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Synthesis of poly[2]catenane having rigid linkage by 1,3-dipolar cycloaddition of diazido[2]catenane with 4,4'-diethynylbiphenyl

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ABSTRACT

A novel poly[2]catenane having rigid triazole rings between [2]catenane moieties was synthesized by the 1,3-dipolar cycloaddition of diazido[2]catenane with 4,4'-diethynylbiphenyl. The reaction proceeded effectively under mild conditions and gave a polymer in high yield. The number average molecular weight (M_n) of the polymers was $1.5 \times 10^4 - 2.5 \times 10^4$. A cyclic dimer consisting of two [2]catenane moieties and two biphenylene units was formed along with the polymer. The cyclodimerization was suppressed by performing the reaction at a low temperature without lowering the yield or molecular weight of the polymer. The novel poly[2]catenane had higher solubility in some solvents than the corresponding non-catenated polymer having a similar primary structure.

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1. Introduction

Catenane, an interlocked compound composed of two or more macrocyclic components has a unique structure [1]. The components are not linked each other but not dissociate because of their topological linkage. Still, there remains much freedom of mechanical movement such as large-amplitude oscillation and rotation in the catenane rings to produce various co-conformers (Scheme 1). We have been interested in incorporating this high degree of mobility into the polymer main chain to develop novel properties of such polymers [2]. For example, a very large loss modulus, low activation energy for viscous flow, and rapid stress relaxation were listed as the expected unusual properties [3]. It is desirable to prepare a polymeric [n]catenane that is composed only of cyclic components; however, it is difficult to design a synthetic procedure leading to such a polymer in reasonable yield. Sauvage, Geerts, and others have prepared poly[2]catenanes by condensing a [2]catenane carrying two hydroxyl groups with a spacer dicarboxylic acid [4]. Urethane linked poly[2]catenane from hydroxymethyl-functionalized [2]catenane and diisocyanate was also reported by Menzer et al. [5]. We thought, however, that it would be rather difficult to extract the effect of flexible [2]catenane units from the properties of such polymer molecules as a whole.

In our previous work, poly[2]catenane was synthesized from carboxy[2]catenane and hydroxyl[2]catenane by esterification







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Scheme 1. Stretched and bent forms of [2]catenanes.

2. Experimental section

2.1. Preparation of N,N'-bis(4-aminobenzyl)-5azidoisophthalamide (**4**)

5-Azidoisophthalic acid (0.829 g, 4.00 mmol) prepared from 5-aminoisophthalic acid, as in the literature [11] and 1hydroxybenzotriazole monohydrate (1.29 g, 8.40 mmol) were dissolved in 20 mL of tetrahydrofuran (THF). To this solution, 10 mL solution of dicyclohexylcarbodiimide (1.73 g, 8.40 mmol) in THF was added and the whole mixture was stirred for 6 h under nitrogen in an ice-water bath. The formed precipitates were removed by filtration and the filtrate was slowly added to a solution of 4-aminobenzylamine (0.95 g, 8.40 mmol) in 20 mL of THF. The mixture was stirred for 24 h under nitrogen at room temperature. The volume of the solvent was then reduced to about half under reduced pressure. Chloroform was added to the mixture and the combined organic phase was washed several times with saturated aqueous solution of sodium bicarbonate. After removal of the solvent under reduced pressure, diamine 4 was obtained in 51% vield as a colorless solid.

2.1.1. N,N'-bis(4-aminobenzyl)-5-azidoisophthalamide (4)

¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.04 (t, *J* = 5.6 Hz, 2H, CONH), 8.18 (t, *J* = 1.6 Hz, 1H, ArH-N₃), 7.70 (d, *J* = 1.6 Hz, 2H, ArH-N₃), 6.98 (d, *J* = 8.4 Hz, 4H, ArH), 6.51 (d, *J* = 8.4 Hz, 4H, ArH), 4.97 (brs, 4H, ArH₂), 4.30 (d, *J* = 5.6 Hz, 4H, CONHCH₂)

¹³C NMR (100 MHz, DMSO-*d*₆): δ = 164.51, 147.60, 139.97, 136.38, 128.41, 126.12, 123.10, 120.14, 113.67, 42.55.

2.2. Preparation of diazido[2]catenane (1)

A solution of 0.30 mL (2.18 mmol) of triethylamine in 250 mL of chloroform was added to a solution of 0.416 g (1.00 mmol) of diamine **4** in 12 mL of heated acetonitrile. Sebacoyl dichloride

(0.21 mL, 1.00 mmol) in 50 mL of chloroform was then added to the mixture over a period of 5 h under a nitrogen atmosphere. The mixture was further stirred at room temperature for 24 h. The formed precipitates were removed by filtration, and the filtrate was first washed with aqueous solution of 1 M HCl and then with saturated aqueous sodium bicarbonate solution. The organic layer was concentrated by partially removing the solvent under reduced pressure. The residue was subjected to preparative thin-layer chromatography on silica gel with chloroform/methanol (93:7) elution to give diazido[2]catenane (**1**) in 11% yield as a colorless solid.

2.2.1. Diazido[2]catenane (1)

¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.68 (brs, 4H, CONH), 8.53 (brs, 4H, CONH), 7.89 (s, 2H, ArH-N₃), 7.57 (s, 4H, ArH-N₃), 7.29 (d, *J* = 8.0 Hz, 8H, ArH), 6.90 (d, *J* = 8.0 Hz, 8H, ArH), 4.08 (brs, 8H, ArCH₂), 2.13 (brs, 8H, NHCOCH₂), 1.30 (brs, 8H, NHCOCH₂CH₂), 0.84 (brs, 16H, NHCOCH₂CH₂CH₂CH₂)

 13 C NMR (100 MHz, DMSO- d_6): $\delta=$ 171.43, 165.03, 139.82, 138.01, 136.46, 132.65, 128.27, 122.21, 120.34, 118.86, 43.02, 36.02, 28.98, 27.96, 25.22.

MALDI TOF-MS: $m/z = 1186 ([M + Na]^+)$

2.3. Preparation of poly([2]catenane-alt-4,4'-diethynylbiphenyl)(3)

To a solution of 20.0 mg (17.2 μ mol) of diazido[2]catenane (1) and 3.5 mg (17.2 μ mol) of 4,4'-diethynylbiphenyl (2) in 0.2 mL of dimethylformamide (DMF) were added 8.6 mg (34.4 μ mol) of copper(II) sulfate pentahydrate, 27.3 mg (137.8 μ mol) of sodium ascorbate, and 0.02 mL of water. After stirring at room temperature for 2 days under a nitrogen atmosphere, additional copper sulfate (8.6 mg) and sodium ascorbate (27.3 mg) were added to the mixture; stirring was continued for another 2 days. The same amounts of copper and ascorbate were added for a third time, and further stirring was carried out for 3 days. The reaction mixture was poured into 5 mL of water, and the precipitate was collected by



Scheme 2. 1,3-Dipolar cycloaddition of diazido[2]catenane with 4,4'-diethynylbiphenyl as a rigid linker.



Scheme 3. Synthesis of diazido[2]catenane (1).

filtration. After removing the solvent under reduced pressure, poly [2]catenane (**3**) was obtained in 88% yield.

2.4. Preparation of poly(2:2 macrocycle-alt-4,4'-diethynylbiphenyl)

To a solution of 20.0 mg (17.2 μ mol) of diazido 2:2 macrocycle and 3.5 mg (17.2 μ mol) of 4,4'-diethynylbiphenyl (**2**) in 0.1 mL of DMF were added 8.6 mg (34.4 μ mol) of copper(II) sulfate pentahydrate, 27.3 mg (137.8 μ mol) of sodium ascorbate, and 0.01 mL of water. After stirring at room temperature for 7 days under a nitrogen atmosphere, the reaction mixture was poured into 5 mL of water and the precipitate was collected by filtration. After removing the solvent under reduced pressure, solvent-insoluble brown solid was obtained in 83% yield.

2.5. Measurements

Mass spectrometric analyses: Analyses were carried out on an Applied Biosystems Voyager RP-PRO MALDI TOF-MS spectrometer.

FT–NMR spectroscopy: Spectra in DMSO- d_6 with TMS as an internal standard were obtained on a JEOL JNM-GX400 spectrometer at 400 MHz.

FT–IR spectroscopy: The solid sample in KBr discs was measured on a Perkin Elmer 1600 Series FT-IR Spectrometer.

Gel permeation chromatography (GPC): The analytical chromatogram was obtained on a Tosoh Co., Ltd. GPC-8020 with a differential refractive index detector CO-8020 and UV–Vis ShimadzuSPD-6A detector. Tosoh Co., Ltd. GPC column TSK gel G2000H_{HR} and TSK gel G4000H_{HR} were used.

Differential scanning calorimetry (DSC): Analyses were carried out on a Seiko Instruments Inc. DSC6100 under N_2 atmosphere at a heating rate of 10 °C/min.

3. Results and discussion

Monomeric [2]catenane was synthesized by the reaction sequences summarized in Scheme 3. [2]Catenane (1) carrying two azido groups, one on each ring ($X = Y = N_3$ in Scheme 1), was prepared starting from 5-aminoisophthalic acid, which was then converted to 5-azidoisophthalic acid. The latter was reacted with 4-

aminobenzylamine using N,N'-dicyclohexylcarbodiimide as a condensing agent to give diamide 4 in 51% yield. The reaction of 4 with sebacoyl dichloride under high dilution at room temperature gave diazido[2]catenane 1 in 11% yield. Uncatenized azido 1:1 macrocycle and diazido 2:2 macrocycle also formed with the [2] catenane in 19% and 4% yield respectively (Fig. 1). The structure of 1 was confirmed by its molecular ion peak in MALDI TOF-MS and the high-field shift of some peaks of the ¹H NMR spectrum (Fig. 2). In ¹H NMR spectra, benzylic and aromatic protons of the 1:1 and 2:2 macrocycles exhibit similar chemical shifts (H_d, H_e, and H_f in Fig. 2), but molecular ion peaks in MALDI TOF-MS are observed at m/ $z = 605 ([M + Na]^+)$ and $m/z = 1186 ([M + Na]^+)$ respectively. In the case of [2]catenane, the molecular ion peak is equal to that of 2:2 macrocycle, however the high-field shift of the H_d, H_e, and H_f caused by interlocked structure are observed clearly in ¹H NMR. Formation mechanism of the amide-type [2]catenanes were already proposed by Vögtle et al, and were also mentioned in our previous work about preparation of [2]catenane having steric hindered group [12]. In this mechanism, a pseudorotaxane intermediate formed by amide-amide hydrogen bonding between the 1:1 macrocycles and the linear diamide (such as **4**) are involved.

A 1,3-dipolar cycloaddition reaction (Click reaction) was carried out to synthesize the poly[2]catenanes. Diazido[2]catenane (**1**) was allowed to react with 4,4'-dietynylbiphenyl (**2**) by the action of copper(II) sulfate pentahydrate and sodium ascorbate under high dilution in aqueous DMF for 7 days at room temperature (~25 °C), in line with Sharpless [10c]. The Click reaction product was obtained in 88% yield and subjected to GPC analyses; the results are summarized in Fig. 3. The presence of poly[2]catenane **3** was confirmed by the observed $M_n = 1.5 \times 10^4$ and $M_w/M_n = 2.0$ in reference to the M_n value of standard polystyrene. When compared with the GPC peak of monomeric catenane **1**, the top of the peak of the polymer was estimated to correspond to 6–7mer. At the same time, we observed that the slope of the high-molecular-weight side of the GPC peak extended to $M_n = 8.0 \times 10^5$.

A sharp peak at $M_n = 7200$ corresponds to the molecular weight of two molecules of **1** plus two molecules of **2**. Both the ¹H NMR signal due to an ethynyl proton at $\delta \sim 4.3$ and IR absorption due to an azido group at ~ 2100 cm⁻¹ were absent for the reaction product, indicating that terminal groups corresponding to **1** and **2**



Fig. 1. Structure of azido 1:1 macrocycle and diazido 2:2 macrocycle.





are absent. Thus, similar to the finding in our previous report, a cyclic dimer (Fig. 4), rather than an open dimer is suggested to be responsible for the GPC $M_n = 7200$ peak. In the case of previous ester-linked poly[2]catenane [6], 37%-56% of the cyclic dimer (calculated from the GPC peak area) was contained. On the other hand, the amount of cyclic dimer that formed from **1** and **2** decreased to 18%. It is suggested that the lowering of the dimer content was due to the rigid linker. The molecular weight of the polymer alone was calculated as $Mn = 3.5 \times 10^4$ by means of eliminating the dimer area from the GPC chart.



Fig. 3. GPC curves of diazido[2]catenane 1 (broken line) and poly[2]catenanes 3 prepared at room temperature (dash-dotted line) and 0 $^{\circ}$ C (solid line) from 4,4'- diethynylbiphenyl as a linker.

The formation of the cyclic dimer suggested the flexibility of the interlocked rings in [2]catenanes. A second Click reaction was then carried out at 0 °C. Other reaction conditions were similar to those for the reaction at room temperature. Poly[2]catenane 3 was obtained in 92% yield with $M_n = 2.5 \times 10^4$ and $M_w/M_n = 1.8$. The yield of the cyclic dimer decreased drastically as shown by the solid curve in Fig. 3 and Table 1. The molecular weight of the polymer without the dimer was calculated as $M_{\rm n} = 3.3 \times 10^4$. Lowering of the polymer yield and molecular weight were not observed in spite of the reaction being at a low temperature. After two molecules of 1 and two molecules of 2 underwent 1,3-dipolar reaction, it is highly likely that an open dimer intermediate with one azido group and one ethynyl group at both terminal positions were formed. This intermediate resides at the branching point along the addition reaction path, with one branch leading to poly[2]catenane **3** (n > 3) and the other to a cyclic dimer. The latter reaction required an unfavorable reaction entropy owing to the special conformation



Fig. 4. Estimated structure of the cyclic dimer forming from 1 to 2.

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Table 1

Composition of polymeric product obtained by poly[2]catenane synthesis.

Product	Total yield (%)	Composition (% in total product) ^a	
		Polymer	Cyclic dimer
3 (r.t.)	88	80	18
3 (0 °C)	92	85	11
Ester-linked poly[2]catenane [6b]	80	63	37

^a Calculated from GPC peak area. Small amount of monomeric [2]catenane was contained.

(bent conformer in Scheme 1) of the interlocked ring that allows both ends to approach for intramolecular 1,3-dipolar reaction.

To evaluate the effect of the catenane structure on polymer properties, polymer containing 2:2 macrocycle instead of [2]catenane was synthesized. Comparing the 2:2 macrocycle and [2]catenane, it is seen that although the primary structures are the same, the topological structures differ. Therefore, it is presumed that the different properties of poly[2]catenane and poly 2:2 macrocycle can be assigned to characteristic properties of the catenane structure.

The polymer-like product was obtained by Click reaction of diazido 2:2 macrocycle and 2. The absence of IR absorption due to the azido group and the ethynyl group shows that the polymerization reaction proceeded, but the molecular weight could not be measured by GPC because of the very low solubility of the product. Since the product was insoluble in any solvent, further purification processes such as reprecipitation, NMR spectroscopy, or measurements of mechanical properties could not be performed. However, the difference in solubility between the poly 2:2 macrocycle and the poly[2]catenane (soluble in DMF or DMSO) is attributable to the difference in their topological structures. It is considered that the insolubility of poly 2:2 macrocycle is due to intermolecular hydrogen bonding of the amide groups in the macrocycle structure, whereas poly[2]catenane having intramolecular hydrogen bonding (between two rings) has fairly high solubility.

Differential scanning calorimetry (DSC) of the poly[2]catenane were also measured. A small endothermic peak is observed at 100 °C, but it has not been revealed whether the peak is caused by crystal melting. The thermal properties of poly[2]catenane will be discussed in detail in a future publication.

4. Conclusions

We have shown that 1,3-dipolar cycloaddition is effective in producing poly[2]catenane by connecting diazido[2]catenane with 4,4'-diethynylbiphenyl. The reaction was superior to the reported esterification and Diels—Alder reaction in terms of the yield and molecular weight of the polymer. Another important finding is that the yield of the polymer is improved, and the yield of dimeric byproduct is decreased by lowering the reaction temperature. The poly[2]catenane had higher solubility in some solvents than did non-catenated polymer having the same primary structure. Our final goal of extracting the effect of flexible [2]catenane units on the macroscopic properties of such polymer molecules remains to be seen by, for example, measuring thermal properties.

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