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Chain-Growth Polymerization for the Synthesis of Polyfluorene via Suzuki−Miyaura Coupling Reaction from an Externally Added Initiator Unit

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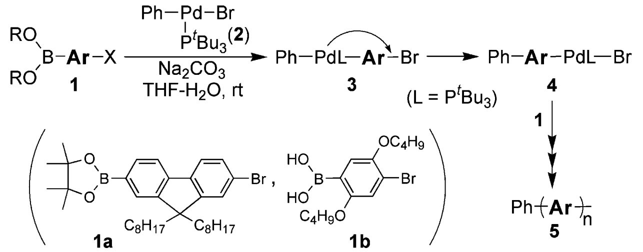
Organometallic polycondensation is a promising and reliable method for the synthesis of π-conjugated polymers.[1] However, the molecular weight and polydispersity of the synthesized polymers have rarely been well controlled, owing to the step-growth polymerization nature of polycondensation. Recently, we have reported that Ni-catalyzed polymerization via Tamao−Kumada reaction of Grignard-type monomers proceeds in a chain-growth polymerization manner to afford poly(3-alkylthiophene)s[2,3] and poly(*p*-phenylene)[4] with controlled molecular weight and a narrow molecular-weight distribution. The polymerization proceeds via a catalyst-transfer polycondensation mechanism involving intramolecular transfer of the nickel catalyst.[5] This is a new type of chain-growth condensation polymerization and is expected to have broad generality for a variety of organometallic polycondensations. However, catalyst-transfer polycondensation using a catalyst containing a metal other than nickel has not yet been reported.

Another attractive feature of catalyst-transfer polycondensation is the progress of the polymerization from an initiator. In the case of the polymerization of above Grignard-type monomers, the initiator is a bithiophene-Ni complex formed in situ by the reaction of one nickel catalyst with two monomers.[5] If the polymerization were started from a surface-bound initiator, it would provide surface-grafted π-conjugated polymers.[6] To develop such a polymerization, we focused on arylpalladium(II) halide complexes containing a bulky phosphine ligand such as ^{t}Bu$_3$PPd(Ph)Br, because they are stable and are easy to handle.[7] If organometallic polycondensation catalyzed by ^{t}Bu$_3$PPd(Ph)Br proceeds in a chain-growth polymerization manner, the phenyl group in ^{t}Bu$_3$PPd(Ph)Br would serve as an initiator unit.

With this idea in mind, we investigated the feasibility of catalyst-transfer Suzuki−Miyaura coupling polymerization of 4-bromo-1,4-dialkyloxybenzeneboric acid[8] and 7-bromo-9,9-dialkyl-9*H*-fluoren-2-ylboric acid ester[9] using ^{t}Bu$_3$PPd(Ph)Br as an arylpalladium(II) halide catalyst for the synthesis of the well-defined polyarylylenes bearing an initiator unit derived from the catalyst. ^{t}Bu$_3$PPd(Ph)Br is a Pd(II) complex formed by oxidative addition of bromobenzene to Pd(0).[7] ^{t}Bu$_3$P was chosen as a bulky ligand because of its known ability to promote the Suzuki−Miyaura coupling reaction.[10] There are several reports of model reactions for chain-growth Suzuki−Miyaura coupling polymerization,[11] but the chain-growth polymerization has not been demonstrated yet. Herein we show that palladium-catalyzed polycondensation of 2-(7-bromo-9,9-dioctyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1a**) proceeds in a chain-growth polymerization manner from an initiator unit derived from the catalyst, and affords well-defined polyfluorenes with narrow polydispersity and controlled molecular weight.

Scheme 1



The polymerization of **1a** and 4-bromo-2,5-dibutyloxybenzeneboric acid (**1b**) was carried out in the presence of ^{t}Bu$_3$PPd(Ph)Br (**2**) as a catalyst. The expected polymerization mechanism is shown in Scheme 1. In accordance with the proposed mechanism of the Suzuki−Miyaura reaction,[12] the polymerization would be initiated by the transmetallation reaction between **1** and **2** to give the Pd complex **3**. If the Pd(0) species, formed through the reductive elimination process, is transferred intramolecularly to the C−Br bond at the end of the same molecule, the polymerization would proceed in a chain-growth polymerization manner from **4** to result in the formation of polyarylylene **5** with a phenyl group at the initiation end.

When **1b** was polymerized with 5 mol % of **2** in a mixture of THF and 2 mol/L aqueous solution of Na$_2$CO$_3$ at room temperature, the polymerization proceeded almost to completion within 30 min. Gel permeation chromatography (GPC) analysis of the crude product showed a unimodal elution curve with $M_n = 11000$ relative to polystyrene standards and $M_w/M_n = 1.53$. On the other hand, polymerization of **1a** under the same conditions also completed in 30 min to afford poly(9,9-dioctylfluorene) with narrower molecular weight distributions ($M_n = 17700$ and $M_w/M_n = 1.33$). These results suggest that the polymerization system is suitable for catalyst-transfer polymerization of fluorene monomer **1b**. Furthermore, poly(9,9-dialkylfluorene) is one of the most attractive π-conjugated polymers owing to its blue electroluminescence.[13] Therefore, we studied the polymerization behavior of **1a** in more detail.

The end groups of the obtained polyfluorene were analyzed by means of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry.[14] As shown in Figure 1, the major peaks of the mass spectrum correspond to the polymer with a phenyl group at one end and a bromine atom at the other end (designated as Ph/Br), and Ph/H ended polymers were also observed as minor peaks. The fact that all the polymers bore the phenyl group at one end strongly supports the proposed initiation mechanism, that is, the polymerization was started by the reaction between **1a** and **2** with introduction of the phenyl group of **2** into **1a** to form **4**. If the polymerization proceeded via a catalyst-transfer mechanism, the propagating end of the polymer would be Ar(polymer)−Pd(P^{t}Bu$_3$)−Br, as in the case of the Ni-catalyzed polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene.[5] Taking into account

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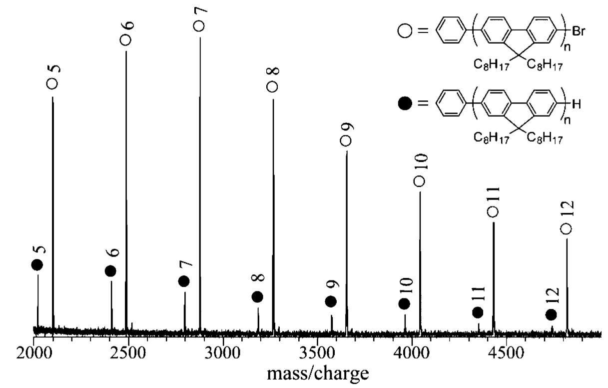

Figure 1. MALDI-TOF mass spectrum of poly(9,9-dioctylfluorene) obtained by the polymerization of **1a** with 5 mol % of **2** in a mixture of THF and 2 mol/L aqueous solution of Na_2CO_3 at room temperature for 30 min. The peaks indicated by the open and closed circles correspond to Ph/Br and Ph/H ended polymers, respectively, and the numbers above the circles represent the degree of polymerization (*n*) of the polymer.

Roy and Hartwig's report that the addition of $\mathrm{P}^t\mathrm{Bu}_3$ to $\mathrm{P}^t\mathrm{Bu}_3$-ligated arylpalladium halide complex induced the reductive elimination of the aryl halide accompanied with formation of the arene and the biaryl as side products,[15] the Br and H ends of the isolated polymers are considered to originate from Ar(polymer)−Pd($\mathrm{P}^t\mathrm{Bu}_3$)−Br polymer propagating groups, which might be converted to Ar(polymer)−Br and Ar(polymer)−H during the quenching of the polymerization reaction.

For clarifying the reaction mechanism, polymerization of **1a** initiated by 5 mol % of **2** was carried out in the presence of 5 mol % of 2-bromo-7-(4-*tert*-butylphenyl)-9,9-dioctylfluorene (**6**) used as a model compound of external Ar(polymer)−Br end.[14] The polymerization proceeded without consumption of **6** to yield the polyfluorene with almost the same M_n (19200) and M_w/M_n (1.34) values as in the case of the polymerization without **6** described above. This data supports the intramolecular transfer of the Pd(0) species from **3** to **4**.

To study the polymerization behavior in more detail, the relationship between the conversion of the monomer **1a** and M_n of the obtained polymer was investigated. Conversion-M_n and conversion-M_w/M_n plots, obtained by the polymerization of **1a** with 5 mol % of **2** in a mixture of THF and 2 mol/L aqueous solution of Na_2CO_3 at room temperature, revealed that M_n increased linearly in proportion to the conversion of **1a** with low polydispersity throughout the polymerization (Figure 2a). Furthermore, as shown in Figure 2b, the molecular weight of the polymer increased linearly in proportion to the feed ratio of **1a** to **2** up to $M_n = 17700$ with a narrow molecular-weight distribution throughout.[16] These linear relationships indicate that the organometallic polycondensation proceeds through a chain-growth polymerization mechanism.

In conclusion, we have demonstrated that the polycondensation of **1a** with a catalytic amount of **2** via Suzuki-Miyaura coupling reaction afforded poly(9,9-dioctyl-2,7-fluorene) with a narrow molecular-weight distribution. The complete introduction of the initiator unit at the polymer end and the linear relationships of conversion-M_n and feed ratio-M_n indicate that the polycondensation proceeded in a chain-growth polymerization manner from an initiator unit derived from the catalyst. These results open the door to the synthesis of well-defined conjugated polymers with designed initiators. Experiments along this line are in progress.

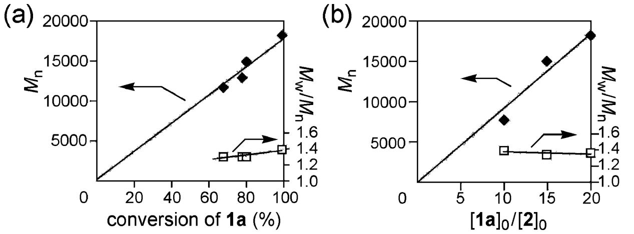

Figure 2. M_n and M_w/M_n values of poly(9,9-dioctylfluorene) as a function of (a) monomer conversion, obtained with **1a** and 5 mol % of **2** and (b) the feed ratio of **1a** to **2** ($[\mathbf{1a}]_0 = 25$ mmol/L; $[\mathbf{2}]_0 = 2.5$ mmol/L (10 mol %), 1.67 mmol/L (6.7 mol %), 1.25 mmol/L (5 mol %)). All the polymerizations were carried out in a mixture of THF and 2 mol/L aqueous solution of Na_2CO_3 at room temperature. M_n and M_w/M_n values were determined by GPC relative to polystyrene standards.

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Supporting Information Available: The experimental details of the polymerization of **1a** and **1b**, ^{1}H and ^{13}C NMR spectra of poly**1a** and poly**1b**, and MALDI-TOF mass spectra of the polyfluorene. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) When the polymerization was carried out with 2.5 mol % of **2** ($[\mathbf{1a}]_0/[\mathbf{2}]_0 = 40$), the molecular weight of the obtained polymer ($M_n = 20700$) deviated from the value expected from the linear relation shown in Figure 2b, and the molecular weight distribution ($M_w/M_n = 1.51$) was broad. This appeared to be due to precipitation of the growing polymer at the late stage of the polymerization.

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