

Synthesis and palladium-mediated cross-coupling reaction of cyclic (*kyklo-*) and open-chain (*kentro-*) telechelic precursors

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Received 10 May 2007; received in revised form 15 June 2007; accepted 20 June 2007

Available online 5 July 2007

Dedicated to Professor Teiji Tsuruta on the occasion of his 88th birthday (Beiju).

Abstract

A series of uniform-size, cyclic poly (THF)s having a bromophenyl (**1a**), a pentynoyl (**1b**) and a phenylboronate (**1c**) group, together with their open-chain, center-functional counterparts having the relevant functional group (**2a** and **2b**), have been prepared in high yields through the esterification of a hydroxyl group of a cyclic (*kyklo-*) and an open-chain (*kentro-*) telechelic precursors. They were subsequently subjected to palladium-mediated, Sonogashira and Suzuki coupling reactions, i.e., **1a** and **1b** as well as **2a** and **2b** for the former, and **1a** and **1c** for the latter, respectively. SEC showed that the Sonogashira process could produce effectively the corresponding cross-coupling products, i.e., an 8-shaped and a 4-armed star polymer, respectively. The Suzuki process, on the other hand, failed to proceed under examined conditions.

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Keywords: Sonogashira reaction; 8-shaped polymer; 4-armed star polymer; Telechelic polymer; Cyclic polymer

1. Introduction

Precise control of polymer topologies has been an ongoing challenge in synthetic polymer chemistry. Hence a variety of new branched, cyclic, multicyclic as well as cyclic-branched hybrid polymer structures have been constructed continuously by intriguing synthetic protocols [1–6]. Nevertheless, a most straightforward means to construct complex polymer architectures remains to be a selective coupling reaction of two complementary polymer precursors having relevant reactive groups at the designated positions.

We have recently proposed a novel synthetic protocol for cyclic, multicyclic as well as cyclic-branched hybrid polymers, optionally having functional groups, such as olefinic or hydroxyl groups at the prescribed positions in these nonlinear polymer constructions [4,7,8]. Moreover, we have demonstrated that polymer precursors having olefinic groups could undergo effective inter- and intramolecular metathesis condensation reactions in the presence of a Grubbs catalyst, to produce unique multicyclic polymer topologies, including an 8-shaped and a δ -graph constructions [9–11]. It should be noted, however, that the synthetic scope of the metathesis process is limited by that the condensation of two different polymer precursors produces concurrently homo- and hetero-coupling

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products. Therefore, it is desirable to develop an alternative polymer reaction process to afford exclusively the hetero cross-coupling product from the two different polymer precursors having complementary reactive groups.

Thus in the present study, we have newly synthesized a series of cyclic and open-chain polymer precursors specifically designed for the palladium-mediated, Sonogashira [12,13] and Suzuki [14–18] coupling reactions. These processes have widely been applied as a versatile hetero cross-coupling means not only in the organic synthesis of complex chemical compounds but also in functional polymer synthesis, by taking advantage of their high efficiency as well as tolerance to the copresence of functional groups. In particular, the Sonogashira process was found to be effective for the preparation of the hetero cross-coupling products from the two relevant polymer precursors.

2. Experimental

2.1. Materials

A cyclic and open-chain poly(THF) having a hydroxyl group were prepared by the method detailed before [19,20]. 4-Bromobenzoyl chloride (Aldrich, 98%) was used as received. 4-Pentynoyl chloride was prepared by the reaction of 4-pentynoic acid (Aldrich, 95%) and thionyl chloride (Kokusai Chemical Co., Ltd., 99.98%) in 40% yield after the distillation under reduced pressure (43 °C/18 mm Hg). 4-Pinacolboranyl benzoyl chloride was prepared by the reaction of 4-pinacolboranyl benzoic acid (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzoic acid), (Aldrich, 97%) and thionyl chloride in 95% yield after evacuation of the volatile reagents. Tetrakis(triphenylphosphine)palladium (Aldrich, 99%) and copper iodide (Aldrich, 99.999%), were used as received. Diisopropylamine (Aldrich, 99%) was distilled over calcium hydride. Other reagents were used as received otherwise noted.

2.2. Synthesis of a cyclic poly(THF) having a bromophenyl group (**1a**)

4-Bromobenzoyl chloride (17.9 mg, 1.68×10^{-2} mmol) was added into a THF solution (2 mL) containing 99.5 mg (1.68×10^{-2} mmol) of a cyclic poly(THF) having a hydroxyl group (M_n (NMR) = 5.9×10^3 , PDI < 1.2) and triethylamine (26.9 mg, 2.67×10^{-1} mmol) at 5 °C. After 1 h, the

reaction mixture was added dropwise into water (<5 °C), and the precipitated product was isolated by filtration and dried in vacuo. The product was then subjected to the preparative TLC with silica gel (Merck, silicagel PF₂₅₄) with *n*-hexane/acetone (65/35 in vol/vol) as an eluent. The yield was 52.5 mg.

¹H NMR (300 MHz, CDCl₃): δ 1.50–1.80 (m, CH₂CH₂O), 3.25–3.50 (m, CH₂CH₂O), 4.38 (t, *J* = 6.0 Hz, 4H CO₂CH₂), 6.64 (m, 6H NPh *o,p*-H), 7.16 (m, 4H NPh *m*-H), 7.67 (d, *J* = 8.1 Hz, 2H Ar-H meta to Br), 8.05 (d, *J* = 8.4 Hz, 2H Ar-H ortho to Br), 8.05 (s, 2H Ar-H ortho to OCO), 8.59 (s, 1H Ar-H para to OCO).

2.3. Synthesis of a cyclic poly(THF) having a pentynoyl group (**1b**)

4-Pentynoyl chloride (9.7 mg, 8.32×10^{-2} mmol) was added dropwise into a THF solution (8 mL) containing 104.8 mg (1.77×10^{-2} mmol) of a cyclic poly(THF) having a hydroxyl group (M_n (NMR) = 5.9×10^3 , PDI < 1.2) and triethylamine (27.8 mg, 2.75×10^{-1} mmol) at 5 °C. After 1 h, the reaction mixture was added dropwise into water (<5 °C). The precipitated product was isolated by filtration and dried in vacuo. The product was then subjected to the preparative TLC with silica gel (Merck, silicagel PF₂₅₄) with *n*-hexane/acetone (65/35 in vol/vol) as an eluent. The yield was 51.9 mg.

¹H NMR (300 MHz, CDCl₃): δ 1.50–1.80 (m, CH₂CH₂O), 2.04 (s, 1H \equiv CH), 2.63 (m, 2H \equiv CCH₂), 2.84 (t, *J* = 7.8 Hz, 2H COCH₂), 3.25–3.50 (m, CH₂CH₂O), 4.37 (t, *J* = 6.9 Hz, 4H CO₂CH₂), 6.65 (m, 6H NPh *o,p*-H), 7.17 (m, 4H NPh *m*-H), 7.93 (s, 2H Ar-H ortho to OCO), 8.54 (s, 1H Ar-H para to OCO).

2.4. Synthesis of a cyclic poly(THF) having a phenylboronate group (**1c**)

4-Pinacolboranyl benzoyl chloride (31.2 mg, 1.17×10^{-2} mmol) in 1 mL of THF was added dropwise into a THF solution (4 mL) containing 93.5 mg of a cyclic poly(THF) having a hydroxyl group (M_n (SEC) = 4.2×10^3 , PDI < 1.2) and triethylamine (16 μ L) at 5 °C. After 14 h, the reaction mixture was added dropwise into water (<5 °C). The precipitated product was isolated by filtration and dried in vacuo. The product was then subjected

to the preparative TLC with silica gel (Merck, silica-gel PF₂₅₄) with *n*-hexane/ethyl acetate (1/1 in vol/vol) as an eluent. The yield was 45.9 mg.

¹H NMR (300 MHz, CDCl₃): δ 1.37 (s, 12H CH₃C), 1.50–1.80 (m, CH₂CH₂O), 3.25–3.50 (m, CH₂CH₂O), 4.38 (t, J = 6.0 Hz, 4H CO₂CH₂), 6.63 (m, 6H NPh *o,p*-H), 7.17 (m, 4H NPh *m*-H), 7.96 (d, J = 8.1 Hz, 2H Ar-H meta to B), 8.17 (d, J = 8.1 Hz, 2H Ar-H ortho to B), 8.03 (s, 2H Ar-H ortho to OCO), 8.59 (s, 1H Ar-H para to OCO).

2.5. Synthesis of an open-chain poly (THF) having a bromophenyl group (2a)

4-Bromobenzoyl chloride (31.5 mg, 1.44×10^{-2} mmol) was added into a THF solution (2 mL) containing 155.6 mg (2.85×10^{-2} mmol) of an open-chain poly(THF) having a hydroxyl group (M_n (NMR) = 5.5×10^3 , PDI < 1.2) and triethylamine (43.6 mg, 4.31×10^{-1} mmol) at 5 °C. After 1 h, the reaction mixture was added dropwise into water (<5 °C), and the precipitated product was isolated by filtration and dried in vacuo. The product was subjected to the preparative TLC with silica gel (Merck, silica-gel PF₂₅₄) with *n*-hexane/acetone (65/35 in vol/vol) as an eluent. The yield was 99.3 mg.

¹H NMR (300 MHz, CDCl₃): δ 1.50–1.80 (m, CH₂CH₂O), 3.25–3.50 (m, CH₂CH₂O), 4.52 (s, 4H PhCH₂), 7.11 (s, 2H Ar-H meta to OCO), 7.18 (s, 1H Ar-H para to OCO), 7.64 (d, J = 8.7 Hz, 2H Ar-H meta to Br), 8.03 (d, J = 9.0 Hz, 2H Ar-H ortho to Br).

2.6. Synthesis of an open-chain poly(THF) having a pentynoyl group (2b)

4-Pentynoyl chloride (65.6 mg, 5.63×10^{-1} mmol) was added dropwise into a THF solution (8 mL) containing 600.3 mg (1.10×10^{-1} mmol) of an open-chain PTHF having a hydroxyl group (M_n (NMR) = 5.5×10^3 , PDI < 1.2) and triethylamine (151.9 mg, 1.50 mmol) at 5 °C. After 1 h, the reaction mixture was evaporated and added dropwise into water (<5 °C). The precipitated product was isolated by filtration and dried in vacuo. The yield was 577 mg.

¹H NMR (300 MHz, CDCl₃): δ 1.50–1.80 (m, CH₂CH₂O), 2.03 (s, 1H \equiv CH), 2.61 (m, 2H \equiv CCH₂), 2.79 (m, 2H COCH₂), 3.25–3.50 (m, CH₂CH₂O), 4.48 (s, 4H PhCH₂), 6.91 (s, 2H Ar-H meta to OCO), 7.00 (s, 1H Ar-H para to OCO).

2.7. Synthesis of an 8-shaped poly(THF) by Sonogashira reaction between 1a and 1b

A THF solution (4 mL) containing **1a** (44.1 mg, 7.46×10^{-3} mmol), **1b** (44.2 mg, 7.49×10^{-3} mmol), tetrakis(triphenylphosphine)palladium (8.2 mg, 7.10×10^{-3} mmol), copper iodide (0.7 mg, 3.62×10^{-3} mmol) in benzene (1 mL) and diisopropylamine (7.7 mg, 1.30×10^{-1} mmol) was stirred for 72 h under reflux. After the reaction mixture was evacuated under reduced pressure, the product mixture was subjected to the preparative SEC fractionation by means of JAI Model LC-908W apparatus with a refractive index detector Model RI-5, using a tandem set of two JAIGEL-3H-AF columns. The eluent was THF at a flow rate of 3.5 mL/min. The purified sample was recovered by evaporating the solvent, and a stabilizer for SEC eluent, i.e., 2,6-di-*tert*-butyl-4-methylphenol, was finally removed by the precipitation of the product into acetone cooled at –78 °C. The yield was 46.6 mg. A portion (30.8 mg) of the product was further purified by the recycling SEC to yield 11.6 mg of the 8-shaped polymer product.

2.8. Synthesis of a 4-armed-star poly(THF) by Sonogashira reaction between 2a and 2b

A THF solution (4 mL) containing **2a** (40.1 mg, 7.43×10^{-3} mmol), **2b** (39.7 mg, 7.27×10^{-3} mmol), tetrakis(triphenylphosphine)palladium (8.5 mg, 7.63×10^{-3} mmol) in THF (0.5 mL), copper iodide (0.2 mg, 1.05×10^{-3} mmol) in benzene (0.5 mL) and diisopropylamine (9.4 mg, 1.57×10^{-1} mmol) was stirred for 24 h under reflux. After the reaction solution was evacuated under reduced pressure, the product mixture was subjected to the SEC analysis to monitor the coupling reaction.

2.9. Measurements

¹H NMR spectra were recorded on a JEOL JNM-AL300 apparatus in CDCl₃. The proton chemical shift (ppm) was referenced to the signal of tetramethylsilane. Size exclusion chromatography (SEC) measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020 and a UV detector model UV 8020 at 254 nm. A column of TSK G3000HXL (300 mm \times 7.8 mm i.d., 5 μ m average particle size) was employed with THF as an eluent at a flow rate 1.0 mL/min at 40 °C. In a typical pro-

cedure, 40 μL of sample solution (sample concentration of 0.5 wt.%) was injected. MALDI-TOF mass spectra were taken on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser ($\lambda = 337 \text{ nm}$) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by a linear-positive ion mode. The sample polymer solution (1 g/L) was prepared in THF. The matrix, 1,8-dihydroxy-9(10H)-anthracenone (dithranol, Aldrich) and sodium trifluoroacetate (Aldrich), was dissolved in THF (10 and 1 g/L, respectively). The polymer solution (50 μL) was then mixed with 50 μL of the matrix solution. A 1 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature. Mass volume were calibrated by the three-point method with insulin plus H^+ at 5734.62, insulin β plus H^+ at 3497.96 and α -cyanohydroxycinnamic acid dimer plus H^+ at 379.35.

3. Results and discussion

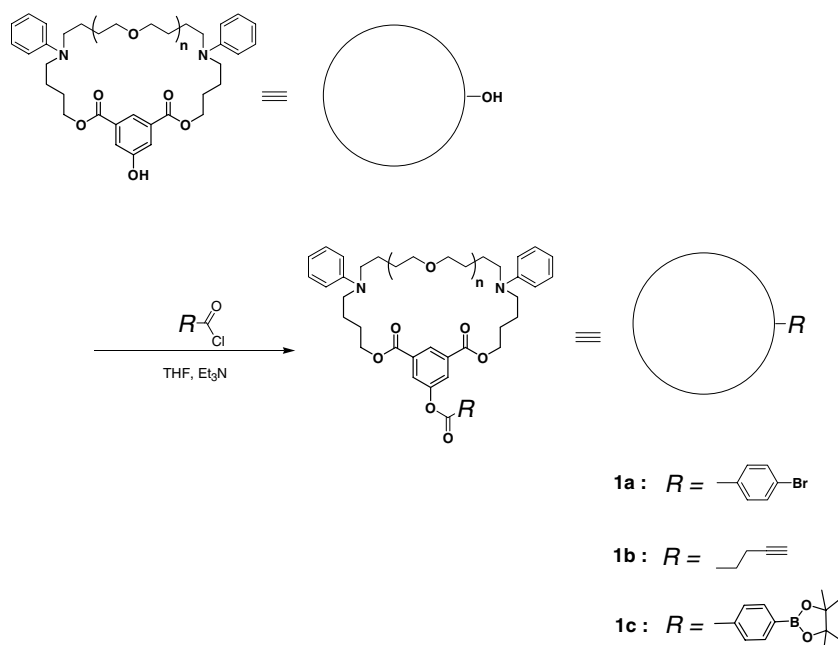
3.1. Synthesis of cyclic poly(THF)s having bromophenyl (**1a**), pentynoyl (**1b**) and phenylboronate (**1c**) groups

A series of cyclic poly(THF)s having bromophenyl (**1a**), pentynoyl (**1b**) and phenylboronate (**1c**)

groups were prepared from a cyclic precursor having a hydroxyl group reported before [19]. (Scheme 1) The subsequent esterification reaction was performed with equimolar amount of the corresponding acid chlorides (4-bromobenzoyl chloride, 4-pentynoyl chloride and 4-pinacolboranyl benzoyl chloride, respectively, either obtainable commercially or prepared from the corresponding free acids) in THF at 5 °C in the presence of triethylamine [21]. The esterification products, **1a**, **1b** and **1c**, were recovered after purification by silica-gel chromatography in 70%, 50% and 49% yield, respectively. These products were fully characterized by means of ^1H NMR and MALDI-TOF mass techniques.

^1H NMR spectra of **1a**, **1b** and **1c** (Fig. 1) showed the signals attributed to the bromophenyl group at 7.67 and 8.05 ppm, to the pentynoyl group at 2.04 (due to an alkyn proton), 2.63 and 2.84 ppm, and to the phenylboronate group at 1.37, 7.96 and 8.17 ppm, respectively, together with those due to the initiator fragment and the linking group signals of the cyclic polymer precursor.

MALDI-TOF mass spectra of **1a**, **1b** and **1c**, (Fig. 2) showed a uniform series of peaks corresponding to poly(THF) (peak interval of 72 mass units), and each peak corresponds exactly to the molar mass summing up the initiator fragment and the linking group, respectively. Thus for **1a**, the peak (assumed to be the adduct with Na^+) at



Scheme 1. Synthesis of cyclic (kyklo-) telechelic poly(THF)s.

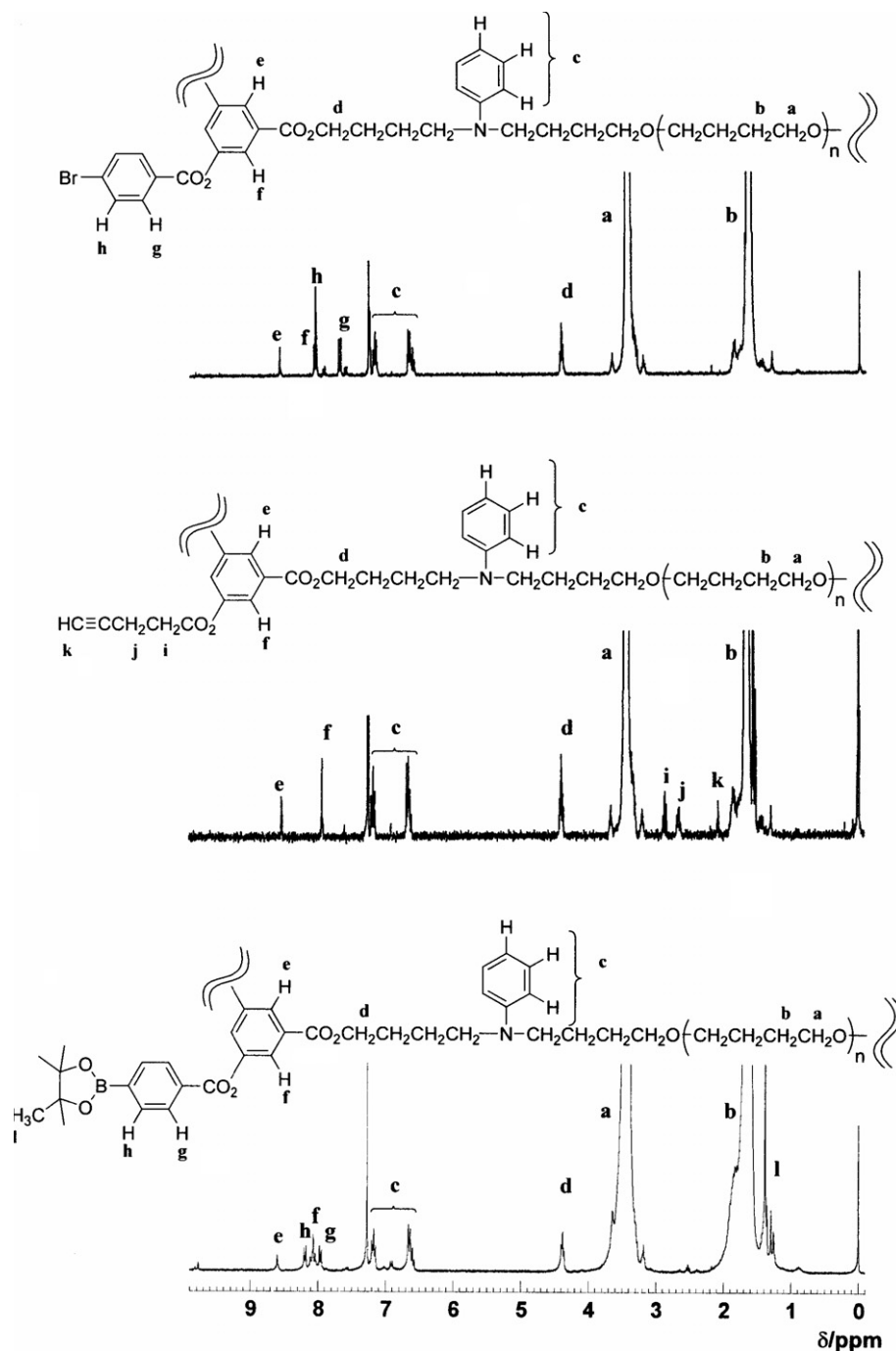


Fig. 1. 300 MHz ^1H NMR spectra of cyclic poly(THF)s having a bromophenyl group, **1a**, (top), a pentynoyl group, **1b**, (middle) and a phenylboronate group, **1c**, (bottom), respectively. (CDCl_3 , 40°C).

5063.6 corresponds to the expected cyclic product having a bromophenyl group, with the DP_n of 60, $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_{39}\text{H}_{41}\text{N}_2\text{O}_6\text{Br}$, plus Na^+ as 5063.10. For **1b** having a pentynoyl group, on the other hand, showed the peak (assumed to be the adduct with Na^+) at 4959.8 corresponding to the

DP_n of 60, $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_{37}\text{H}_{42}\text{N}_2\text{O}_6$, plus Na^+ as 4960.18. Finally for **1c** having a phenylboronate group, the peak (assumed to be the adduct with Na^+) at 5110.6 corresponding to the DP_n of 60, $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_{45}\text{H}_{53}\text{N}_2\text{O}_8\text{B}$, plus Na^+ as 5109.84.

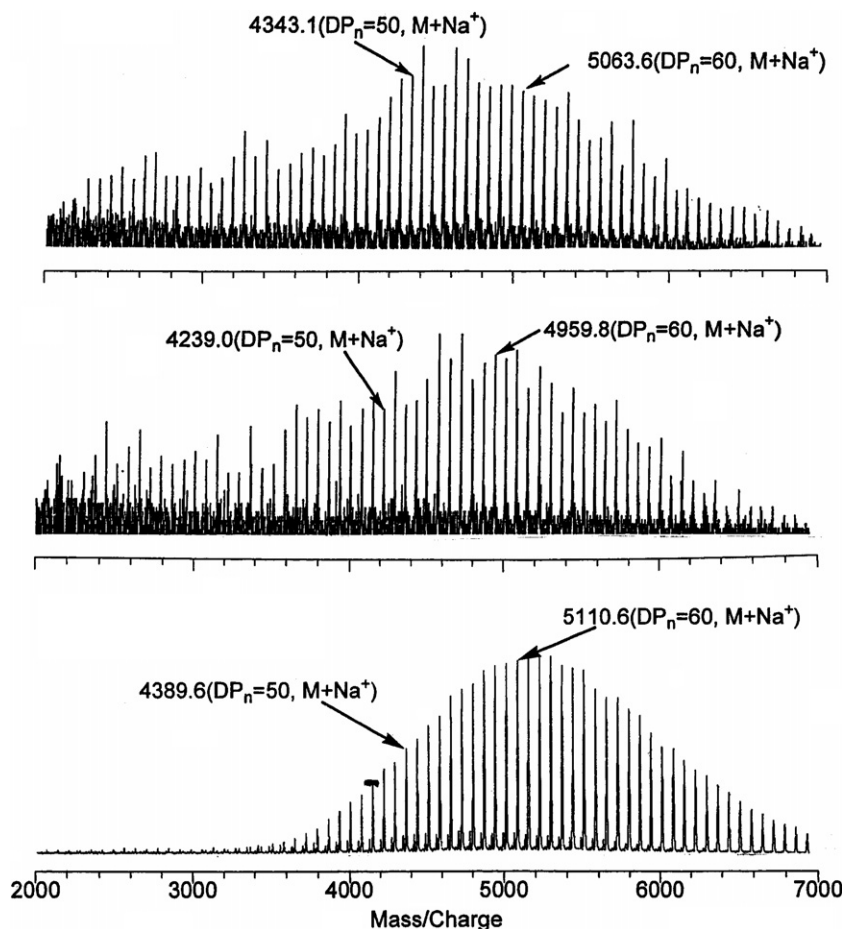


Fig. 2. MALDI-TOF mass spectra of cyclic poly(THF)s having a bromophenyl group, **1a**, (top), a pentynoyl group, **1b**, (middle) and a phenylboronate group, **1c**, (bottom), respectively. (linear mode, matrix: dithranol with sodium trifluoroacetate).

SEC (Fig. 5A: top and middle, respectively) showed that the esterification products, **1a** and **1b**, retained their narrow size distributions ($PDI < 1.2$) as in the precursor having a hydroxyl group, to show the absence of polymer chain degradation during the esterification procedure.

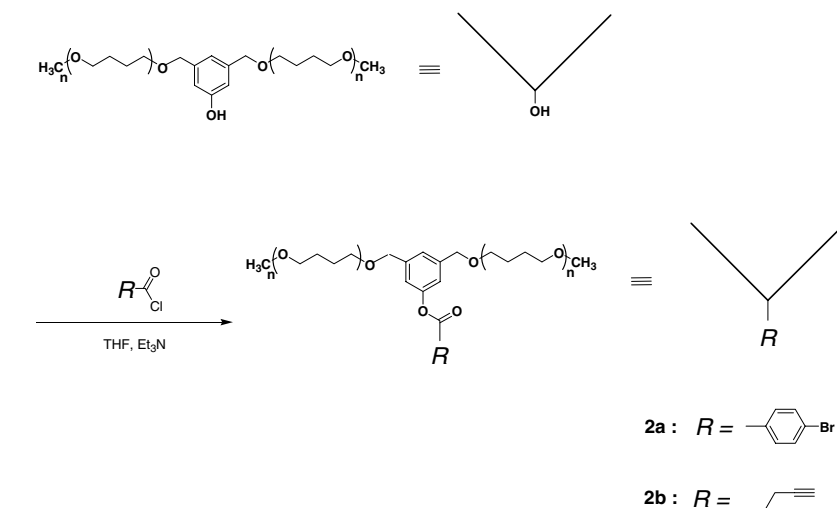
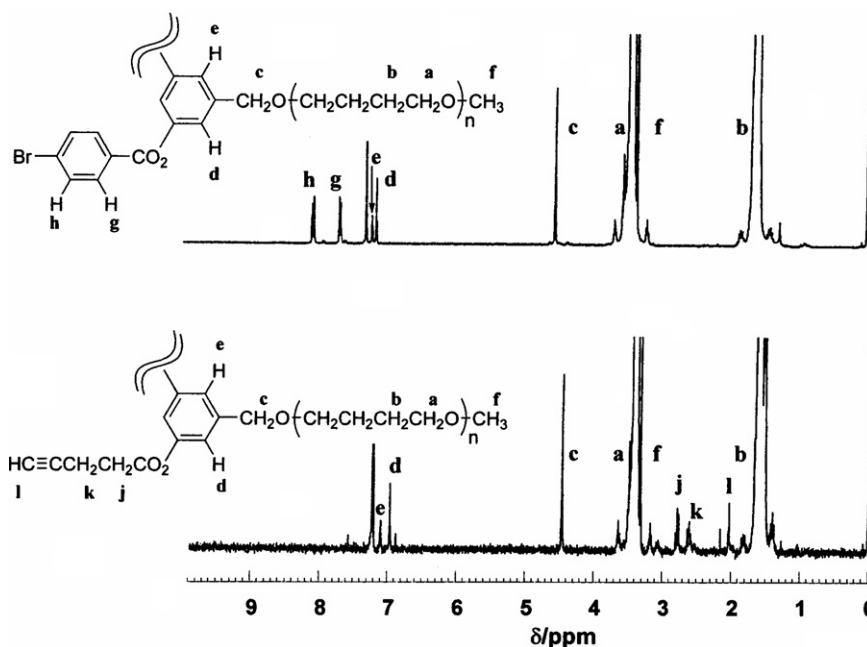
3.2. Synthesis of open-chain poly(THF)s having bromophenyl (**2a**) and pentynoyl (**2b**) groups

A series of open-chain, center-functional poly(THF)s having bromophenyl (**2a**) and pentynoyl (**2b**) groups, respectively, were also prepared from the corresponding precursor having a hydroxyl group obtainable by a functional initiator method [20] (Scheme 2). The subsequent esterification reaction was performed as detailed in the preceding section. The esterification products, **2a** and **2b** were recovered after purification by silica-gel

chromatography in 58% and 96% yield, respectively. These products were then characterized by means of ^1H NMR and MALDI-TOF mass techniques.

^1H NMR spectra of **2a** and **2b** (Fig. 3) showed the signals attributed to the bromophenyl group at 7.65 and 8.05 ppm, and to the pentynoyl group at 2.03 (due to an alkyn proton), 2.78 and 2.61 ppm, respectively, together with those due to the initiator fragment and the linking group of the open-chain polymer precursor.

MALDI-TOF mass spectra of **2a** and **2b** (Fig. 4) again showed a uniform series of peaks corresponding to poly(THF) (peak interval of 72 mass units), and each peak corresponds exactly to the molar mass summing up the initiator fragment and the linking group, respectively. Thus for **2a**, the peak (assumed to be the adduct with Na^+) at 4715.4 corresponds to the open-chain product having a bromophenyl group, **2a**, with the DP_n of 60,

Scheme 2. Synthesis of open-chain (*kentro*-) telechelic poly(THF)s.Fig. 3. 300 MHz ^1H NMR spectra of open-chain poly(THF)s having a bromophenyl group, **2a**, (top), and a pentynoyl group, **2b**, (bottom), respectively. (CDCl_3 , 40 $^\circ\text{C}$).

$(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_{17}\text{H}_{17}\text{O}_4\text{Br}$, plus Na^+ as 4714.65. For **2b** having a pentynoyl group, on the other hand, showed the peak (assumed to be the adduct with Na^+) at 4612.3 corresponding to the DP_n of 60, $(\text{C}_4\text{H}_8\text{O}) \times 60 + \text{C}_{15}\text{H}_{18}\text{O}_4$, plus Na^+ as 4611.73.

SEC (Fig. 5B: top and middle, respectively) showed that the esterification products, **2a** and **2b**, retained their narrow size distributions ($\text{PDI} < 1.2$) as in the precursor having a hydroxyl group, to

show the absence of polymer chain degradation during the esterification procedure.

3.3. Palladium-mediated cross-coupling reaction of cyclic (*kyklo*-) and open-chain (*kentro*-) telechelic poly(THF)s

The two standard palladium-mediated, cross-coupling processes, i.e., Sonogashira and Suzuki

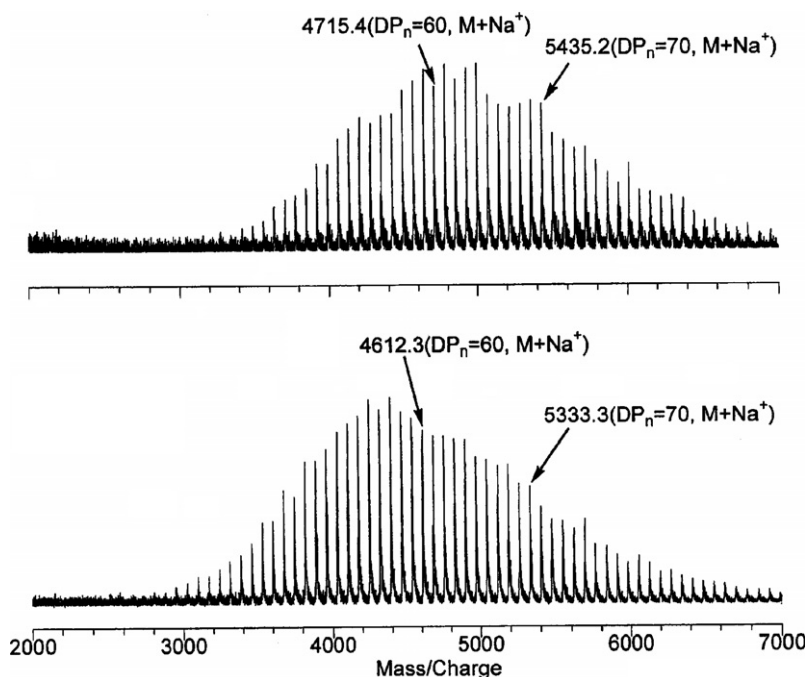


Fig. 4. MALDI-TOF mass spectra of open-chain poly(THF)s having a bromophenyl group, **2a**, (top), and a pentynoyl group, **2b**, (bottom), respectively. (linear mode, matrix: dithranol with sodium trifluoroacetate).

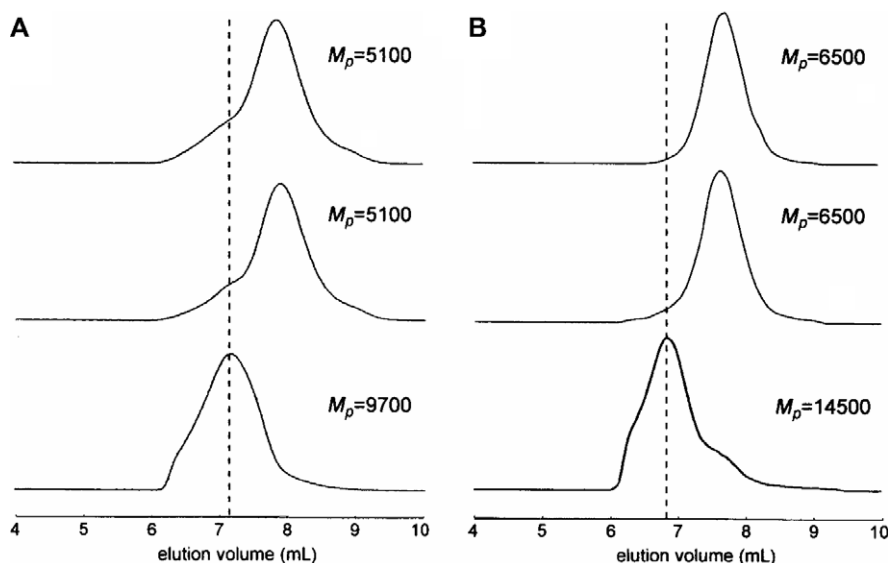
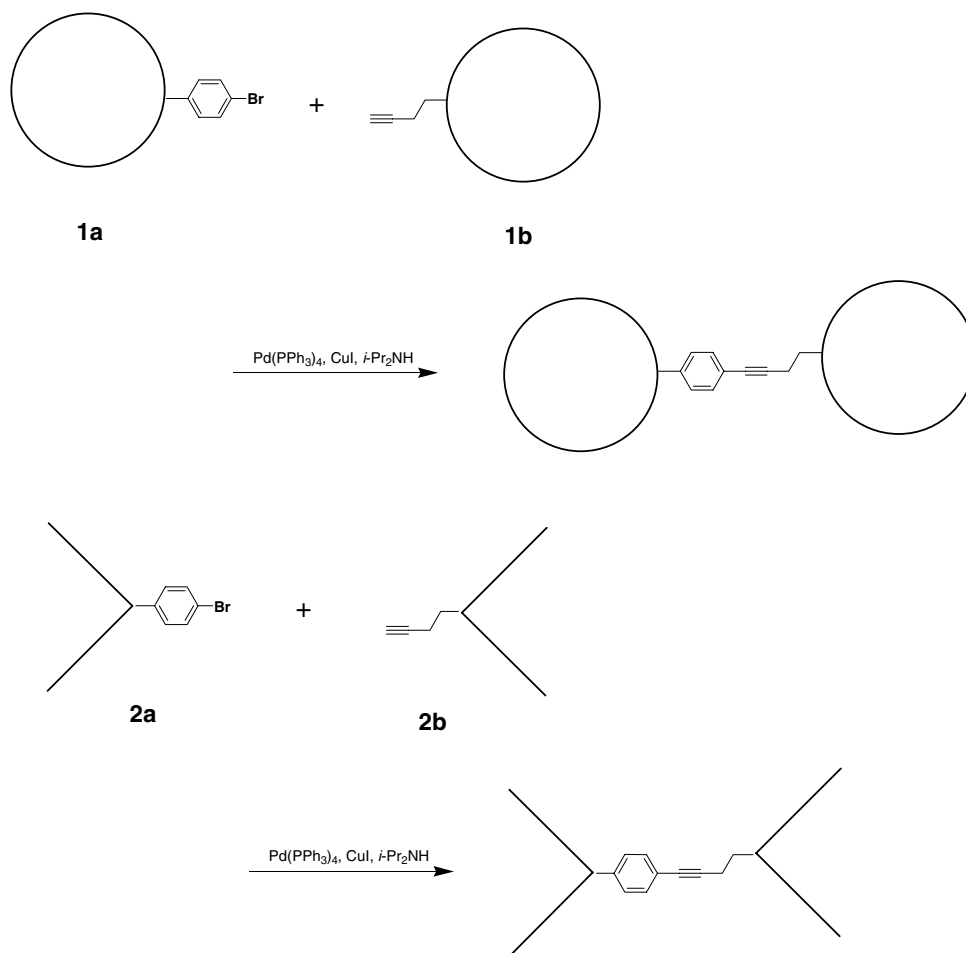


Fig. 5. SEC traces of A: cyclic poly(THF) precursors having a bromophenyl group, **1a**, (top), and a pentynoyl group, **1b**, (middle) and a Sonogashira coupling product (bottom) after the purification by SEC fractionation, and B: open-chain poly(THF) precursors having a bromophenyl group, **2a**, (top), and a pentynoyl group, **2b**, (middle) and a Sonogashira coupling product (bottom). (TSKG3000HXL, eluent: THF 1.0 ml/min).

reactions, have been employed in the present study, by using the above-described cyclic and open-chain precursors having complementary reactive groups. Thus first, the cyclic precursors **1a** and **1b**, as well as the open-chain counterparts **2a** and **2b**, were sub-

jected to the Sonogashira reaction [22] to produce an 8-shaped and a four-armed star polymer, respectively. (Scheme 3) The progress of the reaction could be monitored conveniently by SEC, as the coupling product possesses distinctively higher molecular



Scheme 3. Sonogashira Coupling Reaction of Cyclic and Open-chain Poly(THF) Telechelic Precursors.

weight than that of the precursors. (Fig. 5A and B, respectively) Indeed, the M_p (the peak molecular weight by SEC) of the product (9.7×10^3) obtained by the reaction between **1a** and **1b** was nearly twice of those of the precursors (5.1×10^3). Also, the M_p of the product (14.5×10^3) obtained from **2a** and **2b** was marginally higher than twice of those of the precursors (6.5×10^3). The linking structure, i.e., a phenylacetylene group, formed by Sonogashira reaction is considered to be stiff and extended, and hence could cause the expansion of the hydrodynamic volume of the resulted 8-shaped as well as 4-armed star polymers, otherwise having contracted three-dimensional sizes in comparison with the linear analogue of the same chain length.

It is remarkable that the Sonogashira reaction proceeds even in the equimolar reaction of the two polymer precursors at low concentration of reactive groups, and regardless of the chain topologies of the precursors. And a nearly pure (SEC) 8-shaped cou-

pling product was recovered after purification by SEC preparative fractionation (Fig. 5, A: bottom). From a series of experiments, it has been shown also that the dose of the catalyst as high as an equimolar quantity against the reactive groups was needed to promoted the reaction, that the reflux temperature in THF was required as the reaction at room temperature was prohibitively slow, and that the prolonged reaction time after 24 h was not remarkably effective to increase the coupling product yield.

^1H NMR analysis of the product showed the serious line-broadening of the signals due to the phenylacetylene linking group positioned at a focal point of four polymer segments. This is accounted for by that the segmental motion of the linking group is strongly suppressed to cause rapid T_2 relaxation. MALDI TOF mass analysis was unsuccessful upto now, as the molar masses of the product samples were over 10,000.

The Suzuki coupling reaction between **1a** and **1c** was then attempted under varying such conditions as the dose of the catalyst, the relative charge ratio of the two precursors, the type of base components and the reaction time and temperature. SEC could not show, unfortunately, any noticeable fraction due to the coupling product, but the degradation of the precursors under harsh conditions.

In conclusion, a series of uniform-size, cyclic poly(THF)s having a bromophenyl, a pentynoyl and a phenylboronate group, together with their open-chain counterparts having the relevant functional group, have been prepared in high yields. The subsequent Sonogashira coupling reaction between the relevant cyclic and open-chain polymer precursors proceeded effectively to produce the corresponding hetero cross-coupling products, i.e. an 8-shaped and a 4-armed star polymer, respectively.

Acknowledgement

Authors are grateful to Professor M. Kakimoto for our access to the NMR apparatus. A financial support from Eno Science Foundation is gratefully acknowledged. This work was supported partly by a grant from the Ministry of Education, Culture, Sports, Science and Technology, Japan (17350054).

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