

## ORIGINAL ARTICLE

# Formal aryne/ethylene copolymerization to form polyethylene containing *o*-arylene units in the main chain

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As chain-growth polymerization generally forms aliphatic main chains containing units such as alkylene and alkenylene, the method has rarely been applied to the construction of arylene units. Thus, the formation/introduction of arylene groups via chain-growth polymerization remains a challenging subject in polymer chemistry. In this study, we report a formal aryne/ethylene copolymerization using [2.2.1]oxabicyclic alkenes as aryne equivalents. A palladium-catalyzed copolymerization of [2.2.1]oxabicyclic alkenes with ethylene followed by acid-promoted dehydration produced novel aryne/ethylene copolymers. The use of a bulky phosphine–sulfonate ligand was essential to obtain the desired copolymers with high molecular weight. *Polymer Journal* (2015) 47, 474–480; doi:10.1038/pj.2015.27; published online 13 May 2015

## INTRODUCTION

Chain-growth polymerization is a powerful method that produces a range of polymers with controlled molecular weight, a narrow molecular-weight distribution and defined chain-end functional groups. Among the various types of chain-growth polymerization methods, the most representative examples include radical polymerization of vinyl monomers, coordination polymerization of alkenes/alkynes and metathesis polymerizations, generally forming aliphatic main chains containing units such as alkylene or alkenylene units. In contrast, the introduction of arylene units along with their formation via chain-growth polymerization remains a significant challenge in polymer synthesis. (In this manuscript, chain-growth polymerization of monomers bearing a preformed arylene unit is excluded. For example, see Bunz *et al.*<sup>1</sup>) In this regard, various polymerization methods have been developed for the introduction of *para*-arylene units, including the polymerization of *p*-quinodimethanes<sup>2</sup> or their surrogates,<sup>3,4</sup> the polymerization of *p*-arylene equivalents,<sup>5–8</sup> and the catalyst-transfer chain-growth condensation polymerization of bifunctional monomers.<sup>9–11</sup> However, fewer methods have been developed for the synthesis of *meta*-arylene units<sup>12–15</sup> and *ortho*-arylene units.<sup>16,17</sup> In particular, the formation/introduction of *o*-arylene units into polymer main chains via chain-growth polymerization is a considerable challenge because it generally requires the use of highly reactive monomers that are difficult to control, such as arynes<sup>18,19</sup> or *o*-quinodimethanes.<sup>2,20,21</sup> To expand the variety of polymers bearing *o*-arylene units, the development of novel polymerization methods that can utilize more stable and controllable monomers is desirable.

We have recently developed a formal aryne polymerization using [2.2.1]oxabicyclic alkenes **1** as a monomer, a novel strategy for the

synthesis of poly(*o*-arylene)s.<sup>22</sup> In this reaction, monomer **1** functions as an aryne equivalent through the insertion of **1** followed by dehydration to form *o*-arylene units in the main chain (Scheme 1a). During our ongoing research on this topic, we focused our attention on the copolymerization with ethylene. The introduction of functional groups or different comonomers into linear polyethylenes by the copolymerization method is known to be effective for the modification of both the surface and material properties of the resulting polyethylenes.<sup>23</sup> For such a copolymerization, a range of comonomers, including  $\alpha$ -olefins,<sup>24</sup> styrenes,<sup>25,26</sup> norbornenes,<sup>27,28</sup> polar vinyl monomers,<sup>23,29–31</sup> allyl monomers<sup>32–34</sup> and carbon monoxide,<sup>35–37</sup> has been examined thus far, but the use of aryne or its congeners for the introduction of an *o*-arylene linkage has been unexplored. In this study, we report a formal copolymerization of aryne and ethylene that was successfully catalyzed by palladium/phosphine–sulfonate complexes<sup>23,29,30</sup> to generate the corresponding copolymers containing *o*-arylene units in the main chain (Scheme 1b).

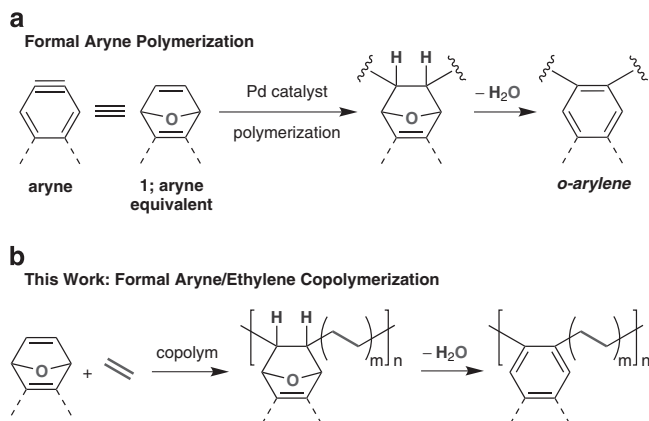
## EXPERIMENTAL PROCEDURE

### General

All manipulations were performed using a glove box and standard Schlenk techniques under an argon atmosphere. All polymerizations were performed using a 50-ml autoclave.

### Materials

Anhydrous toluene and tetrahydrofuran were purchased from Kanto Chemical, Tokyo, Japan (Kanto) and purified by the method of Pangborn *et al.*<sup>38</sup> Ethylene was purchased from the Takachiho Chemical Industrial, Tokyo, Japan and used after passing through columns for drying and deoxygenation. The following



**Scheme 1** (a) Concept of formal aryne polymerization and (b) formal aryne/ethylene copolymerization. A full color version of this figure is available at *Polymer Journal* online.

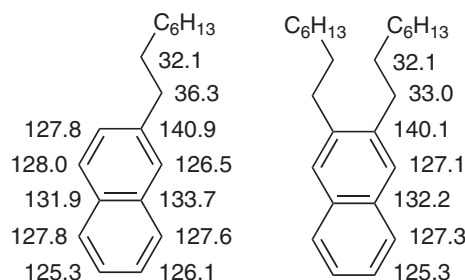
compounds were purchased from commercial suppliers and used as received: 1,4-dihydro-1,4-epoxynaphthalene (**1a**) (Wako Pure Chemical Industries, Osaka, Japan; Wako), furan (Tokyo Chemical Industry, Tokyo, Japan; TCI), butyllithium (1.6 M solution in hexane; Kanto), hydrogen chloride in 1,4-dioxane (Sigma-Aldrich), 1,1,2,2-tetrachloroethane (TCI), 1,1,2,2-tetrachloroethane- $d_2$  (Wako) and dry methanol (Wako). The following compounds were prepared according to procedures in the literature: 1,2-dibromo-4,5-dioctyloxybenzene (for procedure, see Kalashnikova *et al.*<sup>39</sup>; for compound data, see Waghray *et al.*<sup>40</sup>), **1b**,<sup>22</sup> **1d**,<sup>41</sup> **4**,<sup>42</sup> **5**,<sup>43</sup> **6**,<sup>44</sup> **7a**<sup>45</sup> and **7b**.<sup>34</sup>

## Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker BioSpin (Rheinstetten, Germany) Avance III 500 ( $^1\text{H}$ , 500 MHz;  $^{13}\text{C}$ , 126 MHz) NMR spectrometer equipped with a CryoProbe Prodigy or a JEOL ECS400 ( $^1\text{H}$ , 400 MHz;  $^{13}\text{C}$ , 101 MHz) NMR spectrometer. Chemical shift values for protons are referenced to the residual resonance of 1,1,2,2-tetrachloroethane- $d_2$  ( $\delta$  6.0), and values for carbons are referenced to the carbon resonance of 1,1,2,2-tetrachloroethane- $d_2$  ( $\delta$  74.1). Quantitative  $^{13}\text{C}$  NMR analyses of polymers with 0.05-M  $\text{Cr}(\text{acac})_3$  as a relaxation agent were performed at 120 °C using a 30° pulse of 10  $\mu\text{s}$ , a pulse delay time of 2 s, an acquisition time = 1.1 s and the inverse-gated decoupling method with the number of free induction decays (FIDs) collected per sample of 15 000–20 000. Size-exclusion chromatography (SEC) analyses were performed with a Tosoh (Tokyo, Japan) instrument (HLC-8121GPC/HT) equipped with two SEC columns (Tosoh TSKgel GMHHR-H(S)HT) and a refractive index detector by eluting with 1,2-dichlorobenzene at 1.0 ml min<sup>-1</sup> at 145 °C or a Waters (Milford, MA, USA) GPC instrument (ALC/GPC 150C) equipped with three SEC columns (Shodex, Showa Denko, Tokyo, Japan, AD806M/S) and a Foxboro (Schneider Electric, Foxboro, MA, USA) Miran 1A infrared detector by eluting with 1,2-dichlorobenzene at 1.0 ml min<sup>-1</sup> at 140 °C. Molecular weights were determined using narrow polystyrene standards and corrected by universal calibration using the Mark–Houwink parameters of Rudin:  $K=1.75 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$  and  $\alpha=0.67$  for polystyrene and  $K=5.90 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$  and  $\alpha=0.69$  for LLDPE.<sup>46</sup> Differential scanning calorimetry (DSC) measurements were performed on a Seiko Instruments (Chiba, Japan) DSC 7020 analyzer with a heating and cooling rate of 10 °C min<sup>-1</sup>. Infrared spectra were recorded on a Shimadzu (Kyoto, Japan) FTIR-8400 spectrometer equipped with an attenuated total reflection (ATR) system. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo.

## Preparation of 1,4-dihydro-6,7-dioctyloxy-1,4-epoxynaphthalene (**1c**)

Butyllithium (1.6 M solution in hexane, 13.4 ml, 21.4 mmol) was slowly added at -50 °C to a solution of 1,2-dibromo-4,5-dioctyloxybenzene (10.4 g, 21.2 mmol) in anhydrous tetrahydrofuran (200 ml) and furan (45 ml) under an



**Figure 1** Assignment of the  $^{13}\text{C}$  NMR resonances of model compounds ( $\text{Cl}_2\text{CDCDCl}_2$ ). NMR, nuclear magnetic resonance.

argon atmosphere, and the solution was stirred for 2.5 h at -50 °C. After adding distilled water (30 ml) at -50 °C, the mixture was warmed to room temperature. The reaction mixture was extracted with diethyl ether, dried over  $\text{Na}_2\text{SO}_4$ , filtrated and evaporated. Purification by flash chromatography (20% ethyl acetate in hexanes) gave a white solid (5.04 g, 60%);  $R_f=0.42$  on silica gel (20% ethyl acetate in hexane); mp 66.8 °C; infrared (neat,  $\text{cm}^{-1}$ )  $\nu$  2954, 2920, 2850, 1600 (C=C), 1461, 1292, 1207, 1076, 833, 702, 644.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.00 (t,  $J=1.0$  Hz, 2H, H(2) and H(3)), 6.92 (s, 2H, H(5) and H(8)), 5.63 (t,  $J=1.0$  Hz, 2H, H(1) and H(4)), 3.92 (m, 4H,  $\text{OCH}_2$ ), 1.74–1.69 (m, 4H,  $\text{CH}_2$ ), 1.47–1.36 (m, 4H,  $\text{CH}_2$ ), 1.36–1.20 (m, 16H,  $\text{CH}_2$ ), 0.86 (t,  $J=6.9$  Hz, 6H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.2 (2C, C(6) and C(7)), 143.3 (2C, C(2) and C(3)), 141.9 (2C, C(9) and C(10)), 109.9 (2C, C(5) and C(8)), 82.6 (2C, C(1) and C(4)), 70.3 (2C,  $\text{OCH}_2$ ), 31.9 (2C,  $\text{CH}_2$ ), 29.6 (2C,  $\text{CH}_2$ ), 29.5 (2C,  $\text{CH}_2$ ), 29.4 (2C,  $\text{CH}_2$ ), 26.1 (2C,  $\text{CH}_2$ ), 22.8 (2C,  $\text{CH}_2$ ), 14.2 (2C,  $\text{CH}_3$ );  $\text{C}_{26}\text{H}_{40}\text{O}_3$ : calcd. C 77.95, H 10.06; found C 77.78, H 10.28.

## Copolymerization of [2.2.1]oxabicyclic alkenes **1** with ethylene

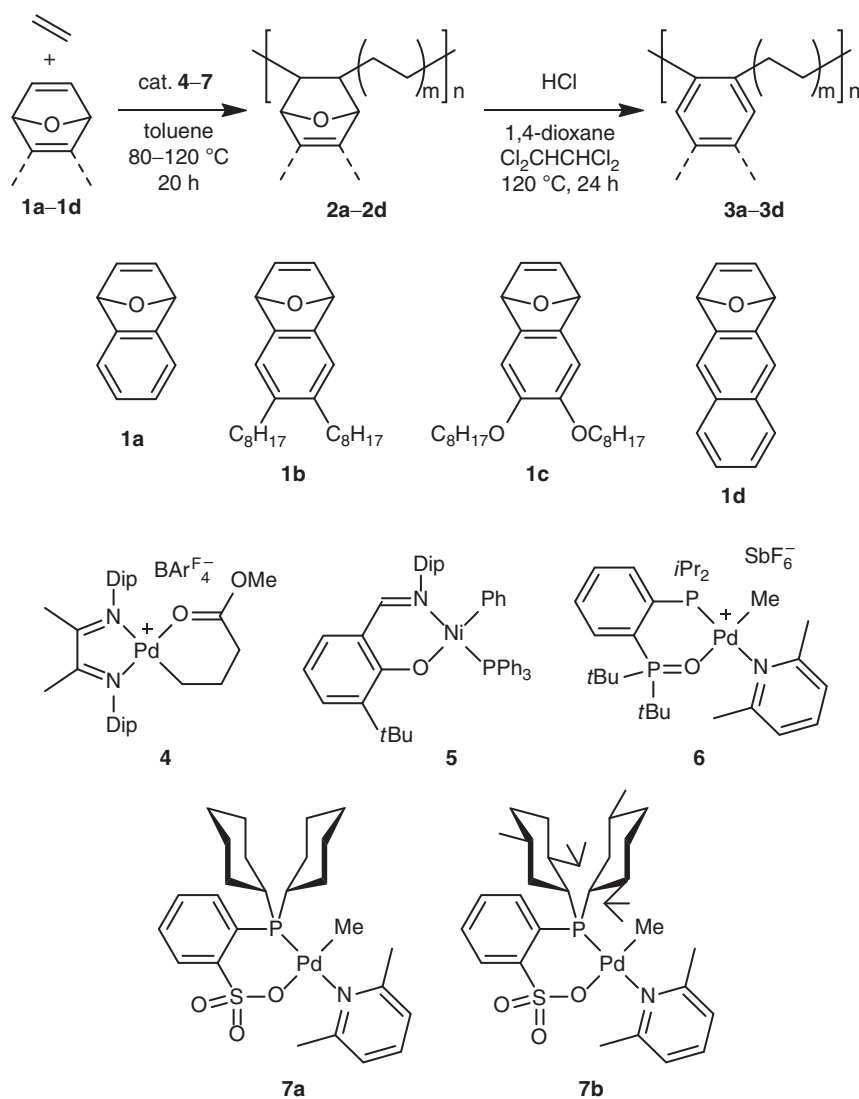
Toluene (10.0 ml) was added at room temperature to a mixture of monomer **1** (1.0 mmol) and palladium complex **7b** (6.9 mg, 0.010 mmol) in a 50-ml stainless autoclave. After charging with ethylene (3.0–5.0 MPa), the resulting mixture was stirred for 20 h at an indicated temperature (80–120 °C). After cooling to room temperature, methanol (50 ml) was added to the autoclave. The polymer was isolated by filtration, washed with methanol and dried under vacuum at room temperature. The obtained copolymers **2** were analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and SEC analyses without further purification.

## Dehydration of polymer **2**

Hydrogen chloride in 1,4-dioxane (4.0 M, 3.0 ml, 12.0 mmol) at room temperature was added to a suspension of polymer **2** (100 mg) in 1,1,2,2-tetrachloroethane (5.0 ml). The mixture was stirred for 24 h at 120 °C. After cooling to room temperature, the suspension was added to methanol (100 ml). The precipitates formed were collected by filtration and washed with methanol using an ultrasound bath. The polymers **3** obtained were analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, SEC and DSC analyses.

## Control experiments

Toluene (10.0 ml) at room temperature was added to a mixture of vinyl acetate or methyl acrylate (10 mmol) and palladium complex **7b** (6.9 mg, 0.010 mmol) in a 50-ml stainless steel autoclave. After charging with ethylene (5.0 MPa), the resulting mixture was stirred for 1 h at 100 °C. After cooling to room temperature, the suspension was added to methanol (100 ml). The precipitates formed were collected by filtration and washed with methanol. The polymers obtained were analyzed by  $^1\text{H}$  NMR and SEC analyses. Copolymerization with vinyl acetate: polymer yield 0.57 g; activity 57  $\text{g mmol}^{-1} \text{ h}^{-1}$ ;  $M_n$  76 000 kDa;  $M_w/M_n$  2.1; incorporation ratio <0.05%. Copolymerization with methyl acrylate: polymer yield 0.86 g; activity 86  $\text{g mmol}^{-1} \text{ h}^{-1}$ ;  $M_n$  36 000 kDa;  $M_w/M_n$  4.3; incorporation ratio 0.5%.



**Scheme 2** Copolymerization of [2.2.1]oxabicyclic alkenes **1** with ethylene and subsequent acid-promoted dehydration.

**Table 1** Catalyst and condition screening for the copolymerization of [2.2.1]oxabicyclic alkene **1a** with ethylene<sup>a</sup>

Entry	Catalyst	Yield of <b>2a</b> (g) <sup>b</sup>	Activity <sup>b</sup> (g mmol <sup>-1</sup> h <sup>-1</sup> )	$M_n^c$ ( $10^3$ )	$M_w/M_n^c$	i.r. (%) <sup>d</sup>
1	<b>4</b>	0	0	—	—	—
2	<b>5</b>	0	0	—	—	—
3	<b>6</b>	0	0	—	—	—
4	<b>7a</b>	2.1	10.5	5.3	3.2	0.3
5	<b>7b</b>	0.30	1.5	10.1	2.3	0.9

Abbreviation: i.r., incorporation ratio.

<sup>a</sup>A mixture of catalyst (0.010 mmol) and monomer **1a** (1.0 mmol) in toluene (10 ml) was stirred for 20 h at 100 °C under an ethylene atmosphere of 3.0 MPa in a 50-ml autoclave.

<sup>b</sup>Isolated yields after precipitation with methanol.

<sup>c</sup>Molecular weights determined by size-exclusion chromatography relative to polystyrene standards and corrected by universal calibration.

<sup>d</sup>Molar incorporation ratio of **1a** determined by <sup>1</sup>H nuclear magnetic resonance analysis.

### NMR assignments

The <sup>13</sup>C NMR resonances of polymers were assigned by comparison with the model compounds shown in Figure 1 that were prepared in our laboratory and assigned by one-dimensional and two-dimensional NMR analyses.

## RESULTS AND DISCUSSION

### Catalyst screening

A range of catalysts were screened for the coordination–insertion copolymerization of 1,4-dihydro-1,4-epoxynaphthalene (**1a**; 1.0 mmol) and ethylene (3.0 MPa) in toluene to generate copolymer **2** (Scheme 2). The molecular weights of the copolymers obtained were determined by SEC analysis using polystyrene standards and corrected by universal calibration (see the Experimental Procedure and Supplementary Information). The incorporation ratios of **1** were determined by <sup>1</sup>H NMR analysis. For some entries, the incorporation ratio of **1** was also determined by quantitative <sup>13</sup>C NMR analysis using the inverse-gated decoupling method, and the obtained values were in good accordance with those determined by <sup>1</sup>H NMR analysis. As monomer **1** can be regarded as a cyclic allylic ether, it is necessary to use transition metal catalysts that are capable of promoting the polymerization of polar monomers as well as that of ethylene. Thus, we screened a number of group-10 metal catalysts that are known to promote polar monomer/ethylene copolymerization (Table 1). The copolymerization using a palladium/ $\alpha$ -diimine complex **4**,<sup>42,47</sup> nickel/imine–phenolate complex **5**,<sup>48</sup> (the copolymerization in the presence

**Table 2** Copolymerization of [2.2.1]oxabicyclic alkenes **1** and ethylene by catalyst **7b** and subsequent dehydration<sup>a</sup>

Entry	Monomer	Amount (mmol)	T (°C)	<b>2</b> (g) <sup>b</sup>	Activity <sup>b</sup> (g·mmol <sup>-1</sup> ·h <sup>-1</sup> )	M <sub>n</sub> <sup>c</sup> (kDa)	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	<b>3</b> (%) <sup>b</sup>	M <sub>n</sub> <sup>c</sup> (10 <sup>3</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	i.r. (%) <sup>d</sup>	T <sub>gm</sub> (°C) <sup>e</sup>
1	<b>1a</b>	1	80	0.37	1.2	17.0	2.0	99	18.2	2.0	0.8	124.0
2	<b>1a</b>	1	100	0.57	2.9	13.8	2.3	96	14.6	2.0	0.9	124.0
3	<b>1a</b>	1	120	0.50	2.5	14.0	2.5	89	14.6	2.3	0.7	126.3
4 <sup>f</sup>	<b>1a</b>	1	100	0.30	1.5	10.1	2.3	98	10.7	2.2	0.9	123.6
5	<b>1a</b>	3	100	0.30	1.5	6.2	2.1	96	7.3	1.9	2.1	115.8
6	<b>1a</b>	6	100	0.27	1.4	3.9	2.3	95	5.8	1.8	3.2	111.9
												109.3
7	<b>1a</b>	10	100	0.073	0.37	2.3	2.3	77	2.0	2.1	5.4	96.1
8	<b>1b</b>	1	100	0.25	1.2	7.3	2.2	93	7.9	2.2	1.1	123.4
9	<b>1c</b>	1	100	0.32	1.6	7.7	2.2	99	8.3	2.2	0.7	126.0
10	<b>1d</b>	1	100	0.27	1.3	19.2	2.5	96	13.2	3.2	0.3	127.1

<sup>a</sup>A mixture of catalyst **7b** (0.010 mmol) and monomer **1** in toluene (10 ml) was stirred under ethylene atmosphere (5.0 MPa) in a 50-ml autoclave for 20 h, unless otherwise noted.

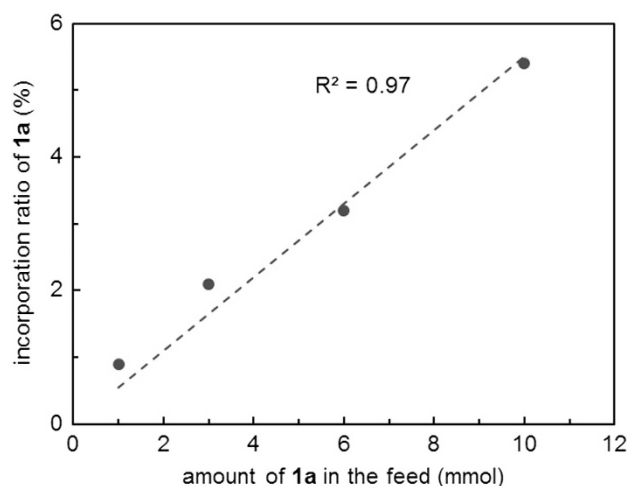
<sup>b</sup>Isolated yields after precipitation with methanol.

<sup>c</sup>Molecular weights determined by size-exclusion chromatography using polystyrene standards and corrected by universal calibration.

<sup>d</sup>Molar incorporation ratio of **1** determined by <sup>1</sup>H nuclear magnetic resonance analysis.

<sup>e</sup>Determined by differential scanning calorimetry analysis.

<sup>f</sup>Reaction was performed under 3.0 MPa of ethylene atmosphere.



**Figure 2** Plot of the incorporation ratio of **1a** in copolymers **3** vs the amount of **1a** in the feed (entries 2 and 5–7 of Table 2).

of Ni(cod)<sub>2</sub> as a co-catalyst was also carried out, resulting in the formation of a homodimer of **1a** presumably via a low-valent nickel-catalyzed dimerization; see Huang and Cheng<sup>49</sup>) and palladium/bisphosphine–monoxide complex **6**<sup>44</sup> yielded no polymeric products. Thus, we found that the use of palladium/phosphine–sulfonate complexes **7** was essential for successful copolymerization and that the substituents on the phosphorus atom have a significant influence on the product structure. Cyclohexyl-substituted ligand **7a**<sup>45</sup> yielded the desired copolymer, but NMR analysis after dehydration revealed that the copolymer contained only a small amount of **1a** (0.3%). However, bulky menthyl-substituted ligand **7b**<sup>34</sup> produced a copolymer with a higher molecular weight of M<sub>n</sub> = 23 × 10<sup>3</sup> and a higher incorporation ratio of 0.9%. The observed catalytic activities were lower than those of previously reported for late transition-metal-catalyzed copolymerization of norbornene with ethylene.<sup>48,50–53</sup>

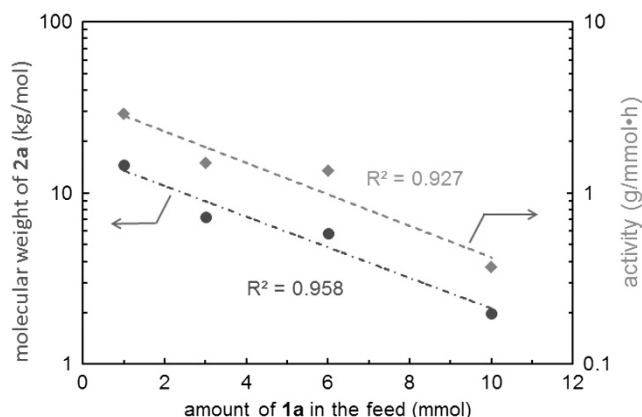
### Copolymerization of monomers **1a–d**

With the optimal catalyst **7b** in hand, we performed the copolymerizations of **1** with ethylene (5.0 MPa) under a range of conditions (Table 2). After the polymerization step, polymers **2** were dehydrated by treatment with hydrogen chloride in 1,4-dioxane/1,1,2,2-

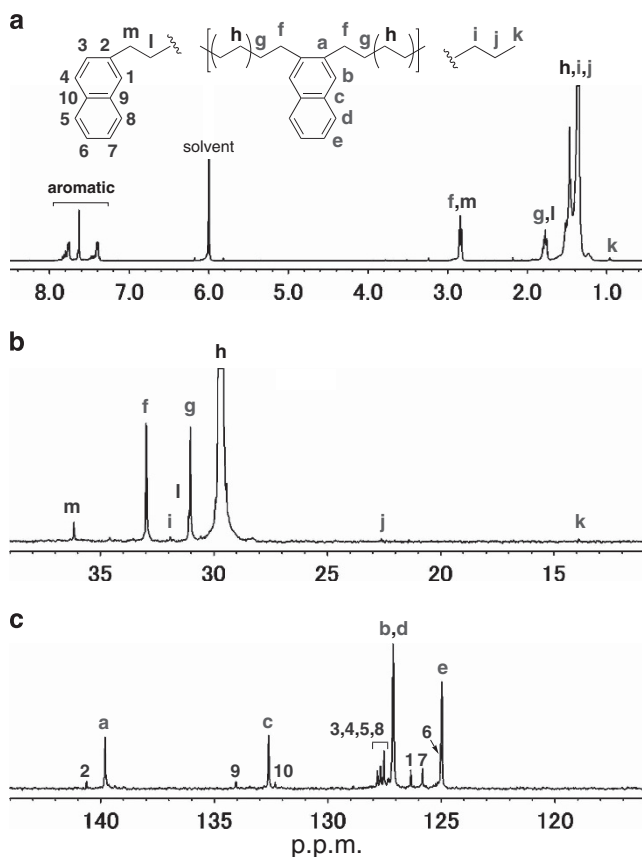
tetrachloroethane at 120 °C to obtain *o*-arylene polymers **3** without a significant decrease in the molecular weight of the polymer. The copolymerizations performed at higher reaction temperatures (compare entries 1–3) or under lower pressures of ethylene (compare entries 2 and 4) did not significantly change the polymerization results in terms of molecular weight and the incorporation ratio of monomer **1a**. When the amount of monomer **1a** in the feed was increased (compare entries 2 and 5–7), the copolymerization/dehydration yielded polymers with higher incorporation ratios up to 5.4% (entry 7). A plot of these values showed an almost linear correlation between the amount of monomer **1a** in the feed and the resulting incorporation ratio of **1a** in copolymer **3a** (Figure 2). The observed incorporation ratios are higher than those of other common polar vinyl monomers; for example, the copolymerization of ethylene with vinyl acetate and methyl acrylate under the same conditions (comonomer 10 mmol, ethylene 5.0 MPa, 100 °C) produced corresponding copolymers with incorporation ratios of <0.05% and 0.5%, respectively. These results suggest that monomer **1a** is more reactive in the copolymerization than other common polar vinyl monomers, and shows comparable reactivity with norbornene derivatives.<sup>48,50–53</sup> Given that a concomitant decrease of polymer yield and molecular weight was observed, it appears that there is a trade-off between catalytic activity/polymer molecular weight and the incorporation ratio of **1a** (Figure 3). The comonomers bearing alkyl (**1b**; entry 8) and alkoxy (**1c**; entry 9) groups were compatible with the copolymerization without changing the incorporation ratios. The polymerization method was applied to the 2,3-didehydroanthracene equivalent (**1d**; entry 10) to form copolymers **2d** and **3d** with higher molecular weights, although the incorporation ratio of **1d** was lower than those of 2,3-didehydronaphthalene equivalents **1a–1c**.

### Characterization of copolymers and mechanistic discussion

Analysis by <sup>1</sup>H NMR (Figure 4a) and <sup>13</sup>C NMR (Figures 4b and c) spectroscopy revealed that the polymers obtained were undoubtedly copolymers rather than a mixture of homopolymers and that these copolymers were composed of linear polyethylene backbones without any detectable alkyl branching. This finding is consistent with the previously reported results obtained using palladium/alkylphosphine–sulfonate catalysts.<sup>32,34,45</sup> The NMR analyses indicated that the naphthalene units were attached to both the main chain as a naphthalene-2,3-diyl group (**a–e**) and to the end of the polymer

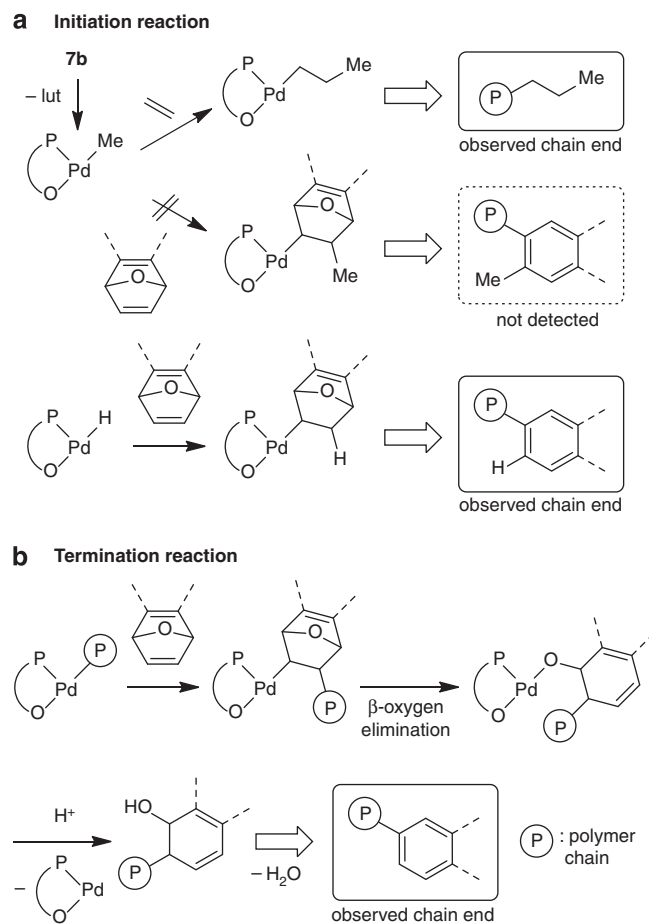


**Figure 3** Plot of the number-averaged molecular weight ( $M_n$ ; circle) and the catalytic activity ( $\text{g mmol}^{-1} \text{h}^{-1}$ ; rhomboid) vs the amount of **1a** in the feed (entries 2 and 5–7 of Table 2). A full color version of this figure is available at *Polymer Journal* online.

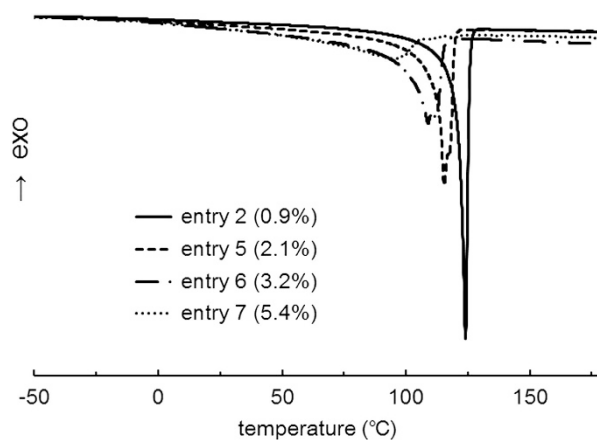


**Figure 4**  $^1\text{H}$  NMR spectrum ((a)  $\text{Cl}_2\text{CDCl}_2$ ,  $120^\circ\text{C}$ ) and  $^{13}\text{C}$  NMR spectra ((b) 11–39 p.p.m. and (c) 116–144 p.p.m.;  $\text{Cl}_2\text{CDCl}_2$ ,  $120^\circ\text{C}$ ) of polymer **3a** obtained in entry 6. NMR, nuclear magnetic resonance. A full color version of this figure is available at *Polymer Journal* online.

chain as a 2-naphthyl group (1–10), with no arylene–arylene units observed. Meanwhile, a saturated alkyl group was found as the initiation chain end (i–k). These results gave useful information on the polymerization mechanism as seen in Scheme 3. The polymerization is initiated by the insertion of ethylene rather than monomer **1** into the Pd–Me bond of the intermediate generated by the dissociation of 2,6-lutidine from catalyst **7b**. The following chain propagation step



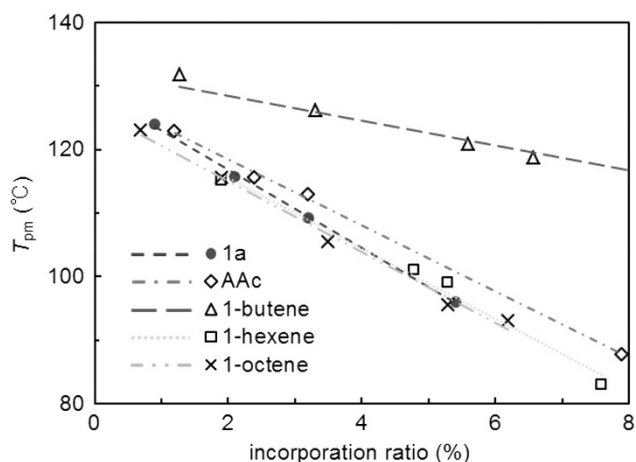
**Scheme 3** Mechanism of (a) initiation and (b) termination for the copolymerization of [2.2.1]oxabicyclic alkenes **1** with ethylene.



**Figure 5** DSC thermograms of polymers **3a** obtained in entries 2 and 5–7 of Table 2 (second heating,  $10^\circ\text{C min}^{-1}$ ). DSC, differential scanning calorimetry.

involves the insertion of both ethylene and monomer **1**. In this step, ethylene insertion is more favorable than the insertion of **1**, and no successive incorporation of **1** takes place. It is worth noting that the homopolymerization of **1** did not proceed when palladium catalysts bearing a bidentate ligand, such as **7b**, were employed. Given that no





**Figure 6** Plot of the melting temperature of copolymers **3a** (entries 2 and 5–7 of Table 2), ethylene/allyl acetate copolymers,<sup>32</sup> ethylene/1-butene copolymers,<sup>56</sup> ethylene/1-hexene copolymers<sup>54</sup> and ethylene/1-octene copolymers<sup>55</sup> vs the incorporation ratio of comonomers. A full color version of this figure is available at *Polymer Journal* online.

terminal or internal alkene units were observed at the end of the polymer chains, the polymerization must have been terminated by  $\beta$ -oxygen elimination after the insertion of monomer **1**. The integration ratio of signals corresponding to naphthyl groups in the quantitative <sup>13</sup>C NMR spectra is greater than that of the terminal alkane chain end, suggesting that the polymerization may also have been initiated by the insertion of **1** into a palladium–hydride complex, somehow generated *in situ* (see Supplementary Information). The origin of the palladium–hydride species is not clear at present, since unsaturated chain ends were not observed in NMR spectra.

### Thermal properties

Thermal properties of polymers **3a–d** were investigated by DSC analysis (see Supplementary Information). Melting temperatures ( $T_m$ ) were determined during the heating process, which was measured at a sweep rate of 10 °C min<sup>-1</sup>. DSC thermograms of polymers **3a** with different incorporation ratios of **1** (entries 2 and 5–7 of Table 2) revealed that an increase in the incorporation ratio of **1** led to a broadening of DSC traces and a decrease in the melting temperature (Figure 5). This result could be due to an increase in the heterogeneity of copolymers **3a** with increasing comonomer content. This behavior was similar to that of linear low-density polyethylenes, such as ethylene/1-hexene copolymers,<sup>54</sup> ethylene/1-octene copolymers<sup>55</sup> and ethylene/allyl acetate copolymers,<sup>32</sup> but was not in accordance with the behavior of ethylene/1-butene copolymers,<sup>56</sup> as seen in Figure 6.

### CONCLUSIONS

In summary, we expanded the formal aryne polymerization strategy using [2.2.1]oxabicyclic alkenes as synthetic equivalents of arynes to aryne/ethylene copolymerization. The use of a bulky phosphine–sulfonate ligand was essential to obtain the desired aryne/ethylene copolymers with high molecular weights. The present study provides a useful method for the introduction of *o*-arylene units into the main chains of polyethylene.

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