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Synthesis and characterization of polyamides based on cubane-1,4-dicarboxylic acid

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Summary

The direct polycondensations of cubane-1,4-dicarboxylic acid with 1,4-phenylenediamine (**2a**), 4,4'-oxydianiline (**2b**), 4,4'-sulfonyldianiline (**2c**), and 9,9'-bis(4-aminophenyl)florene (**2d**) were carried out in *N*-methyl-2-pyrrolidone/pyridine containing triphenylphosphite and lithium chloride at 110 °C for 9 h. Polyamide **3a** obtained from **2a** was scarcely soluble in organic solvent even during heating, and was soluble only in *conc*-H_2SO_4, whereas **3c** and **3d** derived from **2c** and **2d**, respectively, were readily soluble in *N*-methyl-2-pyrrolidone, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, and dimethylsulfoxide. After treating polyamide **3d** with the rhodium complex catalyst in NMP, cubane units were quantitatively converted into cyclooctatetraenes.

Introduction

Since Eaton first synthesized cubane, which is a strained polycyclic aliphatic cage compound,[1] numerous studies have been reported in terms of the synthesis and characterization of cubane derivatives.[2-4] Although cubylcubanes,[5] oligocubanes,[2] and higher cubylcubanes[2] were proposed, demonstrated, and synthesized, there are even fewer reports on the use of cubanes as monomers for polymeric materials leading to polymers with cubane units in their backbone. Therefore, of great interest is the molecular design, synthesis, and characterization of a polymer containing a cubane moiety. In addition, cubanes are treated with a rhodium complex catalyst for quantitative conversion into the corresponding *syn*-tricyclooctadienes which further afforded cyclooctatetraenes by heating.[6,7] For the polymeric cubane system, isomerized cyclooctatetraene units in the polymer are expected to be polymerized with the appropriate cyclic alkene via a ring-opening metathesis mechanism leading to polymers with polyconjugated chains.

Here we report the synthesis of polyamides **3** by the direct polycondensation of cubane-1,4-dicarboxylic acid (**1**) with various aromatic diamines **2**. In addition, the metal-induced ring-opening of cubane units in **3** for conversion into cyclooctatetraenes is investigated, as

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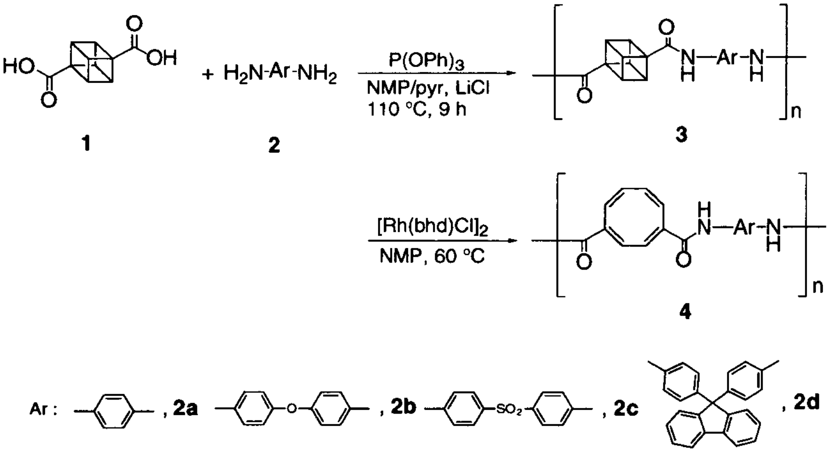

Scheme 1

shown in Scheme 1.

Experimental

Dimethyl cubane-1,4-dicarboxylate, commercially available from EniChem Synthesis, was hydrolyzed to **1**.

A typical example of the direct polycondensation is given as follows: A solution of **1** (769 mg, 4 mmol), **2c** (993 mg, 4 mmol), triphenylphosphite (2.09 mL, 8 mmol), and anhydrous lithium chloride (1.5 g) in NMP (30 mL) and pyridine (10 mL) were heated at 110 °C. After 9 h, the mixture was poured into methanol (1 L). The precipitate was filtered, washed thoroughly with methanol, and dried at 60 °C under vacuum. The cream-colored powdery polymer, **3c**, was obtained. Yield, 1.70 g (100 %). The inherent viscosity of the polymer was 0.16 dL/g as determined in H_2SO_4 at 30 °C. IR (KBr) υ 3244(m), 2994(m), 1660(s), 1589(s), 1519(s), 1327(s); ^{1}H NMR (270 MHz, D_2SO_4, sodium 3-(trimethylsilyl)propionate (TSP)) δ 7.55, 7.25 (br, s, Ar), 4.26 (s, cubyl, CH); ^{13}C NMR (67.5 MHz, D_2SO_4, TSP) δ 179.0 (CONH), 141.1, 140.8 (Ar, C1,C4), 132.6 (Ar, C2), 128.6 (Ar, C3), 57.5 (cubyl, $\underline{\text{C}}$-CO), 52.1 (cubyl, CH).

A typical example of the isomerization is given as follows: A solution of **3d** (300 mg) in NMP (7 mL) and $[Rh(bhd)Cl]_2$ (32 mg, 0.07 mmol) were separately put into each side of a dried H-shaped ampoule. The solution was deoxygenated by several freeze-pump-thaw cycles, and then mixed with $[Rh(bhd)Cl]_2$ under nitrogen at 60 °C for 24 h. The mixture was concentrated by distillation under reduced pressure and poured into methanol (200 mL). The precipitate was filtered using a glass filter, then washed thoroughly with methanol. The obtained yellowish powder was purified by reprecipitation using NMP-methanol, and dried at 60 °C under vacuum. Yield, 298 mg (99 %). IR (KBr) υ 3306 (s), 2993 (w), 1652 (s), 1594 (s), 1513 (s), 1327 (s), 748 (s); ^{1}H NMR (270 MHz, D_2SO_4, TSP) δ 9.56 (broad s, CONH), 7.89, 7.51, 7.31, 7.02 (broad s, Ar), 6.84, 6.35, 6.22, 6.10 (broad s, -CH=); ^{13}C NMR (67.5 MHz, D_2SO_4, TSP) δ 163.9, 150.9, 141.1, 139.0, 139.7, 137.9, 137.5, 133.8, 132.2, 131.9 135.4, 130.2, 127.7, 126.3, 120.8, 120.5, 120.3, 64.4.

Results and Discussion

The direct polycondensations of **1** with aromatic diamines **2** were carried out in *N*-methyl-2-pyrrolidone (NMP)/pyridine (3/1) solution containing triphenylphosphite and lithium chloride at 110 °C for 9 h. The results are listed in Table 1. The polycondensation system for 1,4-phenylenediamine (**2a**) rapidly turned into a heterogeneous solution and the polyamide precipitated, whereas the systems for 4,4'-oxydianiline (**2b**), 4,4'-sulfonyldianiline (**2c**), and 9,9'-bis(4-aminophenyl)florene (**2d**) were homogeneous and turned brown. The yields of the polyamides were almost quantitative in each case. The structures of synthesized polyamides were confirmed by FT-IR and ^{1}H NMR spectrometries. For all the polyamides, the IR spectra were shown the characteristic absorption at 3290-3330 and 1648-1660 cm^{-1} due to the N-H stretching and C=O stretching for the amide groups, respectively. The signal at 4.2 ppm due to the cubyl protons was observed in the ^{1}H NMR spectrum of polyamide **3d** (Figure 1a), therefore, the cubane units were introduced into the polymer backbone.

Table 2 summarizes the qualitative solubility of the polyamides in various solvents. Polyamide **3a** was scarcely soluble in organic solvent even during heating, and was solubleonly in *conc*-H_2SO_4. On the other hand, **3c** and **3d** derived from **2c** and **2d**, respectively, which were flexible or bent diamines, were readily soluble in dipolar aprotic solvents such as NMP, *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO).

Table 1. Polyamides of cubane-1,4-dicarboxylic acid and 1,4-phenylenediamine (2a), 4,4'-oxydianiline (2b), 4,4'-sulfonyldianiline (2c), and 9,9'-bis(4-aminophenyl)florene (2d)[a]

aromatic amine 2	M_w[b]	M_w/M_n[b]	[η][c] dL/g
2a	-	-	0.54
2b	-	-	0.60
2c	39500	3.60	0.16
2d	29800	2.41	0.15

[a] Yields were almost quantitative in each case. [b] Estimated by GPC using polystyrene as standard in DMF. [c] Measured in H_2SO_4 at 30 °C using an Ostwald viscometer.

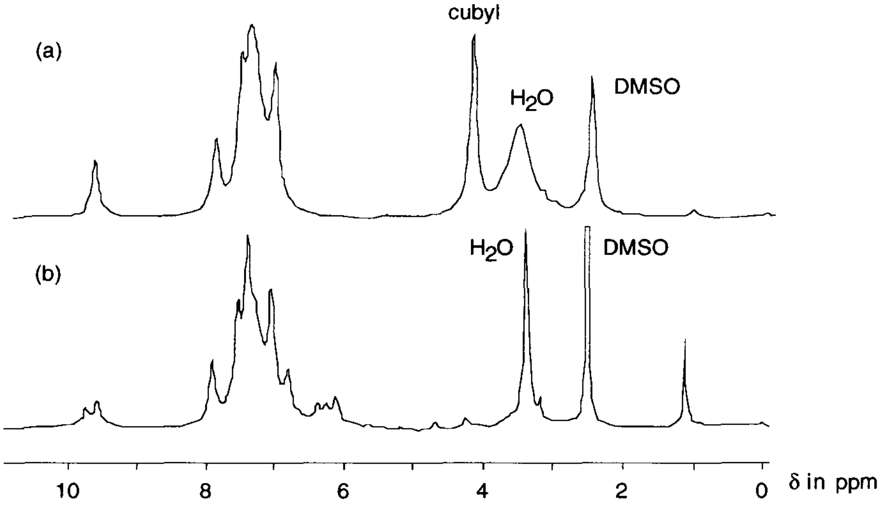

Figure 1. ^{1}H NMR spectra of polyamide **3d** before (a) and after (b) isomerization using $[Rh(bhd)Cl]_2$ (solvent, DMSO-d_6).

The inherent viscosities of the polyamides, which were measured in H_2SO_4 at 30 °C using an Ostwald viscometer, ranged from 0.15 to 0.60 dL/g (Table 1). The viscosities of **3a** and **3b** were relatively higher than those for **3c** and **3d**. Polyamides **3c** and **3d** were soluble in DMF, so that their molecular weights were measured by GPC relative to polystyrene in DMF. For **3c** ([η], 0.16 dL/g) and **3d** ([η], 0.15 dL/g), the weight-average molecular weight (M_w) was 39500 (M_w/M_n, 3.60) and 29800 (M_w/M_n, 2.41), respectively. Since the viscosities of **3a** and **3b** were higher than that of **3c**, the M_ws of **3a** and **3b** should exceed that of **3c**. The powders were structurally characterized by X-ray diffraction, and **3a**, in particular, showed

Table 2. Solubilities of polyamides in various solvents[a]

solvent	polyamide			
	3a	**3b**	**3c**	**3d**
chloroform	–	–	–	–
pyridine	–	–	–	++
NMP	–	+–	+	++
DMAc	–	–	+–	++
DMF	–	–	++	++
DMSO	–	–	++	++
conc-H_2SO_4	++	++	++	++

[a] Determined using 10 mg of polyamide in 2 mL of solvent. Key: ++, soluble at room temperature; +, soluble on heating at 60 °C; +–, partially soluble on heating at 60 °C; –, insoluble. Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethylsulfoxide.

sharp diffraction peaks at $2\theta = 15°$ and $18°$ whose high degree of crystallinity should cause the decrease in solubility for **3a**. These results indicate that the solubility behavior is due to the stiffness of the polymeric chain. Since **3a** had a high degree of crystallinity and its solubility was particularly poor, the backbone structure should be rigid and rod-like. In contrast, **3d** exhibited good solubility, which is caused by the bulky and bent structure of **2d** that prevents any intermolecular hydrogen-bonding interaction.

Eaton et al. reported that the catalytic isomerization of cubane was performed in nonpolar solvents, such as chloroform and carbon tetrachloride. However, **3** were insoluble in nonpolar solvents, therefore, the isomerization was carried out in NMP. A deoxygenated solution of polyamide **3d** and (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) chloride dimer ($[Rh(bhd)Cl]_2$) in NMP was heated at 60 °C for 24 h. The obtained polyamides were yellowish powders. The ^1H NMR spectra of **3d** before and after isomerization are shown in Figure 1. The signal at 4.2 ppm due to the cubane disappeared, while the signals at 6 - 7 ppm due to the olefin protons were observed. Therefore, the cubane units in **3d** were rearranged into cyclooctatetraene units, i.e., polyamide **4d**.

In summary, a novel polyamide incorporating the cubane moiety was prepared by the direct polycondensation of cubane-1,4-dicarboxylic acid with aromatic diamines. The rod-like polyamide derived from 1,4-phenylenediamine had a high molecular weight and high crystallinity. On the other hand, polyamides prepared with flexible or bulky diamines, like 4,4'-sulfonyldianiline and 9,9'-bis(4-aminophenyl)florene, exhibited good solubilities though relatively low molecular weights. After treating the cubane polyamide with the rhodium complex catalyst in NMP, a polymer with a cyclooctatetraene unit was quantitatively obtained.

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