Oxidative Coupling Polymerization of Bishydrazide for the Synthesis of Poly(diacylhydrazine): Oxidative Preparation of Oxidatively Degradable Polymer

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ABSTRACT: The oxidative coupling polymerization of bishydrazide is successfully performed to form poly(diacylhydrazine) (PDAH), which is an oxidatively degradable polymer. Oxone is an effective oxidant, and a mixture of an aprotic polar solvent, water, and acetonitrile or *N*,*N*-dimethylacetamide is necessary as the solvent. On treatment of PDAH with sodium hypochlorite solution or hydrogen peroxide, the PDAH is rapidly oxidized and degraded to the corresponding dicarboxylic acid. When hydrogen peroxide is used as the oxidant, the addition of acetonitrile and potassium carbonate is necessary for effective degradation. PDAH exhibits high thermal stability in air and a high T_g value. No oxidation is observed in air. Thus, PDAH is an oxidatively degradable high-performance polymer that is stable toward oxygen. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: degradation; high perfomance polymers; hydrazide; oxidative coupling polymerization; oxidative degradation; oxone; poly(diacylhydrazine); polycondensation

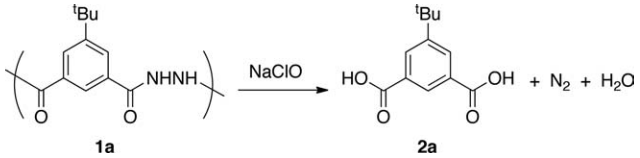
INTRODUCTION Recently, we reported that poly(diacylhydrazine) (PDAH) **1a**, a polyamide for which hydrazine is the diamine component, is a novel degradable polymer that decomposes through the action of an oxidant such as sodium hypochlorite solution (Scheme 1).[1]

1a exhibits some unique features as a degradable polymer: (i) because molecular oxygen does not oxidize the diacylhydrazine moiety, PDAH **1a** is stable in air even at high temperatures ($T_d = 320$ °C in air). (ii) Because sodium hypochlorite is readily available but is not a naturally occurring chemical, decomposition hardly takes place under ambient conditions. However, once **1a** is exposed to sodium hypochlorite, oxidative degradation starts promptly. Therefore, degradation can be initiated at the desired moment. (iii) PDAH **1a** is an ordinary polyamide. Because of the strong hydrogen-bonding interaction between the polymer chains, PDAH **1a** exhibits good thermal and mechanical properties.

Because of unique features of **1a** as a novel degradable polymer, we were interested in the properties of other PDAHs. PDAHs have been prepared as the precursors for whole aromatic poly(1,3,4-oxadiazole)s.[2] Although thermal dehydrative conversion of PDAH to poly(1,3,4-oxadiazole) has been extensively studied, properties of PDAH itself have not been paid much attention. Especially, oxidative degradability of PDAH has not been reported except for our previous reports.[1] Therefore, it is worthwhile to investigate the properties of PDAH, including their oxidative degradability.

PDAH is synthesized by the method used to synthesize polyamides: however, instead of a diamine, hydrazine is used in the condensation reaction with carboxylic acid derivatives.[1(a)] Because hydrazine is a volatile, hygroscopic, corrosive, and toxic compound, it is convenient to use bishydrazide as the hydrazine equivalent.[2,3] In both conventional methods, the nylon-salt technique is not available for the preparation of PDAH because of the low nucleophilicity of the terminal amino group in the hydrazide. Therefore, polycondensation of bishydrazide with a bis(acid chloride) or bis(active ester) has been used, although the use of bis(acid chloride) sometimes causes staining of the product.[1] Therefore, the accessibility of PDAH has been lower than that of other polyamides.

A special method to access diacylhydrazine, that is, the partial oxidation of hydrazine, has been reported.[4] Thus, after hydrazide is oxidized to acyldiimide, the facile nucleophilic attack of a second hydrazide molecule on the highly reactive acyldiimide affords diacylhydrazine (Scheme 2). The eliminated diimide is further oxidized to nitrogen and water. Therefore, theoretically, two moles of two-electron oxidant are necessary for the formation of one mole of diacylhydrazine. Because the oxidation of diacylhydrazine is more



SCHEME 1 Oxidative degradation of **1a**.

difficult than that of hydrazide because of the electron-withdrawing nature of the acyl group, selective oxidation of hydrazide to produce diacylhydrazine is possible.

If this oxidative coupling reaction can be used in polycondensation, we can access PDAH directly from bishydrazide. To produce high-molecular weight PDAH, we have to control the oxidation very precisely: complete oxidation of hydrazide is required, whereas the oxidation of diacylhydrazine has to be thoroughly prevented.

In this article, we report a novel effective method to prepare PDAH: the oxidative coupling polycondensation of bishydrazide. Because various PDAHs were prepared easily with the oxidative coupling poycondensation, we also investigate their oxidative degradability and thermal properties.

EXPERIMENTAL

Materials

5-*tert*-Butylisophthalodihydrazide **3a** was prepared according to the method previously reported[1(b)] and was used after recrystallization from ethanol/water. Reagent-grade aliphatic bishydrazides **3b**–**f** are commercially available and were used without further purification. Dimethyl 5-(octyloxy)isophthalate (**4g**),[5] dimethyl 5-(decyloxy)isophthalate (**4h**),[6] dimethyl 5-phenylisophthalate (**4i**),[7] dimethyl 4,6-bis(octyloxy)isophthalate (**4j**),[8] 4,4′-oxybis(ethyl benzoate) (**4k**),[9] 3,3′-(1,4-phenylene)bis(ethyl propionate) (**4l**),[10] and 3,3′-(1,3-phenylene)bis(ethyl propionate) **4m**[10,11] were prepared according to the literature procedures with some modification. All other chemicals and solvents were reagent-grade, and were used without further purification.

Instruments

NMR spectra were recorded on JEOL JNM-ECP300, JNM-EX400, and JNM-ECP500 spectrometers using tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer. Mass spectra were recorded on a JEOL JMS-T-100LC instrument equipped with a time-of-flight detector and on JMS-AX-505H mass spectrometers. Melting points were observed on a Yanaco MP-500D instrument. Thermal gravimetric analysis was performed on a Rigaku Thermo plus TG-8120 instrument with a temperature gradient of 10 K/min; samples were ramped from room temperature to 500 °C in an aluminum pan under air. Differential scanning calorimetry (DSC) was performed on a Rigaku Thermo plus DSC-8230 with a temperature gradient of 10 K/min; samples were placed in a crimped aluminum pan under air. HPLC analysis was performed using a Shimadzu LC-20AT system with a TOSOH ODS 100V column placed in a CTO-20A oven equipped with RID-10A and SPD-20A detectors. The solvent was degassed using a Shimadzu DGU-20A on-line degasser. Gel permeation chromatography (GPC) was performed using a Shimadzu LC-10AT system with a Polymer Laboratories PolyPore column placed in a CTO-10A oven equipped with RID-10A and SPD-10A detectors. The solvent was degassed using a DGU-12A on-line degasser.

Oxidative Coupling Polymerization: Typical Procedure

Oxone (1.2347 g, 2.01 mmol) was added to a solution of bishydrazide **3a** (246.6 mg, 0.985 mmol) in *N*-methyl-2-pyrrolidone (NMP), water, and acetonitrile (1 mL each). After being stirred for 24 h, the reaction mixture was poured into methanol. The precipitate was washed thoroughly with methanol followed by water and was dried *in vacuo* to obtain polymer **1a** (156.2 mg, 73% yield) as a white powder.

Bishydrazide 3g

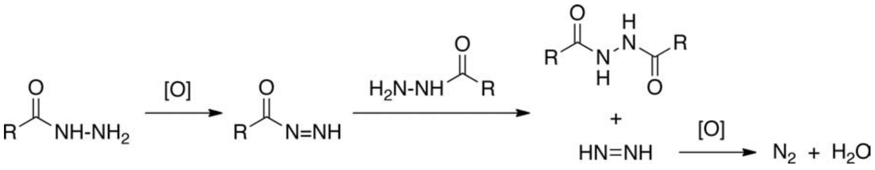
A mixture of ester **4g** (2.8233 g, 9.72 mmol) and hydrazine hydrate (4.5360 g, 90.61 mmol) in ethanol (15 mL) was stirred for 18 h. The reaction mixture was cooled at −30 °C. The precipitate was separated by filtration, washed with a small amount of cold ethanol, and dried *in vacuo* to afford bishydrazide **3g** (2.4380 g, 7.56 mmol, 78% yield).

mp 143.8–145.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.77 (s, 2H), 7.84 (s, 1H), 7.45 (s, 2H), 4.51 (s, 2H), 4.03 (t, J = 6.6 Hz, 2H), 1.69–1.76 (m, 2H), 1.38–1.45 (m, 2H), 1.23–1.36 (m, 8H), 0.83–0.90 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 165.6, 158.3, 135.3, 118.8, 115.7, 68.4, 31.7, 29.2, 29.0, 26.0, 22.6, 14.4.

Bishydrazide 3h

A mixture of ester **4h** (5.6470 g, 16.12 mmol) and hydrazine hydrate (8.0080 g, 160.00 mmol) in ethanol (30 mL) was stirred for 16 h. The reaction mixture was cooled at −30 °C. The precipitate was separated by filtration, washed with a small amount of cold ethanol, and dried *in vacuo* to afford bishydrazide **3h** (4.7726 g, 13.62 mmol, 85% yield).

mp 108.0–111.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.78 (s, 2H), 7.84 (s, 1H), 7.45 (s, 2H), 4.50 (s, 2H), 4.03 (t, J = 6.4 Hz, 2H), 1.69–1.76 (m, 2H), 1.38–1.46 (m, 2H), 1.20–1.36 (m, 14H), 0.82–0.88 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6,



SCHEME 2 Oxidative coupling reaction of hydrazide.

δ): 165.6, 158.9, 135.6, 118.9, 115.7, 68.4, 31.8, 29.4, 29.0, 25.9, 22.6, 14.4.

Bishydrazide 3i

A mixture of ester **4i** (1.2177 g, 4.51 mmol) and hydrazine hydrate (2.0951 g, 41.85 mmol) in ethanol (15 mL) was stirred for 42 h, and heated at reflux for 4 h. The reaction mixture was cooled at −30 °C. The precipitate was separated by filtration, washed with a small amount of cold ethanol, and dried *in vacuo* to afford bishydrazide **3i** (0.6845 g, 2.53 mmol, 56% yield).

mp 189.3–192.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6, δ): 9.96 (s, 2H), 8.26 (s, 1H), 8.22 (s, 2H), 7.81 (d, J = 7.3 Hz, 2H), 7.52 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 4.57 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 165.7, 140.7, 139.4.6, 134.7, 129.5, 128.6, 127.7, 127.5, 125.8; EIMS (m/z): 270, 255, 239, 224, 209, 181, 152.

Bishydrazide 3j

A mixture of ester **4j** (3.1087 g, 6.90 mmol) and hydrazine hydrate (3.5042 g, 70.00 mmol) in methanol (15 mL) was stirred for 24 h. The reaction mixture was cooled at −30 °C. The precipitate was separated by filtration and washed with a small amount of cold methanol. The crude product was recrystallized from methanol to afford bishydrazide **3j** (1.8322 g, 4.07 mmol, 59% yield).

mp 105.4–108.1 °C (ref. [12], 113 °C); ^{1}H NMR (500 MHz, CDCl$_3$, δ): 9.01 (s, 1H), 8.66 (s, 2H), 6.45 (s, 1H), 4.16–4.13 (m, 8H), 1.95–1.89 (m, 4H), 1.52–1.46 (m, 4H), 1.42–1.29 (m, 16H), 0.89 (t, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$, δ): 165.7, 160.3, 136.9, 113.7, 96.3, 69.7, 31.7, 29.2, 29.1, 29.0, 26.0, 22.6, 14.1.

Bishydrazide 3k

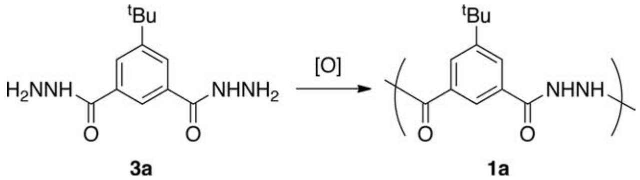
A mixture of ester **4k** (13.8223 g, 43.97 mmol) and hydrazine hydrate (22.2724 g, 444.9 mmol) in ethanol (100 mL) was stirred for 40 h, and heated at reflux for 19 h. The reaction mixture was cooled at −30 °C. The precipitate was separated by filtration, washed with a small amount of cold ethanol, and dried *in vacuo* to afford bishydrazide **3k** (7.5629 g, 26.42 mmol, 60% yield).

mp 224.7–226.9 °C; ^{1}H NMR (500 MHz, DMSO-d_6, δ): 9.74 (s, 2H), 7.87 (d, J = 8.8 Hz, 4H), 7.09 (d, J = 8.8 Hz, 4H), 4.47 (s, 4H).

Bishydrazide 3l

A mixture of ester **4l** (3.1030 g, 11.15 mmol) and hydrazine hydrate (5.5336 g, 110.54 mmol) in ethanol (30 mL) was stirred for 2 days. The reaction mixture was cooled at −30 °C. The precipitate was separated by filtration, washed with a small amount of cold methanol, and dried *in vacuo* to afford bishydrazide **3l** (2.4710 g, 9.88 mmol, 89% yield).

mp 232.7–234.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.94 (s, 2H), 7.08 (s, 4H), 4.14 (s, 4H), 2.76 (t, J = 7.8 Hz, 4H), 2.29 (t, J = 7.8 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, δ): 171.2, 139.2, 128.6, 35.6, 31.1.



3a 1a

SCHEME 3 Oxidative coupling polymerization of **1a**.

Bishydrazide 3m

A mixture of ester **4m** (4.1327 g, 14.85 mmol) and hydrazine hydrate (7.0561 g, 140.95 mmol) in ethanol (30 mL) was stirred for 24 h. The reaction mixture was cooled at −30 °C. The precipitate was separated by filtration, washed with a small amount of methanol, and dried *in vacuo* to afford bishydrazide **3m** (3.2476 g, 12.98 mmol, 87% yield).

mp 199.5–201.0 °C; ^{1}H NMR (300 MHz, DMSO-d_6, δ): 8.94 (s, 2H), 7.19–7.14 (m, 1H), 7.05–6.99 (m, 3H), 4.16 (s, 4H), 2.77 (t, J = 7.8 Hz, 4H), 2.29 (t, J = 7.8 Hz, 4H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6, δ): 170.7, 141.0, 128.1, 125.7, 35.0, 30.9.

Oxidative Degradation by Sodium Hypochlorite: Typical Procedure

A 5% solution of sodium hypochlorite (30 mL) was added to a powder of PDAH **1a** (86.5 mg, 0.40 mmol-unit). Gas evolution ceased within 10 min, and the reaction mixture was stirred for additional 24 h. Concentrated hydrochloric acid was added to give a pH value of < 1. The precipitate was separated by filtration, washed with water, and dried *in vacuo* to afford carboxylic acid **2a** (49.0 mg, 0.22 mmol, 55% yield).

Oxidative Degradation by Hydrogen Peroxide: Typical Procedure

Potassium carbonate (138.5 mg, 1.00 mmol) and 30% hydrogen peroxide solution (1 mL) were added to a solution of PDAH **1a** (105.4 mg, 0.48 mmol-unit) in NMP (1 mL) and acetonitrile (0.5 mL). The reaction mixture was stirred for 24 h. Concentrated hydrochloric acid was added to give a pH value of < 1. The precipitate was separated by filtration, washed with water, and dried *in vacuo* to afford carboxylic acid **2a** (75.0 mg, 0.34 mmol, 70% yield).

IR (KBr): ν = 3423, 2967, 1690, 1453, 1281 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz, δ): 13.24 (s, 2H), 8.31 (s, 1H), 8.18 (s, 2H), 1.41 (s, 9H).

RESULTS AND DISCUSSION

Polymerization Condition

For the optimization of the polymerization condition, the bishydrazide **3a** was used as the monomer (Scheme 3). Because we have already reported PDAH **1a**,[1(b)] we can easily identify the product polymer to evaluate the effectiveness of the oxidation conditions. Polymer **1a** is soluble in aprotic polar solvents. Therefore, the reaction was carried out in NMP as a polar solvent because of its inertness to the oxidation conditions.

TABLE 1 Oxidative Coupling Polymerization of **3a** with Various Oxidants[a]

Run	Oxidant[b] (Equivalent)	Additive[c]	Time (h)	Yield[d] (%)
1	Oxone (1)	Water (1 mL)	24	9
2	Oxone (2)	Water (1 mL)	24	44
3	TBHP (1)	None	24	0
4	mCPBA (1)	None	24	0
5	$K_2S_2O_8$ (1)	None	24	0
6	$PhI(OAc)_2$ (1)	None	48	0[e]
7	$PhI(OCOCF_3)_2$ (1)	None	48	3
8	PhIO (1)	None	48	0[f]
9	$Ph(IO)CO_2H$[f] (1)	None	48	0[g]
10	I_2 (1)	Et_3N (2 equiv.)	24	0[g]
11	$Cu(OAc)_2$ (1)	Water (1 mL)	5 min[g]	0
12	CAN (1)	Et_3N (3 equiv.)	24	27[h]
13	Ag_2O (1)	None	24	0
14	$K_3[Fe(CN)_6]$ (1)	None	48	0[h]

[a] Polymerization of **3a** (1 mmol) was carried out at room temperature in NMP (1 mL).

[b] One equivalent of oxidant consumes four electrons to produce one diacylhydrazine moiety.

[c] Equivalent to hydrazine moiety.

[d] Methanol- and water-insoluble part.

[e] 5-*tert*-Butylisophthalic acid was formed.

[f] 2-Iodosylbenzoic acid.

[g] Microwave irradiation (500 W).

[h] Complex mixture.

For the oxidative coupling polymerization, we had to determine the appropriate oxidant. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$)[4(a)] and (diacetoxyiodo)benzene (DAIB)[4(b)] have been reported to be an effective oxidants for the coupling of hydrazide to obtain diacylhydrazine. Oxidation by copper(II) acetate under microwave irradiation has also been reported.[4(c)] Thus, **3a** was treated with these oxidants and related compounds in NMP. When the oxidant was insoluble in NMP, water was added as a co-solvent. Polymer **1a** was isolated as the methanol- and water-insoluble part, and the product was identified by ^{1}H NMR spectroscopy. The results are summarized in Table 1.

When 1 equivalent of oxone was used as the oxidant, polymer **1a** was obtained, albeit in low yield (run 1). The yield increased as the amount of oxone was increased (run 2). Other peroxides gave no polymeric product (runs 3–5).[4(d)] Although DAIB has been reported to be an effective oxidant for hydrazide for the formation of diacylhydrazine,[4(b)] the oxidative coupling polymerization of **3a** with DAIB was unsuccessful (run 6). The product was an oligomer that was soluble in methanol and/or 5-*tert*-butylisophthalic acid **2a**, the over-oxidation product. To examine the reactivity of DAIB, we treated **1a** with DAIB in NMP, and found that **1a** was slowly oxidized by DAIB. Therefore, DAIB also oxidizes diacylhydrazine, even though the oxidation of hydrazide is faster than that of diacylhydrazine. A small amount of **1a** was obtained when [bis(trifluoroacetoxy)iodo]benzene was used at room temperature (run 7). Other I(III) oxidants were ineffective for the polymerization (runs 8 and 9). The reactivity of iodine itself was so high that only over-oxidation occurred (run 10). We found that Cu(II) acetate[4(c)] was an ineffective oxidant for the oxidative coupling polymerization (run 11). Therefore, we tried other one-electron oxidants (runs 12–14).[4(e)] A polymeric product was obtained when Ce(IV) (CAN) was used as the oxidant, although the ^{1}H NMR spectrum of the product indicated that the desired PDAH **1a** was not produced (run 12).

Because oxone was the only selective oxidant among those we examined, the polymerization conditions were investigated further using oxone as the oxidant to afford the high-molecular weight PDAH **1a**. We found that the solvent significantly affected the result of the polymerization. The results are summarized in Table 2.

Both the water content in the solvent and the concentrations of substrates greatly affected the yield of the polymer. When the amount of water was fixed to 1 mL for 1 mmol of **3a**, the best yield of polymer was obtained when 2 mL of NMP was used (run 2), whereas no polymer was obtained when 3 mL of NMP was used (run 3). No polymer was obtained at higher temperatures because of over-oxidation (run 4). The effect of the organic solvent was also examined. CH_3CN was found to be a good solvent as well as NMP (run 6). Surprisingly, the best result was obtained when NMP was used with CH_3CN (run 7). The yield of polymer simply decreased at lower temperatures (runs 8 and 9); the oxidation was sensitive to the polymerization temperature.

The role of each organic solvent was examined in the NMP/CH_3CN/water tersolvent system. First, CH_3CN was replaced with other organic solvents (runs 10–12). We found that *N*,*N*-dimethylacetamide (DMAc) is as effective as CH_3CN (run 11). It should be noted that the NMP/DMAc/water (1/1/1) system gave better results than the NMP/water (2/1) system (run 2), in spite of the fact that NMP and DMAc are very similar aprotic polar solvents. Next, NMP was replaced by other organic solvents (runs 13–15). Aprotic polar solvents of the amide type, such as DMF and DMAc, also gave good results.

No polymerization occurred without water. It seems that water is necessary only to dissolve the oxone. Because water can be a competitive nucleophile toward the acyldiimide intermediate, we expected that the yield and molecular weight of the polymer would increase in the absence of water. Thus, the oxidative coupling polymerization was carried out without water, but in the presence of phase-transfer catalyst to dissolve oxone in nonaqueous media. However, no polymer was obtained in the presence of 18-crown-6 ether or tetrabutylammonium hydrogen sulfate, even though oxone partially dissolved in the presence of these phase-transfer catalysts. Although the role of water in the oxidation reaction is not clear, it was found that water is essential in the oxidative coupling polymerization of bishydrazide by oxone.

TABLE 2 Oxidative Coupling Polymerization of **3a** Using Oxone as the Oxidant[a]

Run	Solvent (mL)	Temperature	Time (h)	Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	NMP/water (1/1)	rt	48	25	14,000	6.6
2	NMP/water (2/1)	rt	48	34	21,000	6.9
3	NMP/water (3/1)	rt	48	0	–	–
4	NMP/water (2/1)	60 °C	48	0	–	–
5	DMF/water (1/1)	rt	24	15	15,000	6.7
6	CH_3CN/water (1/1)	rt	24	27	18,000	8.0
7	NMP/CH_3CN/water (1/1/1)	rt	48	64	20,000	29
8	NMP/CH_3CN/water (1/1/1)	−40 °C	72	0	–	–
9	NMP/CH_3CN/water (1/1/1)	0 °C	48	41	14,000	18
10	NMP/THF/water (1/1/1)	rt	48	39	23,000	48
11	NMP/DMAc/water (1/1/1)	rt	48	69	20,000	9.6
12	NMP/MeOH/water (1/1/1)	rt	48	24	15,000	42
13	DMF/CH_3CN/water (1/1/1)	rt	48	64	25,000	76
14	DMAc/CH_3CN/water (1/1/1)	rt	48	65	21,000	59
15	THF/CH_3CN/water (1/1/1)	rt	48	48	9,500	150

[a] Polymerization was carried out using **3a** (1 mmol) with oxone (2 mmol).
[b] Methanol- and water-insoluble part.
[c] Estimated by GPC (DMF, PSt standards).

The effect of polymerization time was then examined. The results are shown in Figure 1 with GPC profile. As the polymerization time was increased, both the yield and molecular weight of **1a** increased, and they were saturated around for 24 h. This behavior is unlikely in step polymerization, but likely to occur in chain polymerization. At present, the reason for this unusual behavior is not clear.

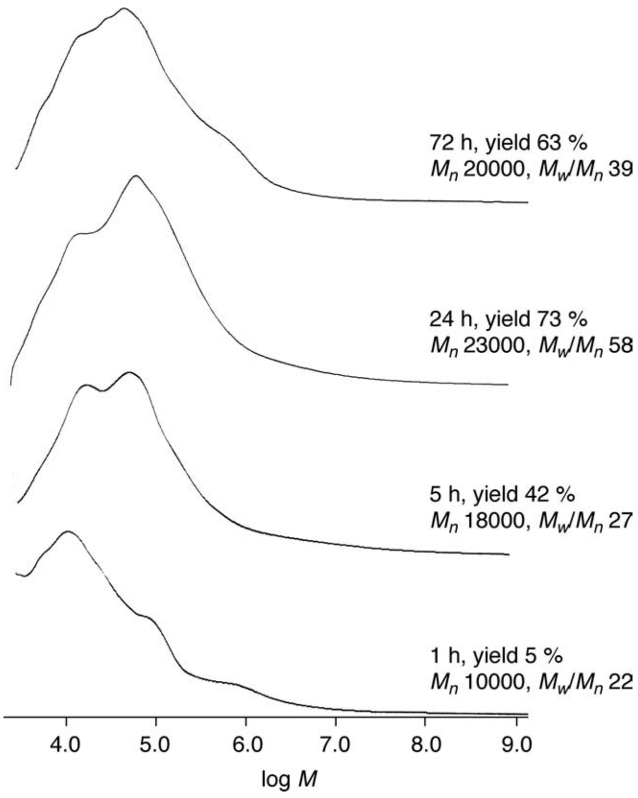
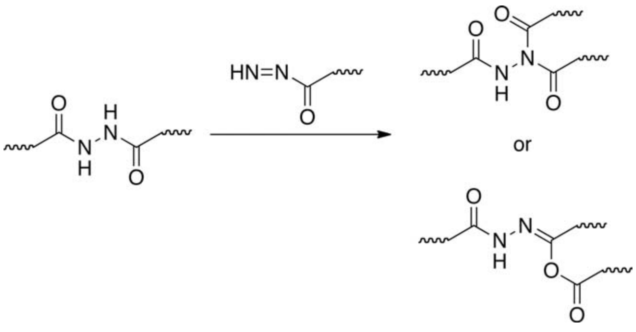
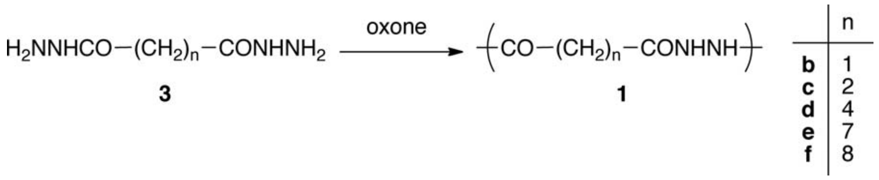


FIGURE 1 The change of the yield and the GPC profile during the polymerization.

A very large molecular weight distribution (MWD) was observed, although no gel fraction was observed even in the case of long polymerization time. In the GPC chart, the considerable amount of the fraction in the very large molecular weight region was observed from the early stage of the polymerization. It can be deduced that partial crosslinking occurred as a side reaction. Because an irregular structure was not detected in the ^1H NMR spectra, there is no spectroscopic information on the branching structure. On the other hand, PDAH with a large MWD was also obtained in the polycondensation system.[1(b)] Therefore, it can be estimated that the main chain of PDAH **1a** reacts with the active polymer terminal. We deduce that the crosslinking reaction occurred via the nucleophilic attack of the diacylhydrazine group on the highly reactive acyldiimide terminal, as shown in Scheme 4, to afford partially branched polymer.[13]



SCHEME 4 Possible crosslinking reaction.



SCHEME 5 Oxidative coupling polymerization of aliphatic dihydrazide.

Because the NMP/CH_3CN system was superior to other solvents for the oxidative coupling polymerization, **3a** was treated with iodine(III) oxidants in NMP/CH_3CN. When [bis(trifluoroacetoxy)iodo]benzene was used, the desired polymer **1a** was obtained in 6% yield (M_n 26,000, M_w/M_n 57). Although the yield was still low, it was better than that obtained in NMP. On the other hand, **1a** was not obtained even in NMP/CH_3CN when DAIB was used as the oxidant.

Oxidative Coupling Polymerization of Bishydrazides

The oxidative coupling polymerization of the commercially available alkanodihydrazides **3b**–**f** was examined in NMP/CH_3CN/water using oxone as the oxidant (Scheme 5). Because of the low solubility of these bishydrazides, however, every polymerization system was heterogeneous. Because hydrazides **3c** and **3d** are insoluble in the solvent system, no polymerization occurred. When **3b**, **3e**, and **3f**, which are slightly soluble in organic solvents, were used as monomers, water- and methanol-insoluble products were obtained in 58–78% yield. However, the products were insoluble in any organic or inorganic solvents, including sulfuric acid and aqueous ammonia solution.[1(a)] Therefore, further characterization of the polymer was not carried out.[14]

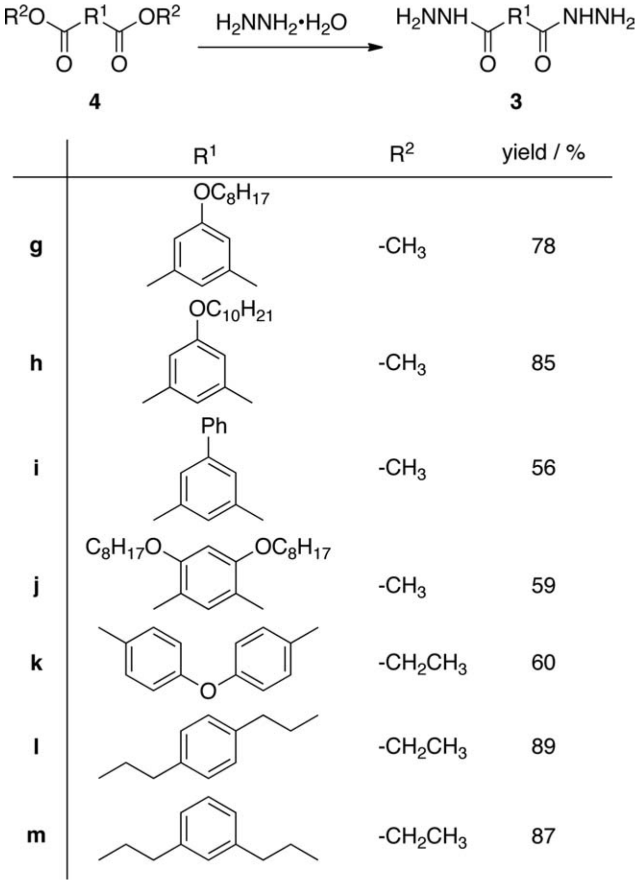
It was supposed that strong intermolecular hydrogen bonding caused the low solubility of hydrazides and PDAH. Therefore, some bishydrazide monomers **3g**–**m**, with a bending structure and hydrophobic side chain to prevent intermolecular hydrogen bonding and the stacking of methylene chains, were prepared. According to the general synthetic strategy,[15] the corresponding diester **4** was treated with excess hydrazine hydrate in alcohol to afford the desired bishydrazide **3** in good yield (Scheme 6). Although these bishydrazides are soluble in aprotic polar solvents, their solubilities were lower than that of **3a**, with the exception of **3i**, which has as good solubility in aprotic polar solvents as **3a**. The rather hydrophobic **3i** and **3j** are also soluble in chloroform, in which other bishydrazides are insoluble.

The oxidative coupling polymerization of **3g**–**m** was carried out in both the NMP/CH_3CN/water and NMP/DMAc/water solvent systems. In the case where the monomer had low solubility in the solvent system, the solution was heated to dissolve the monomer as much as possible, and oxone was added at room temperature before the monomer was precipitated out. The results of the polymerization are summarized in Table 3.

Using oxidative coupling polymerization, we could access various PDAHs very easily. Even though MWDs were so large, no gel fraction was observed. Because **3a** and **3g**–**i** showed rather high solubilities in organic solvents, high-molecular weight PDAH was obtained, whereas the less soluble **3j**–**m** gave low-molecular weight PDAH. Although the effect of the solvent system was small, the molecular weight of PDAH tended to be high in NMP/DMAc/water for the less soluble bishydrazide, because DMAc is a better solvent for PDAH than acetonitrile. Although the hydrophobic **3j** is soluble in chloroform, PDAH **1j** was insoluble in chloroform and DMSO, and only partially soluble in DMF.

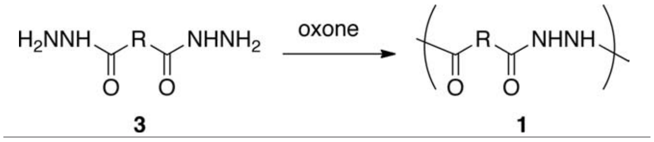
Oxidative Degradation of PDAH

Because various structures of PDAH were obtained, their oxidative degradabilities were examined. First, PDAHs **1a** and **1g**–**m** were treated with sodium hypochlorite solution (5%) at room temperature. Except for **1j**, the PDAHs decomposed immediately with the evolution of nitrogen gas. The decomposition finished within a few tens of minutes to give a clear solution. The decomposition of the aliphatic PDAHs **1l** and



SCHEME 6 Synthesis of bishydrazides.

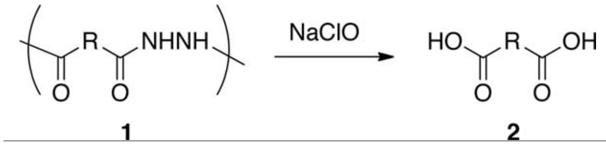
TABLE 3 Oxidative Coupling Polymerization of Bishydrazide **3**[a]



Monomer	Solvent[b]	Yield[c] (%)	M_n[d]	M_w/M_n[d]
3a	A	73	23,000	58
3a	B	72	20,000	9.6
3g	A	85	20,000	33
3g	B	69	16,000	70
3h	A	90	10,000	61
3h	B	92	13,000	160
3i	A	69	16,000	79
3i	B	65	20,000	34
3j	A	76	4,700[e]	140[e]
3j	B	80	4,800[e]	340[e]
3k	A	76	5,000	490
3k	B	80	11,000	75
3l	A	56	5,700	180
3l	B	63	10,000	1,200
3m	A	78	9,000	140
3m	B	68	6,000	850

[a] Polymerization was carried out using **3** (1 mmol) with oxone (2 mmol) at rt for 24 h.
[b] A: NMP/CH_3CN/water (1 mL each). B: NMP/DMAc/water (1 mL/1 mL/0.8 mL).
[c] Methanol- and water-insoluble part.
[d] Estimated by GPC (DMF, PSt standards).
[e] DMF-soluble part.

TABLE 4 Oxidative Degradation of PDAH by Sodium Hypochlorite



PDAH	M_n	Yield[a] (%)
1a	23,000	55
1g	20,000	81
1h	13,000	65
1i	20,000	35[b]
1j	4,800	0 (18)
1k	11,000	38[b]
1l	10,000	36[b]
1m	9,000	56[b]

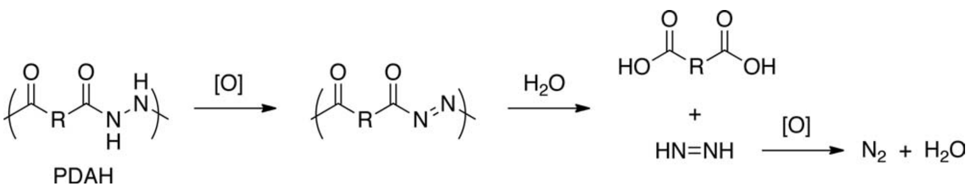
[a] As dicarboxylic acid **2**. Recovery of the starting polymer in parentheses.
[b] Partially chlorinated dicarboxylic acid.

1m proceeded more rapidly than that of the aromatic PDAHs. When the reaction mixture was acidified with hydrochloric acid, the decomposition product was precipitated out. The precipitates were collected by filtration, and the yields are summarized in Table 4.

In the decomposition of **1a**, **1g**, and **1h**, the product was the corresponding carboxylic acid **2**. The decomposition of **1i**, **1k**, **1l**, and **1m** also afforded carboxylic acid, and the products were spectroscopically very similar to the expected carboxylic acids. However, in the ^{1}H NMR spectra of the decomposition products, the integral of the aromatic region was smaller than the expected value for the carboxylic acid **2**. Further, the Beilstein test was positive for these products. These observations clearly indicated that the chlorination of the aromatic ring in the carboxylic acid **2** occurred simultaneously with the oxidative degradation of PDAH by the action of hypochlorite. It should be noted that the aromatic rings in **2i**–**m** have the positions to be attacked by the electrophile, whereas those in **2a**, **2g**, and **2h** are strongly deactivated by the two carbonyl groups. Because the nonregioselective polychlorination was deduced from the ^{1}H NMR spectra of the chlorinated carboxylic acid, further characterization was not carried out.

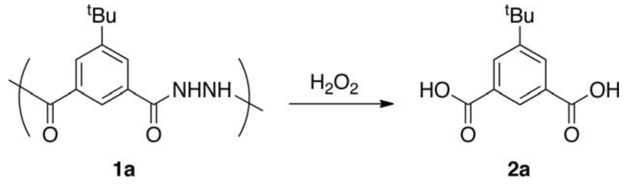
The reaction mechanism for the oxidative degradation of PDAH is shown in Scheme 7. After the oxidation of the diacylhydrazine moiety, the highly reactive azodicarbonyl moiety is rapidly hydrolyzed to afford the carboxylic acid and diimide,[16] which is easily oxidized to nitrogen gas under the reaction conditions used. Because of the high hydrophobicity of **1j**, the approach of the hypochlorite ion to **1j** was so slow that **1j** was recovered without change.

Next, the oxidative degradation with hydrogen peroxide was examined. We have reported that the oxidative degradation of **1a** with hydrogen peroxide was unsuccessful even in the presence of transition metal salts.[1(b)] However, the special solvent effect of acetonitrile on the oxidative coupling polymerization prompted us to re-examine the oxidative degradation of PDAH with hydrogen peroxide. Thus, hydrogen peroxide (30%) was added to a solution or suspension of **1a** (M_n 21,000) at room temperature. The mixture was stirred for 24 h, and the



SCHEME 7 Oxidative degradation of PDAH.

TABLE 5 Oxidative Degradation of **1a** by Hydrogen Peroxide



Solvent	Additive	Yield (%)	Recovery (%)	M_n
NMP	None	0	97	8,000
NMP/CH_3CN	None	0	96	3,500
NMP	K_2CO_3	0	90	10,000
NMP/CH_3CN	K_2CO_3	70	0	–
CH_3CN[a]	K_2CO_3	86	0	–

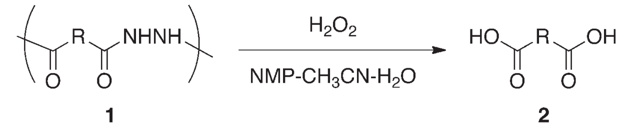
[a] Heterogeneous.

precipitate was collected after acidification of the reaction mixture. The results are summarized in Table 5.

Although oxidative degradation was very slow in NMP, it was accelerated by acetonitrile, and the expected dicarboxylic acid **2a** was obtained in the presence of a base such as potassium carbonate. Oxidative degradation also proceeded without NMP, even though **1a** is insoluble in acetonitrile. At present, the reason for this special effect of acetonitrile is unclear. We deduce that the formation of peroxyimidic acid is responsible for the solvent effect of acetonitrile.[17]

The oxidative degradation of other PDAHs with hydrogen peroxide was examined in NMP/acetonitrile in the presence of potassium carbonate. Except for **1j**, the PDAHs decomposed with the evolution of nitrogen gas. Degradation was scarcely observed in the oxidation of **1j**; the low degradability of **1j** may be attributed to the low solubility and the high hydrophobicity of **1j**, whereas the strong electron-donating nature of two alkoxy groups that deactivate the electrophilic carbonyl groups to reduce the rate of hydrolysis can also be the reason. Although the decomposition was slower than that in sodium hypochlorite solution, the decomposition finished within a few hours to give a clear solution, and the decomposition product was collected as the precipitate after acidification of the reaction mixture. The product yields are summarized in Table 6.

TABLE 6 Oxidative Degradation of PDAH by Hydrogen Peroxide



PDAH	M_n	Yield[a] (%)
1a	23,000	70
1g	20,000	46
1h	13,000	31
1i	20,000	44
1j	4,800	(65)[b]
1k	11,000	63
1l	10,000	(56)[c]
1m	9,000	(78)[d]

[a] Yield of dicarboxylic acid **2**. Recovery of polymer in parentheses.
[b] $M_n = 4{,}800$.
[c] $M_n = 8{,}000$.
[d] $M_n = 2{,}000$.

TABLE 7 Thermal Properties of PDAHs

PDAH	M_n	T_g[a]	T_{d5}[b]
1a	23,000	N	320 °C
1g	20,000	N	306 °C
1h	13,000	N	300 °C
1i	20,000	215 °C	320 °C
1j	4,800	N	298 °C
1k	11,000	N	251 °C
1l	10,000	N	270 °C
1m	9,000	N	257 °C

[a] Measured by DSC (10 K/min, in air). N: not observed under T_d.
[b] 5% weight-loss temperature measured by thermal gravimetric analysis (10 K/min, in air).

Being different from the oxidative degradation with sodium hypochlorite, the decomposition of the aliphatic PDAHs **1l** and **1m** was slower than that of the aromatic PDAHs, and the oligomeric PDAH was recovered instead of the carboxylic acid. In every case, no oxidation of the aromatic ring of the carboxylic acid was observed. Hydrogen peroxide selectively oxidized the diacylhydrazine moiety because hydrogen peroxide is a mild oxidant.

Thermal Properties of PDAH

Stability in air is one of the most important properties of PDAH as an oxidatively degradable polymer. Thus, thermal gravimetric and DSC analyses were performed to measure the thermal properties of the PDAHs. All the measurements were carried out in air to examine the stability of the newly obtained PDAHs in air. The results are summarized in Table 7.

The high-molecular weight PDAHs showed T_{d5} values above 300 °C, whereas T_{d5} values of around 250–270 °C were observed for the rather low-molecular weight PDAHs. The decomposition products were colorless. Thus, it was confirmed that the PDAHs are thermally stable and are hardly oxidized in air. For most PDAHs, no T_g and T_m were observed. T_g was observed only for **1i** at 215 °C. It can be deduced that the other PDAHs have T_g values that are greater than T_d (>300 °C).

CONCLUSIONS

In this article, we have disclosed the novel oxidative coupling polymerization of bishydrazide to form PDAH, an oxidatively degradable polymer. The over-oxidation of PDAH can be prevented by using oxone as the oxidant. For effective polymerization, a tersolvent system (aprotic polar solvent/water/acetonitrile or DMAc) should be used. Various PDAHs of high molecular weight were prepared in good yield when both monomer and polymer exhibited good solubility in the solvent system.

The PDAHs generally showed good oxidative degradability. When PDAH was treated with sodium hypochlorite solution, oxidative degradation was rapid, although chlorination of the electron-rich aromatic ring occurred simultaneously. When hydrogen peroxide was used as the oxidant in an acetonitrile-containing solvent in the presence of potassium carbonate, oxidative degradation proceeded gently, and no side reaction was observed.

We confirmed that PDAH exhibits high thermal stability in air. Even though PDAH is an oxidatively degradable polymer, oxygen is a poor oxidant for the diacylhydrazine moiety. Further, the thermal stability of the *N*—*N* bond is high enough, and the PDAHs are as thermally stable as usual polyamides. Because of the high T_g values, these PDAHs can provide a novel type of high-performance polymer with high degradability.

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