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Mg-mediated Copolycondensation of α,α-Dibromotoluene with Bifunctional Electrophiles

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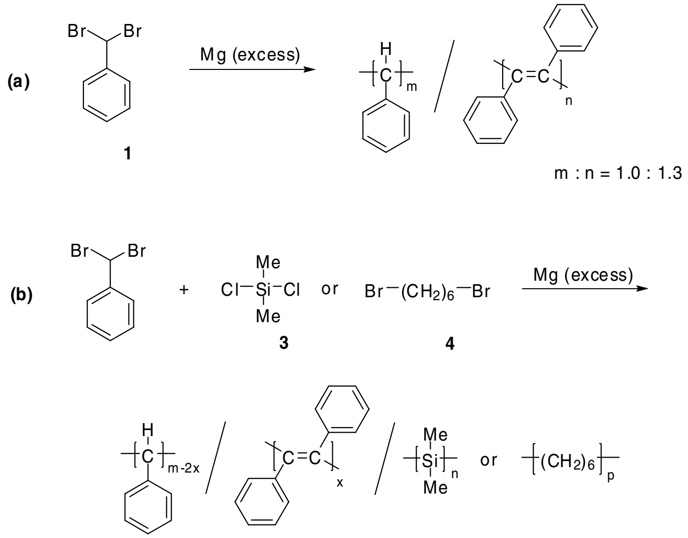
Summary

Copolycondensation of α,α-dibromotoluene (**1**) with α,α'-dibromo-*p*-xylylene (**2**) was found to proceed in the presence of excess Mg via nucleophilic substitution of *in situ* generated Grignard reagents to Br-bearing benzylic carbons. The use of dichlorodimethylsilane (**3**) and 1,6-dibromohexane (**4**) as a comonomer in the ternary copolycondensation with **1** and **2** was effective to give higher molecular weight polymers by improving their solubility. In the series of the copolycondensation, the copolymer with the highest M_n of 8480 was obtained in a 41% yield by the reaction of a feed ratio of [**1**]:[**2**]:[**4**] = 1:1:1 in THF at room temperature.

Introduction

Recently, we have found that α,α-dibromotoluene (**1**) can be polymerized by the reaction with excess Mg to afford a new polymer where each main chain carbon has a phenyl group (Scheme 1a) [1]. Nucleophilc substitution of *in situ* generated bezylic Grignard reagents to Br-bearing carbons was proposed to be propagation, and C=C bonds were formed in the main chain via abstraction of HBr during the propagation. Copolymerization of **1** with dichlorodimethylsilane (**3**) and 1,6-dibromohexane (**4**) also proceeded successfully (Scheme 1b) [1]. However, because of the occurrence of some inevitable side reactions, the (co)polymerization using **1** as a (co)monomer gave rather low molecular weight polymers (M_n < 2000). Although the polymerization of **1** can be regarded as a new method for synthesis of unique polymer structures, the low molecular weight of the products would limit the further application, which prompts us to develop methods for obtaining higher molecular weight polymers derived from **1**.

One of the strategy to obtain higher M_n polymers using **1** as a comonomer would be the use of binfunctional electrophiles with higher reactivity than those of **3** and **4**. Herein, we chose α,α'-dibromo-*p*-xylylene (**2**) [2] as such a reactive comonomer and examined the copolycondensation with **1** under various conditions.



Scheme 1. Homopolymerization of α,α-dibromotoluene (**1**) (a), and copolymerization of **1** with dichlorodimethylsilane (**3**) or 1,6-dibromohexane (**4**) (b).

Experimental

General

^{1}H (400 MHz) NMR spectra were recorded on a Brucker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform-*d* ($CDCl_3$) at 50°C. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-Bowin system (ver. 1.50) equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with polystyrene standards (Aldrich, M_n = 4000, M_w/M_n = 1.07, and M_n = 740, M_w/M_n = 1.04). The column used for the GPC analyses were Styragel HR2 (Waters; 300 mm x 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 20K for polystyrene). Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm x 20 mm i.d., exclusion molecular weight of 70 K for polystyrene) and a JAIGEL-2H (600 mm x 20 mm i.d., exclusion molecular weight of 20 K for polystyrene) using $CHCl_3$ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation.

Materials

THF was dried over Na/K alloy, and distilled before use. After the surface of magnesium (Wako, >98%) was washed with 1 N aqueous HCl solution, H_2O, and MeOH, it was dried under vacuum before use. *α,α*-Dibromotoluene (Acros, 97%) were dried over $CaCl_2$ and used without further purification. Dichlorodimethylsilane (**3**) (Nacalai, 98%) and 1,6-dibromohexane (**4**) (Nacalai, 95%) were dried over CaH_2

and used without further purification. α,α‘-Dibromo-*p*-xylylene (**2**) (TCI, >98%) was used as received. CuBr(PPh$_3$) was prepared according to the literature [3].

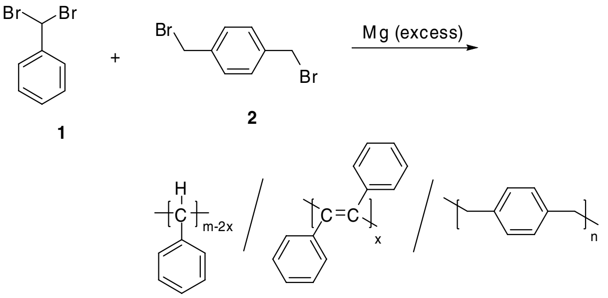
Copolycondensation

As a typical procedure for the copolycondensation, the procedure for run 5 in Table 2 is described as follows. Under nitrogen atmosphere, Mg (0.352 g, 14.5 mmol) and THF (8 mL) were placed in a Schlenk tube, and cooled to 0 °C. α,α-Dibromotoluene (**1**) (0.20 mL, 1.2 mmol), dimethyldichlorosilane (**3**) (0.15 mL, 1.2 mmol), and a THF (17 mL) solution of α,α‘-dibromo-*p*-xylylene (**2**) (0.958g, 3.63 mmol) were consecutively added at 0 °C, and the mixture was stirred at the temperature for 1h, then at room temperature for 15 h. After the volatiles were removed under reduced pressure, 1 N HCl aqueous solution (40 mL) and chloroform (40 mL) were added, and the mixture was stirred until the remaining Mg completely reacted with the acid. The organic layer was separated unig a separatory funnel, and the aqueous phase was extracted with chloroform (30 mL x 2). The combined organic layer was washed with 1 N HCl aqueous solution (40 mL) and water (40 mL), dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure to afford a crude product. Purification with preparative recycling GPC gave the copolymer as a yellow solid in a 34% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ -0.2-0.6 (CH$_3$Si), 1.9-2.7 (benzylic-H), 2.7-3.6 (benzylic-H), 6.6-7.6 (aromatic-H). Other copolycondensations were carried out in similar procedures. Copolymers from **1** and **2**. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.3-3.6 (benzylic-H), 6.2-7.7 (aromatic-H). Copolymers from **1**, **2**, and 1,6-dibromohexane (**4**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.6-1.5 (-[CH$_2$]$_6$-), 2.4-3.4 (benzylic-H), 6.2-7.6 (aromatic-H).

Results and Discussion

Magnesium-Mediated Copolycondensation of α,α-Dibromotoluene (1) with α,α‘-Dibromo-p-xylylene (2)

First of all, copolycondensation of α,α-dibromotoluene (**1**) with α,α‘-dibromo-*p*-xylylene (**2**) was examined in the presence of excess amount of Mg (Scheme 2), which was fixed to [**1**] x 6 + [**2**] x 2. For example, a THF solution of a mixture of **1** and **2** ([**1**]:[**2**] = 5:1) was added to Mg (32 equiv with respect to the total concentration of the monomers) in THF, and the mixture was reacted at room temperature for 15 h to give a polymeric product, whose GPC-estimated M_n (polystyrene standards) was 1630 (run 1 in Table 1). ^{1}H NMR spectrum (Figure 1) of the sample soluble in organic solvents such as CHCl$_3$ and THF exhibits a broad signal assignable to the benzylic protons at 2.3 ~ 3.6 ppm along with a broad C$_6$H$_5$ signals derived from **1** at 6.2-7.7 ppm, whereas the reaction of **2** alone with excess Mg afforded an insoluble product, which was supposed to be poly(*p*-xylylene) [2]. Thus, the spectrum demonstrates that the copolymerization of **1** with **2** actually proceeded through cross-nucleophilc substitution of Grignard reagents to Br-bearing benzylic carbons, where both reactants and substrates were derived from the monomers. According to our proposed mechanism for the homopolymerization of **1** [1], C=C double bonds should be incorporated in the main chain of the copolymer to a certain extent [1]. Based on the integral ratio of the signals in Figure 1, the composition of the two repeating units is estimated to be [**1'**]:[**2'**] = 1.2:1 (**1'** = repeating unit derived from **1**), which indicates that the incorporation of **2** is much more efficient than that of **1**.



Scheme 2. Copolycondensation of α,α-dibromotoluene (**1**) with α,α'-dibromo-*p*-xylylene (**2**).

Table 1. Mg-mediated copolycondensation of α,α-dibromotoluene (**1**) with α,α'-dibromo-*p*-xylylene (**2**).[a]

run	feed ratio [**1**]:[**2**]	yield (%)	M_n[b]	M_w/M_n[b]	copolymer composition[c] [**1'**]:[**2'**]
1	5:1	46	1630	1.72	1.2:1
2	3:1	47	1770	1.67	1.1:1
3	2.5:1	39	2160	1.90	0.9:1
4	2:1	37	2240	1.81	0.8:1
5	1:1	insoluble product			

[a] Conditions: total amount of monomers = 1.8-3.3 mmol, [Mg] = [**1**] x 6 + [**3**] x 2, in THF (10-15 mL), at room temperature for 15 h. [b] M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution. [c] Determined by ^{1}H NMR.

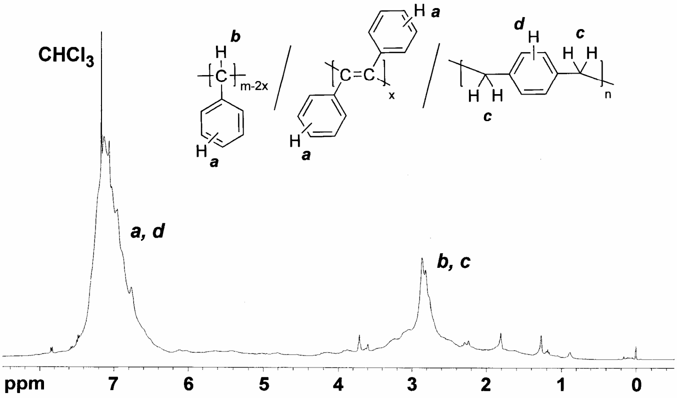


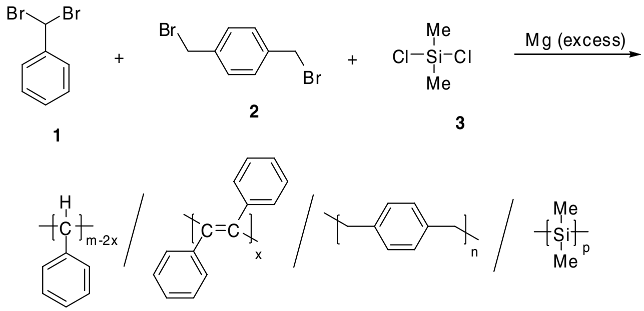
Figure 1. ^{1}H NMR spectrum of a copolymer obtained from **1** and **2** (run 1 in Table 1).

As summarized in Table 1, the copolycondensation was examined with various feed ratios of [**1**]:[**2**]. With the increase of the relative **2** ratio, the content of **2'** in composition and M_n gradually increased while the yield of the copolymers decreased.

The decrease of the copolymer yield can be ascribed to the generation of insoluble products, and the copolymerization with a 1:1 ratio afforded only an insoluble solid (run 5). The results in Table 1 demonstrate that the products of the copolycondensation gave higher M_n polymers than homopolymers of **1** (M_n < 1100), because of the high reactivity of **2** toward the propagation.

*Magnesium-Mediated Copolycondensation of α,α-Dibromotoluene (**1**), α,α'-Dibromo-p-xylylene (**2**), and Dichlorodimethylsilane (**3**)*

In order to improve the solubility of the resulting polymers, we tried to use dimethyldichlorosilane (**3**) as a comonomer in the ternary copolycondensation with **1** and **2**, where no Si-Si linkage should be generated because **3** acts only as an electrophile (Scheme 3). As listed in Table 2, the copolycondensation of **1**, **2**, and **3** in various feed ratios afforded the ternary copolymers, where the incorporation of dimethylsilylene (Me_2Si) unit was confirmed from the CH_3Si signal at -0.2-0.6 ppm in the ^{1}H NMR spectra (Figure 2) and the composition of the repeating units was calculated based on the integral ratio of each signal in the spectra. When the feed ratio of the monomers [**1**]:[**2**]:[**3**] was varied from 3:1:1 to 1:1:1 (runs 1-3), the [**1'**]:[**2'**]



Scheme 3. Copolycondensation of α,α-dibromotoluene (**1**), α,α'-dibromo-*p*-xylylene (**2**), and dichlorodimethylsilane (**3**).

Table 2. Mg-mediated copolycondensation of α,α-dibromotoluene (**1**), α,α'-dibromo-*p*-xylylene (**2**), and dimethyldichlorosilane (**3**).[a]

run	feed ratio [**1**]:[**2**]:[**3**]	yield (%)	M_n[b]	M_w/M_n[b]	copolymer composition[c] [**1'**]:[**2'**]:[**3'**]
1	3:1:1	40	3040	1.72	4.1:4.0:1
2	2:1:1	39	2810	1.62	2.1:2.1:1
3	1:1:1	27	2460	1.56	1.2:1.4:1
4	1:2:1	24	2650	1.57	1:2.4:1.3
5	1:3:1	34	4350	1.55	1:4.0:1.3
6	1:3:3	31	2477	1.39	1:2.0:2.7
7	1:5:2	insoluble product			

[a] Conditions: total amount of monomers = 3.6-6.0 mmol, [Mg] = [**1**] x 6 + [**2**] x 2, in THF (10-25 mL), at room temperature for 15 h. [b] M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution. [c] Determined by ^{1}H NMR.

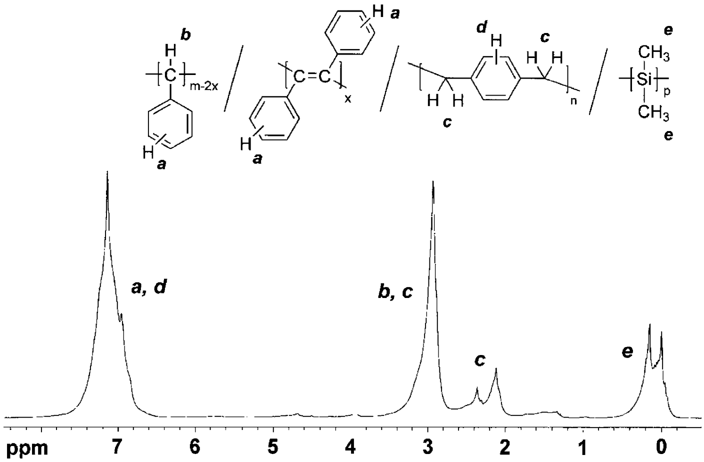
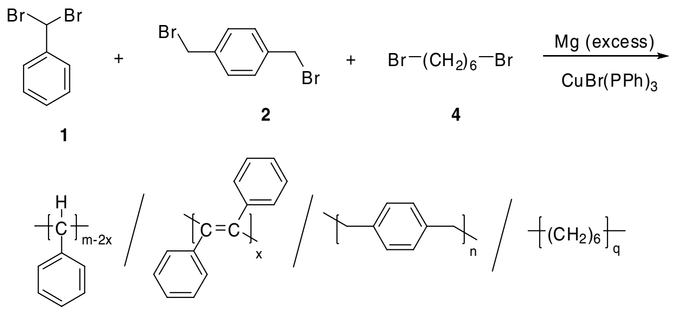


Figure 2. ^{1}H NMR spectrum of a copolymer obtained from **1**, **2**, and **3** (run 5 in Table 2).

ratio remained nearly 1:1 while the total content of **1'** and **2'** in the composition and M_n decreased. In contrast to run 5 in Table 1, the product obtained in run 3 with [**1**]:[**2**]:[**3**] = 1:1:1 was soluble in $CHCl_3$ and THF, because of the **3'** repeating unit imparted solubility to the product. Further increase of the relative feed ratio of **2** in runs 4 and 5 ([**1**]:[**2**]:[**3**] = 1:2:1 and 1:3:1) still afforded soluble products, where the composition roughly corresponded to the feed ratio and M_n increased up to 4350 with 63 mol% of **2'** in the composition in run 5. However, increasing the relative feed ratio of **3** resulted in the lowering of M_n (run 6), and the copolycondensation with a feed ratio of [**1**]:[**2**]:[**3**] = 1:5:2 afforded an insoluble product (run 7).

Magnesium-Mediated Copolycondensation of α,α-Dibromotoluene (1), α,α'-Dibromo-p-xylylene (2), and 1,6-Dibromohexane (4)

In place of **3**, 1,6-dibromohexane **4** was used as a comonomer for solubilizing the product in the copolycondensation with **1** and **2** (Scheme 4). As we described previously, $CuBr(PPh_3)$ was used as a catalyst for efficient incorporation of **4** [1,4].



Scheme 4. Copolycondensation of α,α-dibromotoluene (**1**), α,α'-dibromo-*p*-xylylene (**2**), and 1,6-dibromohexane (**4**).

The presence of **4'** unit in the product was confirmed from the appearance of a CH_2 signal at 0.6-1.5 ppm in the ^1H NMR spectrum (Figure 3), and the integral ratio was used for calculating the repeating unit composition. In runs 1-3 in Table 3 with the feed ratio of [**1**]:[**2**]:[**4**] = 5:1:1 ~ 1:1:1, M_n of the copolymer increased with the decrease of the relative feed ratio of **1**, reaching 8480 in run 3 with the feed ratio of [**1**]:[**2**]:[**4**] = 1:1:1. The **1'** content in the product decreased with the decrease of the feed ratio of **1**, while the [**2'**]:[**4'**] content in the product remained nearly constant at 1.6-1.9:1. Whereas further increase of the relative feed ratio of **2** to [**1**]:[**2**]:[**4**] = 1:2:1 resulted in the formation of an insoluble product (run 4), increase of the feed ratio of **4** led to lowering of M_n (runs 5 and 6). Although the polymerization with [**1**]:[**2**]:[**4**] = 1:2:3 and 1:2:5 afforded soluble copolymers, the M_n increase was not observed (runs 7 and 8). Increasing the feed ratio of **2** to [**1**]:[**2**]:[**4**] = 1:3:5 resulted in the formation of an insoluble product (run 9).

Table 3. Mg-mediated copolycondensation of α,α-dibromotoluene (**1**), α,α'-dibromo-*p*-xylylene (**2**), and 1,6-dibromohexane (**4**).[a]

run	feed ratio [**1**]:[**2**]:[**4**]	yield (%)	M_n[b]	M_w/M_n[b]	copolymer composition[c] [**1'**]:[**2'**]:[**4'**]
1	5:1:1	35	5680	2.22	3.0:1.9:1
2	3:1:1	40	6730	4.09	2.1:1.8:1
3	1:1:1	41	8480	3.20	0.8:1.6:1
4	1:2:1	insoluble product			
5	1:1:2	38	4820	1.94	1:1.8:1.8
6	1:1:5	21	3850	1.35	1:1.5:2.6
7	1:2:3	42	4210	1.77	1:2.4:2.2
8	1:2:5	26	4740	2.18	1:2.6:3.2
9	1:3:5	insoluble product			

[a] Conditions: total amount of monomers = 3.6-6.0 mmol, [Mg] = [**1**] x 6 + [**2**] x 2, [$CuBr(PPh_3)$] = [**4**] x 1/50, in THF (15 mL), at room temperature for 15 h. [b] M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution. [c] Determined by ^1H NMR.

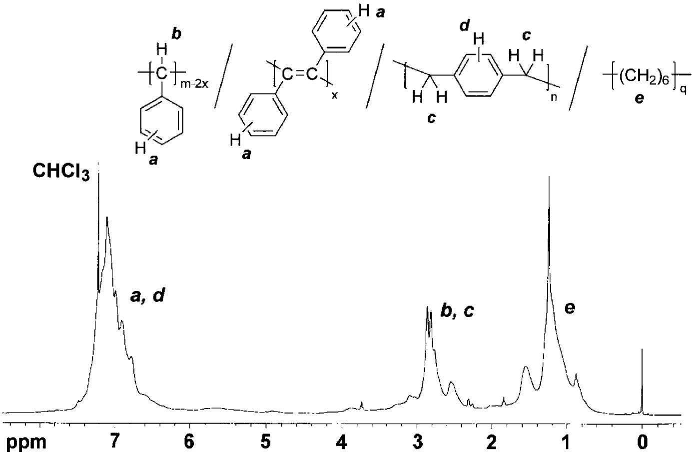


Figure 3. ^1H NMR spectrum of a copolymer obtained from **1**, **2**, and **4** (run 2 in Table 3).

Conclusions

The use of α,α‘-dibromo-*p*-xylylene (**2**) as a comonomer was found to be effective to give high molecular weight copolymers in the Mg-mediated copolycondensation with α,α-dibromotoluene (**1**). The ternary copolycondensation of **1** and **2** with dichlorodimethylsilane (**3**) or 1,6-dibromohexane (**4**) afforded new polymers with unique structures and high solubility in organic solvents, whose highest M_n of 8480 was attained when the feed ratio of [**1**]:[**2**]:[**4**] was 1:1:1.

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