 173—174°C. The IR spectrum (KBr) showed absorptions at ν 3200—3500 (N–H), 1680 (C=O), and 1640 cm^{-1} (C=N). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$:

C, 70.28%; H, 5.48%; N, 17.56%. Found: C, 70.11%; H, 5.50%; N, 17.42%.

N-(*m*-Nitrobenzoyl) benzamidrazone (**3b**). Recrystallization from ethanol gave yellow needles. mp 245–246°C. *Anal.* Calcd for $C_{14}H_{12}N_4O_3$: C, 59.15%; H, 4.26%; N, 19.71%. Found: C, 59.1%; H, 4.3%; N, 19.7%.

N-(*p*-Methoxybenzoyl) benzamidrazone (**3c**). Recrystallization from ethanol gave white needles. mp 195–196°C. *Anal.* Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90%; H, 5.61%; N, 15.60%. Found: C, 66.88%; H, 5.41%; N, 15.30%.

2,5-Diphenyl-1,3,4-oxadiazole (**4a**). **1** (0.135 g, 1.0 mmol) and **2a** (0.122 g, 1.0 mmol) were dissolved in PPMA (1 ml). The solution was stirred at 140°C for 1 h. The product was isolated as described above. The yield was 0.194 g (87%). Recrystallization from ethanol produced white plates. mp 143–144°C (lit.⁷ 138°C). The IR spectrum showed absorptions at ν 1560 (C=N), and 1010 cm^{-1} (C–O–C).

N,N'-Dibenzoylisophthalamidrazone (**6a**). A mixture of **5** (0.192 g, 1.0 mmol) and **2a** (0.244 g, 2.0 mmol) in PPMA (2.0 ml) was stirred at 60°C for 1 h. The product was isolated as described above. The yield was 0.342 g (86%). mp 215–216°C. The IR spectrum showed absorptions at 3200–3400 (N–H) and 1640 cm^{-1} (C=N). *Anal.* Calcd for $C_{22}H_{20}N_6O_2$: C, 65.99%; H, 5.03%; N, 20.99%. Found: C, 65.77%; H, 5.10%; N, 21.05%.

N,N'-Bis(*m*-nitrobenzoyl)isophthalamidrazone (**6b**). Recrystallization from DMF produced yellow powder. mp 189–190°C. *Anal.* Calcd for $C_{22}H_{18}N_8O_6$: C, 53.88%; H, 3.70%; N, 22.85%. Found: C, 53.67%; H, 3.74%; N, 22.27%.

N,N'-Bis(*p*-methoxybenzoyl)isophthalamidrazone (**6c**). Recrystallization from DMF gave white crystals. mp 218–219°C. *Anal.* Calcd for $C_{24}H_{24}N_6O_4$: C, 62.60%; H, 5.25%; N, 18.24%. Found: C, 62.26%; H, 5.13%; N, 18.19%.

2,2'-*m*-Phenylenebis(5-phenyl-1,3,4-oxa-

diazole) (**7a**). **5** (0.192 g, 1.0 mmol) and **2a** (0.244 g, 2.00 mmol) were dissolved in PPMA (2.0 ml). The solution was stirred at 140°C for 1 h. The yield was 0.354 g (97%). Recrystallization from DMF gave white powder. mp 252–253°C. The IR spectrum showed absorptions at 1530 (C=N) and 1010 cm^{-1} (C–O–C). *Anal.* Calcd for $C_{22}H_{14}N_4O_2$: C, 72.12%; H, 3.85%; N, 15.29%. Found: C, 72.0%; H, 4.1%; N, 15.2%.

2,2'-*m*-Phenylenebis[5-(*p*-methoxyphenyl)-1,3,4-oxadiazole] (**7c**). Recrystallization from DMF yielded a faint pink powder. mp 272–273°C. *Anal.* Calcd for $C_{24}H_{18}N_4O_4$: C, 67.60%; H, 4.25%; N, 13.14%. Found: C, 66.50%; H, 4.31%; N, 13.22%.

N,N'-*m*-Phenylenebis[5-(*p*-nitrophenyl)-1,3,4-oxadiazole] (**7d**). Recrystallization from DMF gave yellow powder. mp 373°C (by DTA). *Anal.* Calcd for $C_{22}H_{12}N_6O_6$: C, 57.90%; H, 2.65%; N, 18.41%. Found: C, 57.86%; H, 2.81%; N, 18.81%.

Polymer Synthesis

Typical example of polymerization is as follows.

Polymer (9c) from (5) and (8c). A solution of **5** (0.192 g, 1.0 mmol) and **8c** (0.350 g, 1.0 mmol) in PPMA (2 ml) was stirred at 140°C for 16 h. The resulting solution was poured into ice-water and neutralized with sodium carbonate. The polymer was collected, washed with hot water, and dried in vacuum at 100°C for 2 d. The yield was essentially quantitative. The inherent viscosity of the polymer, in concentrated sulfuric acid was 0.30 $dl\ g^{-1}$ at 30°C. The IR spectrum (KBr) exhibited absorptions at ν 1550 (C=N) and 1000 cm^{-1} (C–O–C). *Anal.* Calcd for $(C_{28}H_{16}N_4O_4 \cdot 3H_2O)_n$: C, 63.88%; H, 4.11%; N, 10.64%. Found: C, 64.56%; H, 3.71%; N, 9.79%.

RESULTS AND DISCUSSION

Model Reaction

The preparation of 1,3,4-oxadiazoles

through intermediate *N*-acylamidrazones has been known for many years. Cyclization of *N*-acylamidrazones leads to the formation of 1,2,4-triazoles or 1,3,4-oxadiazoles depending on the reaction conditions. Conversion of the amidrazones into triazoles takes place in basic solution, while the oxadiazoles are obtained in the presence of acid.⁸

To date, the synthesis of 1,3,4-oxadiazoles **4** by the reaction of amidrazones with carboxylic acids in PPMA has not been reported. Therefore, we first studied the reaction of benzamidrazone **1** with benzoic acid **2a** over a

temperature range from 25°C to 140°C. The reaction was performed by dissolving **1** and **2a** in PPMA. After the reaction was completed, the solution was poured into ice-water and neutralized with sodium carbonate, and the crude product was filtered. These preliminary experiments showed that the condensation at 60°C for 1 h gave *N*-benzoylbenzamidrazone **3a** and the reaction at 140°C for 1 h yielded 2,5-diphenyl-1,3,4-oxadiazole **4a**.

On the basis of these results, various *N*-acylamidrazones **3** and 2,5-disubstituted-1,3,4-oxadiazoles **4** were prepared (eq 1).

The results summarized in Table I indicate that **1** was easily acylated by benzoic acids containing electron donating groups and excellent yields of **4** were obtained. These findings of substituent effects of benzoic acids are explained as due to the stability of the reaction intermediates, acylium ions, as described in

previous papers.¹

Next, bifunctional model compound study was made to determine if the desired model compounds would be formed in quantitative yields, essential for a polymer-forming reaction. The reaction of isophthalamidrazone **5** with **2** was studied in PPMA (eq 2)

Table I. Preparation of *N*-acylbenzamidrazones **3** and 2,5-diaryl-1,3,4-oxadiazoles **4** in PPMA^a

Substituted benzoic acid	Reaction conditions		Product			
	Temp/°C	PPMA/ml	Type	Yield	mp/°C	(lit.)
2a	60	2.0	3a	90	173—174	
2b	60	2.0	3b	22	245—246	
2c	60	2.0	3c	92	195—196	
2a	140	1.0	4a	87	143—144	(138) ⁷
2c	140	1.0	4c	91	152—153	(149—150) ⁹
2d	140	1.0	4d	67	228—229	(207—208) ⁹

^a Reaction was carried out with 1.0 mmol of each reactant in PPMA for 1 h.

The results are summarized in Table II. Similar to the monofunctional model reaction, quantitative yields of the corresponding *N,N'*-diacylisophthalamidrazones **6** and 2,2'-*m*-phenylenebis(5-substituted-1,3,4-oxadiazole)s **7** were obtained from benzoic acid **2** having electron-donating groups at 60°C and 140°C, respectively. The structures of new compounds **3**, **4**, **6**, and **7** were determined by elemental analysis and IR spectroscopy.

Polymer Synthesis

On the basis of the model reactions, the direct polycondensation of **5** with aromatic dicarboxylic acids **8** was carried out in PPMA at 140°C (eq 3).

Table II. Preparation of *N,N'*-diacylisophthalamidrazones **6** and 2,2'-*m*-phenylenebis(5-aryl-1,3,4-oxadiazole)s **7** in PPMA^a

Substituted benzoic acid	Reaction	Product	
	Temp/°C	Type	Yield/%
2a	60	6a	86
2b	60	6b	31
2c	60	6c	95
2a	140	7a	97
2c	140	7c	99
2d	140	7d	89

^a Reaction was carried out with 1.0 mmol of **5** and 2 mmol of **2** in PPMA (2 ml) for 1 h.

The results are listed in Table III. Poly(1,3,4-oxadiazole) **9** was produced in quantitative yield with inherent viscosities up to 0.30 dl g⁻¹.

The polymers were confirmed to be the proposed polymers **9** by comparing their IR spectra with those of the model compounds. The IR spectra showed characteristic absorptions around at 1550 and 1000 cm⁻¹ charac-

teristic of the C=N and C—O—C stretching, respectively. Elemental analysis also supported the formation of the expected polymers.

The polymers were brown solids and soluble in concentrated sulfuric acid, methanesulfonic acid, and *N*-methyl-2-pyrrolidone. The thermal stability of polymers **9** was examined by thermogravimetry (TG). A typical trace for

Table III. Synthesis of poly(1,3,4-oxadiazole)s **9**

Dicarboxylic acid	Reaction conditions		Polymer		
	Time	PPMA	Type	Yield	η_{inh}^b
	h	ml		%	dl g ⁻¹
8a	67	2.0	9a	99	0.21
8b	16	5.0	9b	95	0.28
8c	16	5.0	9c	99	0.30

^a Polycondensation was carried out with 1.0 mmol of each monomer in PPMA at 140°C.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

Figure 1. TG curves of polymer **9c**, (—) in nitrogen and (-----) in air.**Table IV.** Thermal stability of poly(1,3,4-oxadiazole)s **9**

Polymer	Decomposition temp/°C ^a	
Type	In air	In nitrogen
9a	420	420
9b	390	410
9c	445	450

^a 10% weight loss temperature observed by TG.

polymer **9c** is shown in Figure 1. The polymer showed a 10% weight loss in air and under nitrogen at 445 and 450°C, respectively. These data are summarized in Table IV. The good thermal stability of the aromatic poly(oxadiazole)s was comparable to that reported in the literature.^{1f,10}

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