Polymer Journal

Pseudorotaxane-coupled Gel: A New Concept of Interlocked Gel Synthesis by Using Metathesis Reaction

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A unique interlocked gel consisting of an ammonium salt axle having two terminal olefins and a crown ether having two terminal olefins was synthesized by metathesis reaction of pseudorotaxane. The resulting compound showed a swelling in various solvents and showed no solubility.

KEY WORDS: Metathesis Reaction / Pseudorotaxane / Interlocked Compound / Gel / Crown Ether / Ammonium Salt /

Gels are very useful in medical materials and electronic devises. In generally, these gels were categorized as physical gel or chemical gel. However, in recent years, a new type of gel, which is called 'slide-ring gel' or 'topological gel,' has been reported. The new gel was constructed from rotaxane (Figure 1).[1–11]

For example, a gel consisting of cyclodextrin-dimers and poly (ethylene glycol) was reported by Ito *et al.*[12] In addition, Takata *et al.* reported a topologically networked polymer consisting of bisammonium salt axles and poly(crown ether) by using the thiol-catalayzed reversible cleavage of a disulfide linkage;[13] the former is a hydrogel and the later is an organogel. These polymers consisting of rotaxane structure have come under the spotlight as a third type of gel with a high extensibility, swelling, rebound, and impact absorption properties because movable crosslinks were constructed by inclusion effect.

We also have been researching the synthesis of topological gel by metathesis reaction. Metathesis reaction is a very useful tool for syntheses of various olefin compounds, and also has been used for syntheses of rotaxanes[14–17] and catenanes.[18–20] However, a synthesis of rotaxane gel by metathesis reaction has not ever been reported. Moreover, above-mentioned rotaxanes and rotaxane gels must introduce a bulky substituent as a third component into these systems to hold wheel components in axle components. If these stable rotaxane gels are synthesized from two components (a linear axle and a wheel), these synthetic procedures will be simpler. In fact, Gibson *et al.* reported on rotaxane gels consisting of a liner component and a circle component.[21–24]

In this paper, we propose a new strategy of the simple synthesis of rotaxane gel by using the inclusion reaction between ammonium salt compound and crown ether and by the metathesis reaction between the resulting pseudorotaxaenes which have four double bonds. The important point in our concept is to provide two roles for crown ethers: provision of inclusion sites as a host molecule and prevention of release of themselves as a stopper (Figure 2).

EXPERIMENT

General

^{1}H NMR spectra were recorded on JEOL JNM-GX270. Molecular weight and molecular weight distribution were estimated by gel permeation chromatography (GPC) on a shimadzu SPD-10A equipped with an UV detector (257 nm) and a shimadzu HSG-40, HSG-20, HSG-15, HSG-10 column (i.d., 7.9 mm; length, 30 cm; gel particle size 10 μm; theoretical plate numbers, >10,000). THF was used as an eluent at a flow rate of 1.2 mL/min. The molecular weights were calibrated with polystyrene standards. MALDI-TOF mass measurements were performed with Voyager TM DE PRO Y instrument. Elemental analyst was done with a Perkin Elmer 2400 CHNS.

Synthesis of AXLE

***t*-Butyl *N*,*N*-Bis(2-hydoxyethyl)carbamate (1).** To a solution of diethanolamine (15.0 g, 0.014 mol) and 4-(dimethylamino)pyridine (DMAP) (0.175 g, 1.43 mmol) in $CHCl_3$ (250 mL) was added di-*t*-butyl dicarbonate (31.2 g, 0.014 mol) and stirred at room temperature for 3 h. Solvent was removed by evaporation. The resulting residue was purified by SiO_2 column chromatography (EtOAc/MeOH (10:1)) to give **1** (28.1 g, 96%).[25]

^{1}H NMR (270 MHz, $CDCl_3$) δ 3.84–3.72 (s, 4H, HO-CH_2-), 3.45–3.33 (s, 4H, -CH_2-N-), 1.48–1.42 (s, 9H, -COO-C(CH_3)$_3$).

***t*-Butyl *N*,*N*-Bis(2-undec-10-enoyloxyethyl)carbamate (2).** A solution of **1** (14.9 g, 0.0723 mol) and triethylamine (50 mL, 0.362 mol) in THF (50 mL) was cooled at 0 °C. A solution of 10-undecenoyl chloride (44.0 g, 0.217 mol) in THF (50 mL) was added to the mixture, followed by stirring for 10 min. And then, the solution was stirred at room temperature for 86 h. Saturated $NaHCO_3$ was then poured in the solution, followed by extraction with EtOAc. The organic layer was washed with saturated NaCl. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to give a residue as colorless oil. The residue was purified by SiO_2

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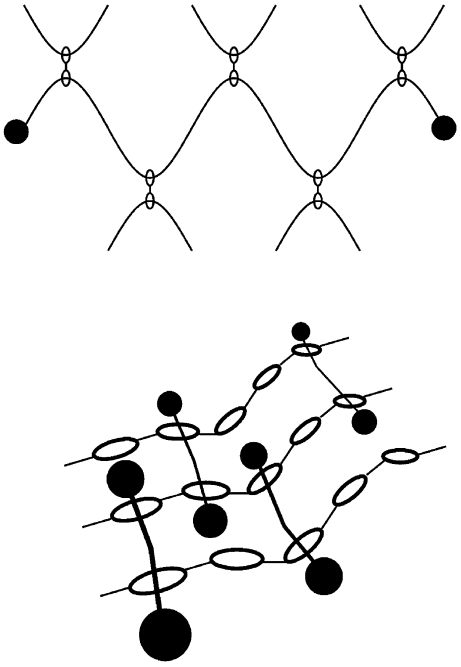


Figure 1. Structures of existing topological polyrotaxane gels.

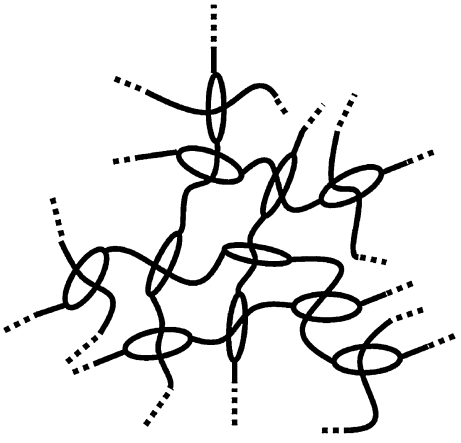


Figure 2. Non-dumbbel-shaped rotaxane gel.

column chromatography (EtOAc/MeOH (9:1, 2:1)) to afford **2** (37.1 g, 95%).

^{1}H NMR (270 MHz, $CDCl_3$) δ 5.89–5.71 (m, 2H, CH_2=C*H*-), 5.03–4.88 (t, 4H, CH_2=CH-), 4.19–4.11 (s, 4H, -COOCH_2-), 3.55–3.41 (s, 4H, -CH_2-N-), 2.35–2.23 (t, 4H, -CH_2COO-), 2.08–1.98 (q, 4H, CH_2=CH-CH_2-), 1.68–1.53 (s, 4H, -CH_2-CH_2COO-), 1.48–1.42 (s, 9H, -COO-C(CH_3)$_3$), 1.41–1.20 (m, 20H, CH_2=CH-CH_2-(CH_2)$_5$-). Anal. Calcd. For $C_{31}H_{55}NO_6$: C, 69.24; H, 10.31; N, 2.60. Found: C, 68.24; H, 10.66; N, 2.78.

***N*,*N*-Bis(undec-10-enoyloxyethyl)ammonium Hexafluorophosphate (AXLE).** To a solution of **2** (3.00 g, 5.58 mmol) in chloroform (3 mL) was added trifluoroacetic acid (3 mL), followed by stirring at room temperature for 4 h. The solution was evaporated *in vacuo*, and the residue was diluted with CH_2Cl_2. The organic layer was washed with saturated ammonium hexafluorophosphate aqueous solution. The organic layer was then dried over $MgSO_4$ and evaporated to give axle component as a white solid (2.25 g, 69%).

mp. 61–62 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.89–5.71 (m, 2H, CH_2=C<u>H</u>-), 5.03–4.88 (t, 4H, C<u>H$_2$</u>=CH-), 4.47–4.35 (s, 4H, -COOC H_2-), 3.48–3.35 (s, 4H, -CH_2-N-), 2.48–2.39 (t, 4H, -C<u>H$_2$</u>COO-), 2.08–1.98 (q, 4H, CH_2=CH-C<u>H$_2$</u>-), 1.68–1.51 (s, 4H, -C<u>H$_2$</u>-CH_2COO-), 1.41–1.20 (m, 20H, CH_2=CH-CH_2-(C<u>H$_2$</u>)$_5$-); MALDI-TOF mass of $C_{26}H_{48}NO_4^+$ Calcd.: 438.66; Found: 437.92 $(M\text{-}PF_6)^+$. Anal. Calcd. For $C_{26}H_{48}F_6NO_4P$: C, 53.51; H, 8.29; N, 2.40. Found: C, 54.31; H, 8.72; N, 2.72.

Synthesis of WHEEL

Triethylene Glycol Monotosylate (3). To a solution of triethylene glycol (90.6 g, 0.600 mol), DMAP (0.147 g, 1.21 mmol), triethylamine (50.4 mL, 0.362 mol) in THF (120 mL) was slowly added *p*-toluenesulfonyl choloride (23.0 g, 0.121 mol) in THF (100 mL), and the solution was stirred at room temperature for 23 h. The reaction mixture was filtrated, and the filtrate was concentrated. The residue was chromatographed over SiO_2 using EtOAc. The aimed compound was isolated as a colorless liquid (30.0 g, 81%).[26]

^{1}H NMR (270 MHz, $CDCl_3$) δ 7.86–7.76 (d, 2H, Ph), 7.43–7.33 (d, 2H, Ph), 4.22–4.15 (t, 2H, Ts-OCH_2-), 3.80–3.58 (m, 10H, Ts-OCH_2-(OCH_2)$_4$CH_2OH), 2.45 (s, 3H, CH_3-Ph).

Ethyl 3,4-Dihydroxybenzoate (4). A mixture of 3,4-dihydroxybenzoic acid (8.0 g, 0.052 mol) and a catalytic amount of *p*-toluenesulfonic acid (0.49 g, 2.60 mmol) was dissolved in EtOH (250 mL), and refluxed for 6 d. The solution was evaporated under reduced pressure, and the resulting concentrate was diluted with EtOAc, followed by washing with water. The organic layer was evaporated to give the product as a white crystalline solid (8.43 g, 89%).[26]

^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73–7.68 (s, 1H, Ph), 7.60–7.53 (d, 1H, Ph), 6.94–6.86 (d, 1H, Ph), 4.38–4.27 (q, 2H, CH_3-CH_2-), 1.39–1.33 (t, 3H, CH_3-CH_2-).

4-Ethyl-1,2-bis[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzoate (5). **4** (8.0 g, 0.040 mol), triethylene glycol monotosylate (29.4 g, 0.097 mol), and K_2CO_3 (15.3 g, 0.10 mol) was dissolved in acetone (240 mL), and refluxed for 17 h. The solution was filtrated, and the filtrate was concentrated. Column chromatography (SiO_2) with MeOH/EtOAc (1:9) yielded a yellowish viscous oil (15.0 g, 76%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.73–7.65 (d, 1H, Ph), 7.63–7.58 (s, 1H, Ph), 6.94–6.86 (d, 1H, Ph), 4.39–4.30 (q, 2H, CH_3-CH_2-), 4.20–4.15 (t, 4H, Ph-OCH_2-), 3.95–3.60 (m, 20H, Ph-OCH_2-(OCH_2)$_4$-CH_2OH), 1.39–1.33 (t, 3H, CH_3-CH_2-).

4-Ethyl-1,2-bis[2-[2-[2-[(4-toluene)sulfonyl]oxy]ethoxy]ethoxy]-ethoxy]benzoate (6). To a solution of diol **5** (15.0 g, 33.6 mmol), DMAP (0.082 g, 0.67 mmol), triethylamine (14.1 mL, 100.0 mmol) in THF (80 mL) was slowly added a solution of *p*-toluenesulfonyl chloride (19.2 g, 100.0 mmol) in THF (50 mL), and the solution was stirred at room temperature for 165 h. The reaction mixture was filtrated and the filtrate was concentrated. The residue was purified by SiO_2 column chromatography (*n*-

hexane/EtOAc (1:1), EtOAc) to afford ditosylate **6** as yellowish viscous oil (22.6 g, 89%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.86–7.76 (d, 4H, Ph (Ts)), 7.73–7.65 (d, 1H, Ph), 7.60–7.55 (s, 1H, Ph), 7.38–7.32 (d, 4H, Ph (Ts)), 6.92–6.86 (d, 1H, Ph), 4.39–4.30 (q, 2H, CH_3-CH_2-), 4.25–4.15 (t, 4H, Ph-OCH_2-), 3.88–3.59 (m, 20H, Ph-OCH_2-(OCH_2)$_4$CH_2OH), 2.40 (s, 6H, CH_3-Ph), 1.41–1.33 (t, 3H, CH_3-CH_2-). Anal. Calcd. For $C_{35}H_{46}O_{14}S_2$: C, 55.69; H, 6.14. Found: C, 56.66; H, 6.39.

Bis(ethoxycarbonylbenzo)-24-crown-8 Ether (7). A suspension of **6** (7.5 g, 9.9 mmol) and cesium carbonate (16.1 g, 49.5 mmol) in acetonitrile (400 mL) was stirred at 60 °C for 30 min. Then, a solution of **4** (1.61 g, 8.91 mmol) in THF (100 mL) was added dropwise. The mixture was heated under reflux for 100 h. The suspension was filtrated, and the filtrate was evaporated under reduced pressure. The resulting residue was diluted with water and extracted with dichloromethane, followed by drying over magnesium sulfate. Upon removal of the solvent, the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH (3:1, 1:1)) to produce the compound **7** as a white solid (2.99 g, 57%).

^{1}H NMR (270 MHz, $CDCl_3$) δ 7.70–7.61 (d, 2H, Ph), 7.58–7.53 (s, 2H, Ph), 6.90–6.83 (d, 2H, Ph), 4.39–4.28 (q, 4H, CH_3-CH_2-), 4.25–4.15 (t, 8H, Ph-OCH_2-), 4.23–3.65 (m, 16H, -CH_2CH_2O-), 1.41–1.33 (q, 6H, CH_3-CH_2-). Anal. Calcd. For $C_{30}H_{40}O_{12}$: C, 60.80; H, 6.80. Found: C, 60.23; H, 6.69.

Bis(hydoxymethylbenzo)-24-crown-8 Ether (8). To a suspension of $LiAlH_4$ (2.25 g, 59.3 mmol) in THF was carefully added a solution of **7** (2.93 g, 4.94 mmol) in THF, and the mixture was refluxed for 60 h. Upon cooling to room temperature, a saturated aqueous solution of $NaHCO_3$ was added to the solution. The solution was filtrated, and the filtrate was extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to give **8** as a white solid (2.47 g, 98%). **8** was used in next reaction without further purification.[27]

^{1}H NMR (270 MHz, $CDCl_3$) δ 6.95–6.80 (m, 6H, Ph), 4.62–4.48 (s, 4H, Ph-CH_2-OH), 4.21–3.65 (m, 24H, -CH_2CH_2O-).

Bis(undec-10-enoyloxymetylbenzo)-24-crown-8 Ether (WHEEL). **8** (2.46 g, 4.84 mmol) was dissolved in THF, and triethylamine (2.70 mL, 19.4 mmol) was added to the solution. To the solution was added dropwise a solution of 10-undecenoyl chloride (3.30 g, 16.3 mmol) in THF. The mixture was stirred at room temperature for 48 h. After the stirring, a saturated aqueous solution of $NaHCO_3$ was poured in the reaction mixture, followed by extraction with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to give a residue as yellow oil. The residue was purified he residue was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc (5:1, 1:1)). The column choromatography yielded the wheel as a white solid (2.78 g, 68%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.94–6.82 (m, 6H, Ph), 5.90–5.73 (m, 2H, CH_2=C*H*-), 5.05–4.95 (m, 8H, CH_2=CH-, Ph-CH_2-O-CO-), 4.18–3.79 (m, 24H, -CH_2CH_2O-), 2.38–2.28 (m, 4H, -CH_2-COO-), 2.10–1.96 (m, 4H, CH_2=CH-CH_2-), 1.70–1.58 (m, 4H, -C$H_2$$CH_2$-COO-), 1.43–1.19 (m, 20H, CH_2=CH-CH_2-(CH_2)$_5$-); MALDI-TOF mass of $C_{48}H_{72}O_{12}Na^+$ Calcd.: 864.07; Found: 862.50 $(M + Na)^+$. Anal. Calcd. For $C_{48}H_{72}O_{12}$: C, 68.54; H, 8.63. Found: C, 68.24; H, 10.66.

Metathesis Reaction of AXLE and WHEEL Mixture

To a solution of **AXLE** (0.05 g, 0.086 mmol) and **WHEEL** (0.073 g, 0.086 mmol) in dichlorometane (0.5 mL) was added a ruthenium carbene complex **9** (7.1 mg, 0.0086 mmol), and the mixture was stirred at 40 °C for 24 h. The reaction was stopped by adding ethyl vinyl ether. The resulting gel compound was wash with dichlorometane and DMF several times, followed by drying to give elastomer as a purple solid (recover rate: 85%).

RESULTS AND DISCUSSION

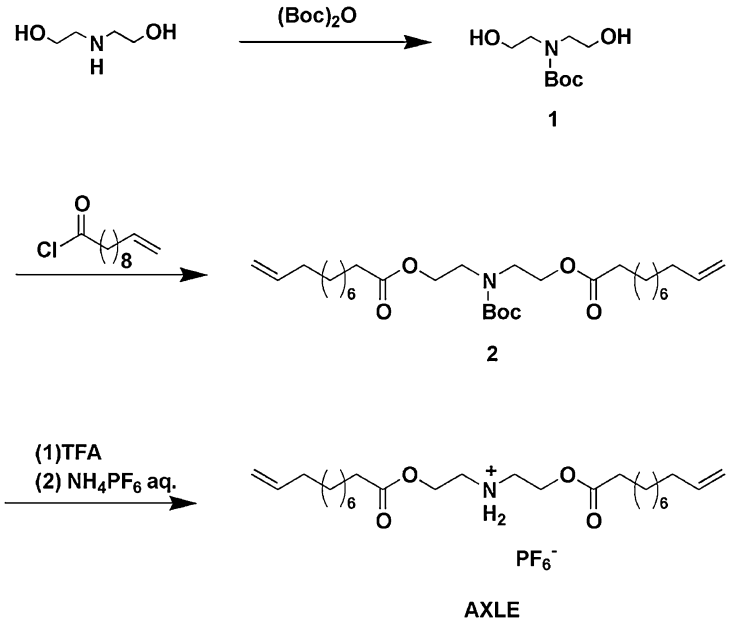
The used **AXLE** and the used **WHEEL** were prepared as shown in Schemes 1 and 2. **AXLE** was synthesized from diethanolamine in 3 steps. **WHEEL** was synthesized from triethylene glycohol in 6 steps. The axle component and the wheel component have two double bonds as a common functional group. As a result, the random metathesis reaction of these double bonds between pseudorotaxanes gives a stable rotaxane gel, which holds axles in wheels by end-capping with other wheels such as shown in Figure 2.

Rotaxane gel was synthesized with the axle, the wheel, and the ruthenium carbene complex **9**,[28–32] as shown in Scheme 3. First, the mixed solution of **AXLE** and **WHEEL** in CH_2Cl_2 was prepared to give a pseudorotaxane (**AXLE/WHEEL** complex) in the solution. And then, the catalyst **9** was added to the mixture solution in order that four olefins of a pseudorotaxane (four-arms-pseudorotaxane) react with olefins of other pseudorotaxans at random. The resulting purple solution was refluxed to give a gel-like solid. The product was washed with DMF and CH_2Cl_2, followed by drying *in vacuo* to afford a purple-red resin as a final product. We tried to purify the gel by washing with various solvents such as DMF and DMSO, but the purple color was not removed from the gel.

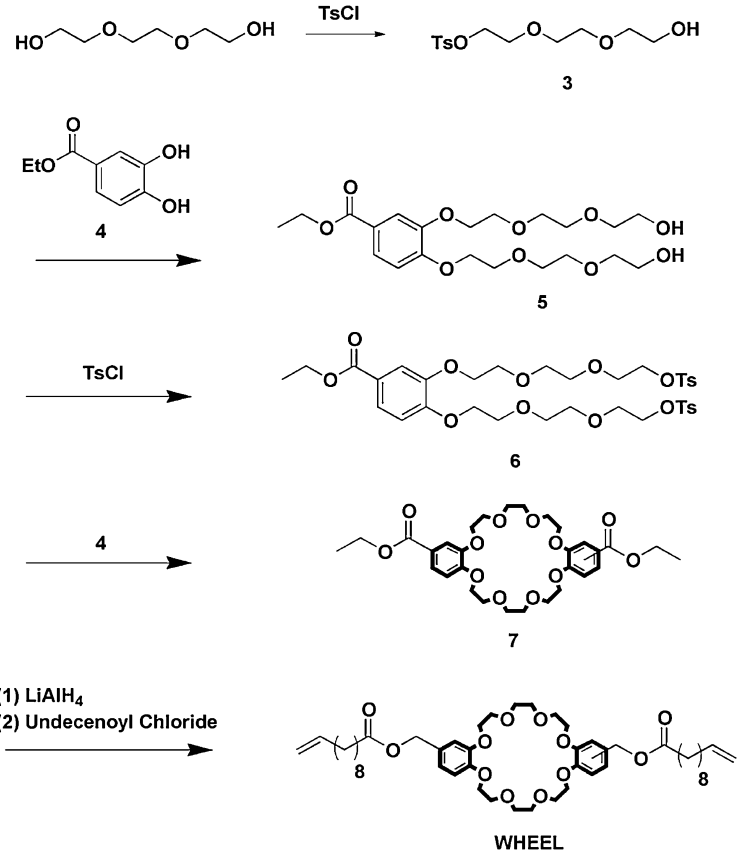
The product showed insolubility and swelling in various organic solvents, and the results of solubility and swelling are listed in Table I. The obtained polymer showed insolubility in all solvent, and tended to increase swelling ability for chloroform, dichloromethane, and aprotic solvents such as *N*,*N*-dimethylformamide (DMF), acetone, and acetonitrile. On the other hand, the polymer showed poor swelling ability for *n*-hexane, diethyl ether, and protic solvents such as methanol and ethanol.

Figure 3 represented photographs of the product before and after swelling in dichloromethane. Although the dry product before swelling was a solid resin, the product after swelling in CH_2Cl_2 became a transparent gel. In addition, the resulting gel held solvent, though the glass vial of gel was turned upside down.

To confirm the formation of network structure by metathesis reaction of four-arms-pseudorotaxane, the gelation process was followed by ^{1}H NMR spectra (Figure 4). The gelation was carried out by heating of a NMR tube that mixed **AXLE**



Scheme 1. Synthesis of **AXLE**.

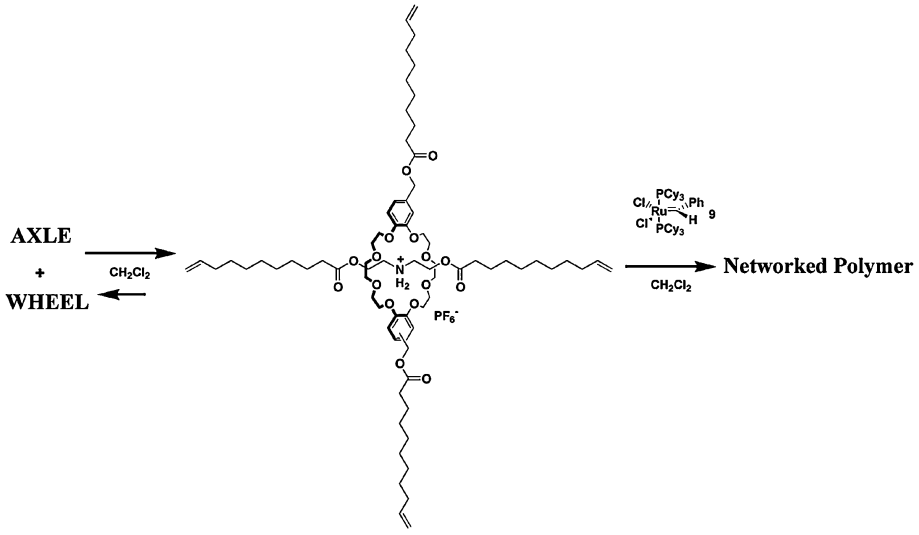


Scheme 2. Synthesis of **WHEEL**.

(0.12 mol/L), **WHEEL** (0.12 mol/L), and catalyst **9** (0.012 mol/L) in CD_2Cl_2.

Before the addition of catalyst **9**, the spectrum of the mixture was different from the superimposed spectrum of **AXLE** and **WHEEL**, and showed the formation of about 95 percent of pseudorotaxane in the system, based on the shift changes of methylene protons H_a and H_b (4.35 ppm and 3.75 ppm) adjacent to ammonium salt units of **AXLE** (Figure 4(A)).

Polymer Journal



Scheme 3. Synthesis of rotaxane gel.

Table I. Swelling Properties of Product

Solvent	Solubility Test	Percentage Swelling[b] [%]
chloroform	I[a]	770
dichloromethane	I	790
acetone	I	390
acetonitrile	I	320
N,N-dimethylformamide	I	1220
benzene	I	370
toluene	I	260
tetrahydrofuran	I	490
ethyl acetate	I	320
n-hexane	I	50
diethyl ether	I	50
methanol	I	60
ethanol	I	80

[a]Insoluble. [b]percentage swelling = (([weigh of swelled gel] − [weight of dried gel])/[weight of dried gel]) × 100.

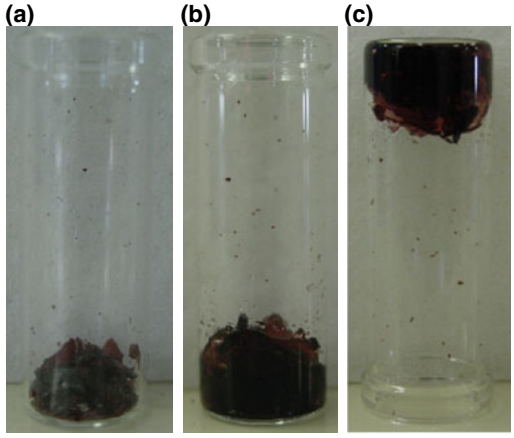


Figure 3. Photographs of the product (a) before swelling, (b) after swelling in CH_2Cl_2, and (c) the inverted glass vial of (b).

After the addition of catalyst **9**, two signal (a) and (b) attributable to terminal olefin of four-arms-pseudorotaxane made less in size, and a new signal (c) attributable to internal olefins appeared in the spectrum of four-arms-pseudorotaxane (Figure 4(B)). The signal intensity of internal olefin increased as time advances, and the solution gelated after 25 h; in fact, the ratio of the formation of internal olefins was calculated to be *ca.* 60% by using ^{1}H NMR spectrum, and ultimately, the ratio reached *ca.* 85% after 95 h. On the other hand, the metathesis reaction between compound **2** and **WHEEL** quantitatively proceeded, but the resulting solution showed no gelation (M_n of the product = 7,000).

These results indicate that that the metathesis reaction of the four-arms-pseudorotaxane consisting of **AXLE** and **WHEEL** was essential for the formation of the desired network polymer, and **WHEEL** played two important roles to make up the rotaxane network structure in the system; inclusion of axle, and protection of other crownethers against dethreading (Figure 5).

CONCLUSION

In conclusion, we have succeeded in synthesizing a new interlocked gel consisting of only two components by metathesis reaction. The resulting polyrotaxane was insoluble and selectively swelled in various organic solvents. Further works on application and structure are currently in progress.

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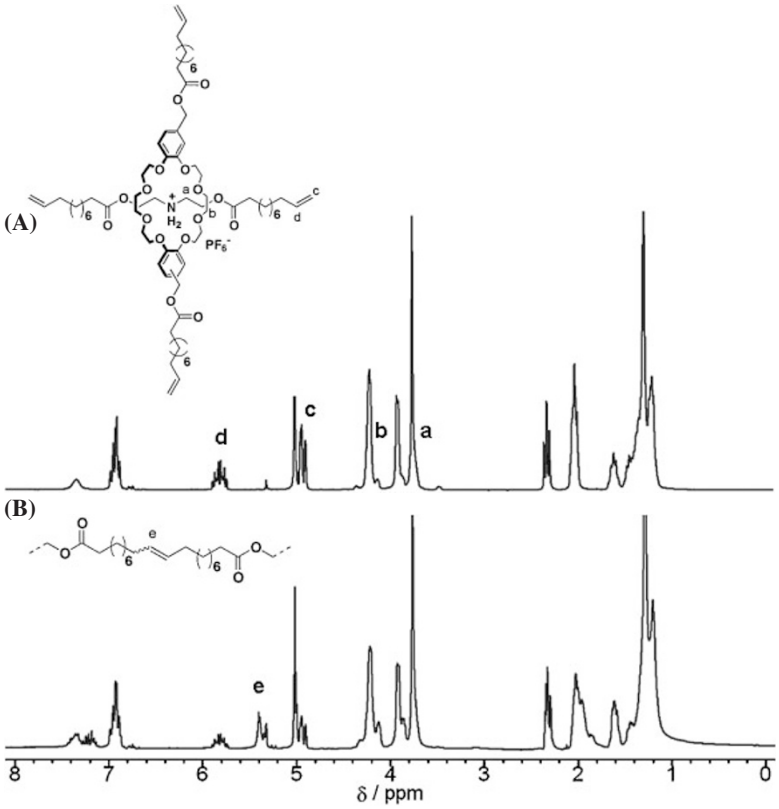

Figure 4. ^{1}H NMR spectral changes during the gelation (270 MHz, CD_2Cl_2). (A) Before adding Grubbs 1st, and (B) 25 h after adding Grubbs 1st. The initial concentrations of the axle and the wheel were 0.12 mol/L.

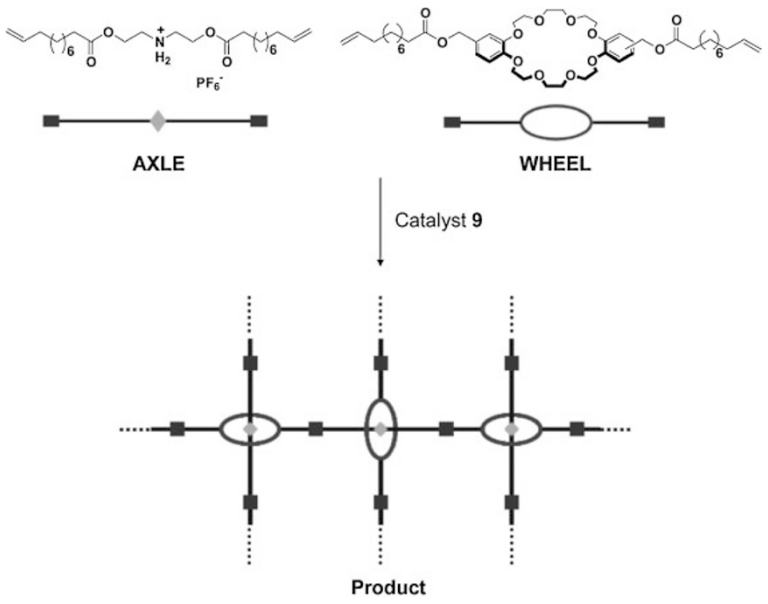

Figure 5. Proposed partial structure of networked polymer.

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