Concise Click/ESA-CF Synthesis of Periodically-Positioned Trifunctional \textit{kyklo}-Telechelic Poly(THFs)

Haruna Wada, Takuya Yamamoto, and Yasuyuki Tezuka*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

**ABSTRACT:** A concise two-step click/ESA-CF process has been developed to prepare a \textit{kyklo}-telechelic poly(tetrahydrofuran), poly(THF), having three functional groups at the constant intervals. Thus, a key linear precursor (I), having \(N\)-phenylpyrrolidinium salt groups at the chain ends and having two hydroxyl groups at the prescribed inner positions, has been prepared through the alkyne–azide addition (click) reaction using one unit of a linear telechelic poly(THF) having a pair of an alkyne and a hydroxyl groups (1) and two units of a linear asymmetric telechelic poly(THF) having an azide and an \(N\)-phenylpyrrolidinium salt group (2). The subsequent polymer cyclization by means of an electrostatic self-assembly and covalent fixation (ESA-CF) process, by employing a dicarboxylate counteranion having an additional alkyne group (3) to I, could produce a trifunctional \textit{kyklo}-telechelic poly(THF) (II), having two hydroxyl and one azide groups positioned at the constant intervals along the ring polymer backbone. The subsequent esterification of the hydroxyl groups in II was performed to give a \textit{kyklo}-telechelic poly(THF) having three azide groups at the constant intervals (III), and a further click reaction of III with 2 was conducted to produce a ring polymer product having three emanating graft segments at the constant intervals along the ring unit (IV), i.e., a three-tail tadpole topology.

**INTRODUCTION**

Cyclic polymers are unique in their architectures by their elimination of chain termini in contrast to their linear and branched counterparts.\(^1\)-\(^4\) A remarkable progress has been witnessed in a recent decade to afford a wide range of single cyclic polymers, relied on innovative end-to-end intramolecular linking processes,\(^5\)-\(^8\) as well as on alternative new ring-expansion polymerizations.\(^9\)-\(^13\) And with the use of newly synthesized cyclic polymers having diverse chemical compositions, unprecedented properties and functions by cyclic polymer topologies have now been revealed.\(^1\),\(^4\),\(^14\)

A current synthetic challenge in this growing area has focused on the precision design of cyclic/linear and cyclic/branched as well as multiple cyclic polymer architectures.\(^1\),\(^15\) A class of tailored cyclic and multicyclic polymer precursors having prescribed reactive groups at designated location (positions), i.e., \textit{kyklo}-telechelics, are crucially important to achieve any ambitious synthetic goals.\(^1\),\(^16\),\(^17\) We have so far reported a wide variety of \textit{kyklo}-telechelics having either hydroxyl, alkynyl, alkynyl, or azide groups based upon an electrostatic self-assembly and covalent fixation (ESA-CF) protocol,\(^1\),\(^18\) where linear or branched prepolymers possessing prescribed cyclic ammonium salt end groups, accompanying plurifunctional carboxylate counteranions having additional functional groups, have been employed as key intermediates.

Notably, moreover, the precise positional control of not only single but also plural functional groups in the \textit{kyklo}-telechelics is a critical prerequisite for the step toward tailored construction of complex polymer topologies. A simple ring polymer having ONE functional group at the prescribed position, as well as those having TWO identical or different functional groups at the opposite positions of the ring structure, are readily accessible by the ESA-CF protocol, by using a center-fuctional linear polymer precursor (\textit{centro}-telechelics) obtained with a bifunctional initiator having an additional functional group.\(^19\) A class of a \textit{spiro}-dicyclic (8-shaped) and \textit{spiro}-tricyclic (trefoil-shaped) polymer precursors, having ONE functional group specifically at the core position, has also been introduced and used to produce a double-eight and a double-trefoil polymers.\(^16\)

Furthermore, a series of tandem \textit{spiro}-dicyclic (8-shaped), \textit{spiro}-tricyclic and \textit{spiro}-tetracyclic polymer precursors having TWO functional (alkenyl) groups at the opposite positions of the multiply linked ring units have been designed upon the ESA-CF protocol, and employed for the construction of tri-, tetra, and even pentacyclic multiply-fused polymer topologies.\(^20\)-\(^22\) Also, a new \textit{kyklo}-telechelics having THREE functional (azide) groups positioned at the constant intervals in the ring backbone segment was recently introduced by an iterative alkyne–azide click addition reaction.\(^23\) This trifunctional \textit{kyklo}-telechelics was employed for the subsequent construction of \textit{spiro}-type tetra- and heptacyclic polymer topologies, where a set of end-group transformation processes, i.e., the azidation of bromoalkyl group and the deprotection of alkyne group on the linear polymer precursors, was applied.

**Supporting Information**

Received: August 17, 2015
Published: August 21, 2015

DOI: 10.1021/acs.macromol.5b01818
repeatedly to undergo the click chain extension as well as the final click polymer cyclization.

We report herein an alternative and concise synthetic means to give the kyklo-telechelics having THREE functional groups at the constant intervals, which will be used for the precision synthesis of a variety of complex multicyclic polymers. Thus, we have employed an orthogonal click/ESA-CF process, by utilizing a key linear precursor (I) having an N-phenylpyrrolidinium salt groups at the chain ends and two hydroxyl groups at the prescribed inner positions. (Scheme 1) The alkyne−azide click reaction was applied to obtain I by using a pair of complementary precursors, namely one unit of a linear telechelic poly(THF) precursor having a set of an alkyne and a hydroxyl groups at the both chain ends, and two hydroxyl groups at the prescribed inner positions. (Scheme 1) The alkyne−azide click reaction was applied to obtain I by using a pair of complementary precursors, namely one unit of a linear telechelic poly(THF) precursor having a set of an alkyne and a hydroxyl groups at the both chain ends, and two hydroxyl groups at the prescribed inner positions. (Scheme 1) The subsequent polymer cyclization of I with the ESA-CF process, by introducing a dicarboxylate counteranion having an additional alkyne group (3) by the ion-exchange reaction, could afford a trifunctional kyklo-telechelic poly(THF) (II) having two hydroxyl and one alkyne groups positioned at the constant intervals along the ring polymer backbone.

The synthetic potential of II has subsequently been demonstrated first by the esterification of the hydroxyl groups in II by 4-pentynoic acid to give a kyklo-telechelic poly(THF), III, having three alkyne groups at the constant intervals, and further by the click reaction of III with 2 to give a ring polymer product having three emanating segment along the ring unit, IV, i.e., a three-tail tadpole topology. (Scheme 2)

RESULTS AND DISCUSSION

1. Synthesis of a Periodically-Positioned Trifunctional kyklo-Telechelic Poly(THF). A pair of complementary reactive telechelic poly(THF) precursors, I and 2, have been introduced in this study for the subsequent use in a click/ESA-CF protocol. The prepolymer 1, having a set of alkyne/hydroxyl groups at the both chain ends, was obtained by the end-capping reaction of a living bifunctional poly(THF) precursor having a set of an alkyne and a hydroxyl groups (1) and two units of a linear asymmetric telechelic poly(THF) precursor having an azide and a cyclic ammonium salt groups (2). The subsequent polymer cyclization of I with the ESA-CF process, by introducing a dicarboxylate counteranion having an additional alkyne group (3) by the ion-exchange reaction, could afford a trifunctional kyklo-telechelic poly(THF) (II) having two hydroxyl and one alkyne groups positioned at the constant intervals along the ring polymer backbone.

The 1H NMR analysis of 1 and 2 (Figure 1, top and bottom, respectively) showed the alkyne end group signal at 2.53 ppm for the former and the azidophenyl and N-phenylpyrrolidinium signals at 7.07/8.03 and at around 2.1–2.5 ppm for the latter, respectively. The MALDI−TOF mass spectra of 1 and 2, after
the covalent conversion of pyrrolidinium group with benzoate anions, (Figure 2, top and bottom, respectively) showed a uniform series of peaks with an interval of 72 mass units corresponding to repeating THF units. Moreover, each peak exactly matched the total molar mass of the expected products having the corresponding end groups. Thus, the peak at \( m/z = 2553.6 \) corresponds to the expected chemical structure of \( 1 \) as the Na⁺ adduct with a DP\(_n\) of 30; \((C_4H_8O) \times 30 + C_{22}H_{22}O_5 \) plus Na⁺ = 2552.62. Also, the peak at \( m/z = 2599.2 \), again assumed to be the adduct with Na⁺, corresponds to the expected chemical structure of the covalent conversion derivative of \( 2 \) with a DP\(_n\) of 30; \((C_4H_8O) \times 30 + C_{24}H_{22}N_4O_3 \) plus Na⁺ = 2600.67.

We managed to obtain the listed MALDI−TOF mass spectra of \( 2 \), in particular, and those in Figure 5 shown later, which exhibited sufficient resolution to determine accurately the peak mass values for their characterization, after several attempts to optimize the MALDI−TOF measurement conditions. We could presume that the presence of a trace amount of contamination including SbF\(_6\) anions, initially introduced as counteranions of cyclic ammonium salt end groups of telechelic precursors (the product \( 2 \), Figure 2, bottom), might cause adverse effects on the ionization process in MALDI−TOF condition, as the relevant counterparts derived from CF\(_3\)SO\(_3\) anions (the product \( 1 \), Figure 2, top) gave comparatively well-resolved MALDI−TOF spectra.

The SEC examination indicated that the prepolymer, \( 1 \), recovered just after the reaction, contained a noticeable portion of the higher MW fraction (the broken line in Figure 3A), and was subjected to the preparative SEC fractionation technique for the purification (the solid line in Figure 3A, \( M_p = 2700 \) and PDI = 1.25). The SEC analysis of \( 2 \), performed after the covalent conversion of pyrrolidinium group with benzoate anions, confirmed the comparable MW (\( M_p = 3200 \) (PDI = 1.17) against the prepolymer \( 1 \). (Figure 3, B)

A pair of the complementary reactive prepolymers \( 1 \) and \( 2 \) were then subjected to the alkyne−azide click reaction in the presence of CuSO\(_4\) and sodium ascorbate in THF/water, where 20 % molar excess of \( 2 \) was charged relative to \( 1 \) to complete the reaction. Notably, N-phenylpyrroldinium salt groups in \( 2 \) were retained intact in the course of the reaction. After the column chromatography purification with silica gel, a linear polymer product, \( I \), having two hydroxyl groups at the constant intervals in the interior positions and having two N-phenylpyrroldinium salts end groups, was recovered. (Scheme 1)

The \(^1\)H NMR analysis of \( I \) (Figure 4, top) confirmed the selective click reaction between the alkyne groups in \( 1 \) and the azide group in \( 2 \). Thus, the signals assigned to the ethynyl proton (2.53 ppm) and to the propynyl methylene protons (4.70 ppm) in \( 1 \) were removed and the new signal was emerged at 5.31 ppm assignable to the methylene protons on the triazole ring unit. The IR analysis (Figure S1) showed that the azide absorption at 2094 cm\(^{-1}\) observed in the precursor \( 2 \) became scarcely visible in the product, \( I \), indicating that the click reaction proceeded effectively.

In order to complete the MALDI−TOF mass and SEC characterization of the product \( I \), the covalently converted derivative was prepared by the ring-opening reaction of the N-
phenylpyrrolidinium salt groups with a benzoate anion. The $^1$H NMR analysis (Figure S2) confirmed the effective covalent conversion of the end groups in 1, with the signal of ester methylene protons visible at 4.25 ppm, together with the signals of $N$-phenyl protons on the dialkyl amine unit at around 6.6 and 7.2 ppm, instead of the $N$-phenyl protons on the pyrrolidinium group at around 7.6 ppm observed before the reaction.

The MALDI−TOF mass spectra of 1 after the covalent conversion the pyrrolidinium end groups (Figure 5, top) showed uniformly separated peaks with an interval of 72 mass units corresponding to repeating THF monomer units. Moreover, each peak corresponded exactly to the total molar mass of the expected products having the respective end/interior groups. Thus, the observed peak at $m/z = 7707.6$ corresponds to the covalently converted derivative of 1 as the Na$^+$ adduct with a DP$_n$ of 90; $(C_5H_9O) \times 90 + C_{70}H_{66}N_8O_{11}$ plus Na$^+$ = 7707.99.

The subsequent SEC comparison of the covalent conversion product from 1 with the starting precursors, i.e., 1 and the covalent conversion product from 2, (Figure 3, chart C against phenylpyrrolidinium salt groups with a benzoate anion. The $^1$H NMR analysis (Figure S2) confirmed the effective covalent conversion of the end groups in 1, with the signal of ester methylene protons visible at 4.25 ppm, together with the signals of $N$-phenyl protons on the dialkyl amine unit at around 6.6 and 7.2 ppm, instead of the $N$-phenyl protons on the pyrrolidinium group at around 7.6 ppm observed before the reaction.

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Figure 2. MALDI−TOF mass spectra of (top) a poly(THF) having a pair of an alkyne and an hydroxyl end groups, 1, and (bottom) a poly(THF) having an $N$-phenylpyrrolidinium salt and an azide end groups, 2, measured after the ring-opening reaction of the $N$-phenylpyrrolidinium salt group by a benzoate anion (linear mode, dithranol with sodium trifluoroacetate as a matrix. DP$_n$ denotes the number of monomer units in the products).

Figure 3. SEC traces of [A] a poly(THF) having a pair of an alkyne and an hydroxyl end groups, 1, (Broken and sold lines show those obtained before and after SEC fractionation, respectively.) [B] a poly(THF) having an $N$-phenylpyrrolidinium salt and an azide end groups, 2, measured after the ring-opening reaction of the $N$-phenylpyrrolidinium salt group by a benzoate anion, [C] an alkyne−azide click reaction product, 1, from 1 and 2, measured after the ring-opening reaction of the $N$-phenylpyrrolidinium salt groups by a benzoate anion, and [D] a trifunctional kyklo-telechelic polymer having two hydroxyl and one alkyne groups positioned periodically along the ring polymer backbone, 11, obtained by the ESA-CF process with 1, after introducing a dicarboxylate counteranion having an additional alkyne group, 3 (THF as an eluent with the flow rate of 1.0 mL/min, using a column of TSK G4000HXL).
charts A and B) showed a noticeable peak shift toward the higher molecular weight region to indicate the effective click linking reaction between 1 and 2. Thus, the peak molecular weight for the covalent conversion product from 1 ($M_p = 8900$, PDI = 1.36) was close to the total sum (9100) of the corresponding $M_p$ of 1 ($M_p = 2700$) and twice that of 2 ($M_p = 3200$).

The linear telechelic precursor, I, initially accompanying SbF$_6$ counteranions on two N-phenylpyrrolidinium salt end groups, was subsequently employed for the ESA-CF procedure after the introduction of a dicarboxylate counteranion having an additional alkyne group, 3. (Scheme 1) In this ion-exchange reaction, we employed a stepwise rather than a direct process first from the SbF$_6$ anion to chloride anion by the treatment with brine, to facilitate the subsequent introduction of a dicarboxylate counteranion. Thus, the precipitation of the acetone solution of the pretreated I was conducted into an ice-cooled aqueous solution containing an excess of 3 as a sodium salt form to result in the high ion-exchange yield (87%).

The $^1$H NMR analysis of the ion-exchanged product, 1/3, (Figure 4, middle) showed the signals assignable to the dicarboxylate counteranion, 3, at 7.75/8.47 as well as 2.54 ppm and the high ion-exchange yield was confirmed from the signal intensity ratio. The obtained ionic product I/3 was then heated
pyrrolidinium salt units. The covalent product, II, was isolated after the silica gel column chromatography in 58% yield.

The $^1$H NMR comparison of II against I/3 (Figure 4, bottom and middle, respectively) confirmed the ESA-CF polymer cyclization to proceed effectively. Thus, the broad methylene proton signal due to the pyrrolidinium ring unit in I/3 observed at around 3.8–4.2 ppm was removed after the reaction, and an alternative triplet signal due to the ester methylene protons became visible at 4.25 ppm, though with overlapping by other ester methylene proton signals. In addition, the N-phenyl proton signal on the pyrrolidinium unit in I/3 observed at around 7.4–7.7 ppm was replaced by the two-set of signals at around 6.6–6.7 and 7.2 ppm in II after the ESA-CF process. The signal of ethynyl proton remained visible at 2.53 ppm.

Moreover, the MALDI–TOF mass analysis of II (Figure 5, middle) showed the peak at $m/z = 7683.4$, corresponding to the expected chemical structure of II as the Na$^+$ adduct with a DP$_n$ of 90; $(C_4H_8O)\times 90 + C_{57}H_{50}N_8O_{12} + Na^+ = 7683.92$.

Finally, the SEC of the cyclized product II in comparison with the linear precursor I (Figure 3, charts D and C, respectively) indicated that the apparent peak MW, $M_n$, of the former (7600) was reduced to 0.85 of the latter (8900), to support the polymer cyclization.

### 2. Reactions of a Periodically-Positioned Trifunctional kyklo-Telechelic Poly(THF).

The synthetic potential of the periodically positioned trifunctional kyklo-telechelic precursor II has subsequently been demonstrated by the selective transformation of functional groups (Scheme 2) Thus, first, the kyklo-telechelics II was subjected to the esterification reaction with 4-pentyenoic acid, to give the product III having THREE alkyne groups at the constant intervals along the cyclic backbone chain.

The $^1$H NMR spectrum of III (Figure 6, top) showed the pentynoyl methin group signal at around 2.5 ppm, together with the ester methylene group signal at 5.05 ppm, by replacing the hydroxymethylene signal visible at 4.67 ppm in II. (Figure 4, bottom)

The MALDI–TOF mass analysis of III (Figure 5, bottom) showed the peak at $m/z = 7843.4$, corresponding to the expected chemical structure of III as the Na$^+$ adduct with a DP$_n$ of 90; $(C_4H_8O)\times 90 + C_{57}H_{50}N_8O_{12} + Na^+ = 7844.10$. The observed mass increase of 161.0 from the precursor II, the peak at $m/z = 7683.4$ (Figure 5, middle), coincides with the two pentynoyl units introduced to II by the esterification. Moreover, the SEC comparison of III against II (Figure 7, top and middle, respectively) confirmed that the respective two profiles were intact during the course of the esterification, to indicate the absence of the chain decomposition under the applied condition.

Finally, the click reaction of the trifunctional kyklo-telechelic precursor II with a linear prepolymers having azide end groups, 2, was conducted to produce a topologically unique polymer IV having a three-tail tadpole form. (Scheme 2) Thus, the precursor III was allowed to react with an excess molar amount of 2 in the presence of a catalyst system of CuSO$_4$ and sodium ascorbate. The product of IV was recovered as a crude form through the column chromatography with silica gel, and was subsequently isolated by the preparative SEC fractionation technique.

The $^1$H NMR inspection of the product IV itself together with its covalently converted derivative (Figure 6, middle and bottom, respectively) showed commonly signals due to the
triazole proton at around 8.2 ppm, by replacing the ethynyl proton signal at around 2.5 ppm observed in III (Figure 6, top), to indicate the selective click linking reaction of III, having three alkyne units, with the linear precursor 2, having an azide end group.

The SEC the covalently converted derivative of IV in comparison with III (Figure 7, bottom and middle, respectively) showed the distinct peak shift toward the higher molecular weight region ($M_p = 13600$, PDI = 1.11), while the value is comparatively smaller than the sum (17200) by one unit of II ($M_p = 7600$) and three units of 2 ($M_p = 3200$). This might correspond to the combined contraction effect by the branch and cyclic structures.
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**Figure 7.** SEC traces of (top) a trifunctional kyklo-telechelics having two hydroxyl and one alkyne groups positioned periodically along the ring polymer backbone, (middle) a trifunctional kyklo-telechelics having three alkyne groups positioned periodically along the ring polymer backbone, III, and (bottom) the product IV, obtained after an alkyne−azide click reaction product of III with 2, measured after the ring-opening reaction of the N-phenylpyrrolidinium salt group by a benzoate anhydride (THF as an eluent at the flow rate of 1.0 mL/min, a column of TSK G4000HXL).

**EXPERIMENTAL SECTION**

**Materials.** 1-Propargyloxy-3,5-bis(hydroxymethyl)benzene, 4-azidobenzoyl chloride, N-phenylpyrrolidinyl, and 5-propargyloxyisophthalate, as well as its sodium salt 3, were synthesized by the method reported before. THF (Kanto Chemical Co., Inc.) was distilled over Na wire. Trifluoromethanesulfonic anhydride (triflic anhydride) (98%, Nacalai Tesque, Inc.) was distilled from P2O5 just before use. Sodium azide (60% oil dispersion, Nacalai Tesque, Inc.) was used after washing by hexane twice and by THF once. Silver hexafluoroantimonate(V) (98%, Aldrich), sodium ascorbate (98.0+%, Wako pure Chemical Industries, Ltd.), CuSO4·SH2O (99.5+%, Wako pure Chemical Industries, Ltd.), 1-ethyl-3-(3-dimethylamino)propyl)carbodiimide hydrochloride (EDAC, > 98.0%, Tokyo Chemical Industry Co., Ltd.), 4-dimethylamino pyridine (DMAP, > 99.0%, Tokyo Chemical Industry Co., Ltd.), 4-pentynoic acid (98%, Acros Organics) were used as received. WakoSil C-300 (Wako Pure Chemical Industries, Ltd.) was used for flash chromatography.

**Synthesis of a Linear Poly(THF) Having a Pair of Hydroxyl and Alkyne Groups at Both Ends (I).** Into a flame-dried flask, THF (50 mL) was introduced to maintain the temperature at 25 °C. Thereupon, trifluoromethanesulfonic anhydride (50 µL, 0.30 mmol) was added, and the mixture was stirred for 4 min. The terminating reagent, prepared separately by the treatment of 1-propargyloxy-3,5-bis(hydroxymethyl)benzene (1.14 g, 5.94 mmol) with sodium hydride (2.38 mg, 5.94 mmol) in THF solution (50 mL), was then added into the polymerization solution, and the mixture was stirred for further 10 min. After removing the unreacted THF by evaporation, the residue was washed by a 3 M aqueous HCl and brine. The product was extracted with CH2Cl2 and the solution was placed in a dry ice/acetone bath to remove the precipitates by the filtration. After removing CH2Cl2 by evaporation, the residual product was reprecipitated twice from acetone into hexane placed in a dry ice/methanol bath. The product was washed by a 3 M aqueous HCl and brine. The product was extracted with CH2Cl2, and the solution was placed in a dry ice/acetone bath to remove the precipitates by the filtration. After removing CH2Cl2 by evaporation, the residual product was reprecipitated twice from acetone into hexane placed in a dry ice/acetone bath. The product was isolated in a yield of 347 mg. (Mw(NMR) = 2.7 kDa, Mw(SEC) = 2.7 kDa).

**Synthesis of a Linear Poly(THF) Having an Azide and an N-Phenylpyrrolidinium Salt End Group (2).** Into a flame-dried flask was prepared a THF solution (30 mL) containing a weighed amount of 4-azidobenzoyl chloride (91 mg, 0.50 mmol) at 0 °C, and a THF solution (5 mL) containing a silver hexafluoroantimonate (155 mg, 450 µmol) was added. The polymerization of THF was allowed to proceed under stirring for 8 min. Thereafter, a measured amount of N-phenylpyrrolidinyl (0.50 mL, 3.38 mmol) was added, and the mixture was stirred for further 2 h. After removing AgCl by the filtration, removing the unreacted THF by evaporation, the residual product was reprecipitated twice from acetone into hexane placed in a dry ice/acetone bath. The product was isolated in a yield of 800 mg. The Mw of the product was determined by the SEC measurement after the ring-opening reaction of the N-phenylpyrrolidinium salt end group of 2 with a benzoate anion (Mw(NMR) = 2.3 kDa, Mw(SEC) = 3.2 kDa, PDI = 1.17).

**Synthesis of a Linear Poly(THF) Having an Azide and an N-Phenylpyrrolidinium Salt End Group (2).** Into a flame-dried flask was prepared a THF solution (30 mL) containing a weighed amount of 4-azidobenzoyl chloride (91 mg, 0.50 mmol) at 0 °C, and a THF solution (5 mL) containing silver hexafluoroantimonate (155 mg, 450 µmol) was added. The polymerization of THF was allowed to proceed under stirring for 8 min. Thereafter, a measured amount of N-phenylpyrrolidinyl (0.50 mL, 3.38 mmol) was added, and the mixture was stirred for further 2 h. After removing AgCl by the filtration, removing the unreacted THF by evaporation, the residual product was reprecipitated twice from acetone into hexane placed in a dry ice/acetone bath. The product was isolated in a yield of 800 mg. The Mw of the product was determined by the SEC measurement after the ring-opening reaction of the N-phenylpyrrolidinium salt end group of 2 with a benzoate anion (Mw(NMR) = 2.3 kDa, Mw(SEC) = 3.2 kDa, PDI = 1.17).

We have demonstrated herein a concise synthetic process of a kyklo-telechelics having THREE functional groups at the constant intervals. Thus, we have introduced a key linear polymer precursor having an N-phenylpyrrolidinium salt groups at the chain ends and two hydroxyl groups at the prescribed inner positions, which was obtained though the alkyne−azide click reaction by using a pair of complementary precursors, namely one unit of a linear telechellic precursor having a set of an alkyne and a hydroxyl groups and two units of a linear asymmetric telechellic precursor having an azide and a pyrrolidinium salt groups. The ESA-CF polymer cyclization technique was then applied by the subsequent introduction of a dicarboxylate counteranion having an additional alkyne group, to produce a trifunctional kyklo-telechelics having two hydroxyl and one alkyne groups positioned at the constant intervals, along the ring polymer backbone. The synthetic potential of this new type of kyklo-telechelics was subsequently been demonstrated first by the synthesis of another kyklo-telechellic derivative having three alkyne groups at the constant intervals, and further by the click synthesis of a novel ring polymer product with a three-tail tadpole topology. A new class of kyklo-telechelics will be accessible by the concise synthetic protocol shown by this work, and they will be utilized in the future to construct a broader range of complex polymer topologies in order to put forward the current frontier of synthetic polymer chemistry.

**CONCLUSION**

We have demonstrated herein a concise synthetic process of a kyklo-telechelics having THREE functional groups at the constant intervals. Thus, we have introduced a key linear polymer precursor having an N-phenylpyrrolidinium salt groups at the chain ends and two hydroxyl groups at the prescribed inner positions, which was obtained though the alkyne−azide click reaction by using a pair of complementary precursors, namely one unit of a linear telechellic precursor having a set of an alkyne and a hydroxyl groups and two units of a linear asymmetric telechellic precursor having an azide and a pyrrolidinium salt groups. The ESA-CF polymer cyclization technique was then applied by the subsequent introduction of a dicarboxylate counteranion having an additional alkyne group, to produce a trifunctional kyklo-telechelics having two hydroxyl and one alkyne groups positioned at the constant intervals, along the ring polymer backbone. The synthetic potential of this new type of kyklo-telechelics was subsequently been demonstrated first by the synthesis of another kyklo-telechellic derivative having three alkyne groups at the constant intervals, and further by the click synthesis of a novel ring polymer product with a three-tail tadpole topology. A new class of kyklo-telechelics will be accessible by the concise synthetic protocol shown by this work, and they will be utilized in the future to construct a broader range of complex polymer topologies in order to put forward the current frontier of synthetic polymer chemistry.
87% ion-exchange yield, in which a trace amount of water was
produced under stirring at ambient temperature for 36 h. Acetone was
then added to the reaction mixture to remove the precipitates by
filtration. After the evaporation to remove the solvents, the residual
product was subjected to silica gel column chromatography
first with acetone/hexane (1/2 v/v), and with acetone. The product I
was isolated in a yield of 114 mg. The M₈ of the product I was determined
by the SEC measurement after the ring-opening reaction of the
N-phenylpyrrolidinum salt end group with a benzoate anion (M₈(NMR) =
8.6 kDa, M₈(SEC) = 8.9 kDa, PDI = 1.36).

1H NMR of I (CDCl₃, δ): 1.33–1.78 (m, CH₂CH₂O), 1.83–2.27
(m, 4H, exo-NCH₂CH₂), 2.26–2.47 (m, 4H, endo-NCH₂CH₂),
2.54 (s, 1H, OCH₂CH₂), 3.20–3.58 (m, CH₂CH₂O), 3.82–4.17
(m, 8H, exo-NCH₂), 4.25 (t, 4H, COOCH₂), 4.48 (s, 4H, ArCH₂O),
4.62–4.81 (m, 6H, ArCH₂OH, OCH₂CH₂), 5.31 (s, 4H, OCH₂-triazole),
5.72–6.16 (m, 6H, Ar–H ortho and para to OCH₂–triazole), 7.38–
7.57 (m, 4H, Ar–H ortho and para to OCH₂–triazole), 7.84–
7.88 (d, 4H, J = 8.6 Hz, Ar–H ortho to triazole), 8.12–8.30
(m, 6H, Ar–H ortho to COO, triazole-H).

Synthesis of a Cyclic Poly(THF) Having Periodically Positioned
Alkylene and Hydroxyl Groups (II). A CHCl₃ solution of I (114 mg, 13
μmol) was treated first with brine in order to facilitate the subsequent introduction of
dicarboxylic counteranion. An acetic solution of the modified product II was then added dropwise into an ice-cooled (< 5°C)
aqueous solution (13 mL) containing sodium salt of dicarboxylate 3
(50 mg, 189 μmol) under vigorous stirring for 30 min, to proceed the
ion-exchange reaction. The precipitated product was then collected by
filtration and dried in vacuo to give the product (1/3, 107 mg) with
87% ion-exchange yield, in which a trace amount of water was
allowed to proceed at reflux for 21 h. The reaction product was
extracted with CH₂Cl₂ and treated with a 3 M aqueous HCl, with a
saturated aqueous NaHCO₃ solution, and finally with brine. After
the collected organic phase was concentrated under reduced pressure, the product III was isolated in a yield of 34 mg by means of the
fractionation with a preparative SEC apparatus (Japan Analytical
Industry Co., Ltd. LC-908 equipped with two columns, JAIGEL-3H
and JAIGEL-2H, and CHCl₃ as an eluent at 3.5 mL/min) (M₈(NMR) =
8.9 kDa, M₈(SEC) = 7.5 kDa, PDI = 1.26).

1H NMR of III (CDCl₃, δ): 1.26–1.86 (m, CH₂CH₂O), 2.34–2.64
(m, 11H, OCH₂CH₂, ArCH₂OCH₂CH₂, ArCH₂OCH₂CH₂OCH₂, OCH₂CH₂CH₂), 3.15–3.52 (m, CH₂CH₂O, ArN(CH₃), 4.18-
4.37 (m, 8H, ArCOOCH₂), 4.44 (s, 4H, ArCH₂O), 4.68 (s, 4H, OCH₂CH₂),
5.05 (s, 4H, ArCH₂O), 5.24 (s, 4H, OCH₂–triazole), 6.48–6.67 (m, 6H, Ar–H ortho and para to NCH₃), 6.79–
7.04 (m, 6H, Ar–H ortho and para to OCH₂–triazole), 7.04–7.17
(m, 4H, Ar–H meta to NCH₃), 7.60–7.72 (m, 4H, Ar–H ortho to OCH₂CH₂), 7.79 (d, 4H, J = 8.4 Hz, Ar–H ortho to triazole), 8.02–
8.30 (m, 7H, triazole-H, Ar–H meta to triazole, Ar–H para to
OCH₂CH₂).

Synthesis of a Three-Tail Tadpole Polymer Product (IV). Into a
THF/water (4/1.0 in mL/mL) solution in a flask a weighed amount of the product III (31 mg, 3.5 μmol) and 2 (43 mg, 19 μmol) were added CuSO₄·5H₂O (21 mg, 82 μmol) and sodium
ascorbate (33 mg, 165 μmol). The resulted suspension solution was
subjected to three cycles of the freeze–pump–thaw treatment, and the reaction was allowed to proceed under stirring at ambient temperature for 42 h. Acetone was then added to the reaction mixture to remove the
precipitates by the filtration. After the evaporation to remove the
solvents, the residual product was subjected to silica gel column chromatography first with acetone/hexane (1/2 v/v), and with acetone. The three-tail tadpole polymer product IV was isolated in a yield of 47 mg. The M₈ of the product IV was determined by the SEC after the ring-opening reaction of the N-phenylpyrrolidinum salt end group with a benzoate anion (M₈(NMR) = 17.8 kDa, M₈(SEC) = 13.6
kDa, PDI = 1.11).

1H NMR of IV (CDCl₃, δ): 1.32–1.79 (m, CH₂CH₂O), 2.08–2.28
(m, 6H, exo-NCH₂CH₂), 2.28–2.45 (m, 6H, endo-NCH₂CH₂),
2.75–3.00 (m, 4H, CH₂CH₂–triazole), 3.23–3.59 (m, CH₂CH₂O,
ArN(CH₃), 3.70–3.83 (m, 6H, exo-NCH₂), 4.19–4.52 (m, 18H,
endo-NCH₂, CH₂OCH₂Ar, triazole–ArCOCH₂CH₂, ArCOOCH₂CH₂CH₂CH₂,)
5.03 (s, 4H, COOCH₂), 5.36 (s, 6H, ArCOCH₂–triazole), 6.68–7.02 (m, 6H, Ar–H ortho and para to
CH₂OCH₂CH₂), 7.34–7.71 (m, 25H, CH₂NAr–H), 7.71–7.98
(m, 12H, Ar–H ortho to triazole, Ar–H ortho to CO₂CH₂ and
ortho to triazole–CH₂OCH₂), 8.10–8.18 (m, 16H, triazole-H, Ar–H meta to
triazole, Ar–H ortho to CO₂CH₂ and CO₂CH₂).

Measurements. 1H NMR spectra were obtained with a JEOL
JNM-AL300 spectrometer at 300 MHz with CDCl₃ as a solvent. SEC
measurements were conducted by a Tosoh model CCP5 at 40 °C
with a column of TSK G4000HXL and with a refractive index detector
model RI 8020. An eluent was THF at the flow rate of 1.0 mL/min.
The molecular weight, M₈(SEC), values were estimated by the
 calibration of polystyrene standard samples with the conversion factor
of 0.536 for poly(THF). MALDI–TOF mass measurements were
 conducted with a Shimadzu AXIMA Performance spectrometer by
 using a nitrogen laser (λ = 337 nm). In the spectrometer operation, an
 accelerating potential of 20 kV in a linear positive ion mode was
 employed with pulsed ion extraction. A solution sample was prepared by mixing a THF solution (10 μL, 10 mg/mL) of a polymer specimen,
 a THF solution (100 μL, 20 mg/mL) of dithranol, and a THF solution
 (100 μL, 10 mg/mL) of sodium trilaurate, and a portion of the
 mixture solution was deposited on a sample target plate. Mass values
 were calibrated by the four-point method using SpheriCal dendrimer
calibrants (Polymer Factory, Sweden), at 3636.44, 4816.89, 5997.34,
and 7263.87 Da (dendrimer plus Na⁺).
REFERENCES


ACKNOWLEDGMENTS

This work was supported partly by KAKENHI (Grants 26288099, 15H01595 and 15K13703 to T.Y., and 26310206 to Y.T.)

AUTHOR INFORMATION

Corresponding Author
*(Y.T.) E-mail ytezuka@o.cc.titech.ac.jp.

Notes
The authors declare no competing financial interest.