

Article

One-Pot Syntheses of [c2]Daisy-Chain Rotaxane Networks via Thiol-Ene Reaction and Its Application to Gel Electrolyte for Secondary Battery

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Abstract: A new topological material, the [c2]daisy-chain rotaxane network, was successfully synthesized via a thiol-ene reaction between a [c2]daisy-chain rotaxane, which consists of a host-guest compound (H-G compound) where a crown ether and a secondary ammonium salt are linked, and a multi-branched thiol compound. The resulting network polymer exhibited higher compressive strength compared to one without the [c2]daisy-chain rotaxane. Additionally, the neutralized [c2]daisy-chain rotaxane network, in which the ammonium salt was neutralized and there was no interaction with the crown ether, showed increased rigidity compared to its state before neutralization. Furthermore, a gel electrolyte was prepared by impregnating the [c2]daisy-chain rotaxane network with an organic electrolyte containing dissolved lithium salts, and its ionic conductivity was investigated. As a result, high ionic conductivity was achieved despite the high polymer content.

Keywords: [c2]daisy-chain rotaxane; network polymer; thiol-ene reaction; gel electrolyte; compression-resistant topological polymer; gel electrolyte



Citation: Kamoto, R.; Onimura, K.; Yamabuki, K. One-Pot Syntheses of [c2]Daisy-Chain Rotaxane Networks via Thiol-Ene Reaction and Its Application to Gel Electrolyte for Secondary Battery. *Reactions* **2024**, *5*, 800–811. <https://doi.org/10.3390/reactions5040041>

Received: 4 September 2024

Revised: 28 September 2024

Accepted: 14 October 2024

Published: 16 October 2024



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1. Introduction

A rotaxane is a supramolecular compound constructed through host-guest interactions, which involves the inclusion phenomena of a cyclic molecule (host, H) and a linear molecule (guest, G) [1–6]. These structures can be quantitatively constructed through precise design. The driving forces for rotaxane formation are known hydrogen bonding, hydrophobic interactions, electrostatic interactions, and π - π interactions. Numerous supramolecular materials based on α -cyclodextrin/polyethylene glycol and secondary ammonium salt/crown ether systems have been reported to date [7–16]. Among these, we are particularly interested in the study of [c2]daisy-chain rotaxanes. The synthesis of [c2]daisy-chain rotaxanes was first reported by Stoddart et al. in 1998 [17]. These rotaxanes can be quantitatively obtained by combining two host-guest compounds (H-G compounds). To elaborate, the [c2]daisy-chain rotaxane is constructed when the host and guest of one H-G compound exchange their inclusion partners with those of another H-G compound. Moreover, many of these studies focus on hydrophilic [c2]daisy-chain rotaxanes that use cyclodextrins as the hosts, or hydrophobic ones that use dibenzo-24-crown-8 ether (DB24C8) [18–27]. In particular, the introduction of functional groups into the benzene rings of DB24C8 is relatively easy, allowing for various molecular designs. Over the past few years, there have been increasing reports of its application to functional polymers [28–37]. Additionally, an essential design factor for obtaining [c2]daisy-chain rotaxanes quantitatively using DB24C8 is not only the interaction between the host and guest but also the precise control of their linking distance. By introducing only a single methylene chain between DB24C8 and the secondary ammonium salt, it is possible to completely suppress the formation of linear rotaxanes (poly[a2]rotaxanes) that multiple molecules align in the same direction or intramolecular ring structures ([c1]rotaxanes)

(Figure 1). Additionally, the structure of the [c2]daisy-chain rotaxane becomes more stable and robust with the contribution of π - π stacking interactions between the benzene moieties derived from DB24C8 units.

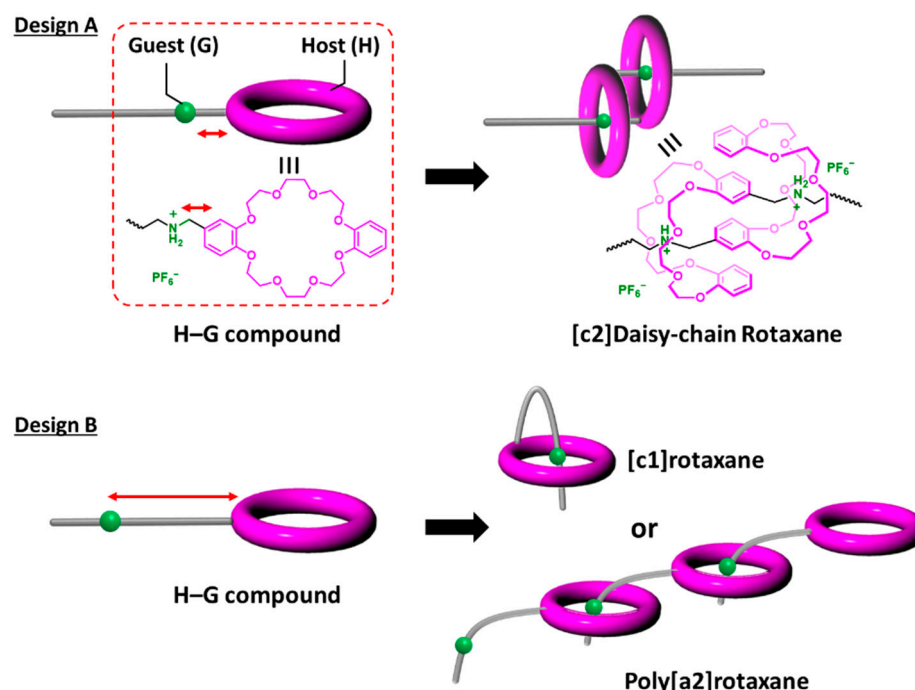


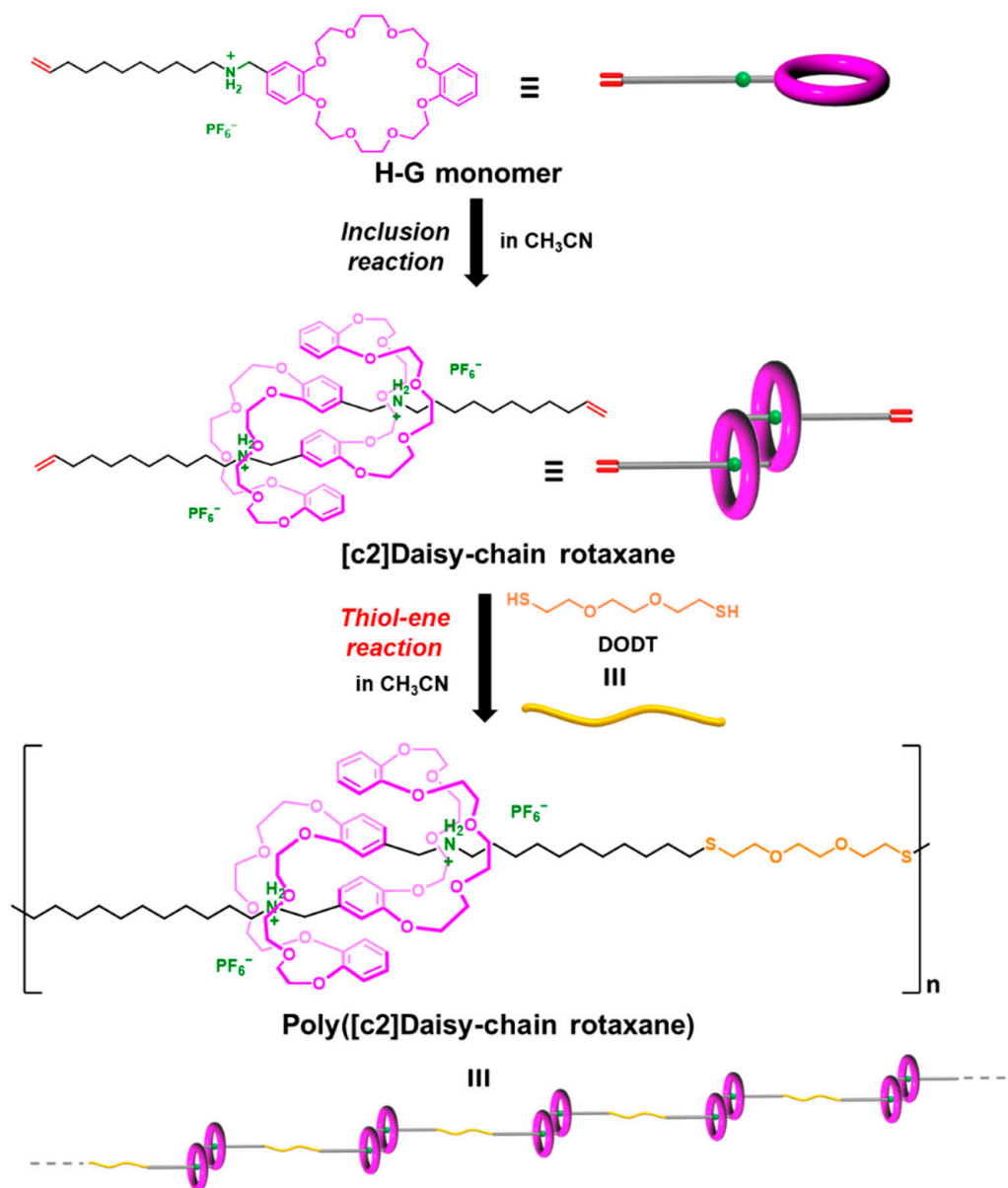
Figure 1. Design of H-G compounds for efficient synthesis of daisy-chain rotaxane (Design A) and other rotaxanes (Design B).

Based on this background, in 2023, we reported our research on poly[c2]daisy-chain rotaxanes [38]. In the previous study, we utilized the stability of crown ether-based [c2]daisy-chain rotaxane units to successfully synthesize a topological polymer (poly[c2]daisy-chain rotaxane) via thiol-ene reaction by linking these units together in large numbers (Scheme 1). The obtained polymers exhibit varying complex stability between the ammonium salts and crown ethers depending on the solvent used. As a result, the distance between the two facing crown ethers changes, making these materials promising for applications requiring excellent expansion-contraction properties.

In 2023, an example of functionalization was reported involving a crown ether-based [c2]daisy-chain rotaxane network polymer with a three-dimensional network structure composed of [c2]daisy-chain rotaxane and a four-branched thiol [39]. This synthesis involves a network polymer using [c2]daisy-chain rotaxane with unconjugated double bonds at both terminal ends, similar to that [c2]daisy-chain rotaxane we have reported. Its topological expansion and contraction properties have been investigated for applications in shape memory and tensile strength. In particular, detailed information about shape memory based on its unique expansion and contraction structure is provided.

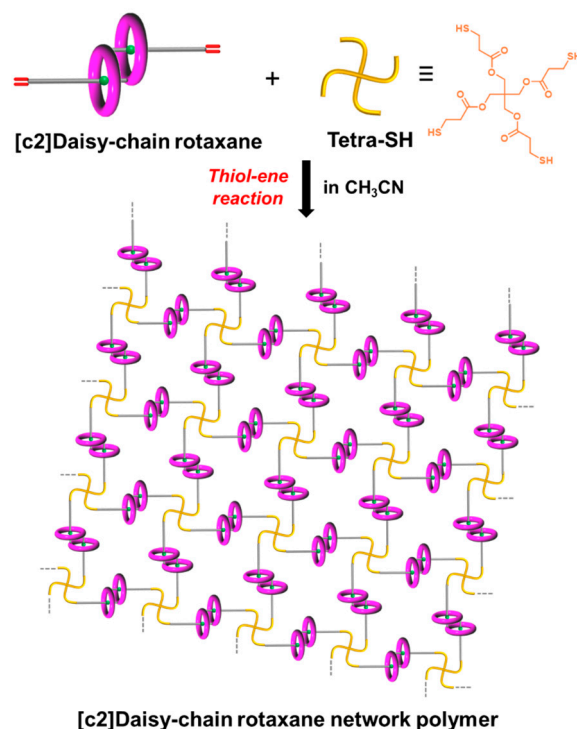
However, we see different potential for this type of [c2]daisy-chain rotaxane network polymer as a functional material. The reason lies in the distance between the two cyclic molecules during the synthesis of [c2]daisy-chain rotaxane. As mentioned earlier, to obtain [c2]daisy-chain rotaxane efficiently and selectively, it is crucial that the binding distance between the host and guest is short. In this configuration, the spacing between the two facing rings (hosts) is at its shortest. In other words, this means that the initial [c2]daisy-chain rotaxane itself is formed in its most extended state. When the [c2]daisy-chain rotaxane in this extended state is arranged in a three-dimensional network, the polymer material will have a larger mesh in its extended form and will be in its most stable state. The point is, we believe that the network polymer made from [c2]daisy-chain rotaxane will exhibit

better properties in response to the change in the compression direction than to one in the extension direction.



Scheme 1. One-pot synthesis of poly([c2]daisy-chain rotaxane) via thiol-ene reaction (our previous work).

In this study, we synthesized novel network polymers incorporating the [c2]daisy-chain rotaxane unit we previously reported, using thiol-ene reactions with a tetrabranched thiol (tetra-SH) (Scheme 2). We investigated their potential as compression-resistant topological polymers and as topological gel electrolytes for secondary batteries. This research aims to explore new developments in topological materials incorporating [c2]daisy-chain rotaxane.



Scheme 2. Illustration of one-pot synthesis of [c2]daisy-chain rotaxane network polymer via thiol-ene reaction (This work).

2. Experimental Section

2.1. Materials and Instruments

Reagent-grade solvents (acetonitrile(CH_3CN), methanol (MeOH)) and other chemicals were used without further purification (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan; Tokyo Chemical Industry Co., Ltd., Tokyo, Japan).

Fourier-transform infrared (FT-IR) spectra were recorded using a JASCO FTIR-6600 (Tokyo, Japan). The glass transition temperature T_g was measured using a highly sensitive differential scanning calorimeter Hitachi High-Tech Science DSC 7020 (Tokyo, Japan). The compression test was conducted using an A&D Company MCT-1150 (Tokyo, Japan). The ionic conductivity was measured using a Bio Logic VSP300 (Seyssinet-Pariset, France).

2.2. Synthesis of H-G Compound

The H-G compound was successfully synthesized based on our previous research [38].

2.3. Synthesis of [c2]Daisy-Chain Rotaxane Network Polymer

A solution of H-G compound (0.100 g, 0.129 mmol) and pentaerythritol tetra(3-mercaptopropionate) as a tetra-SH (0.0160 g, 0.0327 mmol) with a trace amount of benzophenone as an initiator was prepared in acetonitrile. The solution was poured into a cylindrical silicon mold with a diameter of 8 mm and a height of 3 mm and then exposed to UV light (365 nm). The resulting cylindrical gel was washed by soaking in methanol and then dried to obtain an orange transparent resin (0.0948 g, 82% yield). The IR is shown in Figure S4.

2.4. Synthesis of Neutralized [c2]Daisy-Chain Rotaxane Network Polymer

The [c2]daisy-chain rotaxane network polymer (0.0764 g) was impregnated with a mixed solution of triethylamine (1.0 mL) and acetic anhydride (1.0 mL) and then heated and stirred at 80 °C for 24 h. The resulting gel was washed with methanol and dried to give a brown resin (0.0651 g, 96% yield). The IR is shown in Figure S4.

2.5. Synthesis of DB24C8 Network Network

A solution of bisalkenyl-modified dibenzo-24-crown-8 ether (BUOMB24C8) (0.0912 g, 1.12 mmol) and (0.0273 g, 0.0558 mmol) with a trace amount of benzophenone as an initiator was prepared in a chloroform/acetonitrile (volume ratio 1:1) mixed solution. The solution was poured into a cylindrical silicon mold with a diameter of 8 mm and a height of 3 mm and then exposed to UV light (365 nm). The resulting cylindrical gel was washed by soaking in methanol and then dried to obtain a yellow transparent resin (0.0873 g, 74% yield). The IR is shown in Figure S1.

2.6. Compression Test

The test samples were prepared by curing and drying the reaction solution in a silicon mold with a hole of $\Phi 8$ mm and a thickness of 3 mm. After purifying and drying, the test samples (ca. $\Phi 7$ mm, thickness 2.5 mm) were subjected to a compression test under conditions of a measurement temperature of 25 °C, a maximum test force capacity of 500 N, and a compression speed of 10 mm/min.

2.7. Ion Conductivity Measurement

The ionic conductivity of gel electrolytes was measured by alternating current (AC) impedance measurements. The gel electrolytes were prepared by impregnating pre-synthesized and dried [c2]daisy-chain rotaxane network polymers ($\Phi 12$ mm) with a specified amount of 1M lithium Bis(trifluoromethanesulfonyl)imide/triglyme (LiTFSI/G3). The polymer content in gel electrolyte was adjusted according to the amount of electrolyte used. The gel electrolytes were sandwiched between SUS electrodes as blocking electrodes. AC impedance measurements were conducted by cooling from 343 K to 263 K with a frequency range of 1 MHz to 1 kHz and an amplitude of 10 mV. The samples were left to stand at each measurement temperature for at least 90 min before measurement.

3. Results and Discussion

3.1. Preparation of [c2]Daisy-Chain Rotaxane Network Polymer

The [c2]daisy-chain rotaxane network polymer was synthesized using the same method we previously reported for linear poly([c2]daisy-chain rotaxane) [38]. In the synthesis of poly([c2]daisy-chain rotaxane), we employed 3,6-Dithia-1,8-octanediol (DOTD) as a bifunctional dithiol, and synthesis was achieved through a thiol-ene reaction under UV irradiation. In this study, we used pentaerythritol tetrakis(mercaptoacetate) (tetra-SH) as a four-branched thiol instead of the dithiol, conducting a similar reaction to successfully obtain a yellow transparent resin. The obtained resin exhibited swelling behavior without dissolving in any of the tested solvents (acetonitrile and methanol). In acetonitrile, which was also used as the reaction solvent in this study, the resin absorbed 200% of its own weight, demonstrating high swelling property (Figure 2). Notably, even when methanol, an organic solvent that dissociated the inclusion complex of crown ether and ammonium salt through hydrogen bonding and electrostatic interactions, was used, the resin slightly swelled without dissolving. This observation supports the formation of a stable network polymer with stable inclusion complexes serving as cross-linking points. Additionally, DSC measurements revealed a glass transition temperature (T_g) around 50 °C, which suggested the polymerization (Figure S2).

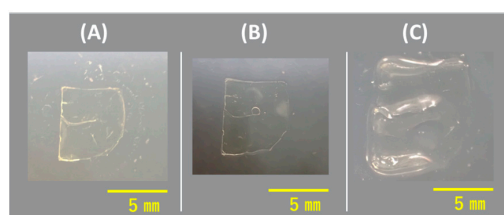


Figure 2. Swelling behavior of [c2]daisy-chain rotaxane network polymer in polar organic solvents: (A) dry state, (B) after methanol immersion, and (C) after acetonitrile immersion.

3.2. Compression Evaluation of [c2]Daisy-Chain Rotaxane Network Polymer

The results of the compression evaluation of the cylindrically-molded [c2]daisy-chain rotaxane network polymer (dry gel) are shown in Figure 3. As a comparative network polymer, the sample composed of bisalkenyl-modified dibenzo-24-crown-8 ether (DB24C8) and tetra-SH, which does not contain the [c2]daisy-chain rotaxane structure, was also evaluated (DB24C8 network polymer, $T_g = -54\text{ }^{\circ}\text{C}$, see Figure S3). Since the initial stress-strain curves of both samples exhibited similar shapes, it was considered that a relaxation phenomenon occurred throughout the polymer chains where the [c2]daisy-chain rotaxane structure was not involved. However, when the thickness of the DB24C8 network polymer before measurement was reduced by approximately 50% in the compression direction, the comparative network polymer was fractured. On the other hand, the [c2]daisy-chain rotaxane network polymer maintained its shape without damage even when compressed by approximately 70% in the compression direction. This flexible and high compressive strength suggests that the excessive stress in the network was relieved by the sliding of the two facing crown ether rings in the [c2]daisy-chain rotaxane units, which were in an extended state, in a direction that causes them to move apart. Moreover, upon the removal of stress, the [c2]daisy-chain rotaxane network polymer quickly returned to its original size, unlike the DB24C8 network polymer. This compression recovery process was repeated for 10 cycles, and it was confirmed that the compression ratio was maintained at a level similar to the first cycle throughout all cycles.

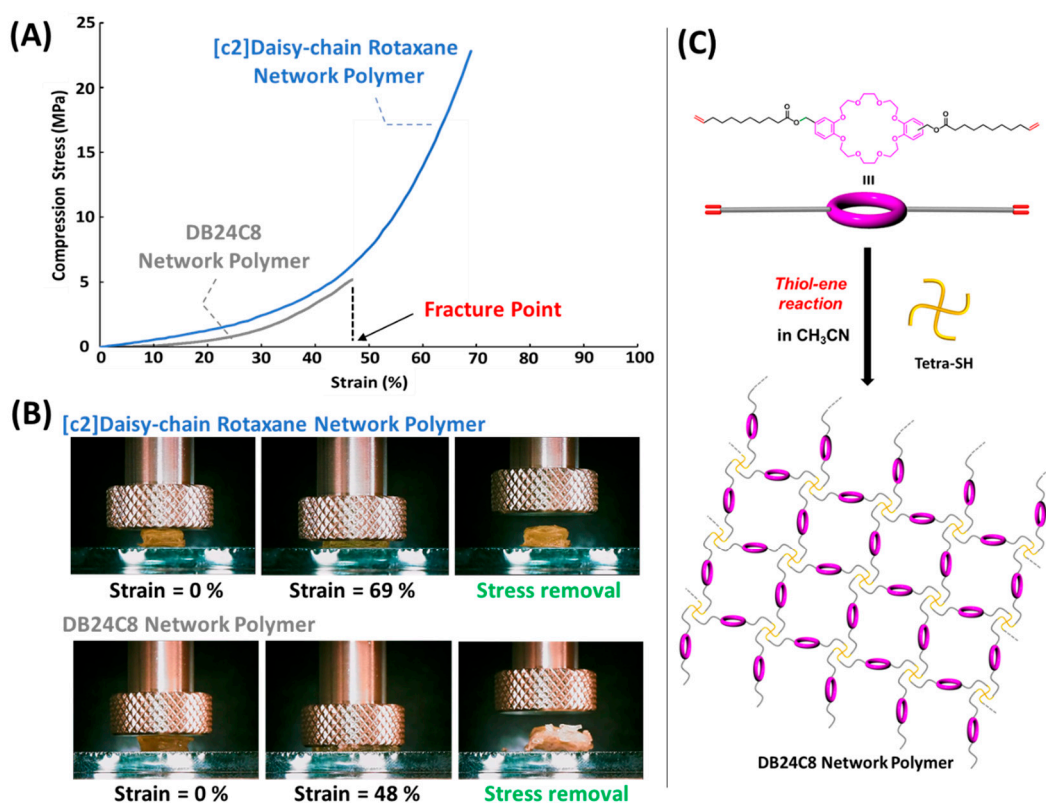


Figure 3. Compression evaluation of [c2]daisy-chain rotaxane network polymer: (A) compression stress-strain curves of network polymers, (B) photographs of network polymers during the compression process, and (C) illustration of DB24C8 network polymer synthesis as a control.

3.3. Compression Evaluation of Neutralized [c2]Daisy-Chain Rotaxane Network Polymer

Next, the neutralization reaction (deionization treatment) of the secondary ammonium salts present in the [c2]daisy-chain rotaxane network polymer was carried out, and various properties were investigated under conditions where the electrostatic interactions with the crown ether were significantly weakened. In the IR spectrum of the resulting brown

resin, an absorption peak attributed to the carbonyl (C=O) group of the amide appeared at 1650 cm^{-1} , and the absorption peak at 860 cm^{-1} derived from the P–F bond of the counter anion species of the ammonium salt was significantly reduced compared to the pre-reaction spectrum, indicating that the neutralization of most of the ammonium salts had proceeded (Figure S4). Additionally, the T_g was $38\text{ }^{\circ}\text{C}$, which was $12\text{ }^{\circ}\text{C}$ lower than before neutralization (Figure S5). This suggests that the strong interaction between the crown ether units and ammonium salt units was weakened by neutralization, leading to an increase in the amorphous regions within the overall network.

The results of the compression tests for the neutralized [c2]daisy-chain rotaxane network polymer (dry gel) are shown in Figure 4. As a result, neither the pre-neutralized nor the post-neutralized [c2]daisy-chain rotaxane was broken under approximately 50% strain compression. However, the neutralized [c2]daisy-chain rotaxane showed nearly a threefold increase in stress values compared to the pre-neutralized state and slow recovery of size, which is a noteworthy result.

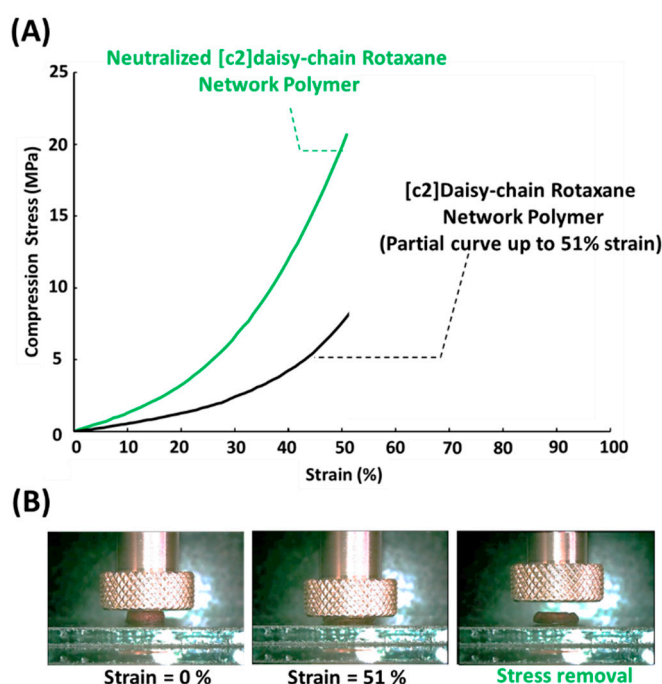


Figure 4. Compression evaluation of neutralized [c2]daisy-chain rotaxane network polymer: (A) compression stress–strain curves of network polymers and (B) photographs of network polymers during the compression process.

In general, topological rotaxane materials composed of separated guest (secondary ammonium salt) and host (crown ether) units lose the interaction between the crown ether and the ammonium salt after neutralization, which makes it easier for the crown ether ring to move along the threaded chain regions. Additionally, given the decrease in the T_g of the neutralized [c2]daisy-chain rotaxane network, we initially predicted that the neutralized network would become easier to deform and experience less stress compared to before neutralization. Contrary to our expectation, the reason why the neutralized polymer exhibited greater stress compared to the pre-neutralized one is likely related to the distance between the facing crown ether rings in each [c2]daisy-chain rotaxane at the onset of compression. In the pre-neutralized [c2]daisy-chain rotaxane, the movement of the crown ether rings is restricted by hydrogen bonding and electrostatic interactions between the crown ether and the secondary ammonium salt, resulting in the rings being in their closest possible proximity before compression. When compression begins, the distance between the cross-linking points in the network is maximally extended, making the polymer more prone to contraction and increasing the overall deformation (Figure 5). On

the other hand, in the neutralized [c2]daisy-chain rotaxane, the crown ethers in the rotaxane become more mobile even before compression. In other words, since the distance between the cross-linking points was already shorter before compression, the polymer became less prone to deformation. In this way, controlling the interactions between the crown ether units and the ammonium salt units means changing the length of the topological [c2]daisy-chain rotaxane units and the resulting network size, which significantly influences the compression properties.

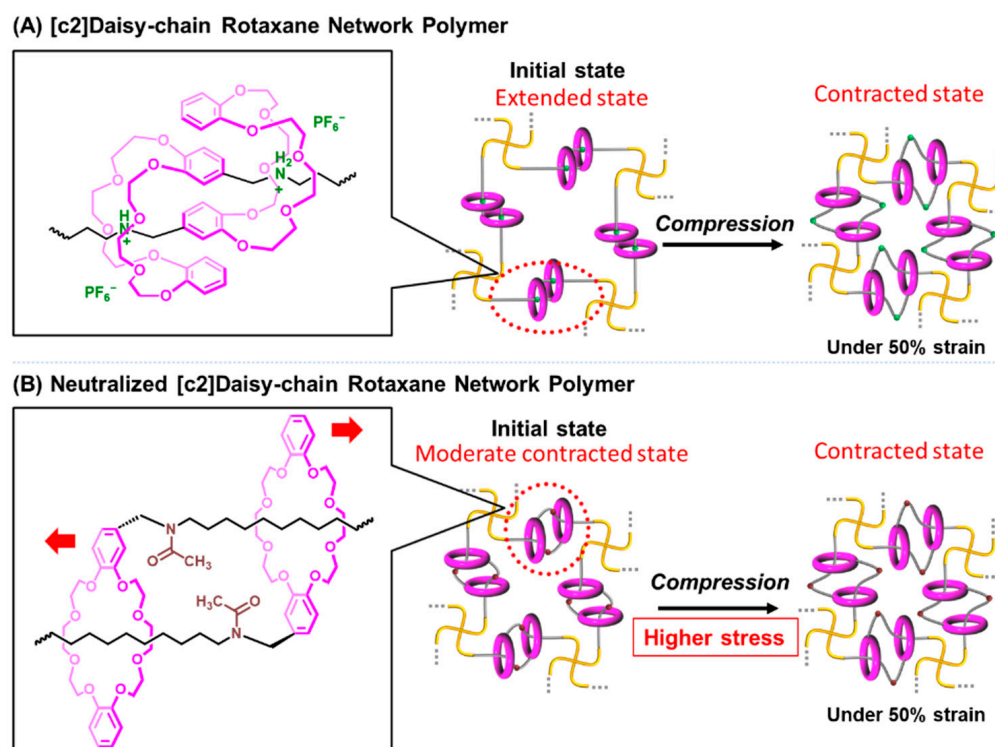


Figure 5. Illustration of the compression process for each network polymer: (A) [c2]daisy-chain rotaxane network and (B) neutralized [c2]daisy-chain rotaxane network.

3.4. Ionic Conductivity of [c2]Daisy-Chain Rotaxane Network Polymer Gel Electrolyte

Additionally, this compressive resistance was utilized to explore applications in polymer electrolytes for storage batteries such as lithium-ion secondary batteries (LIB) [40–43]. Key technologies required for using polymer-based gel or solid electrolytes include (1) achieving good interfacial formation with each electrode and (2) preventing short circuits caused by metal dendrites on the negative electrode surface during charging. Moreover, since laminated and coin-type batteries often require appropriate pressure to achieve high adhesion between the electrodes and the gel electrolyte, as well as to ensure compactness, a functional polymer with excellent compressive resistance is required. Therefore, the potential of this unique material as a gel electrolyte was investigated. In this case, the network polymer composed of tetra-SH and [c2]daisy-chain rotaxane with terminal double bonds had low affinity for Li salt-containing electrolyte solutions, making the preparation of gel electrolytes difficult. Therefore, the strategy of using multiple thiol components, specifically tetra-SH and DODT in a molar ratio of 2:1 (tetra-SH), successfully resolved the issue. The obtained transparent network film (dry state) was turned into a gel electrolyte by incorporating an electrolyte solution composed of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and triethylene glycol (G3) (1M LiTFSI/G3). At this time, the maximum swelling ratio was estimated to be 150%, which implies that the polymer component constitutes 40 wt% of the gel electrolyte. Figure 6 shows the results of ion conductivity measurements performed using the prepared gel electrolyte by the alternating current impedance method.

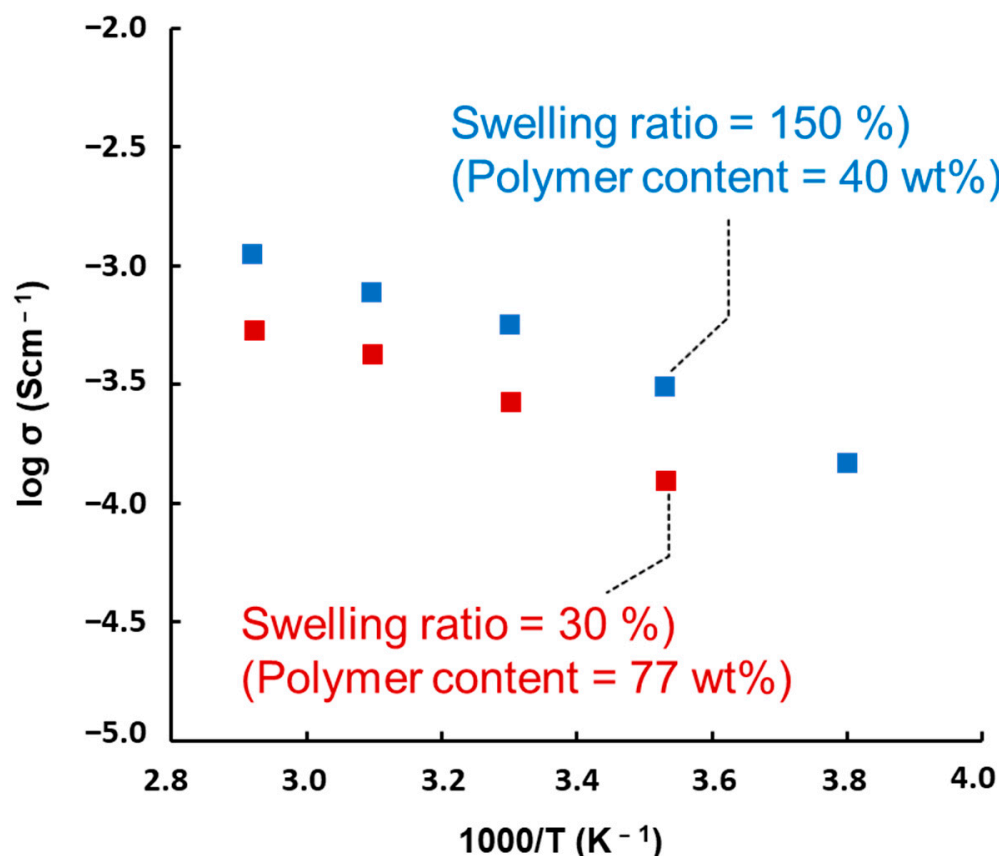


Figure 6. Ionic conductivity as a function of $1000/T$ for gel electrolytes based on [c2]daisy-chain rotaxane network polymers with various swelling ratios (polymer content).

Here, the ion conductivity from 70 °C to −10 °C is shown in Arrhenius plots, demonstrating values above 10^{-4} S/cm over this temperature range. Additionally, although the swelling ratio was 30%, corresponding to 77 wt% polymer content, the ion conductivity in the gel electrolyte was still remarkably high, showing values above 10^{-4} S/cm at 30 °C. Despite the high polymer content, gel electrolytes incorporating rotaxanes that exhibit good ion conductivity have not been reported. This calls for an investigation into the ion conduction mechanism in the future. Currently, we believe that the spontaneous extension and contraction of [c2]daisy-chain rotaxanes contribute to ion transport. LiTFSI/G3 is a highly polar solution, which destabilizes the interactions between the crown ethers and ammonium salts in the rotaxane structure. As a result, the [c2]daisy-chain rotaxane units incorporated throughout the network are capable of undergoing spontaneous expansion and contraction. Ultimately, it was suggested that the polymer matrix, which achieved high mobility, enables efficient ion transport even with a low amount of electrolyte.

4. Conclusions

First, in this study, we successfully developed a three-dimensional network polymer “[c2]daisy-chain rotaxane network polymer” by applying our previously reported synthesis method of chain-like poly[c2]daisy-chain rotaxane, which utilizes the H-G compound composed of crown ether and secondary ammonium salt. The resulting network polymer was insoluble in all tested solvents and exhibited selective swelling behavior.

Next, focusing on the structural characteristics, we evaluated the compression properties of the dry [c2]daisy-chain rotaxane network polymer. The results demonstrated higher flexibility and toughness compared to the crown ether network polymer. Additionally, the network polymer with neutralized ammonium salt exhibited higher stress compared to the pre-neutralized one, suggesting that the extension and contraction state of

the [c2]daisy-chain rotaxane was already coexisting in the neutralized network polymer before compression.

Finally, as a new attempt, we applied the [c2]daisy-chain rotaxane network polymer to a gel electrolyte for LIB. Despite containing over 77 wt% of polymer, it exhibited a high ion conductivity of over 10^{-4} S/cm. The spontaneous elongation and contraction of the [c2]daisy-chain rotaxane within the network is suggested to enhance ion transport conductivity. Further investigation into the details, including the electrochemical properties, is currently underway. The materials with these unique properties have demonstrated potential value in the field of batteries, and it is strongly anticipated that they will exhibit further functionalities and find applications in an expanding range of areas.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/reactions5040041/s1>, Figure S1: IR chart of DB24C8 network polymer; Figure S2: DSC chart of [c2]daisy-chain rotaxane network; Figure S3: DSC chart of DB24C8 network polymer; Figure S4: IR spectra of (A) [c2]daisy-chain rotaxane network polymer and (B) neutralized [c2]daisy-chain rotaxane network polymer; Figure S5: DSC chart of neutralized [c2]daisy-chain rotaxane network polymer.

Author Contributions: Conceptualization, R.K., K.O. and K.Y.; synthesis and structural analysis, R.K.; writing—original draft preparation, K.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author. The data are not publicly available because of the lack of a dedicated server.

Conflicts of Interest: The authors declare no conflicts of interest.

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