

# Formation of Linear Copolymers of Ethylene and Acrylonitrile Catalyzed by Phosphine Sulfonate Palladium Complexes

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Polyethylenes modified by incorporation of functional groups have been of great interest because of potential improvement of various properties such as toughness and adhesion.<sup>1</sup> For example, hydrogenated nitrile butadiene rubbers (HNBRs), which can be regarded as cyano-group-incorporated branched polyethylenes, possess excellent oil, heat, and chemical resistance and have been prepared by radical copolymerization of acrylonitrile with butadiene, followed by hydrogenation.<sup>2</sup>

Transition-metal-catalyzed copolymerization of ethylene with polar vinyl monomers has attracted great attention because, by tuning the catalysts, it would provide superior control over polymer composition and structures to radical processes.<sup>1,3</sup> However, only a limited number of polar vinyl monomers such as alkyl acrylates<sup>4</sup> and vinyl ethers<sup>5</sup> have been efficiently copolymerized with ethylene by coordination–insertion mechanisms.

Acrylonitrile has been particularly recognized as one of the most desirable but challenging monomers for the copolymerization. Extensive and thorough research on reactivity of acrylonitrile with palladium-based olefin polymerization catalysts by Jordan<sup>6a,b</sup> and Piers<sup>6c</sup> has identified a number of drawbacks such as high  $\sigma$ -coordinating ability of the nitrogen atom of cyano groups and low insertion reactivity of  $\alpha$ -CN-substituted alkylpalladium species, which would form aggregates.

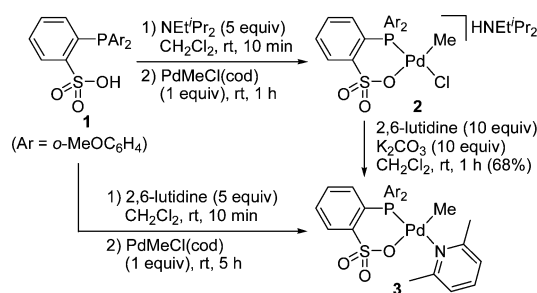
In 2002, Pugh and co-workers reported formation of linear copolymers of ethylene and alkyl acrylates by in-situ-generated Pd catalysts using phosphine-sulfonate ligands.<sup>7</sup> Since then, many researchers,<sup>8</sup> including Claverie,<sup>8a,e</sup> Goodall,<sup>8a–f</sup> Sen,<sup>8g</sup> and us,<sup>9</sup> have worked on olefin copolymerization using phosphine-sulfonate Pd catalysts. Previously, we have reported that anionic methylpalladium(II) complexes with phosphine-sulfonate ligands such as **2** catalyze the formation of linear copolymers of ethylene and methyl acrylate.<sup>9a</sup>

Herein we describe synthesis of ethylene-rich linear copolymers of ethylene and acrylonitrile by isolated phosphine-sulfonate methylpalladium complexes. Insertion of acrylonitrile units into a linear polyethylene chain was observed for the first time. Synthesis of the best catalyst, 2,6-lutidine complex **3**, and characterization of the copolymers are also described.<sup>10–12</sup>

Treatment of **1** with 2,6-lutidine, followed by addition of PdMeCl(cod), afforded complex **3** as a mixture with 2,6-lutidinium chloride, and the structure of **3** was confirmed by X-ray crystallography (Scheme 1). Complex **3** was isolated in a good yield by reaction of **2** with 2,6-lutidine in the presence of K<sub>2</sub>CO<sub>3</sub>.

Copolymerization of ethylene and acrylonitrile was catalyzed by isolated Pd complexes (Table 1, entries 1 and 2). Although blocking of the vacant site on the palladium by 2,6-lutidine was anticipated to retard the polymerization, the use of **3** without any activator showed comparable activity to **2** with NaBARF<sub>4</sub> (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), where the chloride ion is expected to be removed from the palladium by the sodium ion. In addition, copolymers obtained

**Scheme 1**



**Table 1.** Copolymerization of Ethylene and Acrylonitrile<sup>a</sup>

entry	catalyst	activity (g·mol <sup>-1</sup> ·h <sup>-1</sup> )	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>	x:y	T <sub>m</sub> (°C)
1	<b>3</b>	190	2900	1.5	91:9	103.7
2 <sup>b</sup>	<b>2</b> , NaBARF <sub>4</sub>	160	1600	1.7	93:7	101.2
3 <sup>c</sup>	<b>1</b> , Pd(dba) <sub>2</sub>	19 <sup>d</sup>	2400	1.6	nd <sup>e</sup>	nd <sup>e</sup>
4 <sup>f</sup>	<b>3</b>	370	7600	1.9	97:3	114.8
5 <sup>g</sup>	<b>3</b>	40	12300	1.6	98:2	121.4

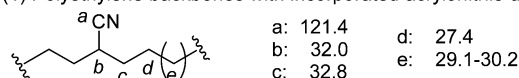
<sup>a</sup> Conditions: 0.01 mmol of Pd complex, ethylene pressure = 3.0 MPa, 2.5 mL of acrylonitrile, 2.5 mL of toluene, 100 °C, 120 h. <sup>b</sup> NaBARF<sub>4</sub> (0.01 mmol) was used. <sup>c</sup> Compound **1** (0.012 mmol) was used. <sup>d</sup> Determined based on the material obtained after washing with DMSO to remove byproducts. See Supporting Information. <sup>e</sup> Not determined. <sup>f</sup> Performed with 0.5 mL of acrylonitrile in 4.5 mL of toluene. <sup>g</sup> Performed with 0.5 mL of acrylonitrile in 4.5 mL of toluene under 4.0 MPa of ethylene at 80 °C for 270 h.

with **3** had both higher molecular weight and degree of acrylonitrile incorporation than those obtained with **2** and NaBARF<sub>4</sub>. In contrast, use of the mixture of **1** and Pd(dba)<sub>2</sub> as a catalyst resulted in formation of a small amount of the copolymer (entry 3), which clearly indicates the importance of preformation of phosphine-sulfonate chelate structures for the copolymerization.

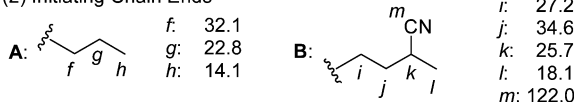
Investigation on the structures of the products by <sup>13</sup>C NMR spectroscopy revealed that linear copolymers of ethylene and acrylonitrile were formed with phosphine-sulfonate Pd complexes. There are no signals corresponding to branching structures found for branched polyethylenes.<sup>13</sup> Acrylonitrile units were found not only at the initiating and terminating chain ends but also in the polyethylene backbones. For example, copolymers obtained with **3** at 100 °C (entry 1) possess acrylonitrile units at initiating and terminating chain ends and in the polymer chains with ca. 1:1:2 ratios. The insertion of acrylonitrile units was confirmed by comparison with reported <sup>13</sup>C NMR data of branched copolymers of ethylene and acrylonitrile produced by a radical method,<sup>14</sup> as well as a model compound, 2-octyldecanenitrile.

Chain propagation should be initiated by ethylene insertion into a Pd–Me bond or insertion of ethylene or acrylonitrile into a Pd–H

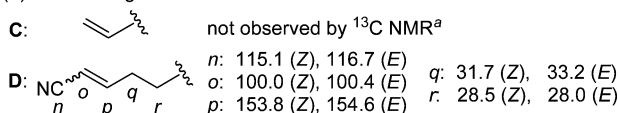
## (1) Polyethylene backbones with incorporated acrylonitrile units



## (2) Initiating Chain Ends



## (3) Terminating Chain Ends



**Figure 1.**  $^{13}\text{C}$  NMR assignments for the copolymers of ethylene and acrylonitrile (in 1,2,4-trichlorobenzene at 120 °C). Chemical shifts for each carbon atom are listed in parts per million. The ratio of C/D was determined to be ca. 0.25 by  $^1\text{H}$  NMR analysis in toluene- $d_8$ .

bond because only two types of initiating chain ends, *n*-alkyl (A) and 3-cyanobutyl (B) groups, were observed. Insertion of ethylene into either a Pd–H or a Pd–Me bond should lead to formation of A, but acrylonitrile insertion should occur into a Pd–H bond, not a Pd–Me bond, selectively in a 2,1-fashion to generate B as only one cyano-incorporated initiating end group (Figure 1).

There are two types of possible terminating chain ends, vinyl (C) and 2-cyanoethenyl (D) groups, formed by  $\beta$ -H elimination or transfer after ethylene and acrylonitrile insertion, respectively. By  $^1\text{H}$  NMR spectrum of the copolymer obtained in entry 1, the C/D ratio was determined to be ca. 0.25, which means chain transfer mostly occurs after acrylonitrile insertion. Reduction of the number of nitrile groups per polymer chain by decreasing the amount of acrylonitrile used led to a significant increase in molecular weight of copolymers (Table 1, entry 4), presumably because it reduced the frequency of chain transfer.  $M_n$  of the copolymer was further increased to 12 300 by increasing the ethylene pressure to 4.0 MPa and lowering the reaction temperature to 80 °C (Table 1, entry 5).

The terminating end group analysis also led us to investigate ethylene homopolymerization because **3** should provide linear polyethylene with high molecular weight and would be a rare Pd catalyst which produces linear polyethylene without any activator such as a large excess of MAO (>60 equiv).<sup>8a,g,15</sup> Polymerization of ethylene using **3** actually produced linear polyethylene (80 °C, 15 h,  $M_n$  63 000,  $M_w/M_n$  2.3, 15 g·mmol<sup>-1</sup>·h<sup>-1</sup>,  $T_m$  131.7 °C).  $^{13}\text{C}$  NMR spectroscopy showed the exceptional high linearity of obtained polyethylenes obtained with **3** (<1 branch/1000 C).<sup>13</sup>

Ethylene-rich copolymers of ethylene and acrylonitrile can be prepared by high-pressure radical copolymerization at high temperature, but a number of branches are formed with this method. Therefore, linear copolymers of ethylene and acrylonitrile should possess different physical properties such as melting points from copolymers produced by radical methods. For example, the linear copolymer produced in entry 5 melts at higher temperature than a copolymer with a similar acrylonitrile incorporation (1.6%) produced by radical method (107.8 °C).<sup>14</sup>

In conclusion, linear copolymers of ethylene and acrylonitrile were prepared using palladium complexes bearing phosphine-sulfonate bidentate ligands. Acrylonitrile units located in the linear polyethylene backbones were detected for the first time by  $^{13}\text{C}$  NMR spectroscopy. Catalyst systems employing isolated palladium complexes such as **3** showed much higher activity for the copolymerization than the in situ generation procedures, and molecular weight of the copolymers and acrylonitrile incorporation were dependent on the palladium complexes. Preliminary studies on the

properties revealed high melting points of the copolymers. Investigations on the mechanism of the copolymerization and physical properties of the linear copolymers are currently in progress.

**Acknowledgment.** The authors are very grateful to Prof. Richard Jordan for helpful discussions. We also thank Prof. Zhaomin Hou for high temperature measurements of polymer molecular weights, and Prof. Takashi Kato for DSC measurements. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas “Advanced Molecular Transformations of Carbon Resources” from the Ministry of Education, Culture, Sports, Science and Technology, Japan. T.K. thanks the Japan Society for the Promotion of Science (JSPS) for a Research Fellowship for Young Scientists.

**Note Added after ASAP Publication.** Due to a production error, the units for activity were incorrect in Table 1, column 3, in the version published ASAP on June 27, 2007. The table was corrected on July 6, 2007.

**Supporting Information Available:** Experimental procedures and characterization (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0725504