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Systematic Synthesis of Block Copolymers Consisting of Topological Amphiphilic Segment Pairs from *kyklo*- and *kentro*-Telechelic PEO and Poly(THF)

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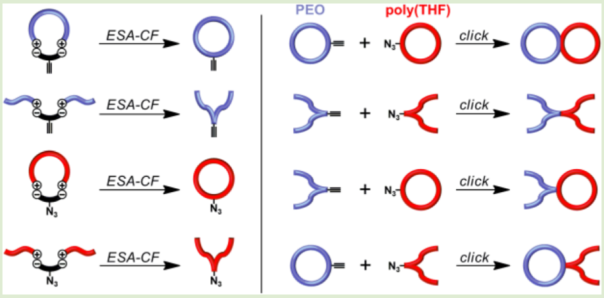
Supporting Information

ABSTRACT: A set of four types of block copolymers consisting of topological amphiphilic segment pairs was effectively synthesized via *kyklo*- (functionalized cyclic) and *kentro*- (center-functionalized linear) telechelic poly(ethylene oxide) (PEO) and poly(tetrahydrofuran) (poly(THF)). Accordingly, *kyklo*- and *kentro*-telechelic PEO with an ethynyl group was newly prepared from relevant linear PEO precursors with quinuclidinium end groups and an ethynyl-functionalized dicarboxylate counteranion by the electrostatic self-assembly and covalent fixation (ESA-CF) process. Similarly, *kyklo*- and *kentro*-telechelic poly(THF) with an azido group was obtained. The PEO and poly(THF) telechelics were subjected to click chemistry to systematically produce amphiphilic block copolymers with two symmetric topological forms, that is, an "8" shape ($\mathbf{I}_\mathrm{C}\cdot\mathbf{II}_\mathrm{C}$) and a four-armed star shape ($\mathbf{I}_\mathrm{L}\cdot\mathbf{II}_\mathrm{L}$), and two asymmetric topological forms, that is, twin-tailed tadpole shapes ($\mathbf{I}_\mathrm{L}\cdot\mathbf{II}_\mathrm{C}$ and $\mathbf{I}_\mathrm{C}\cdot\mathbf{II}_\mathrm{L}$) with respect to the hydrophilic–hydrophobic plane.



The construction of various polymer topologies, particularly cyclic architectures, has become a subject of intense interest, not only due to their appealing geometries but also due to their unusual properties, which are not found in their traditional linear or branched counterparts.[1−3] In addition to the lower viscosity and higher glass-transition temperature that have been frequently reported for cyclic polymers compared to their linear counterparts,[4,5] a variety of distinctive behaviors, namely, topology effects, have been discovered.[6,7] These effects include crystallization behaviors[8] and diffusion properties[9] of cyclic polymers with well-defined structures and selected functionalities. In particular, a micelle formed from a monocyclic amphiphilic block copolymer exhibit significantly higher thermal and salt stability than that from its linear counterpart.[10,11] This is a unique example of controlling/tuning material properties not by the chemical structure or molecular weight of the polymer but by the transformation of the topology.

An increasing number of monocyclic block copolymers were recently synthesized: poly(methyl acrylate)−polystyrene,[12] poly(2-(2-methoxy-ethoxy)-ethyl methacrylate)−poly(oligo-(ethylene oxide) methyl ether methacrylate),[13] and polystyrene−polyisoprene[14] cyclized by click chemistry, poly(ethylene oxide) (PEO)−polystyrene cyclized by Glaser coupling,[15] and cyclic gradient block poly(δ-valerolactone)−poly(ε-caprolactone) by zwitterionic ring-expansion polymerization.[16] Block copolymers composed of cyclic and linear/branched amphiphilic segments have also been reported; Glaser coupling was frequently employed to form one-tailed, two-tailed, and twin-tailed tadpole-shaped[17] topological block copolymers with a cyclic PEO segment.[18−20] On the other hand, the construction of multicyclic architectures with topological block copolymers,[21,22] including hetero[2]catenane,[23] is limited due to the synthetic difficulties to utilize multiple cyclization processes. One of the most elaborate examples is a μ-ABC tricyclic miktoarm star-shaped block copolymer by the orthogonal coupling reactions of click chemistry and nitroxide radical coupling.[24]

To explore the opportunity of the remarkable topology effects by self-assembly of a multitopological amphiphilic block copolymer, a versatile synthetic process to systematically produce the appropriate combinations of topology and solvophilicity of the segment pairs is needed.[10,11] Here we report a novel synthetic method to produce a systematic set of four types of block copolymers with topological and amphiphilic segment pairs through click chemistry using relevant *kyklo*- (functionalized cyclic) and *kentro*- (center-functionalized linear) telechelic PEO and poly(tetrahydrofuran) (poly(THF)) precursors (Scheme 1). These precursors were efficiently obtained using the electrostatic self-assembly and covalent fixation (ESA-CF) process. In this relation, we previously showed that click chemistry, in conjunction with the ESA-CF process, is crucial for the effective synthesis of *bridged*- and *spiro*-multicyclic polymers[25] and for the preparation of the key intermediates that lead to doubly fused tricyclic and triply fused tetracyclic polymers.[26]

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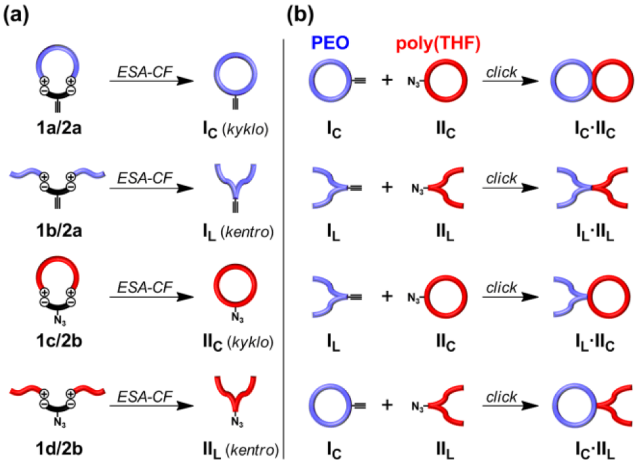
Scheme 1. Schematic Illustration for the Systematic Synthesis of Topological Amphiphilic Block Copolymers ($\mathbf{I_C{\cdot}II_C}$, $\mathbf{I_L{\cdot}II_L}$, $\mathbf{I_L{\cdot}II_C}$, and $\mathbf{I_C{\cdot}II_L}$) by the Combination of (a) the ESA-CF Process and (b) Click Chemistry



In the present study, cyclic and linear PEO with an alkyne group was newly prepared from PEO precursors with quinuclidinium end groups by the ESA-CF process and effectively linked by click chemistry with corresponding cyclic and linear poly(THF) with an azide group. Amphiphilic block copolymers were systematically produced with symmetric topological forms, that is, an "8" shape ($\mathbf{I_C{\cdot}II_C}$) and a 4-armed star shape ($\mathbf{I_L{\cdot}II_L}$), and asymmetric topological forms, that is, twin-tailed tadpole shapes with the opposite amphiphilic compositions ($\mathbf{I_L{\cdot}II_C}$ and $\mathbf{I_C{\cdot}II_L}$) with respect to the hydrophilic−hydrophobic plane (Scheme 1).

First, bifunctional PEO with quinuclidinium end groups (**1a/**$\mathbf{TsO^-}$) and a monofunctional counterpart of approximately half the length (**1b/**$\mathbf{TsO^-}$) were prepared from *α*,*ω*-dihydroxy-PEO (M_n(NMR) = 4600) and its *α*-hydroxy-*ω*-methoxy counterpart (M_n(NMR) = 2000), respectively, by tosylation[27] and subsequent nucleophilic substitution with quinuclidine, according to the method previously reported (Figure 1).[28] The substitution of the tosylate end groups by alternative *N*-phenylpyrrolidine (aniline derivative) failed to proceed due to its lower nucleophilicity in comparison with quinuclidine (aliphatic amine). This is in contrast to the telechelic poly(THF) counterparts, which feature *N*-phenylpyrrolidinium end groups that can be obtained by the end-capping reaction of the highly reactive oxonium groups.

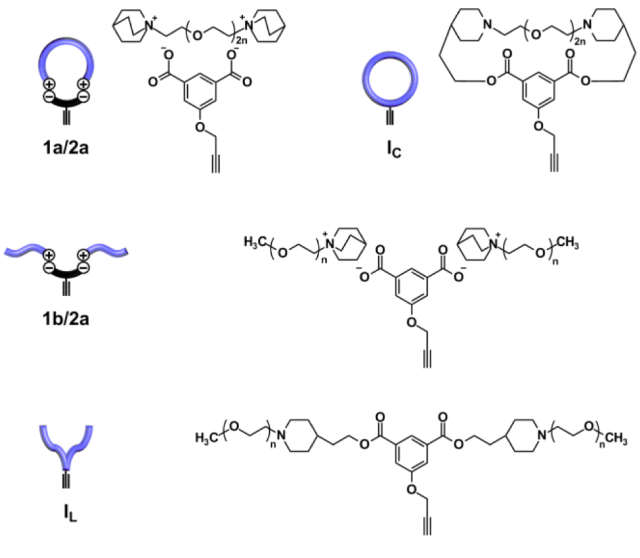


Figure 1. Chemical structures of **1a/2a**, **1b/2a**, $\mathbf{I_C}$, and $\mathbf{I_L}$.

A pair of ethynyl-functionalized *kyklo-* ($\mathbf{I_C}$) and *kentro-*telechelic ($\mathbf{I_L}$) PEO was prepared by introducing an ethynyl-functionalized dicarboxylate (**2a**) as a counteranion to form the ionic polymer precursors (**1a/2a** and **1b/2a**, respectively) shown in Figure 1. The ion-exchange of the water-soluble PEO precursors was successfully achieved by coprecipitation from an acetone solution containing **1a/**$\mathbf{TsO^-}$ or **1b/**$\mathbf{TsO^-}$ and an excess of a tetrabutylammonium salt of **2a** into dry ice/acetone-cooled acetone. A pair of key intermediate ionic polymer precursors (**1a/2a** and **1b/2a** in Figure 1) was thus effectively obtained. Notably, in the preceding study on the cyclization of telechelic PEO with quinuclidinium end groups, an aliphatic dicarboxylate (adipate) counteranion was employed to bring the effective ion-exchange reaction to completion.[28]

The ^{1}H NMR measurements confirmed that the TsO$^-$ counterions were exchanged with ethynyl-functionalized dicarboxylate to form **1a/2a** and **1b/2a**. The signals assignable to **1a/2a** and **1b/2a** ("f" at 8.32 ppm, "g" at 7.72 ppm, "h" at 4.74 ppm, and "i" at 2.52 ppm for **1a/2a** in Figure 2 and "f" at 8.30 ppm, "g" at 7.73 ppm, "h" at 4.74 ppm, and "i" at 2.51−2.56 ppm for **1b/2a** in Figure S3) and the absence of the tosyl groups indicated the completion of the ion-exchange reaction.

The obtained ionic polymer precursors **1a/2a** and **1b/2a** were then subjected to heat treatment to form the covalently linked products $\mathbf{I_C}$ and $\mathbf{I_L}$, respectively (Scheme 1a and Figure 1). Toluene solutions of **1a/2a** and **1b/2a** were refluxed to promote the ring-opening reaction of the quinuclidinium groups through attack by the carboxylate group of **2a**.[29] In the meantime, the pendant ethynyl group remained intact. In addition, for **1a/2a**, the reaction was conducted in a dilute solution (0.20 g/L) to prevent intermolecular reactions.

The reactions were monitored by ^{1}H NMR spectroscopy, and the emergence of a signal for the ester-adjacent methylene protons ("g" at 4.38 ppm) was observed (Figures 2 and S4). Signals for the ethynyl proton ("k" at 2.53−2.68 ppm for $\mathbf{I_C}$ and 2.54−2.72 ppm for $\mathbf{I_L}$, overlapping "b") and the propynyl methylene protons ("j" at 4.80 ppm for $\mathbf{I_C}$ and 4.79 ppm for $\mathbf{I_L}$) were also visible.

The MALDI-TOF mass spectra of $\mathbf{I_C}$ and $\mathbf{I_L}$ are shown in Figure 3. A uniform series of peaks for the repeating ethylene oxide units was observed, and each peak exactly matched the total molar mass of the PEO chain, the linking unit, and the end groups. For example, the peak at m/z = 4432.9, which was assumed to be an adduct with H^+, corresponded to $\mathbf{I_C}$ possessing the expected chemical structure with DP_n of 90; $(C_2H_4O) \times 90 + C_{27}H_{36}N_2O_5$ plus H^+ has a value of m/z = 4434.40. A series of minor peaks observed in the spectrum was assignable to the Na^+ adducts. Likewise, the peak at m/z = 4435.5, which was also assumed to be an adduct with H^+, corresponded to $\mathbf{I_L}$ possessing the expected chemical structure with DP_n of 90; $(C_2H_4O) \times 90 + C_{27}H_{38}N_2O_5$ plus H^+ has a value of m/z = 4435.41.

To determine the size of the polymers in a solvent, peak molecular weight by SEC, M_p(SEC), which represents a hydrodynamic volume, was measured. All M_p(SEC) values in the present study are expressed as a linear poly(THF) homopolymer equivalent for the purpose of comparing the PEO and poly(THF) segments.[30] SEC revealed that $\mathbf{I_C}$ and $\mathbf{I_L}$

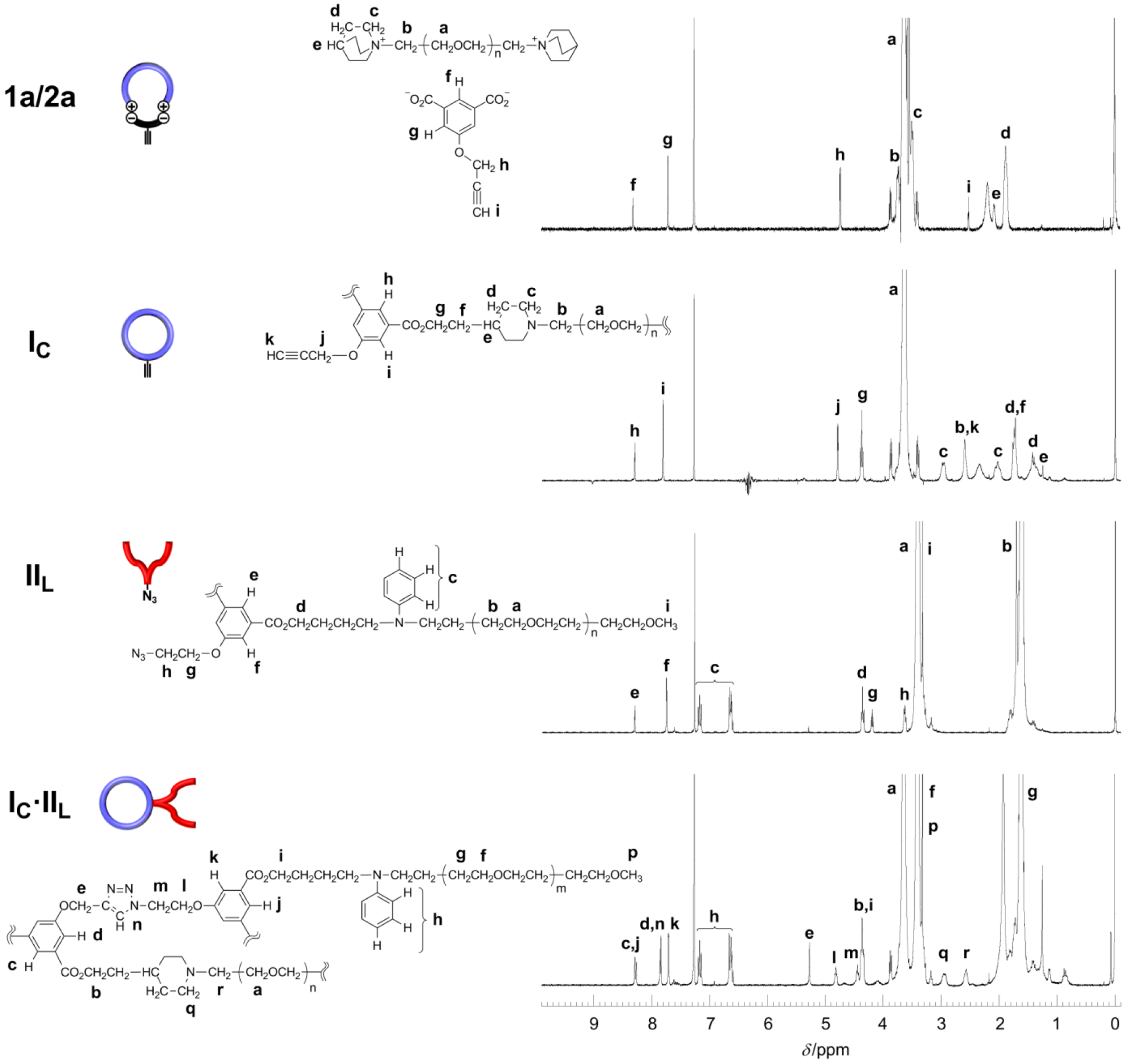


Figure 2. ^{1}H NMR spectra of **1a/2a**, $\mathbf{I_C}$, $\mathbf{II_L}$, and $\mathbf{I_C \cdot II_L}$.

possess M_p(SEC) values of 2.1 and 2.2 kDa[30] with polydispersity index (PDI) values of 1.09 and 1.08, respectively (Figure 4a). The ratio of the M_p(SEC) value of $\mathbf{I_C}$ (2.1 kDa) to that of the corresponding linear starting material, *α*,*ω*-dihydroxy PEO (M_n(NMR) = 4600 and M_p(SEC) = 3.2 kDa),[30] was 0.66, in agreement with the previously reported ratios.[25,26,31,32] On the other hand, the observed M_p(SEC) value for $\mathbf{I_L}$ (2.2 kDa) was almost twice that of the starting material (*α*-hydroxy-*ω*-methoxy PEO with M_n(NMR) = 2000 and M_p(SEC) = 1.2 kDa),[30] indicating that the cyclic topology leads to a decrease in the hydrodynamic volume. $\mathbf{I_C}$ and $\mathbf{I_L}$ were isolated by preparative SEC fractionation to remove the unreacted starting materials and byproducts.

By contrast, *kyklo*- ($\mathbf{II_C}$) and *kentro*-telechelic ($\mathbf{II_L}$) poly(THF) with an azido group was synthesized by the ESA-CF process but using the corresponding *N*-phenylpyrrolidinium-functionalized precursors, as detailed above (Scheme 1a and Figure S1). Thus, *N*-phenylpyrrolidinium-telechelic poly(THF) (**1c/TfO$^-$**) and its *α*-methoxy-*ω*-*N*-phenylpyrrolidinium counterpart of approximately half the length (**1d/TfO$^-$**) were prepared according to the previously reported method.[33] The TfO$^-$ counterions were exchanged with azido-appended dicarboxylate (**2b**) to form **1c/2b** and **1d/2b**. The ionic complexes were refluxed in THF to produce $\mathbf{II_C}$ and $\mathbf{II_L}$, which were characterized by NMR, MALDI TOF-MS, and SEC. SEC revealed that $\mathbf{II_C}$ and $\mathbf{II_L}$ possess M_p(SEC) values of 4.1 and 4.3 kDa, with PDI values of 1.10 and 1.10, respectively (Figure 4a).[30]

The click reaction between the incompatible polymer components of $\mathbf{I_C}$ and $\mathbf{II_C}$ was subsequently performed to selectively produce an 8-shaped amphiphilic block copolymer ($\mathbf{I_C \cdot II_C}$, Scheme 1b and Figure S2). Click chemistry was also applied to $\mathbf{I_L}$ and $\mathbf{II_L}$, $\mathbf{I_L}$ and $\mathbf{II_C}$, and $\mathbf{I_C}$ and $\mathbf{II_L}$. An excess (1.2 equiv) of the poly(THF) prepolymer ($\mathbf{II_C}$ or $\mathbf{II_L}$) was used

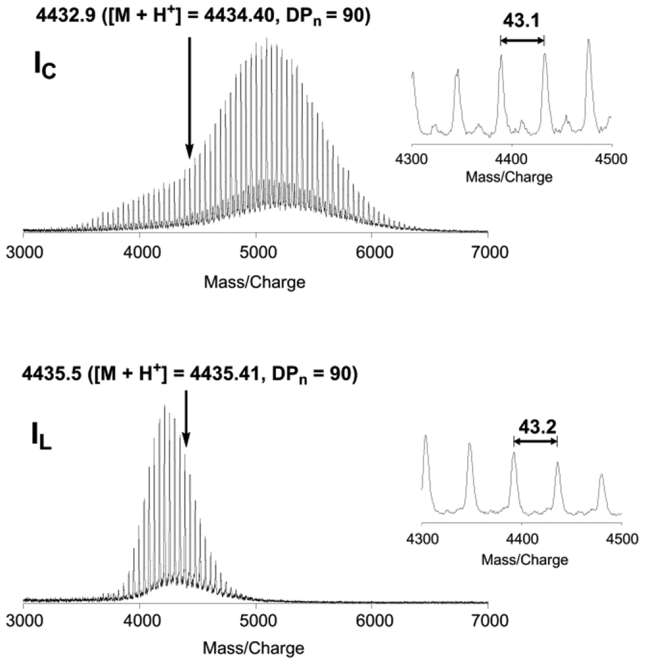


Figure 3. MALDI-TOF mass spectra of $\mathbf{I_C}$ and $\mathbf{I_L}$. DP_n denotes the number of monomer units in the product. Norharmane was used as the matrix.

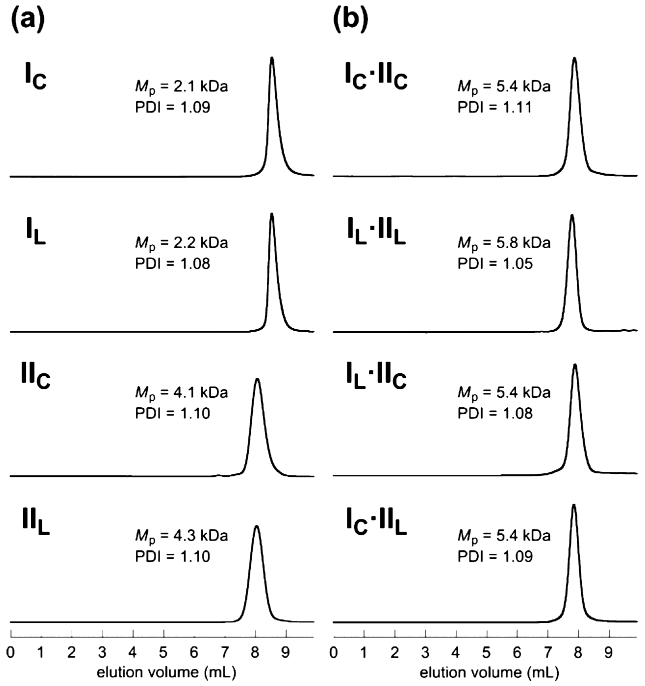


Figure 4. SEC traces of (a) $\mathbf{I_C}$, $\mathbf{I_L}$, $\mathbf{II_C}$, and $\mathbf{II_L}$ and (b) $\mathbf{I_C{\cdot}II_C}$, $\mathbf{I_L{\cdot}II_L}$, $\mathbf{I_L{\cdot}II_C}$, and $\mathbf{I_C{\cdot}II_L}$. The M_p(SEC) values are expressed as a linear poly(THF) homopolymer equivalent for comparison between the PEO and poly(THF) segments.

relative to the PEO counterpart ($\mathbf{I_C}$ or $\mathbf{I_L}$). After the reaction, the unreacted poly(THF) prepolymer was removed by flash column chromatography. Thus, a THF solution of the reaction mixture was loaded on a silica gel column. The unreacted poly(THF) prepolymer was eluted first with THF, and the block copolymer product was retained on the silica gel due to the presence of the PEO segment. Subsequently, other hydrophobic impurities were eluted with *n*-hexane. Finally, the product remaining on the silica gel was collected by elution with dichloromethane/methanol (9/1 vol/vol).

By comparing the ^{1}H NMR spectra of product $\mathbf{I_C{\cdot}II_C}$ with prepolymers $\mathbf{I_C}$ and $\mathbf{II_C}$ as well as those of $\mathbf{I_L{\cdot}II_L}$ with $\mathbf{I_L}$ and $\mathbf{II_L}$, $\mathbf{I_L{\cdot}II_C}$ with $\mathbf{I_L}$ and $\mathbf{II_C}$, and $\mathbf{I_C{\cdot}II_L}$ with $\mathbf{I_C}$ and $\mathbf{II_L}$ (Figures 2, S4, and S6), the selective reaction between the ethynyl and azido groups to form a 1,2,3-triazole group was confirmed. This was observed in that the signals of the propynyl methylene protons ("j" at 4.79−4.80 ppm in $\mathbf{I_C}$ and $\mathbf{I_L}$) and the methylene protons second adjacent to the azido group ("g" at 4.20 ppm in $\mathbf{II_C}$ and $\mathbf{II_L}$) were replaced with those of the methylene protons adjacent to the 4-position ("e" at 5.27−5.29 ppm in $\mathbf{I_C{\cdot}II_C}$, $\mathbf{I_L{\cdot}II_L}$, $\mathbf{I_L{\cdot}II_C}$, and $\mathbf{I_C{\cdot}II_L}$) and second adjacent to the 1-position ("l" at 4.82 ppm in $\mathbf{I_C{\cdot}II_C}$, $\mathbf{I_L{\cdot}II_L}$, $\mathbf{I_L{\cdot}II_C}$, and $\mathbf{I_C{\cdot}II_L}$) of the triazole ring, respectively. Moreover, the signal of the proton at the 5-position of the triazole ring ("n") emerged at 7.86−7.89 ppm in the products.

The SEC traces in Figure 4b demonstrate that the cross-coupled products possess a narrow size distribution (PDI = 1.05−1.11). The observed M_p(SEC) value for $\mathbf{I_C{\cdot}II_C}$ (5.4 kDa), which is expressed as a poly(THF) homopolymer equivalent,[30] was marginally smaller than the sum of those for the precursors, $\mathbf{I_C}$ and $\mathbf{II_C}$ (2.2 kDa + 4.2 kDa = 6.4 kDa).[34] Likewise, the M_p(SEC) values for $\mathbf{I_L{\cdot}II_L}$ (5.8 kDa), $\mathbf{I_L{\cdot}II_C}$ (5.4 kDa), and $\mathbf{I_C{\cdot}II_L}$ (5.4 kDa) were also smaller than the sums of the individual M_p(SEC) values of the prepolymers $\mathbf{I_L}$ and $\mathbf{II_L}$ (2.3 kDa + 4.3 kDa = 6.6 kDa), $\mathbf{I_L}$ and $\mathbf{II_C}$ (2.3 kDa + 4.1 kDa = 6.4 kDa), and $\mathbf{I_C}$ and $\mathbf{II_L}$ (2.2 kDa + 4.3 kDa = 6.5 kDa), respectively.[34] The decrease in the M_p(SEC) values is likely due to a reduction in the hydrodynamic volumes upon the formation of the product polymers with higher topological complexities.[25,26,31,35]

In conclusion, *kyklo*- and *kentro*-telechelic PEO and poly(THF) precursors were obtained by the ESA-CF process. Click chemistry of the precursors effectively produced a set of four types of block copolymers with topological and amphiphilic segment pairs: two amphiphilic block copolymers with symmetric topological forms, that is, an "8" shape ($\mathbf{I_C{\cdot}II_C}$)[36] and a 4-armed star shape ($\mathbf{I_L{\cdot}II_L}$), and two asymmetric forms, that is, two twin-tailed tadpole shapes with the opposite amphiphilic compositions ($\mathbf{I_L{\cdot}II_C}$ and $\mathbf{I_C{\cdot}II_L}$). Considering that the topology-based properties of polymeric materials have recently become an innovative subject in polymer chemistry,[10,11,37−39] the present versatile method would serve as an effective means for the synthesis of a new class of topological solvophilic block copolymers. On the basis of the novel topologies of the amphiphilic block copolymers, we are currently investigating self-assembly and the associated topology effects.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental section, chemical structures, ^{1}H NMR spectra, and MALDI-TOF mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(34) The M_p(SEC) values of $\mathbf{I}_C$, $\mathbf{I}_L$, and $\mathbf{II}_C$ are slightly different from those in Figure 4a due to the use of different batches.

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(36) The MALDI-TOF mass spectrum of $\mathbf{I}_C\cdot\mathbf{II}_C$ (data not presented) showed complex signals at $m/z \sim 8000$ due to the copolymer composition. A series of peaks in a lower molecular weight region assignable to precursor $\mathbf{I}_C$ was also detected despite no residue of $\mathbf{I}_C$ was observed either by the NMR or SEC analysis of the product. We reasoned that MALDI-TOF MS is more sensitive to $\mathbf{I}_C$ due to the lower molecular weight even when the amount is very small. Additionally, due to the chemical structure, the PEO precursor likely had a higher ionization efficiency than the poly(THF) counterpart.

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