Investigation of Mizoroki-Heck Coupling Polymerization as a Catalyst-Transfer Condensation Polymerization for Synthesis of Poly(*p*-phenylenevinylene)

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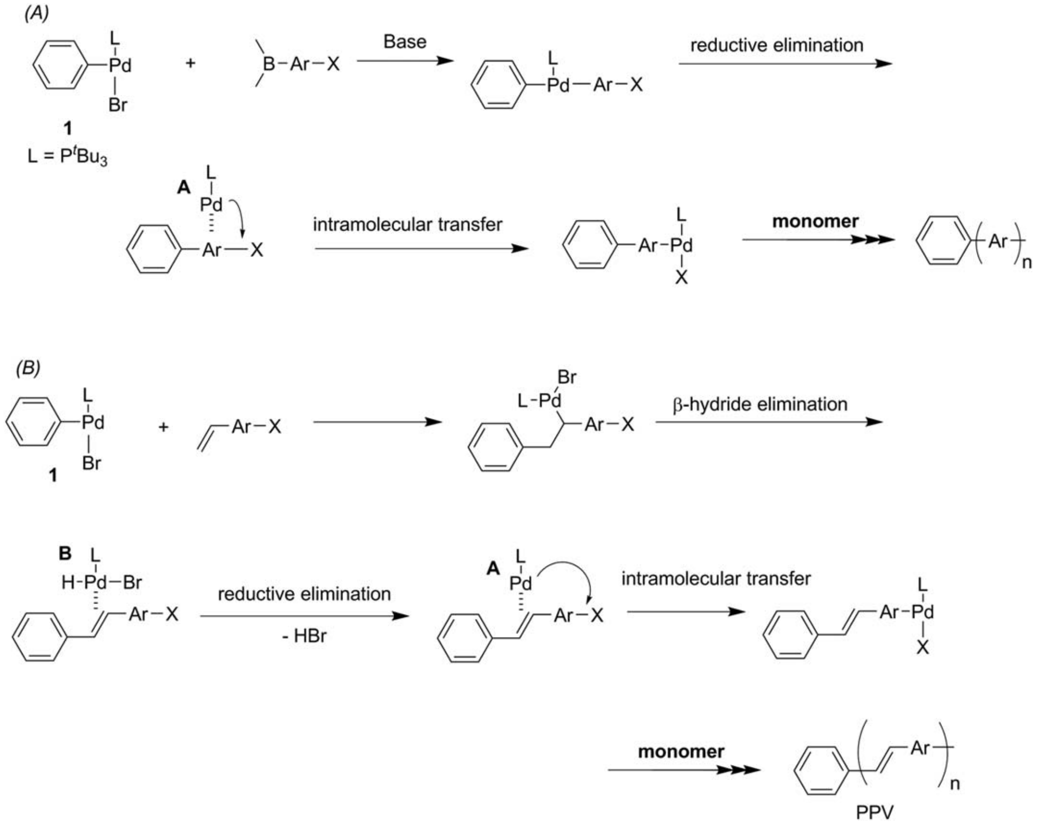
ABSTRACT: Mizoroki-Heck coupling polymerization of 1,4-bis[(2-ethylhexyl)oxy]-2-iodo-5-vinylbenzene (**1**) and its bromo counterpart **2** with a Pd initiator for the synthesis of poly(phenylenevinylene) (PPV) was investigated to see whether the polymerization proceeds in a chain-growth polymerization manner. The polymerization of **1** with ^{t}Bu$_3$PPd(Tolyl)Br (**10**) proceeded even at room temperature when 5.5 equiv of Cy$_2$NMe (Cy = cyclohexyl) was used as a base, but the molecular weight distribution of PPV was broad. The polymerization of **2** hardly proceeded at room temperature under the same conditions. In the polymerization of **1**, PPV with H at one end and I at the other was formed until the middle stage, and the polymer end groups were converted into tolyl and H in the final stage. The number-average molecular weight (M_n) did not increase until about 90% monomer conversion and then sharply increased after that, indicating conventional step-growth polymerization. The occurrence of step-growth polymerization, not catalyst-transfer chain-growth polymerization, may be interpreted in terms of low coordination ability of H-Pd(II)-X(^{t}Bu$_3$P) (X = Br or I), formed in the catalytic cycle of the Mizoroki-Heck coupling reaction, to π-electrons of the PPV backbone; reductive elimination of H-X from this Pd species with base would take place after diffusion into the reaction mixture. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 543–551

KEYWORDS: catalyst-transfer condensation polymerization; conjugated polymers; catalysts; MALDI-TOF mass spectra; Mizoroki-Heck coupling reaction; poly(phenylenevinylene)

INTRODUCTION π-Conjugated polymers have received much attention due to potential applications in thin film transistors (TFTs),[1] organic light-emitting diodes (OLEDs),[2] and photovoltaic cells.[3] Among π-conjugated polymers, poly(*p*-phenylenevinylene) (PPV) has been intensively investigated, especially for application to OLEDs.[2] General synthetic procedures for PPV include the Gilch route, Witting reaction, and transition metal-catalyzed cross-coupling reactions.[3] These polymerizations proceed through a step-growth polymerization mechanism, and it is difficult to control molecular weight and to obtain polymers with low polydispersity. However, Galvin and co-workers prepared well-defined PPV by means of stepwise synthesis, and they found that OLED devices made from PPV with narrow polydispersity showed better external quantum efficiency as compared to those made from PPV with broad polydispersity.[4] Therefore, precision synthesis of PPV is an important research goal. Turner and co-workers succeeded in controlled synthesis of PPV by ring-opening metathesis polymerization of cyclophane monomers.[5] Junkers and co-workers carried out controlled anionic and radical polymerization of quinodimethane monomers containing a sulfinyl group, followed by thermal elimination to obtain well-defined PPV.[6,7] However, these polymerization methods can afford only block copolymers of PPV with different substituents.

On the other hand, development of catalyst-transfer condensation polymerization (CTCP) with a transition metal catalyst has made it possible to synthesize well-defined π-conjugated polymers.[8] We have proposed that this polymerization involves intramolecular catalyst transfer on the polymer backbone. Furthermore, block copolymers consisting of different π-conjugated polymers can also be obtained in one pot.[8(a,b)] Therefore, if PPV could be synthesized by means of CTCP, it would be easy to obtain well-defined π-conjugated

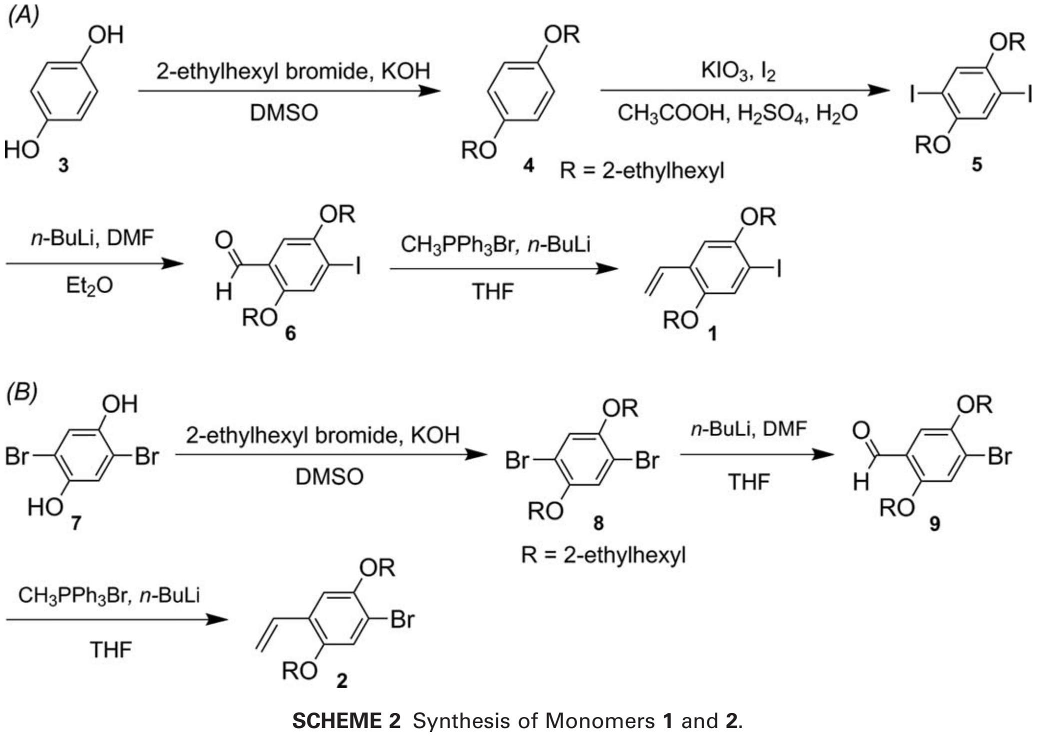
Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Proposed Pd-CTCP mechanism of (a) Suzuki-Miyaura coupling polymerization and (b) Mizoroki-Heck coupling polymerization.

block copolymers of PPV and other π-conjugated polymers such as poly(3-hexylthiphene), opening an entry into a new class of π-conjugated materials.

In the previous report, we investigated Ni-catalyzed Kumada-Tamao coupling polymerization and Pd-catalyzed Suzuki-Miyaura coupling polymerization of phenylenevinylene



SCHEME 2 Synthesis of Monomers **1** and **2**.

monomers to see whether these polymerizations would proceed in the CTCP manner to afford well-defined PPV. However, Ni-catalyzed Kumada-Tamao coupling polymerization was not suitable for the synthesis of PPV. On the other hand, Pd-catalyzed Suzuki-Miyaura coupling polymerization afforded the corresponding PPV with high molecular weight within a few minutes, but the molecular weight distribution was broad, probably due to dehalogenation and disproportionation side reactions.[9]

In the present article, we focused on Mizoroki-Heck coupling reaction for CTCP leading to PPV. This reaction does not require metalation of monomers, unlike other cross-coupling reactions, and therefore it is easy to prepare monomers.[3] Furthermore, Mizoroki-Heck coupling polymerization has recently been reassessed as an atom-efficient, greener synthetic method involving direct arylation.[10] Although direct arylation has been employed for CTCP,[11] the feasibility of Mizoroki-Heck CTCP has not been investigated. Mastrorilli and co-workers conducted Suzuki/Heck copolymerization of dibromofluorene and potassium vinyl trifluoroborate for the synthesis of poly(fluorenylene vinylene), and they observed that the polymerization proceeded in a chain-growth polymerization manner until the middle stage, while the formed oligomers were coupled in a step-growth polymerization manner in the final stage.[12] They proposed that the polymerization of fluorenylene vinylene monomer generated in situ might proceed in the CTCP manner, but the details of polymerization mechanism remained unclear.

Mizoroki-Heck coupling reaction is generally carried out under reflux condition,[3] though Fu and co-workers reported an exceptionally mild Mizoroki-Heck coupling reaction in the presence of Cy_2NMe (Cy = cyclohexyl) and Pd/^{t}Bu$_3$P, which proceeds even at room temperature.[13] They proposed that the catalytically active species might be PdP^{t}Bu$_3$ (**A**). On the other hand, it turned out that **A** has an intramolecular transfer property in Suzuki-Miyaura coupling reactions,[14] and we succeeded in Suzuki-Miyaura CTCP by using ^{t}Bu$_3$PPd(Ar)Br as an external initiator.[8(o–q)] Therefore, it occurred to us that Mizoroki-Heck polymerization with this Pd initiator might proceed at room temperature in a CTCP manner.

However, the reaction mechanism of Mizoroki-Heck coupling reaction differs from that of other cross coupling reactions, such as Suzuki-Miyaura coupling reaction. In the case of Pd-catalyzed Suzuki-Miyaura CTCP, palladium(0) complex **A**, which has three unshared coordination sites, would be generated after reductive elimination and would move to the terminal C-X bond of the elongated monomer unit through coordination of π orbitals of the polymer main chain. By contrast, in the case of Mizoroki-Heck coupling polymerization, threefold coordinated palladium(II) complex **B** is generated after carbopalladation and β-hydrogen elimination.[15] If reductive elimination of HX from **B** occurs with coordination of the polymer main chain, CTCP can proceed. On the other hand, if reductive elimination occurs after the diffusion of **B** into the reaction mixture, because of low coordination ability of **B**, intermolecular transfer of **A** will occur, resulting in step-growth polymerization (Scheme 1). The present article reports an investigation of Mizoroki-Heck coupling polymerization with ^{t}Bu$_3$PPd(Ar)Br as a new candidate for CTCP leading to PPV.

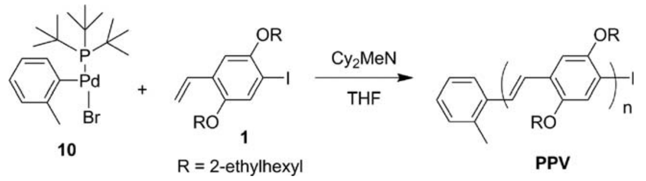
EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-600 spectrometers. The internal standard for ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm) and the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm). Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto), dehydrated diethyl ether (Kanto), dehydrated dimethyl sulfoxide (DMSO) (Kanto) and dehydrated *N*,*N*-dimethylformamide (DMF) (Wako) were used as dry solvents. *n*-Butyllithium (1.6 M solution in hexane, Kanto) was used as received. ^{t}Bu$_3$PPd(*o*-tolyl)Br (**10**) was prepared as described.[16] The M_n and M_w/M_n values of polymers were measured on a Tosoh HLC-8020 gel permeation chromatography (GPC) unit (eluent, THF; calibration, polystyrene standards) with two TSK-gel columns (2 × Multipore H_{XL}-M). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus in the reflectron ion mode by use of a laser ($\lambda = 337$ nm). Dithranol (1,8-dihydroxy-9[10*H*]anthracenone) was used as the matrix for the MALDI-TOF mass measurements. Synthetic procedures for Monomers **1** and **2** were described in Supporting Information.

General Procedure for Mizoroki-Heck Coupling Polymerization

All glass apparatus was dried prior to use. Addition of reagents to the reaction flask and withdrawal of small aliquots of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under an argon atmosphere. Monomer **1** or **2** (0.1 mM) and *N*,*N*-dicyclohexylmethylamine (0.55 mM) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (0.1 mL) was added to the flask via a syringe, and the mixture was degassed with argon. A solution of **10** (0.005 mM, 5.0 mol %) in dry THF (0.3 mL, degassed with argon) was added via a syringe, and the reaction mixture was stirred at the



SCHEME 3 Polymerization of **1** with **10** for the synthesis of PPV.

TABLE 1 Polymerization of **1** with 5 mol % of **10** and Cy_2NMe

Entry	Equivalent of base	Temperature (°C)	Time (h)	M_n (M_w/M_n)[a]
1[b]	1.1	rt	54	1,630 (1.08)[d]
2[c]	1.1	rt	81	2,450 (1.33)[d]
3[c]	1.1	50	125	11,260 (2.04)
4[c]	1.1	30	288	4,850 (1.73)[d]
5[c]	5.5	50	1	10,130 (2.16)
6[c]	5.5	rt	3.5	8,280 (2.07)

[a] Estimated by GPC based on polystyrene standards (eluent: THF).
[b] $[\mathbf{1}]_0 = 0.025$ M.
[c] $[\mathbf{1}]_0 = 0.25$ M.
[d] Monomer remained.

appropriate temperature (see Tables). After 1–312 h, 1 M hydrochloric acid was added. The mixture was extracted with chloroform, and the organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give PPV.

RESULTS AND DISCUSSION

Synthesis of Monomers

In general, Mizoroki-Heck coupling polymerization employs A_2 and B_2 type monomers, but investigation of CTCP requires AB type monomers. We prepared iodophenylenevinylene Monomer **1** and its bromo counterpart **2** to compare their reactivity (Scheme 2). To increase the solubility of PPV, 2-ethylhexyloxy groups were introduced into both monomers.

Etherification of hydroquinone with 2-ethylhexyl bromide was carried out according to the literature,[17] and then two iodine atoms were introduced. One of the iodines of **5** was reacted with *n*-butyllithium, followed by DMF, resulting in conversion to a formyl group. Finally, the formyl group of the obtained **6** was subjected to Wittig reaction to yield the iodine Monomer **1**.[18] The bromo Monomer **2** was similarly prepared from commercially available 2,5-dibromohydroquinone **7**.

Mizoroki-Heck Coupling Polymerization of Iodo Monomer 1

Since Pd-CTCP is well-controlled at lower temperature,[8(q)] polymerization of **1** with palladium initiator **10** ($[\mathbf{1}]_0/[\mathbf{10}]_0 = 20$) was first carried out in the presence of 1.1 equiv of Cy_2NMe in THF at room temperature according to Fu's procedure (Scheme 3).[13] However, the polymerization was slow, and **1** remained even after 54 hours, resulting in oligomer formation (Table 1, Entry 1). A higher monomer concentration (increased from 0.025 M to 0.25 M) gave a similar result (Entry 2). We next examined the polymerization temperature. Following a report of Mizoroki-Heck coupling polymerization that employed the same catalyst ligand and base,[19] the polymerization of **1** was carried out at 50 °C for 5 days to afford high-molecular-weight PPV ($M_n > 10000$) with a broad molecular weight distribution (Entry 3). To obtain PPV with a narrower molecular weight distribution through CTCP, the polymerization of **1** was then carried out at 30 °C, resulting in a lower molecular weight and a slightly narrower molecular weight distribution (Entry 4). Thus, it turned out that the polymerization of **1** with **10** was very sensitive to polymerization temperature.

We next increased the amount of Cy_2NMe from 1.1 to 5.5 equiv. This dramatically increased the rate of polymerization, and the reaction was completed within 1 h at 50 °C (Entry 5), implying that the rate-determining step of polymerization is reductive elimination of HI from the Pd catalyst. Furthermore, the polymerization proceeded even at room temperature, and **1** was consumed within 3.5 h (Entry 6). To our knowledge, there is no previous report of Mizoroki-Heck coupling polymerization occurring at room temperature. Unfortunately, however, the molecular weight distribution was broad, contrary to our expectation.

The MALDI-TOF mass spectrum of PPV (Entry 6) obtained at 15 min showed several series of peaks, but the major peaks can be assigned to PPV in which one end is a hydrogen atom and the other is an iodine atom (designated as H/I); the tolyl group of Pd initiator **10** was not introduced into the polymer

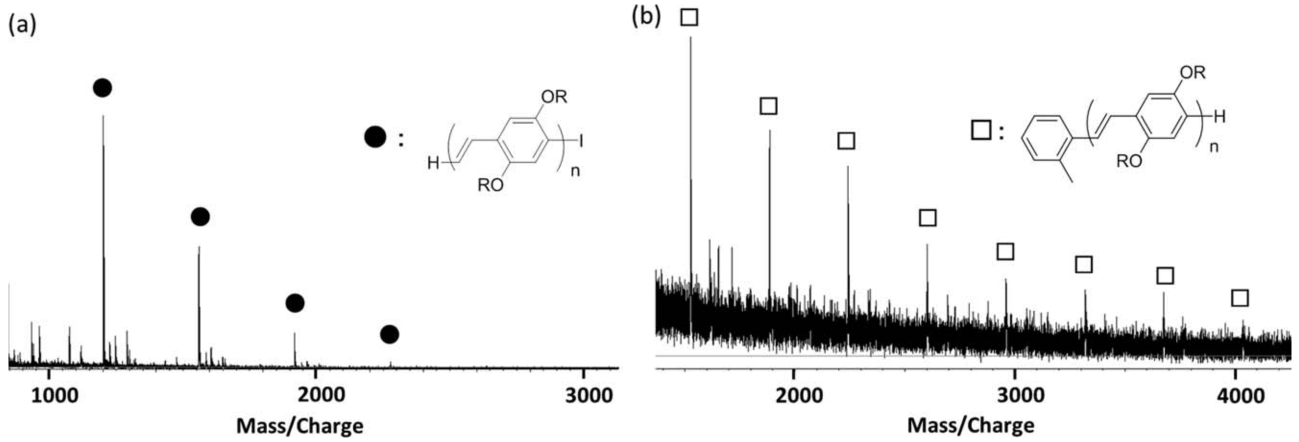


FIGURE 1 MALDI-TOF mass spectra of products obtained by polymerization of **1** in the presence of 5.5 equiv of Cy_2NMe and 5.0 mol % of **10** at room temperature in THF ($[\mathbf{1}]_0 = 0.25$ M) for (a) 15 min, ($M_n = 1570$, $M_w/M_n = 1.25$) and (b) 240 h, ($M_n = 9700$, $M_w/M_n = 2.51$).

TABLE 2 Polymerization of **2** with 5 mol % of **10** and 5.5 equivalent of Cy_2NMe

Entry	Temperature (°C)	Time (h)	M_n (M_w/M_n)[a]	Conv. of **2**[b] (%)
1	rt	168	1,060 (1.24)	40
2	50	312	4,230 (1.99)	100

[a] Estimated by GPC based on polystyrene standards (eluent: THF).
[b] Estimated by GC using naphthalene as an internal standard substance.

end [Fig. 1(a)]. This result indicated that the polymerization of **1** proceeded mainly by conventional step-growth polymerization with intermolecular transfer of the Pd catalyst (chain transfer). Surprisingly, however, in the polymerization for 10 days the polymer ends became almost uniformly Tolyl/H [Fig. 1(b)]. Accordingly, the polymerization of **1** presumably proceeded by step-growth polymerization, and then the H atom of the vinyl end group of PPV was converted into the tolyl group derived from **10** in the final stage. The other hydrogen end might be formed by hydrolysis of the C-Pd-I end or by deiodination of the polymer end as a side reaction (see "Proposed Mechanism of Polymerization" below).

Mizoroki-Heck Coupling Polymerization of Bromo Monomer 2

We next examined polymerization of bromo Monomer **2** to examine the effect of halogen in the monomer. The polymerization of **2** was first carried out at room temperature, but **2** remained even after 7 days (Table 2, Entry 1). At 50 °C, Monomer **2** was consumed after 13 days to afford PPV, the molecular weight of which was less than half that in the case of the polymerization of **1** at 50 °C. The molecular weight distribution was similarly broad (Entry 2). The MALDI-TOF mass spectrum of the obtained PPV (Entry 2) showed major H/Br peaks, indicating that polymerization of **2** was not initiated by the Pd initiator **10** and that conventional step-growth polymerization took place (Supporting Information Fig. S1).

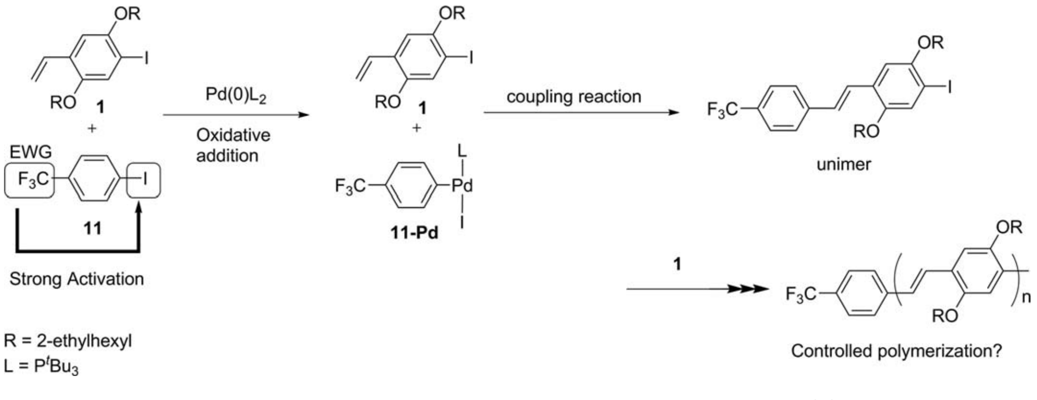
As compared with **1**, slower polymerization is accounted for by the lower oxidative addition reactivity of C-Br for Pd(0). Accordingly, the Pd catalyst might be inactivated during prolonged reaction, resulting in lower molecular weight of PPV. Therefore, it turned out that the iodo Monomer **1** is more appropriate than the bromo Monomer **2**, especially in Mizoroki-Heck coupling polymerization at room temperature.

Polymerization of 1 in the Presence of Active Aryl Halide

We next conducted polymerization of **1** with Pd(0) complex in the presence of active aryl halide **11**. Because of the higher reactivity of C-I of **11** than C-I of **1**, Pd(0) would be rapidly inserted into **11** to generate **11-Pd**, followed by polymerization of **1**, resulting in $CF_3C_6H_4$-ended PPV (Scheme 4). We considered that this might result in decreased polydispersity, even though intermolecular transfer of Pd(0) occurs in the Mizoroki-Heck coupling polymerization.

Polymerization of **1** was carried out with 0.05 equiv of bis[tri(*tert*-butyl)phosphine]palladium(0) and **11** instead of **10** in the presence of 5.5 equiv of Cy_2NMe. Contrary to our expectation, the polymerization was slower than that using **10**; **1** remained even after 19 days, and low-molecular-weight PPV was formed.[20] The reason for the slow polymerization is not clear at present, but might be interpreted in terms of low activity of this Pd(0) complex having two $(tert\text{-Bu})_3P$ ligands toward aryl halides. The MALDI-TOF mass spectra of PPV obtained at 2 days showed mainly H/I and an unidentified series of peaks [Fig. 2(a)]. Since the latter peaks were also observed in the polymerization of **1** with bis[tri(*tert*-butyl)phosphine]palladium(0) without addition of **11**, they could be due to end groups derived from excess tri(*tert*-butyl)phosphine (Fig. S2). The PPV obtained at 9 days showed only H/I peaks [Fig. 2(b)], while that obtained at 19 days showed not only H/I peaks, but also H/H and $CF_3C_6H_4$/I as minor peaks.

Accordingly, it turned out that selective coupling reaction of **1** occurred even in the presence of reactive **11** and that introduction of **11** at the polymer end required a long reaction time. Van der Boom and coworkers demonstrated that the reaction of $Ni(PEt_3)_4$ with a bromostilbene derivative resulted in selective η^2-C=C coordination, which was kinetically preferable at low temperature, followed by intramolecular "ring walking" of the metal center and intramolecular



SCHEME 4 Proposed initiation of polymerization of **1** with **11** and Pd(0) catalyst.

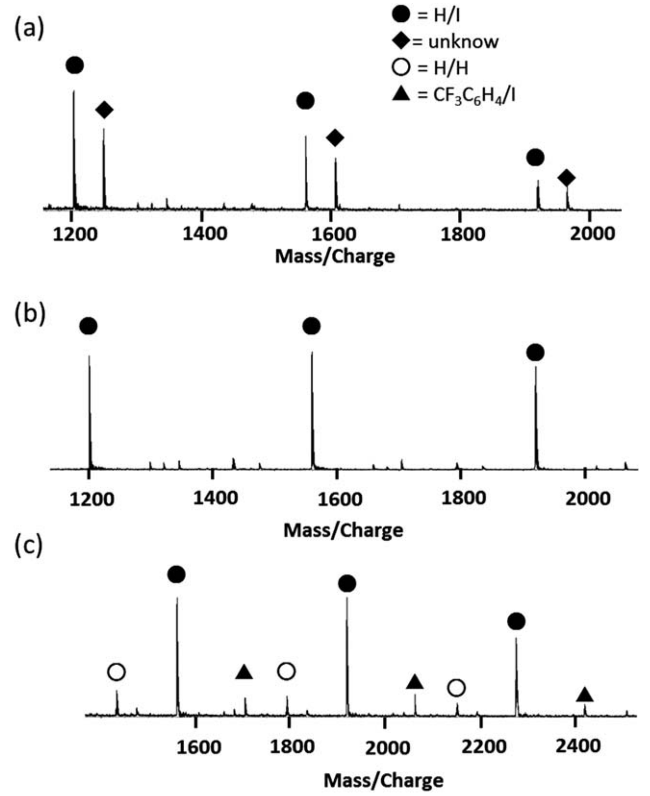


FIGURE 2 MALDI-TOF mass spectra of products obtained by polymerization of **1** in the presence of 5.5 equiv of Cy_2NMe and 5.0 mol % of **11** and bis[tri(*tert*-butyl)phosphine]palladium in THF ($[\mathbf{1}]_0 = 0.25$ M) at room temperature for (a) 49 h (conversion of $\mathbf{1} = 53\%$, $M_n = 990$, $M_w/M_n = 1.22$), (b) 216 h (conversion of $\mathbf{1} = 82\%$, $M_n = 1370$, $M_w/M_n = 1.22$), and (c) 456 h (conversion of $\mathbf{1} = 96\%$, $M_n = 1370$, $M_w/M_n = 1.40$).

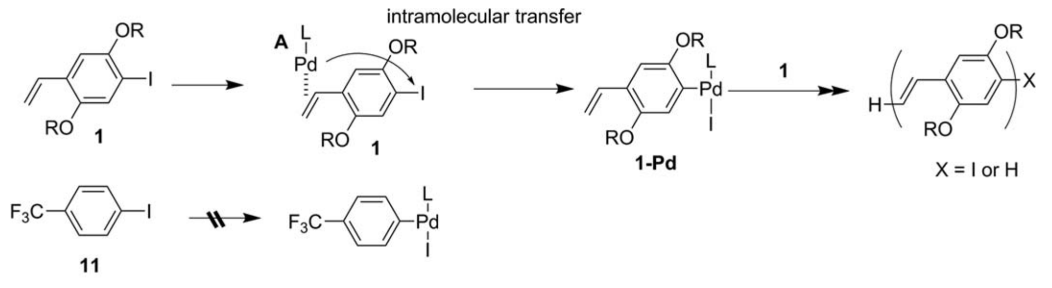
oxidative addition of aryl bromide, which was thermodynamically preferable when the temperature was raised.[21] This report, even though the central metal is different from palladium, indicates that Pd(0) **A** might preferentially coordinate to the C=C of **1** rather than be inserted into the C-I bond of reactive **11**, followed by intramolecular transfer and insertion into the C-I bond of **1** (Scheme 5).

Proposed Mechanism of Polymerization

To investigate the polymerization mechanism, we followed the monomer conversion, M_n, and changes of polymer ends with polymerization time. The M_n did not increase until the conversion of **1** reached 90%, but sharply increased after that, indicating a conventional step-growth polymerization mechanism (Fig. 3). The MALDI-TOF mass spectrum of PPV obtained at 5.5 h (conversion of $\mathbf{1} = 90\%$, $M_n = 1380$, $M_w/M_n = 1.43$) contained one major series of H/I peaks, as well as a minor series of Tolyl/I peaks [Fig. 4(a,b)]. After 6 days (conversion of $\mathbf{1} = 100\%$, $M_n = 3730$, $M_w/M_n = 1.95$), all of **1** was consumed, and the intensity of the Tolyl/I peaks was increased [Fig. 4(c,d)]. The spectrum at 13 days (conversion of $\mathbf{1} = 100\%$, $M_n = 7690$, $M_w/M_n = 2.16$) showed a major series of Tolyl/I peaks and a minor series of Tolyl/H peaks [Fig. 4(e,f)].

On the basis of the above results, we propose the following reaction mechanism for the polymerization of **1** with **10** (Scheme 6). Polymerization is initiated by carbopalladation of **1** with **10**, followed by β-hydrogen elimination with concomitant generation of Pd(II) complex **B**. Since the coordination ability of **B** toward C=C bond is low, reductive elimination of HI takes place after the diffusion of **B** into the reaction mixture to afford unimer and Pd(0) complex **A** (Scheme 6, Step 1). The C=C bond of **1** coordinates to **A** and induces intramolecular oxidative addition at the C-I bond, followed by coupling reaction with another **1** to afford dimer. After that, H/I-ended oligomers are formed in a step-growth polymerization manner (Step 2). After consumption of **1**, H/I-ended oligomers react with Tolyl/I-ended oligomers to afford Toly/I-ended PPV (Step 3). Finally, deiodination of polymer partially occurs by hydrolysis of the C-Pd-I end of PPV, which is generated by oxidative addition of the C-I end of PPV with **A** (Step 4).

Thus, there appear to be two reasons why Mizoroki-Heck coupling polymerization did not proceed in a CTCP manner. First, Pd(II) complex **B**, formed in the catalytic cycle of Mizoroki-Heck coupling reaction, does not have strong coordination ability to the polymer backbone, and reductive elimination of H-I from **B** presumably occurs after diffusion of **B** into the reaction mixture. Second, **A** diffuses into the



R = 2-ethylhexyl
L = P^tBu_3

SCHEME 5 Proposed mechanism of Mizoroki-Heck coupling polymerization of **1** with **11** and Pd(0) catalyst.

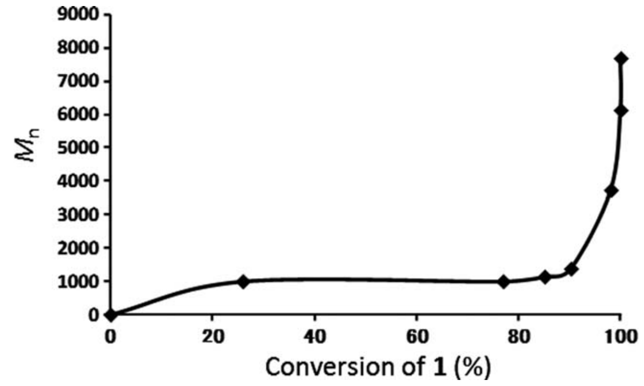


FIGURE 3 M_n values of products as a function of monomer conversion in polymerization of **1** in the presence of 5.5 equiv of Cy_2NMe and 5.0 mol % of **10** in THF ($[\mathbf{1}]_0 = 0.25$ M) at room temperature.

reaction mixture, where it preferentially coordinates to the C=C bond of **1**, followed by intramolecular oxidative addition of C-I of **1**, which would induce step-growth polymerization.

CONCLUSION

The feasibility of CTCP by means of Mizoroki-Heck coupling reaction for the synthesis of well-defined PPV was investigated. The polymerization of 1-iodo-4-vinylbenzene Monomer **1** with ^{t}Bu$_3$PPd(Tolyl)Br (**10**) proceeded even at room temperature when 5.5 equiv of Cy_2NMe was used. However, the molecular weight distribution of the obtained PPV was broad, and MALDI-TOF mass spectra indicated that PPV molecules with H/I end groups, which would not have been initiated by **10**, were formed at the early stage, implying that the polymerization proceeds via chain transfer of the

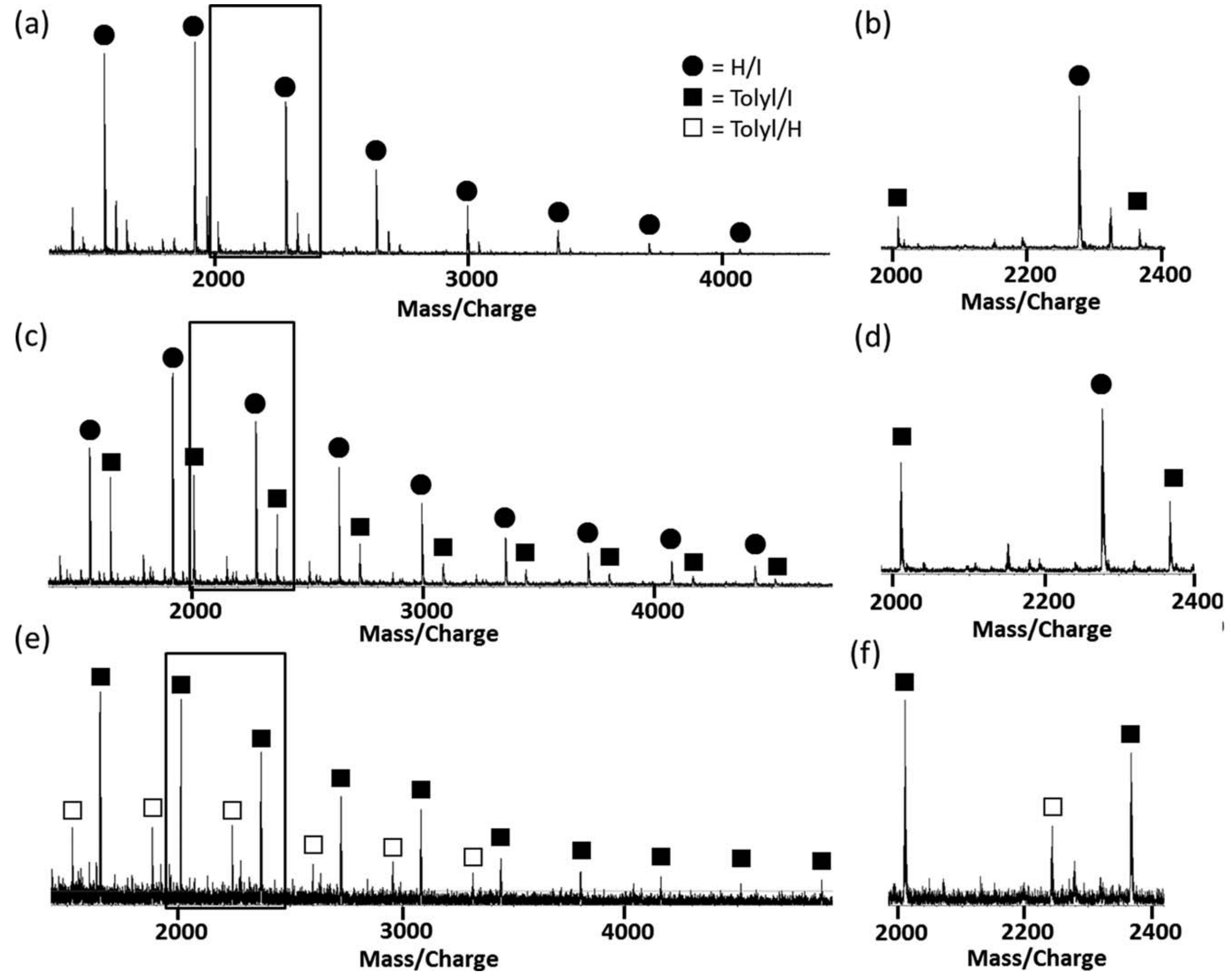
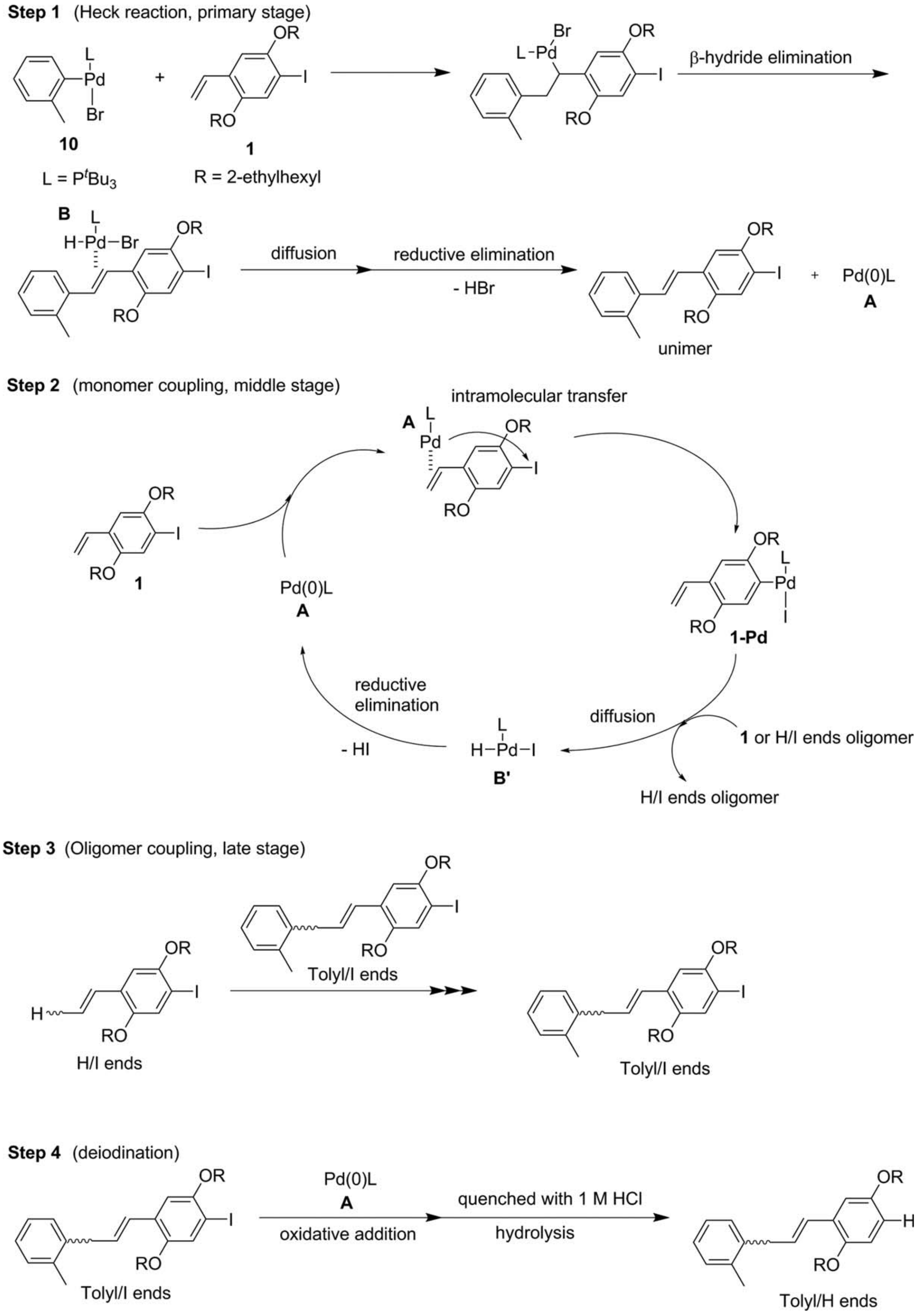


FIGURE 4 MALDI-TOF mass spectra of products obtained by polymerization of **1** in the presence of 5.5 equiv of Cy_2NMe and 5.0 mol % of **10** in THF ($[\mathbf{1}]_0 = 0.25$ M) at room temperature for (a, b) 5.5 h (conversion of $\mathbf{1} = 90\%$, $M_n = 1380$, $M_w/M_n = 1.43$), (c, d) 6 days (conversion of $\mathbf{1} = 100\%$, $M_n = 3730$, $M_w/M_n = 1.95$), and (e, d) 13 days (conversion of $\mathbf{1} = 100\%$, $M_n = 7690$, $M_w/M_n = 2.16$). (b), (d), and (f) are expanded (a), (c), and (e), respectively.



SCHEME 6 Proposed mechanism of Mizoroki-Heck coupling polymerization of **1** with **10**.

catalyst. Furthermore, it turned out that selective coupling reaction between the monomers occurred even in the presence of active 4-iodobenzotrifluoride. The relationship between monomer conversion and M_n also supported a conventional step-growth polymerization mechanism. The observed lack of CTCP behavior in Mizoroki-Heck coupling polymerization is presumably due to low coordination ability of H-Pd-I complex **B** to the polymer backbone; Pd(0) complex **A**, which enables Suzuki-Miyaura CTCP, is generated by reductive elimination of H-I from **B** after diffusion into the reaction mixture. Although the molecular weight distribution of PPV obtained by Mizoroki-Heck coupling polymerization of **1** was broad, the polymer end groups were controlled to some extent.

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REFERENCES AND NOTES

1 A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, A. Salleo, *Chem. Rev.* **2010**, *110*, 3–24.

2 A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897–1091.

3 Y. Pang, In Design and Synthesis of Conjugated Polymers; Wiley-VCH Verlag GmbH & Co.: KGaA, **2010**, pp 147–174.

4 A. Menon, H. Dong, Z. I. Niazimbetova, L. J. Rothberg, M. E. Galvin, *Chem. Mater.* **2002**, *14*, 3668–3675.

5 C. Y. Yu, M. L. Turner, *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 7797–7800.

6 I. Cosemans, J. Wouters, T. Cleij, L. Lutsen, W. Maes, T. Junkers, D. Vanderzande, *Macromol. Rapid Commun.* **2012**, *33*, 242–247.

7 J. Vandenbergh, I. Cosemans, L. Lutsen, D. Vanderzande, T. Junkers, *Polym. Chem.* **2012**, *3*, 1722.

8 (a) T. Yokozawa, A. Yokoyama, *Chem. Rev.* **2009**, *109*, 5595–5619; (b) T. Yokozawa, Y. Ohta, *Chem. Commun.* **2013**, *49*, 8281–8310; (c) A. Yokoyama, R. Miyakoshi, T. Yokozawa, *Macromolecules* **2004**, *37*, 1169–1171; (d) R. Miyakoshi, A. Yokoyama, T. Yokozawa, *Macromol. Rapid Commun.* **2004**, *25*, 1663–1666; (e) R. Miyakoshi, A. Yokoyama, T. Yokozawa, *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547; (f) I. Adachi, R. Miyakoshi, A. Yokoyama, T. Yokozawa, *Macromolecules* **2006**, *39*, 7793–7795; (g) E. E. Sheina, J. S. Liu, M. C. Iovu, D. W. Laird, R. D. McCullough, *Macromolecules* **2004**, *37*, 3526–3528; (h) M. C. Iovu, E. E. Sheina, R. R. Gil, R. D. McCullough, *Macromolecules* **2005**, *38*, 8649–8656; (i) A. Yokoyama, A. Kato, R. Miyakoshi, T. Yokozawa, *Macromolecules* **2008**, *41*, 7271–7273; (j) R. Miyakoshi, K. Shimono, A. Yokoyama, T. Yokozawa, *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013; (k) A. Sui, X. Shi, S. Wu, H. Tian, Y. Geng, F. Wang, *Macromolecules* **2012**, *45*, 5436–5443; (l) Y. Nanashima, A. Yokoyama, T. Yokozawa, *Macromolecules* **2012**, *45*, 2609–2613; (m) V. Senkovskyy, R. Tkachov, H. Komber, M. Sommer, M. Heuken, B. Voit, W. T. S. Huck, V. Kataev, A. Petr, A. Kiriy, *J. Am. Chem. Soc.* **2011**, *133*, 19966–19970; (n) R. J. Ono, S. Kang, C. W. Bielawski, *Macromolecules* **2012**, *45*, 2321–2326; (o) A. Yokoyama, H. Suzuki, Y. Kubota, K. Ohuchi, H. Higashimura, T. Yokozawa, *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237; (p) T. Yokozawa, H. Kohno, Y. Ohta, A. Yokoyama, *Macromolecules* **2010**, *43*, 7095–7100; (q) T. Yokozawa, R. Suzuki, M. Nojima, Y. Ohta, A. Yokoyama, *Macromol. Rapid Commun.* **2011**, *32*, 801–806; (r) E. Elmalem, A. Kiriy, W. T. S. Huck, *Macromolecules* **2011**, *44*, 9057–9061; (s) S. Kang, R. J. Ono, C. W. Bielawski, *J. Am. Chem. Soc.* **2013**, *135*, 4984–4987.

9 M. Nojima, Y. Ohta, T. Yokozawa, *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2643–2653.

10 K. Okamoto, J. Zhang, J. B. Housekeeper, S. R. Marder, C. K. Luscombe, *Macromolecules* **2013**, *46*, 8059–8078.

11 (a) S. Tamba, K. Shono, A. Sugie, A. Mori, *J. Am. Chem. Soc.* **2011**, *133*, 9700–9703; (b) S. Tamba, S. Tanaka, Y. Okubo, H. Meguro, S. Okamoto, A. Mori, *Chem. Lett.* **2011**, *40*, 398–399.

12 R. Grisorio, G. P. Suranna, P. Mastrorilli, *Chem. Eur. J.* **2010**, *16*, 8054–8061.

13 A. F. Littke, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 6989–7000.

14 (a) C.-G. Dong, Q.-S. Hu, *J. Am. Chem. Soc.* **2005**, *127*, 10006–10007; (b) S. K. Weber, F. Galbrecht, U. Scherf, *Org. Lett.* **2006**, *8*, 4039–4041.

15 W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2–7.

16 J. P. Stambuli, C. D. Incarvito, M. Buhl, J. F. Hartwig, *J. Am. Chem. Soc.* **2004**, *126*, 1184–1194.

17 S. Wen, J. Pei, Y. Zhou, P. Li, L. Xue, Y. Li, B. Xu, W. Tian, *Macromolecules* **2009**, *42*, 4977–4984.

18 J. Hou, B. Fan, L. Huo, C. He, C. Yang, Y. Li, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1279–1290.

19 H. Skaff, K. Sill, T. Emrick, *J. Am. Chem. Soc.* **2004**, *126*, 11322–11325.

20 High-molecular-weight PPV was obtained under the same conditions at 50 °C.

21 O. V. Zenkina, A. Karton, D. Freeman, L. J. W. Shimon, J. M. L. Martin, M. E. van der Boom, *Inorg. Chem.* **2008**, *47*, 5114–5121.