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Synthesis of furan dimer-based polyamides with a high melting point

Naoki Miyagawa, Toyoko Suzuki, Kentaro Okano, Takuya Matsumoto, Takashi Nishino, and Atsunori Mori

Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan

Correspondence to: Atsunori Mori (E-mail: *amori@kobe-u.ac.jp*)

((Additional Supporting Information may be found in the online version of this article.))

ABSTRACT

Polyamide composed of furan dimer, which is prepared from biomass-derived organic molecule 2-furfural, is synthesized. The reaction of 2,2'-furan dimer 5,5'-dicarbonyl chloride with several 1,ω-diamines was carried out with a solution or interfacial polycondensation leading to the corresponding polyamide. Measurement of the melting point was performed resulting to exhibit a higher temperature compared with the related polyamide bearing a single furan ring composed of furan-2,5-dicarboxylic acid (FDCA). Thermal analyses (TG-DTA) also indicated higher temperatures of decomposition than those of FDCA derived polyamide.

KEYWORDS: Biomass, furfural, furan dimer, polyamide, FDCA, thermal analyses

INTRODUCTION

Utilization of biomass-derived organic molecule toward preparation of organic or polymer materials recently attracts much attention to replace the established petrochemical process with a system employing non-edible feedstock biomass cellulose cascade.[1,2] Since furfural derivatives, which involves five-membered heteroaromatic structure, can be readily obtained by degradation of cellulose through the formation of C5 and C6 monosaccharides.[3-6] We have recently shown that furan dimer dicarboxylate, which is converted by the transformation of furfural through several steps, reacts with 1, ω-diols by polycondensation and leads to biopolyesters.[7,8] Those melting points were shown to be superior to those of the related polyesters composed of a single furan ring 2,5-furan dicarboxylate unit.[9] Since such polyesters involve potential use as a surrogate of petro-derived terephthalates representative as PET (polyethylene terephthalate), it is remarkable that polyester derived from furan dimer shows a comparable melting point with PET that is recognized as widely available plastics.[10] On the other hand, polyamides bearing a rigid aromatic framework serve as engineering plastics due to the multiple interchain hydrogen bonds.[11-13] Our further concern employing furan dimer to biomass-derived polymer materials has turned to prepare polyamides bearing furan dimer, which would also show highly rigid structure. Herein, we report that a bifunctional acid chloride composed of furan dimer reacts with 1,ω-diamines leading to polyamides to show thermal stability based on the rigid structure.

EXPERIMENTAL

General

Melting points were measured on a Yanaco MP-J3 Model melting point apparatus. Measurements of ^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (100 MHz) NMR spectra were performed with JEOL ECZ 400 as a $CDCl_3$, DMSO-d_6, or TFA-d (CF_3CO_2D)

solution. HRMS were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). Thermal analyses were carried out with RIGAKU Thermo plus EVO DSC8230 and EVO2 TG-DTA 8121. Synthesis of (2,2'-bifuryl)-5,5'-dicarboxylic acid diethyl ester (**1**) was performed according to our previous report[7] and 1,ω-diamines (ω = 4, 5, 6, 10) were purchased and used without further purification. NMP (*N*-methylpyrrolidone; anhydrous grade) and distilled water were purchased from Wako Pure Chemicals Industries, Ltd. THF (anhydrous grade) was purchased from Kanto Chemicals, Ltd. and passed through a Glass Contour MINI Ultimate solvent system prior to use.

(2,2'-Bifuryl)-5,5'-dicarboxylic acid:[14] To a 500 mL of two-necked flask equipped with a magnetic stirring bar and reflux condenser were added THF (90 mL) and water (60 mL). To the mixture were added 5,5'-(diethoxycarbonyl)-2,2'-bifuryl (**1**) (5.63 g, 20 mmol) and 22 g of KOH and heated at 90 °C for 4 h. After cooling to room temperature the mixture was poured into 6 M hydrochloric acid to form precipitates and filtered off. The residue was washed with water and ethanol to afford 4.30 g of dicarboxylic acid as a solid (97%). ^{1}H NMR (DMSO-d_6) δ 7.08 (d, J = 3.7 Hz, 2H), 7.36 (d, J = 3.7 Hz, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6) δ 110.1, 119.7, 145.0, 147.2, 159.1. IR (ATR) 3131, 2688, 2570, 1672, 1572, 1456, 1311, 1166, 1029, 953, 918, 883, 812, 761 cm^{-1}. The obtained product was used for the following reaction without further purification.

(2,2'-Bifuryl)-5,5'-dicarbonyl dichloride (2): To a 200 mL of two-necked flask equipped with a magnetic stirring bar was added (2,2'-bifuryl)-5,5'-dicarboxylic acid (2.02 g, 9.1 mmol), which was dissolved in 10 mL of dichloromethane and the resulting solution was cooled to 0 °C in an ice bath. Oxalyl chloride (3.4 mL, 40 mmol) and DMF (0.1 mL) were then added to the mixture and stirring was continued at 0 °C to room temperature for 15 h. The mixture was concentrated under reduced pressure to leave a crude solid, which was purified by column chromatography on silica gel using $CHCl_3$ as an eluent to afford 2.06 g of (2,2'-bifuryl)-5,5'-dicarbonyl dichloride (**2**). (87%) Mp 138-140 °C, ^{1}H NMR ($CDCl_3$) δ 7.08 (d, J = 3.7 Hz, 2H), 7.59 (d, J = 3.7 Hz, 2H). Attempted measuremant of ^{13}C{^{1}H} NMR in $CDCl_3$ was found unsuccessful because of difficulties in the solubility, while attempted measurement in DMSO-d_6 resulted in observing the hydrolyzed product as well as in the measurement of HRMS. ^{13}C{^{1}H} NMR (DMSO-d_6) δ 110.2, 119.8, 145.1, 147.2, 159.1. IR (ATR) 3138, 3132, 1732, 1548, 1429, 1240, 1035, 967, 884, 827, 807, 693, 550 cm^{-1}. HRMS (DART+) Calcd for $C_{16}H_{19}O_8$ $[M+H]^+$: 258.9564; found : m/z 258.9568.

General procedure of polyamide synthesis (Method A): To a 20 mL Schlenk tube equipped with a magnetic stirring bar were added (2,2'-bifuryl)-5,5'-dicarbonyl dichloride (**2**, 130 mg, 0.5 mmol), NMP (1.0 mL), triethylamine (0.21 mL, 1.5 mmol), and 1,10-diaminodecane (86.2 mg, 0.5 mmol) under a nitrogen atmosphere. The resulting mixture was heated at 100 °C for 144 h. After cooling to room temperature, the mixture was poured into water to form precipitates, which were washed with water and methanol. The residue was dissolved in 1,1,1-trifluoroethanol/chloroform (2 mL/2 mL) and the solution was added into 20 mL of methanol to form precipitates, which were filtered off. The residue was washed with chloroform repeatedly and dried under reduced pressure with heating at 80 °C to afford 66 mg of **4b** (37%).

Poly[{2,2'-bifuryl)-5,5'-dicarbonyl}-(1,6-diaminohexyl)] (4a): The reaction was carried out in a similar manner to the above procedure employing (2,2'-bifuryl)-5,5'-dicarbonyl dichloride (**2**, 130 mg, 0.5 mmol), NMP (1.0 mL), triethylamine (0.21 mL, 1.5 mmol), and 1,6-diaminohexane (58.1 mg, 0.5 mmol) to yield 48 mg of **4a** (48%). ^{1}H NMR (TFA-d/$CDCl_3$: 9:1 v/v) δ 1.48-1.70 (m, 4H), 1.71-2.04 (m, 4H), 3.26-3.36 (m, 0.12H), 3.48-3.88 (m, 4H), 6.94-7.07 (m, 2H), 7.42-7.59 (m, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6) δ 25.8, 28.7, 38.3, 108.4, 114.2, 145.4, 147.6, 157.0. IR

(ATR) 3324, 3270, 3252, 2927, 2853, 1649, 1568, 1534, 1473, 1455, 1305, 1179, 1020, 798 cm^{-1}.

Poly[(1,10-diaminodecan-*N*,*N*'-diyl)-{(2,2'-bifuryl)-5,5'-dicarbonyl}] (4b): ^{1}H NMR (TFA-*d*/$CDCl_3$) δ 1.36-1.61 (m, 12H), 1.71-1.94 (m, 4H), 3.28 (t, *J* = 7.2 Hz, 0.18H), 3.56-3.78 (m, 4H), 6.96-7.08 (m, 2H), 7.48-7.60 (m, 2H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6) δ 26.5, 28.8, 29.0, 29.3, 38.6, 108.9, 115.0, 145.8, 147.7, 157.3. IR (ATR) 3315, 3284, 2926, 2854, 1739, 1634, 1587, 1529, 1474, 1455, 1366, 1300, 1229, 1216, 1015, 806 cm^{-1}.

General procedure of polyamide synthesis by interfacial polycondensation (Method B): To a 20 mL screw-capped test tube equipped with a magnetic stirring bar was dissolved acid chloride **2** (78 mg, 0.3 mmol) in 1.0 mL of dichloromethane. To the resulting solution was slowly added aqueous 1 M solution of KOH (0.3 mL) to result in phase separation. Then, 1,6-diaminohexane (35 mg, 0.3 mmol) dissolved in 1 M KOH (0.7 mL) was added. The resulting mixture was vigorously stirred to initiate the polymerization for 1 h. The formed precipitates were filtered off and the residue was washed with H_2O, methanol, and dichloromethane, successively to leave 55 mg of poly[(1,6-diaminohexan-*N*,*N*'-dilyl)-{(2,2'-bifuryl)-5,5'-dicarbonyl}] (**4a**). (61% yield)

Synthesis of poly[(1,4-diaminobutan-*N*,*N*'-diyl)-{(2,2'-bifuryl)-5,5'-dicarbonyl}] (**4c**) and poly[(1,5-diaminopentan-*N*,*N*'-diyl)-{(2,2'-bifuryl)-5,5'-dicarbonyl}] (**4d**) were carried out in the above manner for 1 h with 1,4-diaminobutane and for 4 h with 1,6-diaminohexane, respectively.

Poly[(1,4-diaminobutan-*N*,*N*'-diyl)-{(2,2'-bifuryl)-5,5'-dicarbonyl}] (4c): 71% yield. ^{1}H NMR (TFA-*d*/$CDCl_3$: 9:1 v/v) δ 1.81-2.12 (m, 4H), 3.35-3.45 (m, 0.05 H), 3.60-3.87 (m, 4H), 7.00 (d, *J* = 3.6 Hz, 2H), 7.50 (d, *J* = 3.6 Hz, 2H) $^{13}C\{^{1}H\}$ NMR (DMSO-d_6) δ 25.9, 38.0, 108.6, 114.4, 145.5, 147.7, 156.9. IR (ATR) 3300, 3271, 2933, 1643, 1586, 1531, 1475, 1455, 1298, 1218, 1170, 1017, 810 cm^{-1}.

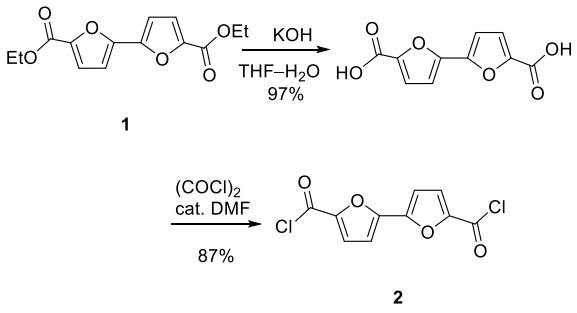
Poly[(1,5-diaminopentan-*N*,*N*'-diyl)-{(2,2'-bifuryl)-5,5'-dicarbonyl}] (4d): 48% yield. ^{1}H NMR (TFA-*d*/$CDCl_3$: 9:1 v/v) δ 1.46-1.75 (m, 2H), 1.75-2.15 (m, 4H), 3.28-3.38 (m, 0.11H), 3.53-3.92 (m, 4H), 6.82-7.19 (m, 2H), 7.41-7.65 (m, 2H). $^{13}C\{^{1}H\}$ NMR (DMSO-d_6) δ 23.6, 28.5, 38.3, 108.4, 114.2, 145.4, 147.6, 157.0. IR (ATR) 3329, 3285, 2947, 2936, 1642, 1584, 1527, 1475, 1453, 1298, 1018, 812, 800, 753 cm^{-1}. Synthesis of model compound **5a** for the estimation of the degree of polymerization was carried out in a similar manner to Method A with acid chloride **2** (0.3 mmol), triethylamine (0.9 mmol), and 1,6-diaminohexane (**3a**) (6.0 mmol). After stirring the mixture at 100 °C for 1 h, an aliquot of the reaction mixture was taken and poured into water to form a precipitate, which was subjected to the measurement of ^{1}H NMR spectrum in TFA-*d* to observe signals at δ = 3.31 (0.38H) and 3.69 (4H).

RESULTS AND DISCUSSION

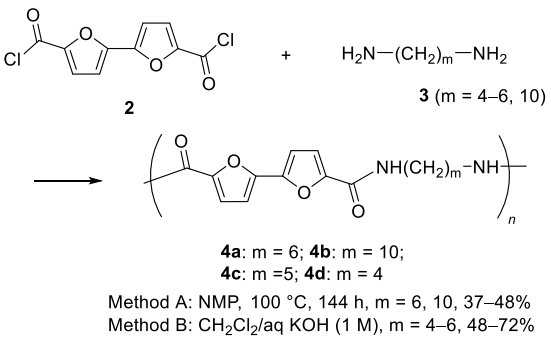
Preparation of acid chloride of the furan dimer **2** as a monomer species was carried out by the hydrolysis of the corresponding diethyl ester **1**[13] and following treatment with thionyl chloride. The obtained **2** was subjected to the polymerization with 1,ω-diamine **3** as shown in Scheme 1 and 2. We initially examined solution polymerization in NMP in the presence of triethylamine (3.0 equiv).[14] When the reaction was carried out employing 1,6-diaminohexane (**3a**), the corresponding polymer **4a** was obtained in 48% isolated yield after stirring at 100 °C for 144 h. The reaction with 1,10-diaminodecane (**3b**) was also performed in a similar manner to afford 37% of polymer **4b** (isolated yield). Although the similar polymerization of 1,ω-diamines of a shorter chain length (ω = 3-5) was attempted, little polymer was obtained under similar conditions. Synthesis of such polymers was found to be achieved using interfacial polycondensation under biphasic conditions.[15] The reaction was performed with a dichloromethane solution of acid chloride **2** and diamine **3a** (ω = 6) in aqueous 1 M KOH solution at room temperature.

Vigorous stirring of the mixture initiated the polymerization at the interface and immediate precipitation resulted to form polymer **4a** in 61% yield. The reaction of 1,4-diaminobutane (**3c**) and 1,5-diaminopentane (**3d**) also afforded the corresponding polymers **4** in 71% and 48% yields, respectively, while the attempted polymerization of 1,3-diaminopropane was unsuccessful.

The use of 1,ω-diamine **3** composed of a long alkylene chain seems to favor solution polymerization, while polymer **4** employed by **3** of a shorter chain length was smoothly obtained by interfacial polycondensation. However, polyamide composed of 1,3-propanediamine was not obtained even by interfacial polycondensation to result in forming a solid, which was easily dissolved in methanol. We consider that polyamide bearing a short alkylene chain with less rotation freedom only formed oligomers and the rigid structure of bifuryl moiety caused propagation of the polymer, accordingly.

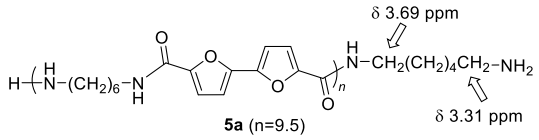


SCHEME 1 Preparation of carboxylic acid chloride of furan dimer



SCHEME 2 Polymerization of furan dimer **2** with 1,ω-diamine **3** by solution or interfacial polycondensation

Although attempted SEC analysis was unsuccessful due to the extremely inferior solubility of polymers **4** in chloroform and THF, measurement of NMR spectra showed formation of polyamide and allowed to estimate the degree of polymerization (DP) as 23-79. Comparing the ^{1}H NMR spectrum of **4a** with that of model compound **5a**, which is the product by the reaction of **2** with excess amounts of diamine **3a**, little signal derived from the end group observed at 3.31 ppm was detected in **4a**.



SCHEME 3 The model compound **5a** for the estimation of the degree of polymerization by ^{1}H NMR.

The obtained polymer **4** either by solution or interfacial polycondensation was then subjected to analyses of DSC and DG-DTA. These results are summarized in Table 1. Thermal properties of polyamide **4a** prepared by solution and interfacial polycondensations were found to be similar suggesting that the property is irrespective of the method of polymerization. Compared with those of polyamide **6a** composed of a single furan ring,[16-18] polyamide **4a** suggested thermally more stable showing higher temperatures at values of 5-50% mass loss and no remarkable mass loss was observed up to ca. 400 °C in polyamides **4a**. The melting point of **4a** was also found to be higher than **6a**. The thermal stability of polyamide **4** was revealed to be comparable irrespective of the chain length of 1,ω-diamine **3**.[19-21] Melting points of polyamide **4a** and **4d** (ω = 6 and 5, respectively) exhibited mostly similar values, while it was found slightly lower in that of **4c** (ω = 4) and that of **4b** composed of 1,10-

TABLE 1 Thermal analyses of polyamide **4**.[a]

Entry	4 (ω)	yield (%)	M_n (NMR)[b]	T_d^5, °C[c]	T_d^{10}, °C[d]	T_d^{50}, °C[e]	T_m, °C[f]
1	**4a** (6)	48	9700	386	413	449	211
2	**4b** (10)	37	7900	393	414	453	163
3	**4a** (6)	61	23900	408	418	454	215
4	**4c** (4)	71	22800	377	407	444	198 (283)[g]
5	**4d** (5)	48	10000	297	406	437	213
	6a (6)[h]			287±5		355±5	
	6c (4)[h]			275±6		350±4	

[a] Measurements of thermal analyses were carried out by TG/DTA and DSC at a heating rate of 10 °C/min under N_2 flow. [b] The molecular weight measured by 1H NMR analysis. [c] The temperature at 5% mass loss by TG/DTA.[d] The temperature at 10% mass loss by TG/DTA. [e] The temperature at 50% mass loss by TG/DTA. [f] The melting point by DSC. [g] The peak top of the main endotherm was defined as melting point. [h] Results of polyamide derived from 1,ω-diamine (ω = 4 or 6) and 2,5-furan dicarbonyl dichloride. See ref 18.

decanediamine (**3b**) was much lower (T_m = 163 °C) because of higher freedom of the rotation of methylene chains. As we have recently shown in thermal properties of polyesters composed of furan dimer,[3] improved thermal stabilities of polyamides **4** was also observed by the introduction of the dimeric heteroaromatic furan moiety and melting points of polyamide was much higher than that of the related polyester (T_m of **4a** and the polyester of 1,6-hexanediol: 211-215 °C vs. 161 °C) because of stronger hydrogen bond of amide

CONCLUSIONS

In conclusion, we have shown that bifunctional acid chloride **2** composed of furan dimer dicarboxylic acid reacted with several 1,ω-alkanediamines **3** to undergo polycondensation to give polyamide **4**. The reaction proceeded both with solution or interfacial polymerization and the obtained **4** showed higher melting points compared with the related furan dimer polyester. It was also found that thermal analyses of polyamides **4** indicated superior temperatures of T_d^{50} to those of furan dimer polyesters as well as those composed of a single furan ring **6**. The obtained polyamide **4** can be available as a new class of bioplastics of high thermal stabilities.

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GRAPHICAL ABSTRACT

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Synthesis of furan dimer-based polyamides with a high melting point

Bifunctional acid chloride of furan dimer, which is converted from furfural, reacts with 1, ω-diamine to give polyamide showing high thermal stability. Comparing thermal stability with that of the related polyamide composed of a single furan ring, it is found to show higher decomposition temperatures.