4438 *Macromolecules* **2010**, *43*, 4438–4440
DOI: 10.1021/ma100537d

Macromolecules
COMMUNICATION TO THE EDITOR

Grignard Metathesis Chain-Growth Polymerization for Poly(bithienylmethylene)s: Ni Catalyst Can Transfer across the Nonconjugated Monomer

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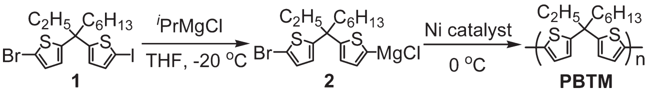
Received March 9, 2010
Revised Manuscript Received April 19, 2010

Pioneered by McCullough and Yokozawa, Ni-complex-catalyzed Grignard metathesis (GRIM) chain-growth polymerization has become an attractive method for the synthesis of conjugated polymers.[1−3] Polythiophenes (PThs),[4−11] polyphenylenes (PPs),[12] and polypyrroles (PPys)[13,14] with defined molecular weights and narrow polydispersities (PDIs) can be synthesized. Utilizing the living property of these polymerizations, related rod−coil[15−19] and rod−rod[6,13,20−22] block copolymers have been prepared. Besides, by using appropriate catalyst, polymer brushes[23−25] and "hairy" polymer particles[26] have also been prepared via surface-initiated GRIM polymerization. For the monomers with longer molecular length, such as fluorenes,[14,27,28] carbazoles,[14] and oligothiophenes,[29] the polymerizations also follow the chain-growth manner but are not living probably due to inefficient catalyst transfer.

Intramolecular transfer of the Ni catalyst[5] or an associated pair formed by the growing polymer chain and Ni catalyst[6] is believed to be essential for this type of chain-growth polymerization. It has been suggested that Ni complex could rest on π-system and transfer to the chain termini via "ring walking",[30−34] which should be the key of the efficient intramolecular catalyst transfer for GRIM chain-growth polymerization. Contrary to this mechanism, one can imagine that the catalyst should be able to transfer across the neighboring aromatic rings that are nonconjugated but appropriately arranged in space; thus, GRIM chain-growth polymerization is also applicable to the synthesis of nonconjugated polymers. In the current contribution, we have achieved this goal with a bithienylmethane derivative (**2**, Scheme 1) as the monomer, in which two thiophene rings are connected via a saturated carbon. The polymerization proceeded in a chain-growth manner to afford well-defined poly(bithienylmethylene)s (PBTMs). Moreover, copolymerizations of **2** with 2-bromo-5-chloromagnesio-3-hexylthiophene (**4**) in the monomer addition order of **2**/**4** and **4**/**2** were both successful.

The polymerization route is depicted in Scheme 1. The magnesium−halogen exchange was carried out with 0.98 equiv of ^{i}PrMgCl at −20 °C by taking advantage of the selectivity of iodine over bromine.[27] The reaction was over in 1 h with a conversion of **1** > 96%. Polymerizations were first carried out at 0 °C with four different Ni(II) catalysts. The results are listed in Table 1, and the corresponding gel-permeation chromatography (GPC) elution curves are shown in Figure S5. All catalysts gave PBTM with high yields. Ni(PPh$_3$)$_2$Cl$_2$ (PPh$_3$ = triphenylphosphine) and Ni(dppf)Cl$_2$ (dppf = 1,1′-bis(dipenylphosphino)ferrocene) both afforded polymers with broad PDIs. With Ni(dppp)Cl$_2$ (dppp = 1,3-bis(diphenyl phosphino)propane) as the catalyst, the PDI of the obtained PBTM was as narrow as 1.27, but the number-average molecular weight (M_n) was much higher than the theoretical value calculated by assuming that the polymerization is living, and the polymerization went on very fast and was over around 0.5 min. With Ni(dppe)Cl$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) as the catalyst, the polymerization afforded PBTM with a narrow PDI of 1.28 and a M_n close to the theoretical value. Meanwhile, the polymerization rate was moderate with a conversion of 91% in 70 min. Thus, we chose Ni(dppe)Cl$_2$ as the catalyst for further investigation.

Scheme 1. Synthesis of PBTM by the GRIM Polymerization



We found that the actual M_ns of the polymers with relatively lower molecular weights could be calculated from ^{1}H NMR spectra (Figure S6). For polymers from 10, 4, and 2 mol % catalyst (entries 4−6), the actual M_ns are 2.6×10^3, 6.7×10^3, and 1.2×10^4, respectively, which are close to the values measured by GPC (Table 1). However, calculations for the polymers with higher molecular weights are unreliable because the ^{1}H NMR signals of the terminal groups are very weak for these polymers. Accordingly, M_ns measured by GPC are still employed in the following discussion. Figure 1A shows the M_ns and PDIs of the polymers at different monomer conversions with 2 mol % Ni(dppe)Cl$_2$. M_n is linear to conversion over the whole polymerization process with PDI ≤ 1.3. The polymerizations with different ratios of Ni(dppe)Cl$_2$ to **2** were also carried out. M_ns and PDIs are shown in Figure 1C along with corresponding GPC profiles reported in Figure 1D. M_ns of the polymers increase in proportion to [converted **2**]/[Ni(dppe)Cl$_2$] with PDIs ≤ 1.3. These results clearly indicate that the polymerization follows the chain-growth mechanism with living characteristics, like those for PThs, PPs, and PPys,[4−14] proving our speculation about the possibility of the spatial catalyst transfer across the neighboring nonconjugated aromatic rings. Moreover, as shown in Figure 1B, similar to the polymerization for poly(3-hexylthiophene) (P3HT) with Ni(dppp)Cl$_2$ as the catalyst,[6] the semilogarithmic kinetic plot of the polymerization for PBTM is linear until the polymerization is over (conversion ~91%). This indicates a first-order dependence of the polymerization rate on the monomer concentration. Recently, McNeil et al. found that the polymerization for P3HT with Ni(dppe)Cl$_2$ exhibited a zeroth-order dependence on the monomer concentration since reductive elimination was the rate-determining step.[35] This difference implies that the kinetics of GRIM polymerization depends on both monomer and catalyst.

A polymerization with 50 mol % Ni(dppe)Cl$_2$ was also carried out, and the dimer was separated for structural analysis. High-performance liquid chromatography (HPLC, Figure S7) and ^{1}H NMR spectrum (Figure S8) indicate that the dimer has H/Br end groups. That means 2 equiv of **2** first reacted with Ni(II) complex, and then the generated Ni(0) was immediately inserted into one C−Br bond of the dimer via an intramolecular process. This initiation process is identical to that for P3HT.[5] Matrix-assisted

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Table 1. Polymerizations with Various Ni Catalysts[a]

entry	catalyst	amount of catalyst (%)	polymerization time (min)	conversion of **2** (%)	M_n ($\times 10^{-4}$)	PDI	yield[b] (%)
1	Ni(dppp)Cl_2	2	5	95	2.83	1.27	80
2	Ni(dppf)Cl_2	2	60	88	1.36	1.71	70
3	Ni$(PPh_3)_2Cl_2$	2	430	88	1.26	1.96	76
4	Ni(dppe)Cl_2	2	70	91	1.28	1.28	80
5	Ni(dppe)Cl_2	10	16	95	0.30	1.12	64[c]
6	Ni(dppe)Cl_2	4	35	92	0.87	1.09	84
7	Ni(dppe)Cl_2	1	140	93	3.12	1.17	85
8	Ni(dppe)Cl_2	0.5	280	93	5.51	1.24	89

[a] Grignard metathesises were carried out by treatment with 0.98 equiv of ^{i}PrMgCl in THF at −20 °C for 1 h with conversions of **1** >96%. Polymerizations were conducted at 0 °C ($[\mathbf{1}]_0$ = 0.10 mol/L). [b] Overall yields are based-on the sum of added **1**. [c] The low yield is attributed to the loss in the precipitation process due to the low M_n of the product. PPh_3 = triphenylphosphine; dppf = 1,1′- bis(dipenylphosphino)ferrocene; dppp = 1,3-bis(diphenyl phosphino)propane; dppe = 1,2-bis(diphenylphosphino)ethane.

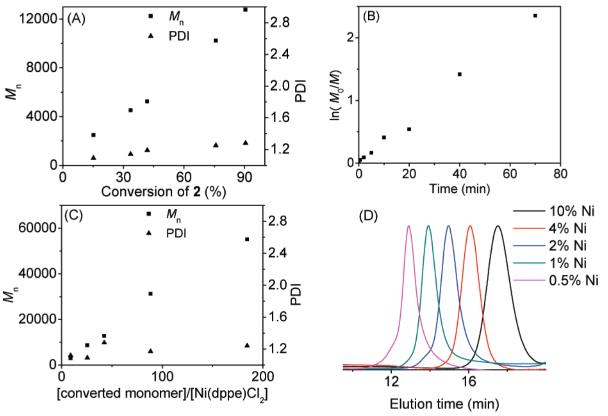


Figure 1. (A) Number-average molecular weight (M_n) and polydispersity (PDI) as a function of the conversion. (B) Logarithm of the concentration of **2** as a function of time. (C) M_n and PDI of PBTM as a function of [converted **2**]/[Ni(dppe)Cl_2]. (D) Gel-permeation chromatography (GPC) elution curves of PBTMs with different M_ns. The polymerizations were carried out with 2 mol % Ni(dppe)Cl_2 for (A) and (B), while those for (C) and (D) were conducted with 0.5, 1, 2, 4, and 10 mol % Ni(dppe)Cl_2. $[\mathbf{1}]_0$ = 0.10 mol/L for all polymerizations.

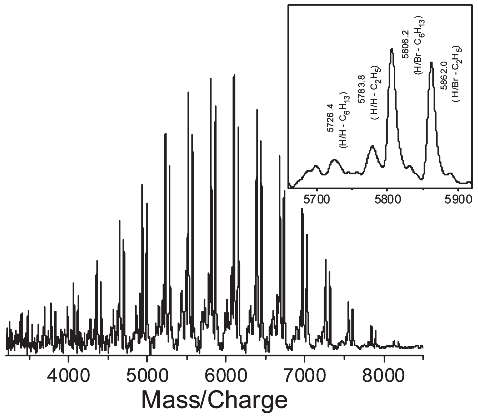


Figure 2. MALDI-TOF mass spectrum of PBTM (M_n = 8700, PDI = 1.09 determined by GPC). The polymerization was carried out with 4 mol % Ni(dppe)Cl_2. $[\mathbf{1}]_0$ = 0.10 mol/L.

laser desorption ionization time-of-flight (MALDI-TOF) mass spectra of PBTM were also recorded. As shown in Figure 2, two series of major peaks are in good agreement with the values calculated by the formula of 290.5 (mass of monomer unit) $\times\, n +$ 1 (mass of H) + 79.9 (mass of Br) − 85.2 (mass of side chain C_6H_{13}) and $290.5n + 1 + 79.9 - 29.0$ (mass of side chain C_2H_5) and correspond to H/Br end-capped PBTM with cleavage of C_6H_{13} and C_2H_5 side chains, respectively. This indicates that H/Br end groups dominated PBTM, which is consistent with ^{1}H NMR spectroscopic analysis (Figure S6). These results are consistent with the chain-growth mechanism. Two series of weaker peaks can also be found in the spectrum, which meet the values calculated by the formula of $290.5n + 1 \times 2 - 85.2$ and $290.5n + 1 \times 2 - 29.0$ and is ascribed to H/H end-capped PBTM with cleavage of C_6H_{13} and C_2H_5 side chains, respectively.

Block copolymerization can further prove the chain-growth mechanism of the polymerization. Here, we choose **4** as the second monomer. As shown in Figure 3A, the block copolymerization in the order of **2** and then **4** yielded a block copolymer with monomodal GPC profile and narrow PDI. This indicates that the PBTM chain is active and can initiate the polymerization of **4** to afford diblock copolymer and further confirms the chain-growth mechanism of the polymerization of **2**. According to the previous report,[13,21,22] the result of GRIM copolymerization significantly depends on monomer addition order. Therefore, we also carried out the diblock copolymerization in the order of **4** and then **2**. As shown in Figure 3B, after the diblock copolymerization, monomodal GPC profile with relative narrow PDI still remains, indicating the success of copolymerization. Inspired by this success, triblock copolymerizations were carried out in two routes (Scheme 2). As shown in Figure 3, after the addition of the third portion of monomer, there are tails in the GPC profiles for both routes. However, the tail is negligible in the route B, while that in the route A is more significant. In the previous report,[22] we found that significant amount of Br/Br ended P3HT presented with Ni(dppe)Cl_2 as the catalyst. Therefore, one of the main reasons for the imperfect triblock copolymerization might be the partially deactivation of P3HT chain ends. ^{1}H NMR spectra indicate that the compositions of the diblock and triblock copolymers from the route B are consistent with the converted monomer ratios (Figure S9). Thus, the chain-growth mechanism of the polymerization of **2** is unambiguous according to above results.

In the previous reports,[14,27−29] probably due to the inefficient intramolecular catalyst transfer across the long monomer units, significant chain transfer/termination was found in the GRIM polymerizations of the monomers comprising ≥2 aromatic rings, such as thiophene dimers/trimers, fluorene, and carbazole. Therefore, it was difficult to prepare polymers with well-defined molecular weights and narrow PDIs from the polymerizations of these monomers. However, the polymerization of **2**, which also has two aromatic rings and long monomer molecular length, shows the quasi-“living” feature as discussed above, which may be ascribed to the appropriate arrangement of the nonconjugated thiophene rings in space to enable the efficient intramolecular catalyst transfer.

In conclusion, we have first demonstrated that GRIM chain-growth polymerization is also applicable to the synthesis of well-defined polymers comprising nonconjugated aromatic repeating

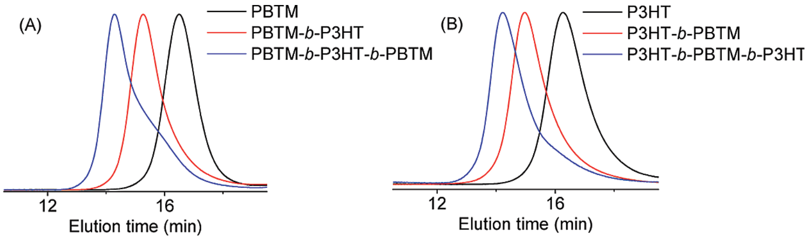
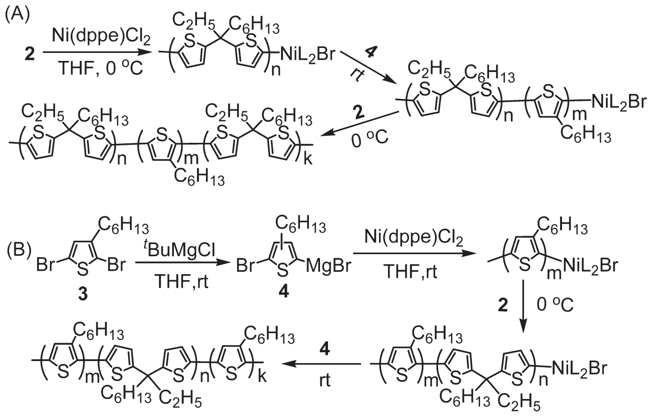


Figure 3. GPC profiles of the polymers obtained by copolymerizations. (A) Monomer addition order: **2**, **4**, and then **2**. PBTM ($M_n = 5.5 \times 10^3$, PDI = 1.13), PBTM-*b*-P3HT ($M_n = 9.7 \times 10^3$, PDI = 1.26), and PBTM-*b*-P3HT-*b*-PBTM ($M_n = 1.4 \times 10^4$, PDI = 1.40). (B) Monomer addition order: **4**, **2**, and then **4**. P3HT ($M_n = 5.0 \times 10^3$, PDI = 1.30), P3HT-*b*-PBTM ($M_n = 1.1 \times 10^4$, PDI = 1.38), and P3HT-*b*-PBTM-*b*-P3HT ($M_n = 1.6 \times 10^4$, PDI = 1.40).

Scheme 2. Synthesis of Triblock Copolymers PBTM-*b*-P3HT-*b*-PBTM (A) and P3HT-*b*-PBTM-*b*-P3HT (B)



units. Diblock copolymers with P3HT can also be synthesized. These results imply that GRIM chain-growth polymerization is a universal method for the preparation of the polymers based on aromatic units with a diversity of structures.

Acknowledgment. This work is supported by National Basic Research Program of China (973 Project, No. 2009CB623603) of Chinese Ministry of Science and Technology, NSFC (Nos. 20921061 and 50833004).

Supporting Information Available: Synthesis and characterization of monomer, details for polymerizations, GPC profiles of PBTM synthesized with various catalysts, HPLC profile and ^{1}H NMR spectrum of the dimer, and ^{1}H NMR spectra of PBTMs with different M_ns and copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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