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Reactive & Functional Polymers 67 (2007) 1233–1242

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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.

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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doi:10.1016/j.reactfunctpolym.2007.06.013

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 (Kokusan 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) $= 5.9 \times 10^3$, 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 PF_{254}) with *n*-hexane/acetone (65/35 in vol/vol) as an eluent. The yield was 52.5 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50–1.80 (m, CH_2CH_2O), 3.25–3.50 (m, CH_2CH_2O), 4.38 (t, $J = 6.0$ Hz, 4H CO_2CH_2), 6.64 (m, 6H N*Ph o,p-H*), 7.16 (m, 4H N*Ph 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) $= 5.9 \times 10^3$, 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 PF_{254}) with *n*-hexane/acetone (65/35 in vol/vol) as an eluent. The yield was 51.9 mg.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.50–1.80 (m, CH_2CH_2O), 2.04 (s, 1H $\equiv CH$), 2.63 (m, 2H $\equiv CCH_2$), 2.84 (t, $J = 7.8$ Hz, 2H $COCH_2$), 3.25–3.50 (m, CH_2CH_2O), 4.37 (t, $J = 6.9$ Hz, 4H CO_2CH_2), 6.65 (m, 6H N*Ph o,p-H*), 7.17 (m, 4H N*Ph 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) $= 4.2 \times 10^3$, PDI < 1.2) and triethylamine (16 μL) 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