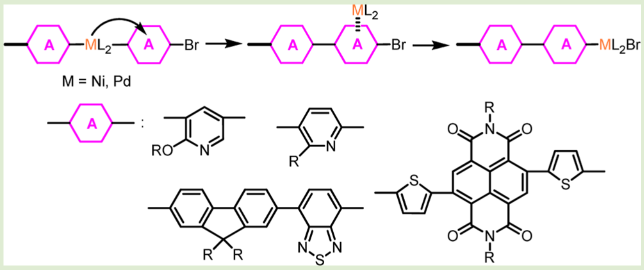
ACS Macro Letters
Viewpoint
pubs.acs.org/macroletters

Precision Synthesis of n-Type π-Conjugated Polymers in Catalyst-Transfer Condensation Polymerization

Tsutomu Yokozawa,* Yutaka Nanashima, and Yoshihiro Ohta

Department of Material and Life Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan



ABSTRACT: Recent developments in catalyst-transfer condensation polymerization, which proceeds in a chain-growth polymerization manner, have made it possible to synthesize well-defined π-conjugated polymers with controlled molecular weight and low polydispersity, as well as block copolymers and gradient copolymers. However, catalyst-transfer condensation polymerization has been limited to the polymerization of donor monomers (such as thiophene) for the synthesis of p-type π-conjugated polymers. Here, we highlight several recent advances in catalyst-transfer condensation polymerization leading to n-type π-conjugated polymers. The Kumada−Tamao coupling polymerization of Grignard pyridine monomers yields well-defined poly(pyridine-3,5-diyl) and poly(pyridine-2,5-diyl) with a broad molecular weight distribution. Monomers consisting of strong acceptor and weak donor moieties also undergo catalyst-transfer polymerization; well-defined poly(fluorene benzothiaziazole) was obtained by Suzuki−Miyaura coupling polymerization and poly(bithiophene naphthalene diimide) was obtained by an unusual Ni-catalyzed coupling polymerization of an anion radical generated from a bromothiophene naphthalene diimide bromothiophene monomer and activated zinc.

Conjugated polymers are an increasingly important class of materials, because they can be fabricated by low-cost solution processing and hence offer economic advantages in the production of thin film transistors,[1] organic light-emitting diodes,[2] and photovoltaic cells.[3] Many π-conjugated polymers have been conventionally synthesized by means of polycondensation involving transition metal-catalyzed cross-coupling reaction, but they did not exhibit well-defined structures, owing to the involvement of the step-growth polymerization mechanism.[4,5] However, the development of chain-growth condensation polymerization with a transition metal catalyst has made it possible to synthesize well-defined π-conjugated polymers.[6,7] We have proposed that this polymerization involves intramolecular catalyst transfer on the polymer backbone.[8] In catalyst-transfer Kumada−Tamao coupling polymerization with a Ni catalyst, well-defined poly(3-alkylthiophene)s (P3ATs),[8−11] poly(*p*-phenylene),[12] poly(*m*-phenylene)s,[13] and poly(*N*-alkylpyrrole)[14,15] have been synthesized. Among these polymerizations, the catalyst-transfer condensation polymerization leading to P3ATs has been extensively developed; many kinds of block copolymers[7] and gradient copolymers[16] containing the P3AT segment have been synthesized, and the mechanism, including the role of ligands on the catalyst, has been thoroughly investigated.[17−23] Furthermore, isolable Ni-initiators[24−28] were formed and applied to the production of polythiophene brushes from a substrate surface[24,26,29−31] and of star polymers.[32] In the case of catalyst-transfer Suzuki−Miyaura coupling polymerization with a Pd catalyst, polyfluorenes,[33,34] poly(*p*-phenylene),[35] and P3AT[36] can be obtained in a controlled manner by using an isolable Pd(II) complex initiator, as well as all π-conjugated block copolymers of these polymers.

However, catalyst-transfer condensation polymerization has been limited to the polymerization of donor monomers for the synthesis of p-type π-conjugated polymers. The catalyst-transfer condensation polymerization of acceptor monomers faces the following difficulties: (1) some electron-withdrawing groups, such as the carbonyl group, in acceptor monomers cannot tolerate the conditions used for formation of the Grignard monomer; (2) the solubility of n-type π-conjugated polymers is generally lower than that of p-type ones, because acceptor aromatics have stronger $\pi-\pi$ stacking interactions than donor aromatics do; (3) the weaker π-donation of the n-type polymer backbone to zerovalent metal catalyst may not sufficiently assist intramolecular catalyst transfer.

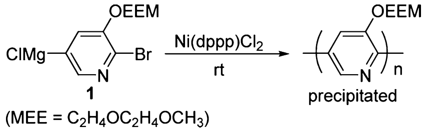
Most n-type π-conjugated polymers have been synthesized by Stille[37,38] or Suzuki[39,40] coupling polymerization of difunctional stannyl or boronic acid (ester) aromatics and dibromo aromatics containing base-sensitive heterocyles or electron-withdrawing groups. Therefore, few studies have been reported concerning the coupling polymerization of AB type acceptor monomers consisting of a single arene, except for Yamamoto coupling polymerization of dibromo acceptor monomers with an equimolar zerovalent Ni complex.[5] However, pyridine Grignard monomers can be formed from dihalopyridine with alkyl Grignard reagents without decomposition of the monomer under these conditions,[41] and so we have set out

Received: June 4, 2012
Accepted: June 19, 2012
Published: June 22, 2012

to explore the catalyst-transfer condensation polymerization of pyridine monomers as an acceptor monomer.

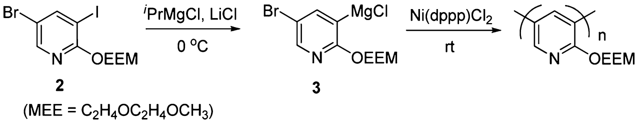
We first investigated the Kumada–Tamao coupling polymerization of 2-bromo-5-chloromagnesio-3-(2-(2-methoxyethoxy)-ethoxy)pyridine **1** with a Ni catalyst, since we have found that di- and trioxaalkyl groups are effective for increasing the solubility of aromatic polyester[42] and polythiophene.[43] However, the polymer (M_n = 25 000, M_w/M_n = 1.33) was unexpectedly precipitated during the polymerization (Scheme 1), although the obtained polymer was soluble in dichloromethane and chloroform.[44]

Scheme 1. Polymerization of 1



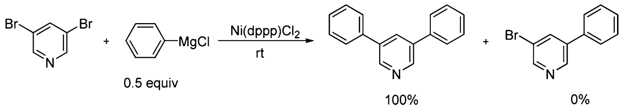
Only if the polymer is soluble in the reaction solvent would we be able to establish whether this acceptor monomer unit undergoes Kumada–Tamao catalyst-transfer condensation polymerization. Therefore, we changed the polymerization position of this monomer unit from the 2,5-position (*para* type) to the 3,5-position (*meta* type) while retaining the same side chain, although the obtained polypyridine lacks conjugation between the repeat units in the polymer.[45] We used 5-bromo-3-iodo-2-(2-(2-methoxyethoxy)ethoxy)pyridine (**2**) as a monomer precursor, hoping for quantitative generation of Grignard monomer **3** via a more facilitated magnesium-iodo exchange reaction. Indeed, the reaction of **2** with 1.0 equiv of ^{i}PrMgCl smoothly proceeded at 0 °C for 1 h to quantitatively afford Grignard monomer **3**. The polymerization of **3** with Ni(dppp)Cl$_2$ was carried out in the presence of LiCl (2 equiv to **3**) (Scheme 2). When the M_n and M_w/M_n values of the crude polymer were plotted against monomer conversion, the M_n value increased in proportion to conversion, and the M_w/M_n ratio was 1.34 or below over the whole conversion range, indicating chain-growth polymerization behavior. Furthermore, the M_n value also linearly increased in proportion to the feed ratio of monomer precursor **2** to the Ni catalyst (M_n = 5000–10000). The matrix-assisted desorption ionization time-of-flight (MALDI-TOF) mass spectrum of the obtained polymer contained one major series of peaks and one minor series of peaks. The major peaks correspond to the Na$^+$ adducts of polypyridine with bromine at one end and hydrogen at the other (designated as Br/H). The minor peaks correspond to polypyridine with Br/H ends. The polymerization behavior and the MALDI-TOF mass spectrum strongly support the involvement of a catalyst-transfer polymerization mechanism.

Scheme 2. Polymerization of 3 from Precursor 2



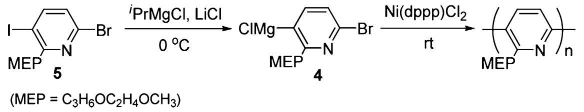
We further examined whether the Ni catalyst would move intramolecularly on the pyridine ring by means of a model reaction, as McCullough had done in the investigation of the catalyst-transfer polymerization of thiophene monomer.[46] Thus, 3,5-dibromopyridine was reacted with 0.5 equiv of phenylmagnesium chloride in the presence of a catalytic amount of Ni(dppp)Cl$_2$ (dppp = 1,3-bis(diphenylphosphino)-propane) in tetrahydrofuran (THF) at ambient temperature. It turned out that only 3,5-diphenylpyridine was quantitatively formed (Scheme 3). This result indicated that successive coupling reactions took place via intramolecular transfer of the Ni(0) catalyst on the pyridine ring, even though the π-donation ability of pyridine is weaker than that of donor monomers such as thiophene.

Scheme 3. Model Reaction of 3,5-Dibromopyridine with Phenylmagnesium Chloride



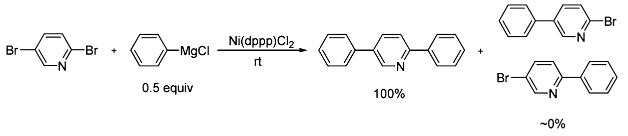
The polypyridine in Scheme 2 is a nonconjugated polymer, and the electron-donating alkoxy group decreases the electron acceptor nature of the pyridine repeat unit. Accordingly, we should consider polymerization of *para*-substituted pyridine monomer bearing an alkyl side chain for the synthesis of well-defined n-type π-conjugated polymers. Thus, the polymerization of 6-bromo-3-chloromagnesio-2-(3-(2-methoxyethoxy)-propyl)pyridine **4**, formed from the corresponding bromoiodo precursor **5**, with a Ni catalyst was investigated (Scheme 4).[47]

Scheme 4. Polymerization of 4 from Precursor 5



We first examined whether the Ni catalyst would intramolecularly walk on the acceptor pyridine ring even between the *para* positions by means of a model reaction. Thus, 2,5-dibromopyridine was reacted with 0.5 equiv of phenylmagnesium chloride in the presence of a catalytic amount of Ni(dppp)Cl$_2$ in THF at ambient temperature. We found that 2,5-diphenylpyridine was quantitatively formed, indicating that successive coupling reactions took place via intramolecular transfer of Ni(0) catalyst on the pyridine ring, as in the case of the model reaction using 3,5-dibromopyridine (Scheme 5).

Scheme 5. Model Reaction of 2,5-Dibromopyridine with Phenylmagnesium Chloride

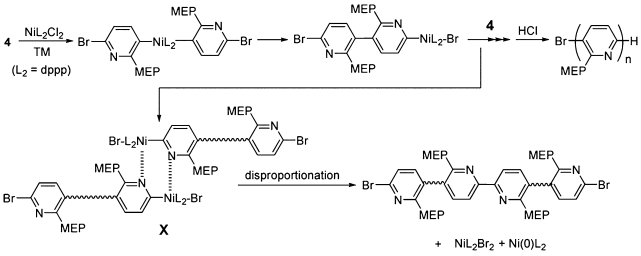


Therefore, we expected that the polymerization of *para*-substituted pyridine monomer bearing an alkyl group would also proceed via a catalyst-transfer chain-growth polymerization mechanism to yield poly(pyridine-2,5-diyl) with a well-defined molecular weight and low polydispersity.

However, the polymerization of **4** with Ni(dppp)Cl$_2$ in the presence of 1.0 equiv of LiCl afforded polymer with a broad molecular weight distribution (M_n = 10 300, M_w/M_n = 4.35). The MALDI-TOF mass spectrum of the obtained polypyridine contained one major series of peaks, corresponding to the K$^+$

adducts of the Br/Br-ended polymer, accompanied by two minor series of peaks. The two minor series of peaks correspond to the K$^+$ adducts of polymer with Br/H ends and the Na$^+$ adducts of polymer with Br/Br ends. We followed the time course of the polymerization to clarify when the polymer with Br/Br ends was formed. In the MALDI-TOF mass spectra, the major peaks were always those of Br/Br-ended polymers from the early stage to the final stage. This result indicated that disproportionation occurred continually from the initial stage of polymerization. Thus, the polymerization of **4** with Ni(dppp)Cl$_2$ proceeds essentially via an intramolecular catalyst-transfer polymerization mechanism to afford polymer with Br/H ends after hydrolysis of the polymer−Ni−Br complex, but the disproportionation reaction continually occurs to afford polymer with Br/Br ends, as well as Ni(II) and Ni(0) complexes, which can initiate the polymerization from **4** and insert into the terminal C−Br bond followed by repropagation, respectively (Scheme 6). The tendency for occurrence of disproportionation in the polymerization of pyridine monomer **4** can presumably be attributed to coordination of the nitrogen in the pyridine−Ni−Br end to the Ni in another pyridine−Ni−Br end, as shown in complex X in Scheme 6. Suzuki−Miyaura coupling polymerization of a pinacol boronate monomer, having the same substituted pyridine structure, with *o*-tolylPd(^{t}Bu$_3$P)Br was also accompanied with disproportionation.[47]

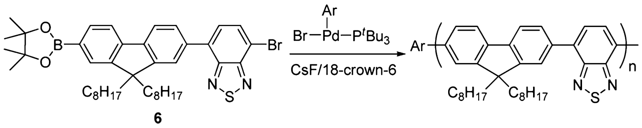
Scheme 6. Proposed Mechanism of Polymerization of 4



TM = transmetalation

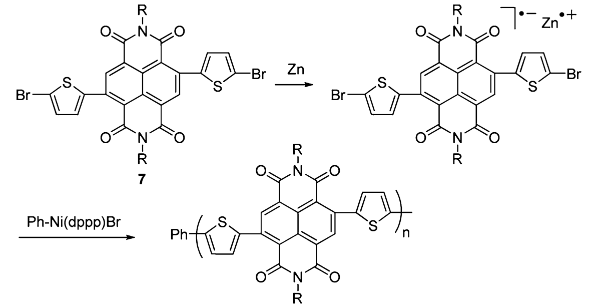
Huck and Kiriy investigated the polymerization of AB type monomers consisting of a strong acceptor arene and weak donor arene. Solubilizing side chains are introduced into the donor unit of the monomers. AB type monomer **6** composed of fluorene boronic acid ester and bromobenzothiadiazole was synthesized, and Suzuki−Miyaura coupling polymerization with ArPd(^{t}Bu$_3$P)Br (Ar = Ph and pyrenyl) was conducted in the presence of CsF and crown ether.[48] The molecular weight of the obtained polymer increased with reaction time (M_n = 3300−7400), and the molecular weight distribution remained narrow ($M_w/M_n \leq 1.27$), indicating a chain-growth polymerization mechanism. Furthermore, the MALDI-TOF mass spectra showed two series of peaks corresponding to polymer with Ar/Br and Ar/H ends. The presence of an aryl group on every polymer chain strongly supports the chain-growth polymerization from the Pd complex initiator (Scheme 7).

Scheme 7. Polymerization of 6



Symmetrical dibromo monomer **7**, consisting of thiophene, naphthalenediimide, and thiophene, was also investigated.[49] The first attempt to form a Grignard monomer from **7** for Kumada−Tamao coupling polymerization failed. Activated Zn was next reacted with **7** for generation of an organozinc monomer. Remarkably, however, the acidic workup of the prepared **7**/Zn complex resulted in recovery of **7**, but not the hydrized monobromo compound. Electron paramagnetic resonance measurements revealed that the **7**/Zn complex was a radical anion; single electron transfer from Zn to the electron-deficient **7** occurred. This radical anion was polymerized with Ni(dppp)Br$_2$ or PhNi(dppp)Br at room temperature. The polymerization behavior showed a chain-growth polymerization mechanism: the molecular weight increased with increasing feed ratio of monomer to the Ni catalyst, with retention of low polydispersity (M_n = 25 000−104 000, M_w/M_n = 1.3−1.7), and the phenyl group was introduced into the polymer end group when PhNi(dppp)Br was used (Scheme 8).

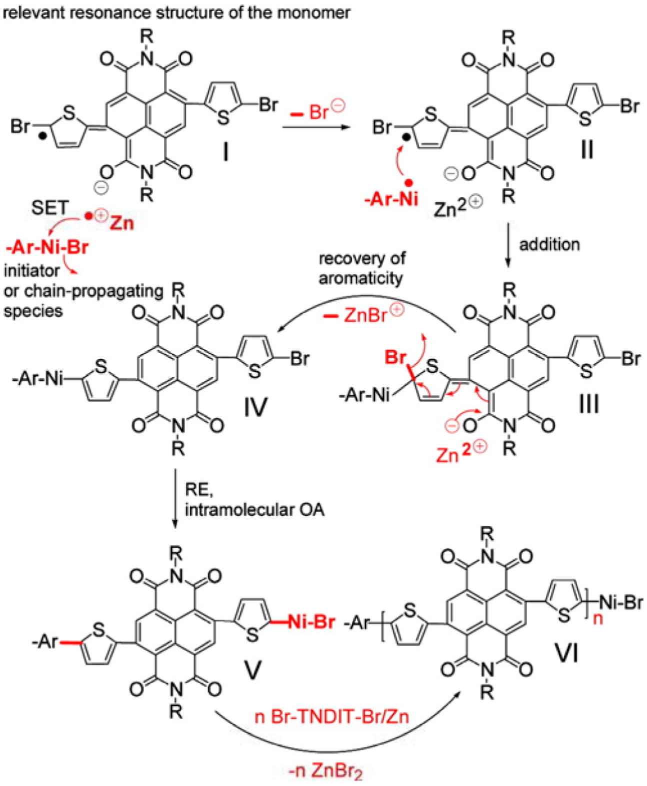
Scheme 8. Polymerization of 7



The proposed polymerization mechanism is shown in Scheme 9. The first step of a "quasi-transmetalation" process involves a single electron transfer (SET) from Zn$^+$ to Ni(II) with concomitant elimination of Br$^-$, leading to Ni(I) species (I → II, Scheme 9). The next step is the addition of Ar−Ni(I) to the terminal carbon of the monomer (II → III). Finally, the aromaticity of the system is recovered by elimination of Br$^-$ and Zn^{2+} (III → IV). After this quasi-transmetalation, reductive elimination (RE) and intramolecular oxidative addition (OA) take place as in the case of catalyst-transfer condensation polymerization of donor monomers.

As mentioned in the introduction, we first thought that catalyst-transfer condensation polymerization of acceptor monomers would be a challenge, because the weaker π-donation of the n-type polymer backbone to the zerovalent metal catalyst may not sufficiently assist intramolecular catalyst transfer on the basis of the fact that well-defined π-conjugated block copolymers were not obtained by successive polymerization from a monomer with a high π-donor ability to a monomer with a low π-donor ability.[14,35,36,50] However, the results cited in this report have at least revealed that Ni catalyst can undergo intramolecular transfer on pyridine and naphthalenediimide, and Pd catalyst can do so on benzothiaziazole. Accordingly, it should be feasible to polymerize more acceptor monomers via the catalyst-transfer mechanism to yield a variety of n-type π-conjugated polymers if the difficulties of (1) formation of organometallic monomers and (2) low solubility of n-type π-conjugated polymers, mentioned in the introduction, are overcome. The use of two or three aromatic monomers consisting of strong acceptor and weak donor arenes is a good approach for this purpose, although the donor

Scheme 9. Proposed Mechanism of Polymerization of 7/Zn Complex with a Ni Catalyst (Reprinted from ref 49. Copyright 2011 American Chemical Society)



unit slightly increases the HOMO levels of the n-type π-conjugated polymers. Nucleophilic boronic ester and stannyl moiety can be introduced into the donor unit under strongly basic conditions before linking to the base-sensitive acceptor unit to prepare monomers. The solubilizing side chain can be attached to either donor or acceptor unit. One might wonder if the catalyst can move on long monomer units consisting of two or three aromatics in this approach, but the catalyst-transfer condensation polymerization indeed took place in the polymerization of the above two or three aromatic monomers, as well as in a recent study of the polymerization of a thiophene and phenylene Grignard monomer with a Ni catalyst.[51]

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yokozt01@kanagawa-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are appreciative of funds from a Grant-in-Aid (No. 21350067) for Scientific Research from Japan Society for the Promotion of Science and a Scientific Frontier Research Project from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

■ REFERENCES

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

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

(3) Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607–632.

(4) Babudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem.* **2004**, *14*, 11–34.

(5) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 431–455.

(6) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009**, *109*, 5595–5619.

(7) Yokozawa, T. In *Conjugated Polymer Synthesis*; Chujo, Y., Ed.; Wiley-VCH: Weinheim, 2010; pp 35–58.

(8) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.

(9) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.

(10) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663–1666.

(11) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.

(12) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013.

(13) Ohshimizu, K.; Takahashi, A.; Higashihara, T.; Ueda, M. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 2709–2714.

(14) Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271–7273.

(15) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2009**, *42*, 30–32.

(16) Locke, J. R.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8709–8710.

(17) Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573–16579.

(18) Boyd, S. D.; Jen, A. K. Y.; Luscombe, C. K. *Macromolecules* **2009**, *42*, 9387–9389.

(19) Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J.-U.; Kiriy, A. *J. Am. Chem. Soc.* **2010**, *132*, 7803–7810.

(20) Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8039–8044.

(21) Lanni, E. L.; Locke, J. R.; Gleave, C. M.; McNeil, A. J. *Macromolecules* **2011**, *44*, 5136–5145.

(22) Verswyvel, M.; Verstappen, P.; De Cremer, L.; Verbiest, T.; Koeckelberghs, G. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 5339–5349.

(23) Bryan, Z. J.; Smith, M. L.; McNeil, A. J. *Macromol. Rapid Commun.* **2012**, *33*, 842–847.

(24) Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626–6632.

(25) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894–12895.

(26) Senkovskyy, V.; Tkachov, R.; Beryozkina, T.; Komber, H.; Oertel, U.; Horecha, M.; Bocharova, V.; Stamm, M.; Gevorgyan, S. A.; Krebs, F. C.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 16445–16453.

(27) Smeets, A.; Van den Bergh, K.; De Winter, J.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2009**, *42*, 7638–7641.

(28) Senkovskyy, V.; Sommer, M.; Tkachov, R.; Komber, H.; Huck, W. T. S.; Kiriy, A. *Macromolecules* **2010**, *43*, 10157–10161.

(29) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Bocharova, V.; Simon, F.; Nitschke, M.; Stamm, M.; Grotzschel, R.; Kiriy, A. *Macromolecules* **2008**, *41*, 7383–7389.

(30) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Horecha, M.; Stamm, M.; Uhrich, C.; Riede, M.; Leo, K.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 153–161.

(31) Sontag, S. K.; Marshall, N.; Locklin, J. *Chem. Commun.* **2009**, 3354–3356.

(32) Yuan, M.; Okamoto, K.; Bronstein, H. A.; Luscombe, C. K. *ACS Macro Lett.* **2012**, *1*, 392–395.

(33) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.

(34) Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695–2698.

(35) Yokozawa, T.; Kohno, H.; Ohta, Y.; Yokoyama, A. *Macromolecules* **2010**, *43*, 7095–7100.

(36) Yokozawa, T.; Suzuki, R.; Nojima, M.; Ohta, Y.; Yokoyama, A. *Macromol. Rapid Commun.* **2011**, *32*, 801–806.

(37) Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dotz, F.; Kastler, M.; Facchetti, A. *Nature* **2009**, *457*, 679−686.

(38) Durban, M. M.; Kazarinoff, P. D.; Segawa, Y.; Luscombe, C. K. *Macromolecules* **2011**, *44*, 4721−4728.

(39) Izuhara, D.; Swager, T. M. *J. Am. Chem. Soc.* **2009**, *131*, 17724−17725.

(40) Zhou, E.; Cong, J.; Zhao, M.; Zhang, L.; Hashimoto, K.; Tajima, K. *Chem. Commun.* **2012**, *48*, 5283−5285.

(41) Yamamoto, T.; Nakamura, T.; Fukumoto, H.; Kubota, K. *Chem. Lett.* **2001**, *30*, 502−503.

(42) Iwashita, K.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4109−4117.

(43) Adachi, I.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2006**, *39*, 7793−7795.

(44) Nanashima, Y.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1054−1061.

(45) Nanashima, Y.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2012**, *45*, 2609−2613.

(46) Sheina, E. E.; Liu, J. S.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526−3528.

(47) Nanashima, Y.; Shibata, R.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, in press.

(48) Elmalem, E.; Kiriy, A.; Huck, W. T. S. *Macromolecules* **2011**, *44*, 9057−9061.

(49) Senkovskyy, V.; Tkachov, R.; Komber, H.; Sommer, M.; Heuken, M.; Voit, B.; Huck, W. T. S.; Kataev, V.; Petr, A.; Kiriy, A. *J. Am. Chem. Soc.* **2011**, *133*, 19966−19970.

(50) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Chem. Lett.* **2008**, *37*, 1022−1023.

(51) Ono, R. J.; Kang, S.; Bielawski, C. W. *Macromolecules* **2012**, *45*, 2321−2326.