Polyrotaxane Networks Formed via Rotaxanation Utilizing Dynamic Covalent Chemistry of Disulfide

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ABSTRACT: Polyrotaxane networks were synthesized from a mixture of poly(crown ether)s (**2**–**5**) as a trunk polymer and dumbbell-shaped bifunctional secondary ammonium salt **6** bearing a disulfide linkage and bulky end caps as a cross-linking agent in the presence of a catalytic amount of benzenethiol via a reversible thiol–disulfide interchange reaction. Trunk polymers **2**–**4** were prepared by copolymerization of bis(hydroxymethyl)dibenzo-24-crown-8-ether **1** and comonomers. Poly(crown ether) **5** bearing a poly(tetrahydrofuran) (PTHF) spacer was also synthesized from **1** and PTHF with 4,4′-methylenebis(phenyl isocyanate) (MDI) in *N*,*N*-dimethylacetamide (DMAc) at room temperature. The treatment of these poly(crown ether)s (**2**–**5**) with axle component **6** in the presence of benzenethiol gave the corresponding polyrotaxane networks (**7**–**10**) in quantitative yields. We confirmed the cross-linking process by monitoring the ^{1}H NMR spectral change during the polymerization. Thermal properties, swelling, and dynamic viscoelasticity of these polyrotaxane networks were evaluated. Polyrotaxane network **10** bearing **5** afforded higher swelling and elasticity than those of other networks because of the flexibility of the trunk polymer as wheel components.

Introduction

Among network polymers, polyrotaxane networks that have the rotaxane structures on the cross-linking points are the most interesting class of cross-linked polymers, which are characterized in terms of both the unique structure and specific properties on the basis of their mechanical cross-linking.[1] Synthetic methods of such polyrotaxane networks are divided into two types (Figure 1). One type is the statistical method, in which monomers with sufficiently large macrocycles are polymerized or copolymerized to give mechanically cross-linked polymers[2–5] through the accidental penetration of the propagation end into the cavity of the large macrocycles in the polymer produced in situ, which eventually leads to the cross-linking (Figure 1, (I)). The other type is the strategical method, that is, the cross-linking by the direct linking of polyrotaxane at the wheels (Figure 1, (II)) or the precise rotaxanative cross-linking of the macrocycle-containing polymer by the threading of two or more macrocycles (Figure 1, (III)).[6–9]

Gibson's group reported the first polyrotaxane networks as mechanically networked polymers possessing the rotaxane structures on the cross-linking points.[2] For example, the polyamide-type polyrotaxane network was formed as a gelled product by the polycondensation of a ditopic amine and a 32-membered macrocyclic dicarboxylic acid. In this case, the propagation end was accidentally threaded to form 3D polyrotaxane networks. Zilkha's group,[3] Tezuka's group[4] and Kubo's group[5] also reported the synthesis of mechanically cross-linked polymers through the radical copolymerizations of vinyl monomers with large macrocycles. Meanwhile, Ito et al. strategically prepared a polyrotaxane network by the intramolecular binding of wheel moieties of a polyrotaxane consisting of α-cyclodextrin and poly(ethylene glycol).[6] Yui's group also developed a biodegradable polyrotaxane network with an ester end-capping group by a similar protocol.[7,8]

In the course of our rotaxane chemistry utilizing a *sec*-ammonium axle and a crown ether wheel,[9] we have recently reported a novel approach to the polyrotaxane network that exploits strategic rotaxanation as the cross-linking reaction.[10] In a typical example, the treatment of a bifunctional *sec*-ammonium axle component bearing a central disulfide linkage and two bulky end caps with poly(crown ether) as the trunk polymer afforded the corresponding polyrotaxane network by cross-linking via the catalytic thiol–disulfide interchange reaction (Figure 2).[11] This protocol was characterized by the reversible cross-linking (Figure 2).[12] Because the reaction that occurred during the cross-linking is that of only the axle component in this system, no trunk polymer takes part in the cross-linking, (i.e., no trunk polymer is injured after the cross-linking). From another viewpoint, there is no apparent chemical bond formation or breaking during the cross-linking because both the wheel and axle component do not change structure before and after the cross-linking but only change position, as shown in Scheme 1. Thus, this cross-linking protocol is unique enough to be noteworthy from both basic and applied points of view. Additionally, we became intrigued by the potential usefulness of the crown ether moiety as a cross-linking point for versatile polymers. If the sparse crown ether moiety in the polymer chain was successfully available as a cross-linking point, then an attachment of topological characteristics to the desired polymer would be possible.

Herein we describe in detail the synthesis of polyrotaxane networks that consist of various poly(crown ether)s and a dumbbell-shaped bifunctional *sec*-ammonium salt bearing a central disulfide linkage and two bulky end caps by utilizing the dynamic covalent chemistry[13] of the S–S bond in the formation of an interlocked bond, along with their properties.

Experimental Section

General. ^{1}H spectra were recorded on JEOL AL-270 NMR (270 MHz) and AL-400 NMR spectrometers (400 MHz) in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on a JEOL AL-400 NMR spectrometer operating at 100 MHz. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Molecular weight and molecular weight distribution were estimated by gel permeation chromatography (GPC) on a JASCO HSS-1500 system equipped with consecutive TOSOH TSKgel G5000HXL, G4000HXL, and G2500HXL eluted with

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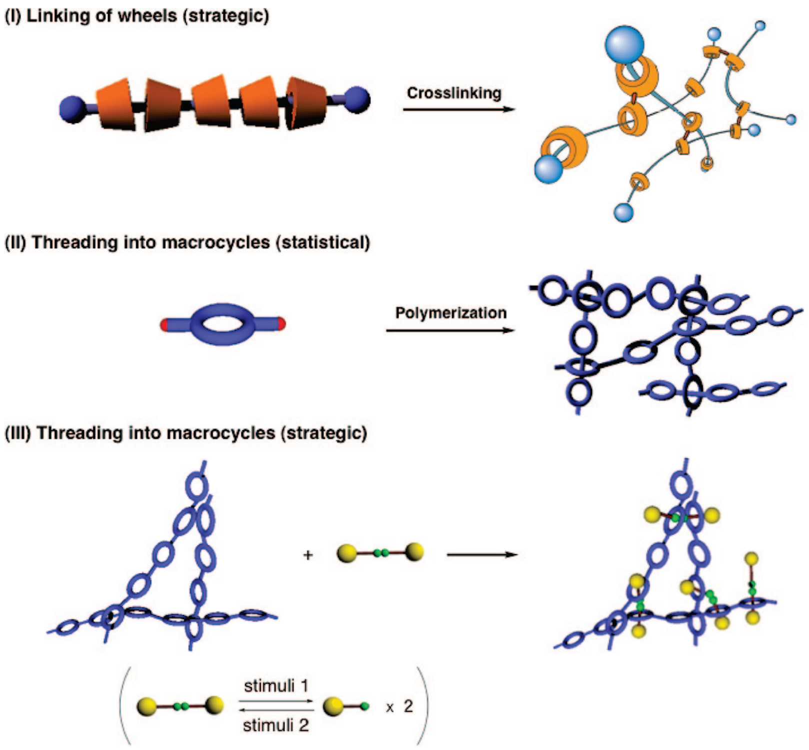


Figure 1. Synthetic methods for polyrotaxane networks.

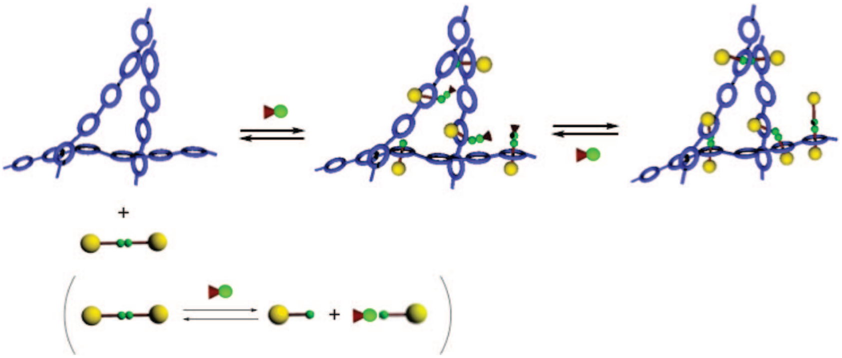
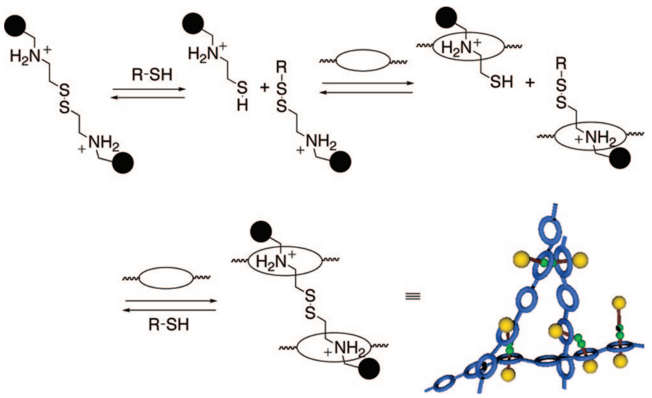


Figure 2. Synthesis of polyrotaxane network using dynamic covalent chemistry.

Scheme 1. Rotaxanation−Cross-Linking Utilizing Reversible Disulfide Linkage

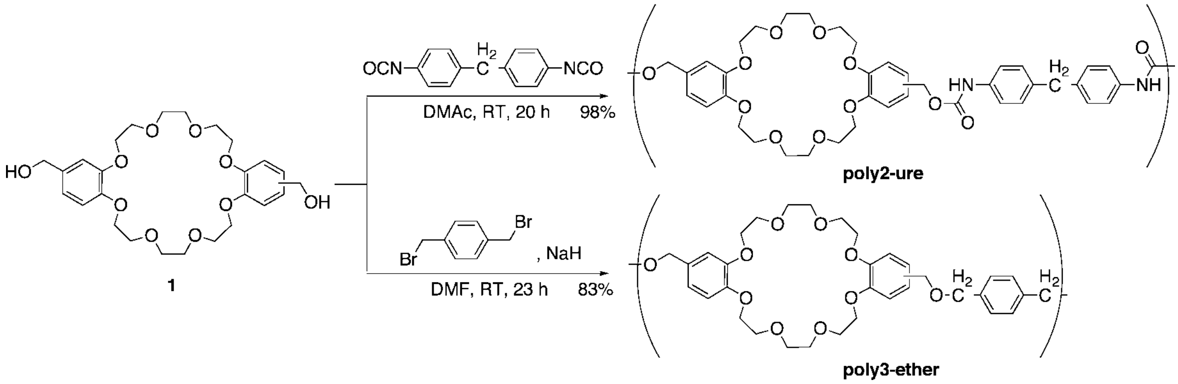


CHCl$_3$ at a flow rate of 1.0 mL/min calibrated by polystyrene standards. The decomposition temperature was obtained with a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min. DSC was performed on a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under N$_2$ atmosphere at a flow rate of 40 mL/min. Glass transition temperature was recorded as a temperature at the middle of the thermal transition from the second heating scan. MALDI-TOF MS analyses were made on a SHIMADZU, Mass AXIMA-CFR-S instrument. Dynamic mechanical properties of polyrotaxane network films were evaluated at a temperature range of −120 to 140 °C by the use of an IT-DVA200s (ITK, Japan) apparatus. The measurement was conducted in the oscillatory tensile mode at a frequency of 10 Hz and a heating rate of 5 °C/min.

Bisammonium salt **6**[10a] and bis(hydroxymethyl)dibenzo-24-crown-8 **1**[14] were prepared according to the literature. Commercial grade 4,4′-methylenebis(phenyl isocyanate) (MDI) was distilled under reduced pressure before use. Commercial grade *N*,*N*-dimethylacetamide (DMAc) was used after distillation over calcium hydride. Other chemicals were reagent grade and were used without further purification.

Preparation of Poly2-ure. *Typical Procedure.* To a solution of MDI (388 mg, 1.55 mmol) in DMAc (1.1 mL) was added **1** (830 mg, 1.63 mmol) under an Ar atmosphere. The mixture was stirred for 5 h at 50 °C, and the reaction was stopped by being poured in water to precipitate the polymer. The precipitate was collected by filtration and was dried at room temperature overnight to give **poly2-ure** (1.19 g, 98%) as a white solid. M_n = 2.4 kDa, M_w/M_n = 3.7, T_{d10} = 279 °C, T_g = 80 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, δ): 9.61 (s, 2H, NH), 7.34 (d, J = 7.0 Hz, 4H, ArH), 7.08−6.93 (m, 10H, ArH), 5.02 (s, 4H, ArCH$_2$O), 4.05−3.64 (m, 26H, CH$_2$).

Scheme 2. Synthesis of Poly(crown ether)s Poly2-ure and Poly3-ether



Scheme 3. Synthesis of Poly(crown ether) Poly4-ket

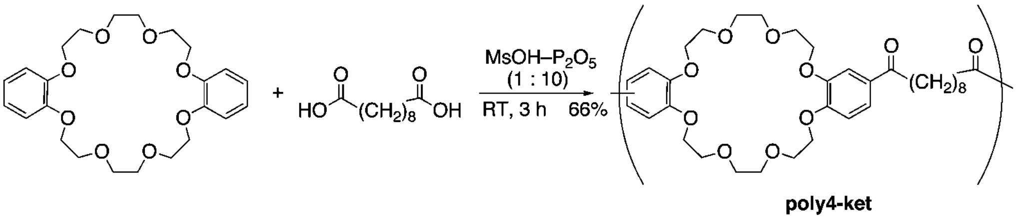


Table 1. Synthesis of Poly(crown ether)s

entry	poly (crown ether)	M_n (kDa)[a]	M_w (kDa)[a]	M_w/M_n[a]	T_{d10} (°C)[b]	T_g 1 (°C)[c]	yield (%)
1	**poly2-ure**	2.4	8.8	3.7	279	80	98
2	**poly3-ether**	5.5	8.3	1.5	310	18	83
3	**poly4-ket**	2.9	4.9	1.7	412	125	66

[a] Estimated by GPC on the basis of polystyrene standards. [b] 10% weight-loss temperature: T_{d10}. [c] Measured by DSC at a heating rate of 10 °C/min.

^{13}C NMR (100 MHz, CDCl$_3$, 298 K, δ): 63.6, 66.6, 69.7, 70.0, 71.3, 114.3, 114.5, 114.7, 115.1, 118.9, 119.3, 122.1, 122.4, 129.5, 129.9, 122.4, 136.3, 136.4, 137.8, 149.0, 149.1, 154.2. IR (KBr, cm^{-1}) ν: 3329 (N−H), 1718 (C=O). Anal. Calcd for $C_{41}H_{46}N_2O_{12}$: C, 64.90; H, 6.11; N, 3.69. Found: C, 64.10; H, 6.42; N, 3.66.

Preparation of Poly3-ether. *Typical Procedure.* To a suspension of NaH (288 mg, 7.20 mmol) in DMF (3.0 mL) was added **1** (1.53 g, 3.00 mmol) at room temperature under an Ar atmosphere, and the mixture was stirred for 30 min at room temperature. *m*-Xylylene dibromide (792 mg, 3.00 mmol) was added to the suspension, and the stirring was continued for 22 h at the same temperature. The reaction was stopped by the addition of water (3.0 mL). The precipitate formed was collected by filtration, washed with MeOH, and dried under vacuum to give **poly3-ether** (1.29 g, 2.11 mmol, 83%) as a white solid. M_n = 5.5 kDa, M_w/M_n = 1.50, T_{d10} = 310 °C, T_g = 18 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, δ): 7.50 (s, ArH, 4H), 6.89−6.85 (m, ArH, 6H), 4.47 (s, CH$_2$, 4H), 4.41 (s, CH$_2$, 4H), 4.06 (s, CH$_2$, 8H), 3.78−3.68 (m, CH$_2$, 16H).

Preparation of Poly4-ket. A mixture of sebacic acid (127 mg, 0.625 mmol) and dibenzo-24-crown-8 (DB24C8) (280 mg, 0.625 mmol) in phosphorus pentoxide/methanesulfonic acid (PPMA) (1.5 mL, 1/10) was stirred at room temperature for 3 h. The reaction was stopped by being poured in ice water (300 mL). The precipitated fibrous polymer was filtered, and the polymer was triturated in water (300 mL) for 1 day. The polymer was collected by filtration, washed with hot water, and dried in vacuo to give **poly4-ket** (270 mg, 0.439 mmol, 66%) as a white solid. M_n = 2.8 kDa, M_w/M_n = 1.7, T_{d10} = 412 °C, T_g = 125 °C. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K, δ): 7.55−7.53 (m, 4H, ArH), 6.87−6.83 (m, 2H, ArH), 4.19 (s, 8H, CH$_2$), 3.93−3.83 (m, 16H, CH$_2$), 2.88−2.86 (m, 4H, COCH$_2$), 1.68 (s, 4H, CH$_2$), 1.34 (s, 8H, CH$_2$). ^{13}C NMR (400 MHz, CDCl$_3$, 298 K, δ): 24.6, 29.3, 38.1, 69.4, 69.7, 71.3, 111.5, 112.2, 113.8, 121.3, 122.9, 130.3, 148.5, 152.8, 199.2. IR (KBr, cm^{-1}) ν: 1672 (C=O). Anal. Calcd for $C_{34}H_{48}O_{11}$: C, 64.54; H, 7.65. Found: C, 63.91; H, 7.36.

Preparation of Copoly5-(36). *Typical Procedure.* To a mixture of **1** (126 mg, 0.25 mmol) and poly(tetrahydrofuran) (PTHF, M_n

Scheme 4. Syntheses of Copoly5s

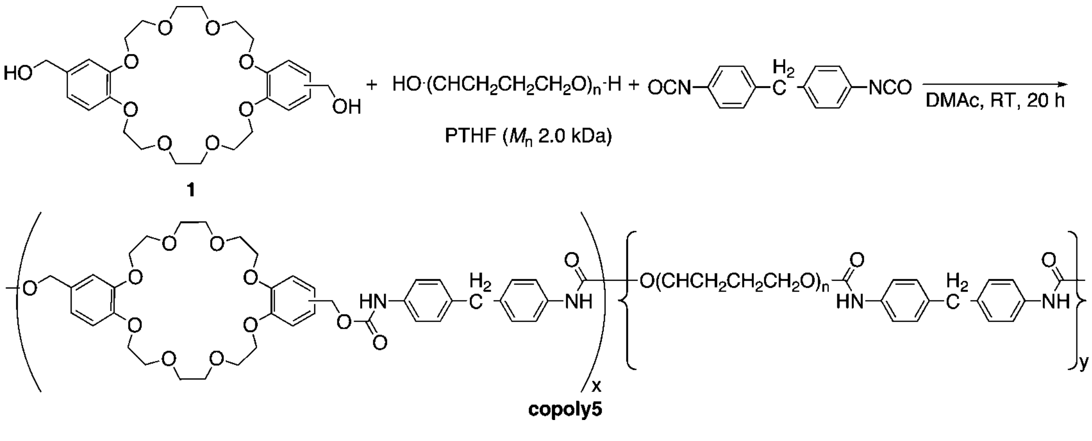


Table 2. Synthesis of Copoly(crown ether)s

entry	feed ratio (*x*/*y*)	poly(crown ether) (composition ratio)	M_n (kDa)[a]	M_w (kDa)[a]	M_w/ M_n[a]	yield (%)
1	1/0.5	**copoly5-(66)**	14.6	71.4	4.9	99
2	1/1	**copoly5-(50)**	25.7	105.0	4.1	99
3	1/1.8	**copoly5-(36)**	18.0	64.0	3.6	98
4	1/2	**copoly5-(33)**	45.7	144.0	3.2	99
5	1/3	**copoly5-(25)**	49.5	149.0	3.0	99

[a] Estimated by GPC on the basis of polystyrene standards.

= 2.0 kDa, 1.51 g, 0.75 mmol) in DMAc (1.6 mL) under an argon atmosphere at 50 °C was added MDI (250 mg, 1.00 mmol). The mixture was stirred for 20 h at room temperature, and the reaction was stopped by the addition of MeOH (1 mL). The mixture was diluted with $CHCl_3$ (5 mL), and the resulting mixture was poured in MeOH (100 mL). The precipitate formed was collected by filtration, washed with MeOH, and dried under vacuum to give **copoly5-(36)** (448 mg; 0.24 mmol; 98%; crown ether/PTHF 36/64, determined by the integral ratio of terminal protons on ^{1}H NMR spectrum). M_n =18 kDa, M_w/M_n = 3.6, T_{d10} = 280 °C, T_g 1 = −72 °C, T_g 2 = 70 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.28 (s, 8H, ArH), 7.09−7.07 (m, 6H, ArH), 5.04 (brs, 2H, NH_2), 4.16−4.14 (m, 8H, CH_2), 3.87−3.81 (m, 10H, CH_2 and Ar−CH_2−Ar), 3.41 (s, 166H, CH_2), 1.61 (s, 171H, CH_2). IR (KBr, cm^{-1}) ν: 3436 (N−H), 1733 (C=O). Anal. Calcd for $C_{62}H_{73}N_4O_{16}$: C, 65.88; H, 6.51; N, 4.96. Found: C, 66.49; H, 9.15; N, 1.69.

Preparation of Polyrotaxane Network Gel7-ure. *Typical Procedure.* To a mixture of **poly2-ure** (200 mg, 0.26 mmol) and **axle 6** (56.8 mg, 0.066 mmol) in $CHCl_3/CH_3CN$ (3/1 v/v, 0.90 mL) was added a 2.0 M solution of benzenethiol in $CHCl_3$ (65.5 μL, 13.3 μmol). The mixture was allowed to stand at 50 °C for 1 day. The insoluble material formed was collected by filtration and washed with $CHCl_3$ and MeOH to give polyrotaxane network **gel7-ure** (256 mg, 100%). T_g = 45 °C, T_{d10} = 265 °C.

Results and Discussion

Synthesis of Poly(crown ether)s. Scheme 2 features the construction of poly(crown ether)s as the trunk polymers of polyrotaxane networks. Poly(crown ether)s **poly2-ure** and **poly3-ether** were synthesized using bis(hydroxymethyl)dibenzo-24-crown-8 **1** as the monomer. The synthesis of **poly4-ket** was carried out by the direct polycondensation of sebacic acid with dibenzo-24-crown-8-ether (DB24C8) in the presence of a phosphorus pentoxide/methanesulfonic acid mixture (1/10 w/w, PPMA) as the condensation agent and solvent at room temperature (Scheme 3).[15] The results are summarized in Table 1. We found that mild reaction conditions including a low reaction temperature (below 25 °C) and a controlled amount of PPMA (in the case of **poly4-ket**) were absolutely needed in all synthetic processes for the poly(crown ether)s because treatment at a higher temperature or with an excess amount of PPMA gave only the cross-linked polymers. This was most likely because of the accidental penetration of the propagation end into the cavity of the crown ethers.[16,17] This is in good accordance with the reports of Gibson et al.[2] We found that T_{d10} and T_g of **poly4-ket** were higher than those of other polymers probably because of its thermally stable ketone linkage.

Copolymer **5** with PTHF spacer was synthesized by a similar polycondensation of a mixture of **1**, PTHF (M_n = 2.0 kDa), and MDI in DMAc at room temperature (Scheme 4). The polymerizations with various feed ratios of **1** and PTHF gave the corresponding polymers shown in Table 2. Table 2 summarizes the results of the polymerization. **Copoly5**s with higher molecular weights than those of polymers of Table 1 due to the use of the PTHF spacer showed two T_g values: T_g 1 for the PTHF chain and T_g 2 for the urethane chain. These polymers were well soluble in organic solvents such as $CHCl_3$, nitrobenzene, and THF but were insoluble in MeOH, hexane, and Et_2O.

Synthesis of Polyrotaxane Networks. With various poly(crown ether)s as the trunk polymers in hand, we examined the synthesis of polyrotaxane networks. Dumbbell-shaped bisammonium salt **6** as a ditopic cross-linker was prepared according to the literature.[10a] Prior to the preparation of polyrotaxane

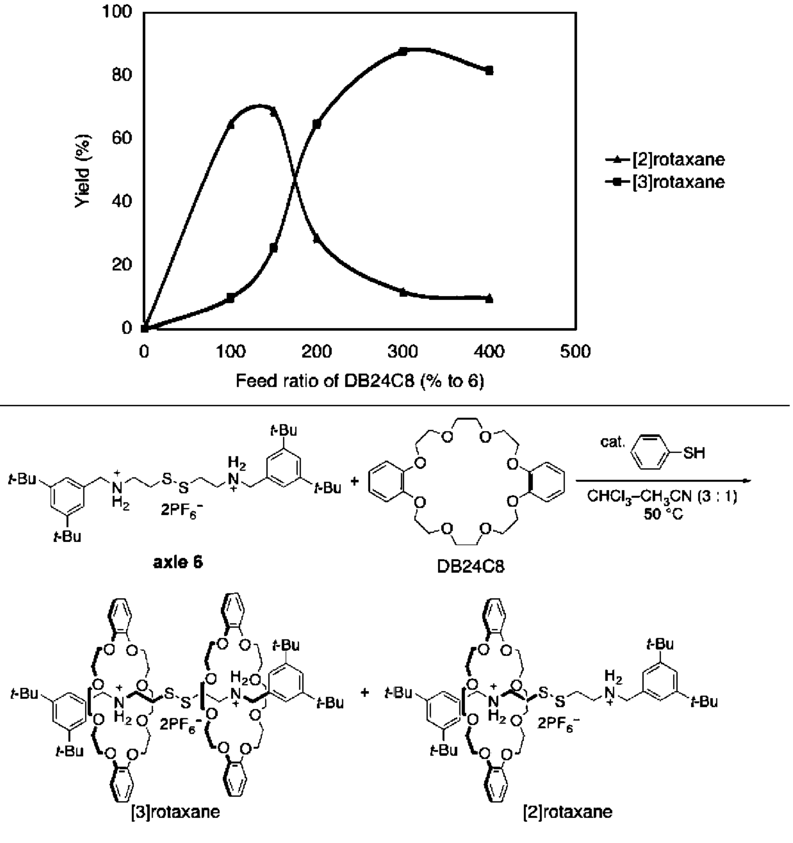
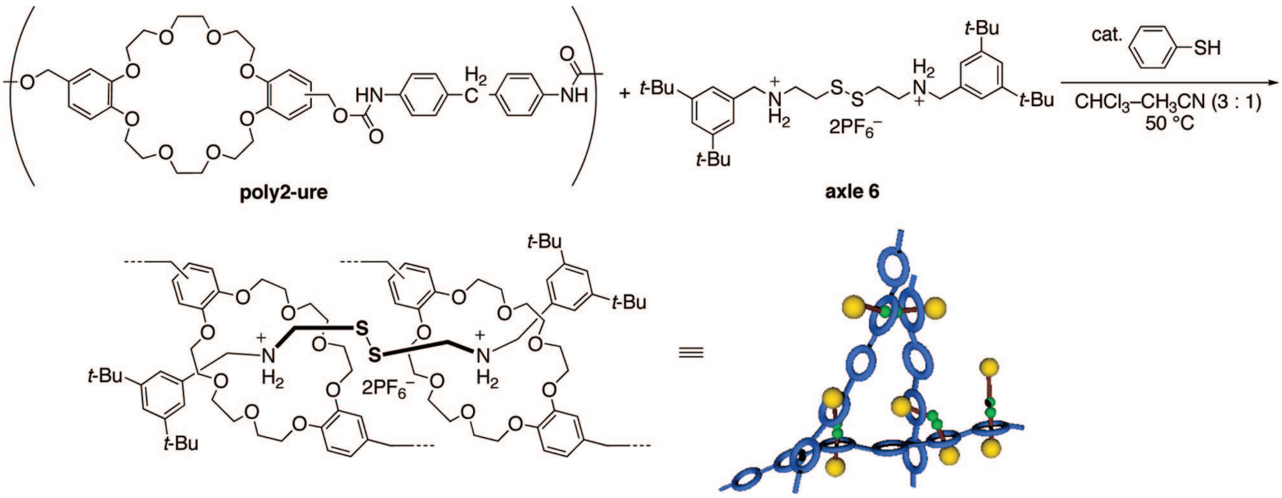


Figure 3. Yield of rotaxanes depending on concentration of DB24C8.

Scheme 5. Synthesis of a Polyrotaxane Network



networks, the reversible rotaxanation reaction between DB24C8 and bisammonium salt **6** in the presence of a catalytic amount of benzenethiol was examined under varying concentration, as shown in Figure 3. The yields of [2]rotaxane and [3]rotaxane were plotted against the feed ratio of DB24C8/**6**. When an equimolar mixture of DB24C8 and **6** was employed, [2]rotaxane was preferentially obtained in 65% yield at 50 °C. Increasing the DB24C8/**6** ratio dramatically shifted the equilibrium to [3]rotaxane. Thus, we could control the yields of [2]- and [3]rotaxanes by changing a feed ratio of DB24C8 to the axle **6**. If poly(crown ether) is employed in place of DB24C8 as the wheel component, then the resulting product is expected to involve both the inter- and intramolecular cross-links. On the basis of these model studies, the cross-linking reaction was carried out according to Scheme 5 using **6**, poly(crown ether)s, and benzenethiol (5 mol %) in a mixed solvent of $CHCl_3$ and CH_3CN at 50 °C. The reaction mixture changed to a transparent insoluble material after ca. 20 h (for **poly2-ure−poly4-ket**), whereas it took a much longer time (3−10 days) for **copoly5**s because the crown ether units as the cross-linking points are placed far from each other. (The calculated mean distance between the crown ether moieties is ca. 50 nm for **copoly5-(25)**.) The resulting cross-linked polymers were repeatedly washed with $CHCl_3$ and dried under reduced pressure at room temperature overnight to yield the corresponding polyrotaxane networks (quantitative yields).

The cross-linking process leading to the polyrotaxane network could be directly confirmed by observing the NMR spectral change of a mixture of reactants and catalyst, as shown Figures 3 and 4. Figure 4 reveals the NMR spectra of the model compounds where three kinds of methylene signals around the ammonium moiety are separately observed and change according to the degree of the rotaxanation. In particular, two sets of signals assigned to methylene protons and two *tert*-butyl protons appeared in the case of [2]rotaxane, which clearly indicated the sufficiently sluggish shuttling of the wheel component DB24C8 between the two ammonium stations on the axle. Referring to the NMR results of the model compounds (Figure 4), we confirmed the occurrence of the cross-linking by directly monitoring the NMR spectral change of a mixture of the

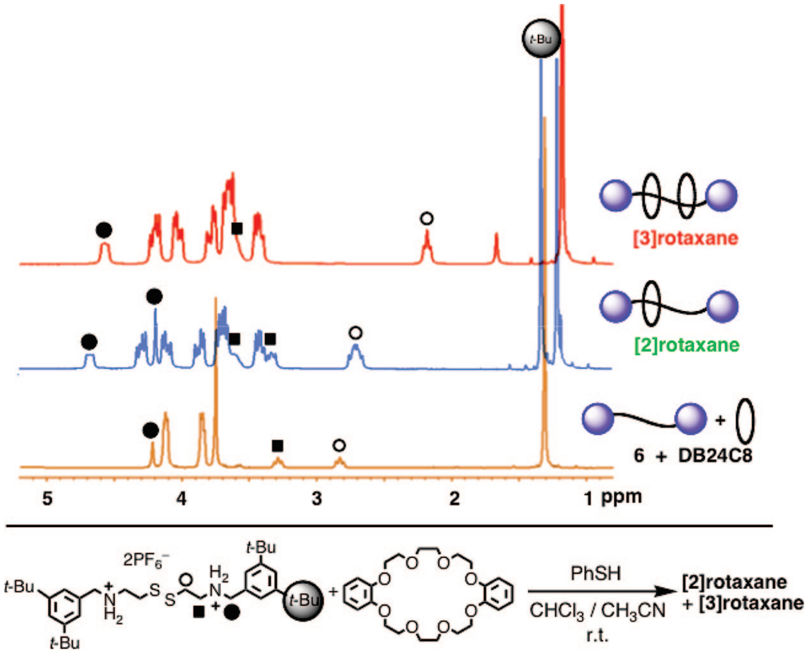


Figure 4. Partial NMR spectra (400 MHz, $CDCl_3$, 298 K) of a mixture of **6** and DB24C8 (bottom), [2]rotaxane (center), and [3]rotaxane (top). Chemical shift changes in three methylene signals (●, ■, ○) and a *tert*-butyl signal (*t*-Bu) are shown.

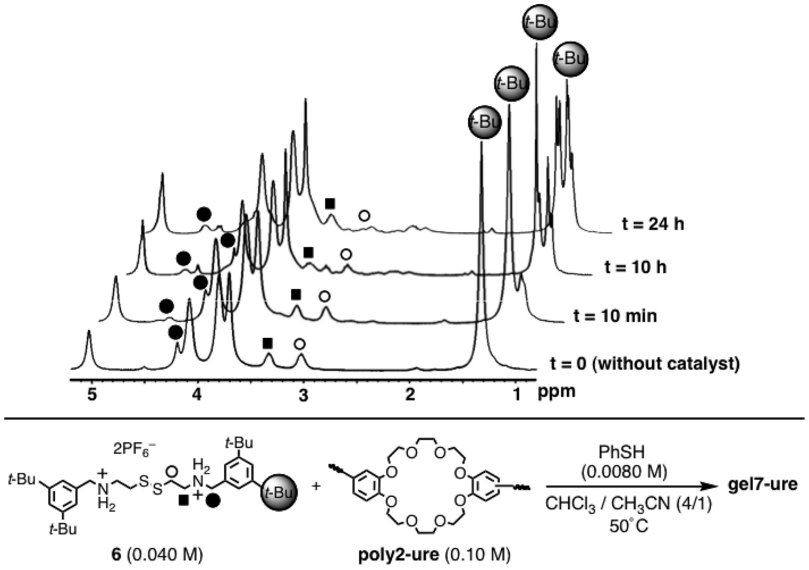


Figure 5. Time-dependent NMR spectral change (270 MHz, $CDCl_3/CD_3CN$ (4/1), 333 K) of the reaction of **6** and poly(crown ether) **poly2-ure** catalyzed by benzenethiol. Changes in spectral pattern and chemical shift of three methylene signals (●, ■, ○) and a *tert*-butyl signal (*t*-Bu) are shown.

Table 3. Synthesis of Polyrotaxane Networks[a]

entry	poly (crown ether)	time (h)	product	yield (%)	T_{d10} (°C)[b]	T_g 1 (T_g 2) (°C)[c]
1	**poly2-ure**	20	**gel7-ure**	98	265	45
2	**poly3-ether**	20	**gel8-ether**	98	176	48
3	**poly3-ether**	20	**gel9-ket**	98	305	58
4	**copoly5-(66)**	24	**gel10-(66)**	93	268	−75 (66)
5	**copoly5-(50)**	72	**gel10-(50)**	98	271	−73 (75)
6	**copoly5-(36)**	72	**gel10-(36)**	97	265	−79 (74)
7	**copoly5-(33)**	240	**gel10-(33)**	97	263	−73 (68)
8	**copoly5-(25)**	240	**gel10-(25)**	97	280	−72 (70)

[a] The gelation reaction was carried out by using poly(crown ether) (0.25 mol/L) and axle component **6** (0.063 mol/L) in the presence of benzenthiol (0.013 mol/L) in $CH_3CN/CHCl_3$ (1/3) at 50 °C. [b] Measured by DSC from −100 to 120 °C at a heating rate of 10 °C/min. [c] Measured by TGA at a scanning rate of 10 °C/min.

Table 4. Effect of Molar Ratio on the Property of Cross-Linked Polyrotaxane

entry	**poly2-ure** (mol/L)[a]	**axle 6** (mol/L)	[**6**]/[**2**]	percent swelling[b]	T_g (°C)[c]
1	0.25	12.5	0.50	75	60
2	0.25	6.25	0.25	97	53
3	0.25	2.50	0.10	240	32
4	0.17	4.25	0.25	170	49

[a] Based on cyclic unit of poly(crown ether). [b] The polyrotaxane network was immersed in chloroform at room temperature for 30 h. The percent swelling was calculated according to the following equation: percent swelling = {[weight of swelled gel] − [weight of dried gel]}/[weight of dried gel] × 100. [c] Measured by DSC at a scanning rate of 10 °C/min.

Table 5. Swelling Behavior of Polyrotaxane Networks Gel7-Ure and Gel9-Ket

	percent swelling[a]	
solvent	**gel7-ure**	**gel9-ket**
DMF	1400	650
DMSO	840	320
$CHCl_3$	240	230
CH_3CN	62	370
MeOH	27	170

[a] The polyrotaxanes were immersed in solvent for 30 h at room temperature. The percent swelling was calculated according to the following equation: percent swelling = {[weight of swelled gel] − [weight of dried gel]}/[weight of dried gel] × 100.

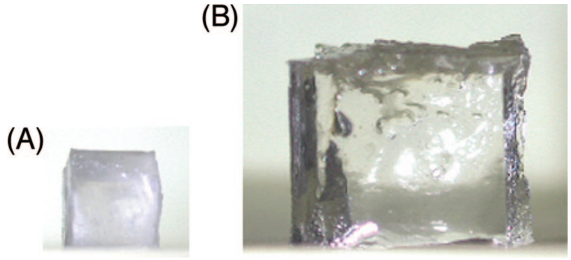


Figure 6. Pictures of polyrotaxane network **gel7-ure** (A) before and (B) after swelling in DMF.

dumbbell-shaped ammonium disulfide **6**, poly(crown ether) **poly2-ure** as the linearly linked polymacrocycle, and benzenethiol as the catalyst (5 mol %) (Figure 5). First of all, the *tert*-butyl signal split to several signals, suggesting the formation of a few possible structures. Notably, three methylene signals of **6** that were the same as those of the model compounds made changes similar to those of Figure 4, although the signals became broad as the reaction progressed. The estimated complexation ratio between the crown ether cavity and *sec*-ammonium group after 24 h was 74%, as calculated from the integral ratio. This value consists of the sum of both [2]- and [3]-rotaxane structures for axle **6** and indicates that the degree of rotaxanation to [3]rotaxane structure is at least 48%, which can be regarded as the degree of cross-linking, although the value should be lower because a certain amount of [2]rotaxanation would occur within a poly(crown ether) molecule. Thus, the obtained results undoubtedly prove that the mechanical linkage between the two polymers caused the cross-linking.

The cross-linked polyrotaxanes (**gel7-ure**, **gel8-ether**, and **gel9-ket**) were elastic and transparent in the swelled state, whereas they became hard translucent solids with plasticity when dried under reduced pressure. **Gel10**s were very elastic in both swelled and dried states, probably because of the incorporation of the PTHF spacer. Thermal properties (T_{d10} and T_g) of the polyrotaxane networks are summarized in Table 3. The decomposition and glass transition temperatures clearly depended on the polymer structure. For example, polyketone-type network polymer **gel9-ket** showed high thermal stability (T_{d10} = 305 °C, T_g = 58 °C), whereas **gel8-ether** had lower thermal stability (T_{d10} = 176 °C, T_g = 48 °C). **Gel10**s, like **copoly5**s, had two T_g values that perhaps originated from the polyether and polyurethane moieties.

Table 6. Thermal Properties of Polymer Films of Polyrotaxane Networks Gel7-Ure, Gel9-Ket, and Gel10-(36)

	12.5 mol %[a]			25 mol %[a]			50 mol %[a]		
polyrotaxane network	T_{d10}[b]	T_g 1 (T_g 2)[c]	yield (%)	T_{d10}[b]	T_g 1 (T_g 2)[c]	yield (%)	T_{d10}[b]	T_g 1 (T_g 2)[c]	yield (%)
gel7-ure	[d]	[d]	[e]	265	45	95	188	49	98
gel0-ket	285	46	98	285	55	98	255	52	09
gel10-(36)	292	−76 (74)	98	265	−79 (74)	98	256	−55 (119)	98

[a] Feed ratio of **6** to cyclic units of poly(crown ether). [b] Measured by TGA at a scanning rate of 10 °C/min. [c] Measured by DSC from −100 to 120 °C at a heating rate of 10 °C/min. [d] Not measured. [e] Not determined.

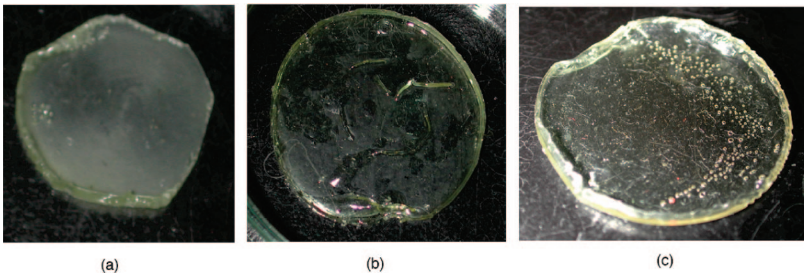


Figure 7. Pictures of the films of polyrotaxane networks **gel10-(36)**. These films were prepared by using (a) 50, (b) 25, and (c) and 12.5 mol % of the axle component **6** as the cross-linking agent.

Effect of Concentration of the Cross-Linker (6). To clarify the effect of the concentration of the cross-linker (i.e., dumbbell-shaped ammonium disulfide **6**) on the property of polyrotaxane network **gel7-ure**, their thermal and swelling behaviors (percent swelling) were examined in terms of concentration and feed ratio (Table 4). Dry **gel7-ure** was prepared according to Scheme 5 after drying under reduced pressure at room temperature overnight, whereas swelled **gel7-ure** was obtained by immersion in $CHCl_3$ at room temperature for 30 h. The percent swelling value increased as the feed ratio of **6** decreased (entries 1−3). These results simply suggested that the treatment with a large amount of **6** resulted in the formation of a densely cross-linked network that loses the elasticity. Meanwhile, low concentration resulted in a high degree of swelling due to a low degree of cross-linking (entries 2 and 4), which is in accordance with the thermodynamic nature of the cross-linking reaction.

Swelling Behavior of Polyrotaxane Networks. Table 5 features the percent swelling ratio of polyrotaxane networks **gel7-ure** and **gel9-ket**. Both **gel7-ure** and **gel9-ket** were swollen in *N*,*N*-dimethylformamide (DMF). **Gel7-ure** was swollen in DMF to 1400% and in DMSO to 840%, whereas the swelling ratio of **gel9-ket** was half the value of **gel7-ure**, which is most likely due to the low affinity for such solvents. Although **gel7-ure** was hardly swollen in MeOH and acetonitrile (MeOH percent swelling = 27%, CH_3CN percent swelling = 62%), **gel9-ket** was moderately swollen in MeOH (percent swelling = 170%) and CH_3CN (percent swelling = 370%). Figure 6 illustrates the pictures of **gel7-ure** before and after swelling in DMF. Translucent polymer in the dry state changed to transparent after swelling in DMF.

Preparation of Polyrotaxane Network Film. We examined the thermal properties of polyrotaxane networks of **gel7-ure**, **gel9-ket**, and **gel10-(36)** in the dry state. For this purpose, polymer films were prepared using different concentrations of **6** (50, 25, and 12.5 mol %). Self-standing polymer films were obtained by cold curing of a mixture with **gel10-(36)**, axle **6**, and a catalytic amount of benzenethiol in $CHCl_3/CH_3CN$ (3/1). Thermal properties of the films were evaluated by TGA and DSC. The results are summarized in Table 6. When the concentration of **6** increased, the T_g value became higher in accordance with the increasing amount of cross-linked points. Figure 7 depicts the pictures of the films of **gel10-(36)** where the film became turbid with increased concentration of **6** possibly because of the partial aggregation of the axle components.

Dynamic Viscoelasticity of Polyrotaxane Network Films. Dynamic mechanical properties of polyrotaxane network films (**gel10-(36)**) with various feed ratios of **6** were evaluated in a temperature range of −120 to 140 °C by the use of an IT-DVA200s apparatus (ITK, Japan). The measurement was conducted in the oscillatory tensile mode at a frequency of 10 Hz and a heating rate of 5 °C/min. The dimensions of a rectangular specimen were 5.0 mm in width and 0.15 (feed ratio of **6**: 12.5 mol %), 0.20 (25 mol %), or 0.25 (50 mol %) mm in thickness, and the distance between clamps was 10 mm. Figure 8 shows the temperature dependence of the dynamic viscoelastic properties: (a) tensile storage modulus E', (b) tensile loss modulus E'', and (c) tensile loss tangent tan δ. Two relaxation modes clearly appeared from −90 to −40 °C and from 10 to 50 °C, mostly depending on the T_g of **gel10-(36)**. Both E' and E'' increased with the increase in the feed ratio of **6** from 0 to 100 °C, and a plateau region in E' appeared at temperatures of $>$20 °C, suggesting the formation of a network structure. These results also suggested that the dumbbell-shaped disulfide **6** worked well as the cross-linker of poly(crown ether) from the viewpoint of dynamic viscoelastic properties. In addition, it was also revealed that the crown ether moieties that are sparsely placed in the polymer chain of **copoly5-(36)** take part in the cross-linking.

Conclusions

This article has demonstrated the synthesis of polyrotaxane networks consisting of poly(crown ether)s as the trunk polymers and the dumbbell-shaped *sec*-ammonium axle component **6** with a central disulfide linkage as the cross-linking agent via the reversible thiol−disulfide interchange reaction (i.e., the dynamic covalent chemistry of disulfide bond). The combination of poly(crown ether)s with **6** quantitatively afforded the polyrotaxane networks, which showed the thermal properties depending on the trunk polymer structure. The swelling property, film-forming property, and dynamic viscoelasticity of the polyrotaxane networks also depended on the cross-linker concentration. Thus, the present protocol provides a new procedure for the network polymers by utilizing the combination of dynamic covalent chemistry and supramolecular chemistry in which both the trunk polymer and the cross-linking agent change position without an apparent change in their chemical structures during the cross-linking reaction. Moreover, this protocol would also render a new manner for topological cross-linking to afford an attachment of topological characteristics to a desired polymer, which was

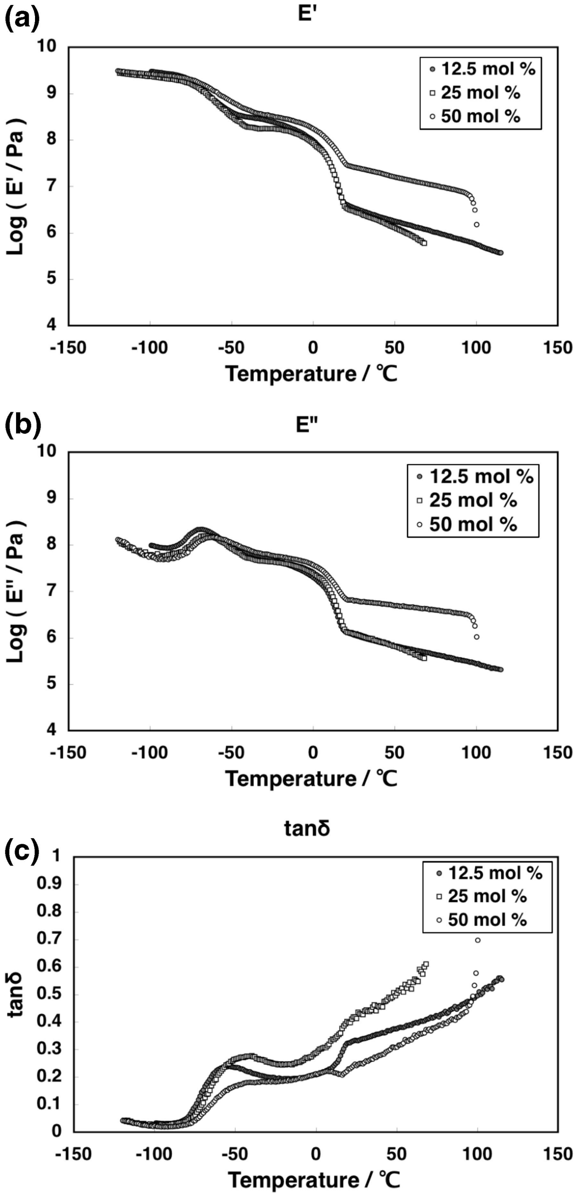


Figure 8. DMA profiles of polyrotaxane network **gel10-(36)**: (a) storage modulus E', (b) loss modulus E'', and (c) loss tangent tan δ profiles. Changes in intensities of three feed ratios (●, 12.5; □, 25; and ○, 50 mol %) are shown.

demonstrated by exploiting copolymers that possess a PTHF spacer. Further applications directed toward the decomposition of polyrotaxane networks that exploit the reversible S−S linkage would be an important future work from the viewpoint of recyclable polymers.

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