Notes

Grignard Metathesis Chain-Growth Polymerization for Polyfluorenes

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Received July 8, 2008
Revised Manuscript Received October 14, 2008

Introduction

Conjugated polymers are of current interest due to their promising optoelectronic properties.[1−4] To date, most of those are synthesized via organometallic polycondensations. As typical step-growth polymerizations, the molecular weight and polydispersity of the resulting polymers are rarely well controlled.[5] Moreover, monomers with sufficient purity are required.

Compared to step-growth polymerizations, chain-growth polymerizations can often be controlled to afford polymers with high molecular weights and narrow molecular weight distributions, even under relatively undemanding conditions. Recently, the Ni(II)-catalyzed quasi-"living" chain-growth polymerization for poly(3-alkylthiophene)s (PThs) was reported by McCullough[6−10] and Yokozawa.[11−14] This new type of polymerization was then successfully applied to the synthesis of polyphenylenes (PPs),[15] polythiophene bearing ester groups,[16] and thiophene-based diblock and triblock copolymers.[17] The resulting polymers have narrower molecular weight distributions and defined chain-ends, and their molecular weights can be controlled by adjusting the ratio of the catalyst to the monomer. Further mechanism studies showed that the Ni complex repetitively transferred to the chain-end via an unclear intramolecular process for further chain propagation,[9,11] compared to the conventional Kumada organic cross-coupling reactions, which follow a distinct "oxidative addition−transmetallation−reductive elimination" three-step process.[18]

Based on the propagation mechanism of above quasi-"living" chain-growth polymerization proposed by McCullough and Yokozawa, the length of the monomer must severely affect the transfer of the Ni complex to the chain end. Actually, it is unclear yet whether the intramolecular transfer of the Ni complex to the chain-end for a longer monomer, such as fluorene, can proceed smoothly for chain propagation, although a chain-growth polymerization based on Pd-catalyzed Suzuki−Miyaura coupling reaction for poly(9,9-dioctylfluorene) with controlled molecular weight and narrow polydispersity has been reported.[19] In the current paper, we first report the Ni(II)-catalyzed polymerization of fluorenyl Grignard reagent for polyfluorenes, one of the most important classes of conjugated polymers.[3] The polymerization also follows a chain-growth mechanism, and poly(9,9-dioctylfluorene) with number average molecular weights (M_n) up to 8.60×10^4 have been synthesized. In contrast to aforementioned quasi-"living" chain-growth polymerization for PThs and PPs, noticeable chain termination occurs, possibly due to reductive elimination.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker AV 300 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. The gel-permeation chromatography (GPC) analysis was conducted on a Waters 2414 system equipped with Waters HT4 (7.8 × 300 mm, bead diameter: 10 μm) and HT3 (7.8 × 300 mm, bead diameter: 10 μm) column-assembly and a Waters 2414 refractive index detector (eluent, chloroform; flow rate, 1.00 mL/min; temperature, 40 °C; standard, polystyrene). Gas chromatography−mass spectroscopy (GC-MS) measurements were carried out on an Agilent 5975/6890N GC-MS instrument equipped with an Agilent HP-5 column (30 m) with 1,4-bishexyloxy benzene as an internal reference. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR Kompact MALDI Mass Spectrometer with anthracene-1,8,9-triol as the matrix.

Materials. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Isopropylmagnesium chloride (*i*-PrMgCl, 2.0 M solution in THF, Aldrich), $Ni(dppp)Cl_2$ (1,3-bis(diphenylphosphino) propane nickel dichloride, Pacific ChemSource, Inc. (Zhengzhou, China), 98%), $Ni(dppe)Cl_2$ (1,2-bis (diphenylphosphino) ethane nickel dichloride, Pacific ChemSource Inc. (Zhengzhou, China), 98%), $Ni(dppf)Cl_2$ (1,1′-bis(diphenylphosphino) ferrocene nickel dichloride, Pacific ChemSource Inc. (Zhengzhou, China), 98%), and $Ni(PPh_3)_2Cl_2$ (bis(triphenylphosphine) nickel dichloride, Pacific ChemSource Inc. (Zhengzhou, China), 98%) were used as received without further purification. Lithium chloride (LiCl, Acros) was heated at 130 °C in vacuum for 5 h prior to use. 2-Bromo-7-iodo-9,9-dioctylfluorene (**1**)[20] and 1,4-bishexyloxy benzene[21] were synthesized according to the references. The purity of **1** was 99.7% according to GC-MS.

General Procedure for Polymerization (an Example). Freshly distilled THF (40 mL) was added into a mixture of **1** (1.19 g, 2.00 mmol), LiCl (0.0848 g, 2.00 mmol), and 1,4-bis(hexyloxy)benzene (0.278 g, 1.00 mmol) in a Schlenk tube under argon. After the mixture had been stirred at −20 °C for 10 min, *i*-PrMgCl (2.0 M solution in THF, 1.0 mL, 2.0 mmol) was added via syringe and the mixture was maintained at −20 °C for 1 h under stirring. Then the mixture was allowed to warm to 0 °C, and 2.0 mL solution was withdrawn via syringe for GC-MS analysis (the conversion of **1** to **2** was 98%). $Ni(dppp)Cl_2$ (10.3 mg, 0.019 mmol) was added to the mixture under the protection of argon atmosphere. After the reaction mixture was stirred at 0 °C for 30 min (93% of **2** was converted), aqueous HCl (5 M) was added to terminate the polymerization. Then the mixture was extracted with $CHCl_3$, and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, and then concentrated under reduced pressure. The crude product was washed with petroleum ether to afford poly(9,9-dioctylfluorene) in a yield of 67%. $M_n = 6.24 \times 10^4$, and $M_w/M_n = 1.49$ by GPC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85−7.82 (br,

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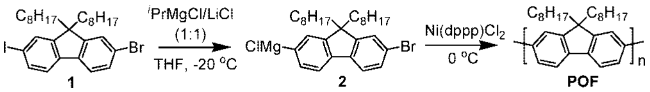
10.1021/ma801538q CCC: $40.75

Scheme 1. Synthesis of Poly(9,9-dioctylfluorene) by the Grignard Metathesis Method[a]



[a] THF = tetrahydrofuran, dppp = 1,3-bis(diphenylphosphino) propane.

Table 1. Polymerization of 2-Bromo-7-chloromagnesio-9,9-dioctylfluorene (2) with Various Ni(II) Catalysts[a]

entry	*i*-PrMgCl to **1**	conv of **1**[b] (%)	catalyst	$M_n \times 10^{-4}$ [c]	PDI[c]	yields of the polymers[d] (%)
1	1.0	77	Ni(dppp)Cl$_2$	1.35	1.86	23
2	1.0	98	Ni(dppp)Cl$_2$	6.24	1.49	67
3	1.0	86	Ni(dppf)Cl$_2$	no polymer		
4	1.0	96	Ni(PPh$_3$)$_2$Cl$_2$	0.58	1.64	15
5	1.0	96	Ni(dppe)Cl$_2$	3.25	2.23	68
6	0.85	77	Ni(dppp)Cl$_2$	5.96	1.60	57
7	0.70	67	Ni(dppp)Cl$_2$	5.19	1.57	53
8	0.60	59	Ni(dppp)Cl$_2$	4.41	1.56	46

[a] Carried out by treatment of **1** with *i*-PrMgCl in tetrahydrofuran ($[\mathbf{1}]_0$ = 0.05 M) at −20 °C for 1 h with (entries 2−8) and without (entry 1) LiCl (*i*-PrMgCl/LiCl = 1:1), followed by polymerization at 0 °C for 30 min with 1.0 mol % Ni(II) catalyst to added **1**. **1** = 2-bromo-7-iodo-9,9-dioctylfluorene; M_n = number-average molecular weight; PDI = weight-average molecular weight (M_w)/M_n. [b] Determined by gas chromatography−mass spectroscopy. [c] Estimated by gel-permeation chromatography with polystyrene as the standard and CHCl$_3$ as eluent. [d] Calculated according to $[\mathbf{2}]_0$.

2H, protons at the 4,5-positions of the fluorene unit), 7.76−7.58 (br, 4H, protons at the 1,3,6,8-positions of the fluorene unit), 2.11 (br, 4H, -C$\boldsymbol{H}_2$C$_7$H$_{15}$), 1.22−1.02 (m, 20H, -(CH$_2$)$_2$(C$\boldsymbol{H}_2$)$_5$CH$_3$), 0.81 (br, 10H, -CH$_2$C$\boldsymbol{H}_2$C$_6$H$_{13}$ and -(CH$_2$)$_7$C$\boldsymbol{H}_3$).

Results and Discussion

To test the magnesium-halogen exchange, compound 2-bromo-7-iodo-9,9-dioctylfluorene (**1**, 2.0 mmol) was treated with 1.0 equiv of *i*-PrMgCl/LiCl (1:1) in anhydrous THF (40 mL) at −20 °C. GC-MS measurements revealed that only two compounds, that is, **1** and 2-bromo-7-chloromagnesio-9,9- dioctylfluorene (**2**), presented in the resulting mixture, and the exchange reaction was almost over in 1 h with a conversion up to 98%. This indicates that the magnesium-halogen exchange selectively takes place with iodine group and only gives a single Grignard reagent **2** as shown in Scheme 1.

The polymerization of **2** was carried out at 0 °C with Ni(dppp)Cl$_2$ as the catalyst. For the polymerization with 98% conversion of **1** to **2** and 1.0 mol % catalyst, poly(9,9-dioctylfluorene), with the number-average molecular weight (M_n) of 6.24 × 10^4 and the polydispersity index (PDI = M_w/M_n) of 1.49 was obtained with a polymerization time of 30 min (Table 1, entry 2). The PDI is noticeably lower than that from Suzuki polycondensations. Without LiCl, the magnesium−iodine exchange reaction could still proceed but with lower conversion (77%), and meanwhile, the polymerization only afforded lower molecular weight product with lower yield (Table 1, entry 1). This indicates that LiCl can promote both the magnesium−iodine exchange and polymerization. These functions of LiCl have been previously reported in the references for the preparation of phenyl magnesium chloride with functional groups[22] and the Ni-catalyzed polymerization for PPs.[15]

Nickel catalysts with other ligands, that is, Ni(dppe)Cl$_2$, Ni(dppf)Cl$_2$, and Ni(PPh$_3$)$_2$Cl$_2$ were also used in the polymerization. Ni(dppf)Cl$_2$ gave no polymeric product while Ni(PPh$_3$)$_2$Cl$_2$ and Ni(dppe)Cl$_2$ afforded polymers with lower molecular weight and broader PDI. (Table 1, entries 3−5).

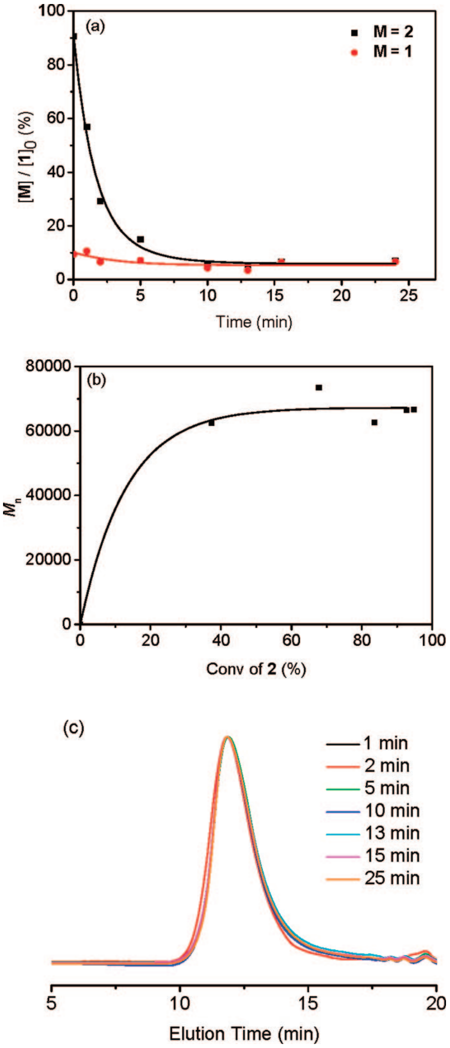


Figure 1. Conversions of 2-bromo-7-iodo-9,9-dioctylfluorene (**1**) and 2-bromo-7-chloromagnesio-9,9-dioctylfluorene (**2**) vs polymerization time plot (a), number-average molecular weight (M_n) values vs conversion of **2** plot (b), and gel-permeation chromatography profiles of poly(9,9-dioctylfluorene) at different polymerization time (c). For polymerization, **1** (0.05 M) in tetrahydrofuran was first treated with 1 equiv *i*-PrMgCl/LiCl (1:1) at −20 °C for 1 h (conversion of **1** to **2** was 91%), which was followed by polymerization at 0 °C for 30 min with 1.0 mol % Ni(dppp)Cl$_2$ (dppp = 1,3-bis(diphenylphosphino) propane) as the catalyst.

To ascertain if the current polymerization follows the chain-growth polymerization mechanism, different ratios of *i*-PrMgCl/LiCl (1:1) to **1** were employed for tuning the content of **1** in polymerization mixture. If high molecular weight poly(9,9-dioctylfluorene) can still be obtained at the presence of a considerable amount of **1**, the polymerization should proceed in a chain-growth manner. As shown in Table 1, the polymerization proceeds smoothly even at low conversions of **1** to **2**. With *i*-PrMgCl/LiCl (1:1) to **1** of 0.85, 0.70, and 0.60, the conversions of **1** to **2** were 77, 67, and 59%, respectively. The corresponding polymerization with 1.0 mol % Ni(dppp)Cl$_2$ afforded poly(9,9-dioctylfluorene) with M_n/PDI of 5.96 × 10^4/1.60, 5.19 × 10^4/1.57, and 4.41 × 10^4/1.56, respectively (Table 1, entries 6−8). This indicates that the chain-growth mechanism dominates the polymerization.

The conversions of **1** and **2** and M_n at different polymerization time were measured by GC-MS and GPC, respectively. As shown in Figure 1, the polymerization proceeded very fast and

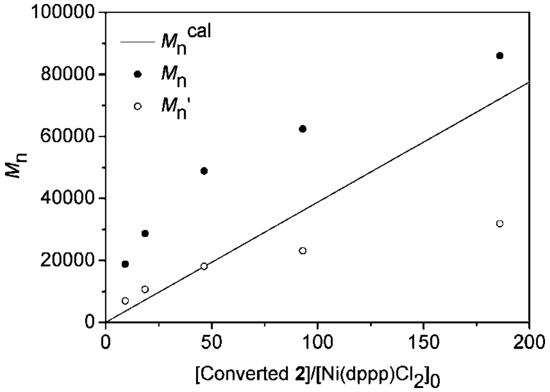


Figure 2. Number-average molecular weight (M_n), corrected molecular weight (M_n'), and calculated molecular weight (M_n^{cal}) as a function of the ratio of converted 2-bromo-7-chloromagnesio-9,9- dioctylfluorene (**2**) to Ni(dppp)Cl_2 (dppp = 1,3-bis (diphenylphosphino) propane). M_n' is calculated by dividing M_n with 2.7, according to ref 23. M_n^{cal} is calculated by assuming that the polymerization follows living mechanism. For polymerization, 2-bromo-7-iodo-9,9-dioctylfluorene (**1**, 0.05 M) in tetrahydrofuran was first treated with 1 equiv *i*-PrMgCl/LiCl (1:1) at −20 °C for 1 h, which was followed by polymerization at 0 °C for 30 min.

was almost over in 10 min. High molecular weight poly(9,9-dioctylfluorene) was obtained just in the very beginning and the M_n almost kept identical at different conversion of **2**. With a lower magnesium-halogen exchange conversion, the polymerization also exhibited similar phenomena. These results further solidify the chain-growth nature of the polymerization, and meanwhile indicate the presence of chain termination.

The polymerizations at different r = [converted **2**]/[Ni(dppp)Cl_2] were also carried out. The dependence of the M_n on r is depicted in Figure 2. The M_n increases as r increases, and varies in the range of 1.88×10^4 to 8.60×10^4. Moreover, the PDI of the resulting polymers is in the range of 1.49−1.77. For more accurate depiction of the molecular weight, the GPC measured M_n values were divided by a factor of 2.7 to give M_n' (as reported in ref 23, the M_n of PFs measured by GPC with PS as the standard is overestimated about 2.7 times.), and then M_n' is compared with the calculated molecular weight (M_n^{cal}) based-on the eq 1 (straight line in Figure 2), assuming that polymerization follows living mechanism, which means one Ni catalyst forms one polymer chain with absence of chain termination.

$$M_n = 388 \times [\text{converted } \mathbf{2}]/[\text{Ni(dppp)Cl}_2]_0 \qquad (1)$$

As shown in Figure 2, the M_n' is higher and lower than the corresponding M_n^{cal} at the low and high r region, respectively. The lower M_n' than M_n^{cal} in high r region should be ascribed to the chain termination, and the higher M_n' than M_n^{cal} in low r region can be attributed to the low solubility of Ni(dppp)Cl_2 in THF and the fast propagation of the polymer chain, thereby some of catalyst is not involved in the polymerization. In fact, we found that some of the Ni catalyst still remained in the polymerization mixture after the polymerization completion as the ratio of Ni(dppp)Cl_2 to added **1** was ≥5 mol %.

Because fluorene unit is much longer than thiophene and benzene, we suspect that the reductive elimination may compete with intramolecular catalyst transfer to induce chain termination, therefore the resultant polymer should be mainly Br/Br ended. Shown in Figure 3 is the ^{1}H NMR spectrum of poly(9,9-dioctylfluorene) with M_n of 1.88×10^4. According to refs 24−26, the signals at 7.3−7.4 and 7.4−7.5 ppm can be assigned to the protons at a “H” end (H_{1-3}) and those at a “Br” end

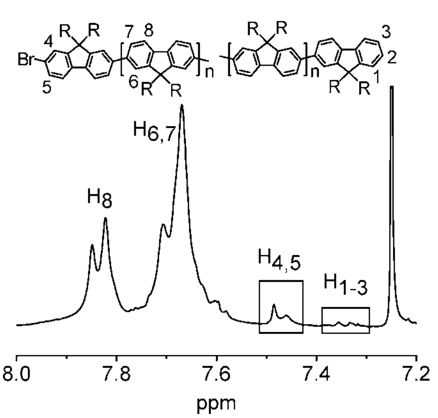


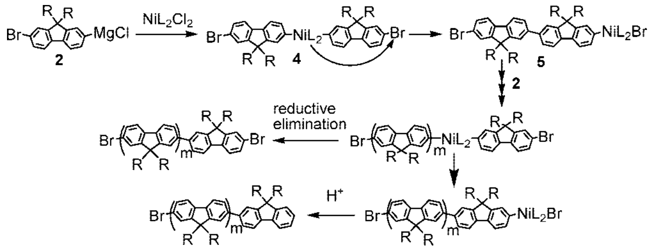
Figure 3. ^{1}H NMR spectrum of the poly(9,9-dioctylfluorene) with a number-average molecular weight of 1.88×10^4 and a polydispersity index of 1.54. The assignment is determined according to the references.[24−26] The signals of protons other than H_{1-5} in terminal fluorenes, which overlap with those of H_8 and $H_{6,7}$, cannot be distinguished.

($H_{4,5}$), respectively. The integral ratio of H_{1-3} to $H_{4,5}$ is about 1:2. Accordingly, the ratio of “H” ends and the “Br” ends is about 1:3. This indicates that noticeable amount of polymer chains are Br/Br ended (If all the polymers have “Br/H” ends, the integral ratio of H_{1-3} to $H_{4,5}$ should be 3:2), which is consistent to our assumption. For ease of mass spectra measurements, a polymerization with 50 mol % Ni(dppp)Cl_2 was carried out, and dimers, trimers and higher oligomers were separated by column chromatography on silica gel. As shown in MALDI-TOF spectra of these oligomers (Figures S1−3, Supporting Information), Br/Br ended oligomers dominate Br/H ended ones. This result also strongly supports above discussion.

To further confirm the presence of the chain termination, a “monomer addition” experiment was carried out. Ni(dppp)Cl_2 (1 mol %) was added into a solution of **1** and **2** containing 94% **2** to start a polymerization. The second part solution of **1** and **2** was added to the reaction mixture after 10 min for further polymerization for 30 min. After the first 10 min, 96% of compound **2** were converted, and poly(9,9-dioctylfluorene) with M_n of 6.89×10^4 and PDI of 1.43 were obtained. Most importantly, compound **2** in the second part was also consumed with an identical conversion, but M_n remained almost unchanged. This indicates the termination of poly(9,9-dioctylfluorene) chain at the first polymerization period and presence of reinitiation. It was found that **1** unconverted to **2** was also partially consumed during the polymerization process, as observed in *polymerization time−monomer conversion* experiments. For example, **1** decreased from 9% to 4% in a typical experiment as shown in Figure 1a. It is well-known that the C−I bond can undergo oxidation addition at much milder condition than the C−Br bond does. Therefore, we surmise that the residual **1** in polymerization mixture can reinitiate the chain growth via the oxidative addition to Ni(0) produced by reductive elimination for chain termination.

Based on the above discussion, a polymerization mechanism is proposed as shown in Scheme 2. The chain initiation and propagation are similar to that for PThs and PPs. However, chain-termination caused by reductive elimination is noticeable due to a much longer length of fluorene than thiophene and benzene, which significantly diminishes the possibility of the intramolecular transfer of Ni complex and results in polymer with “Br/Br” ends. Yamamoto et al. have reported that electron-accepting compounds could promote reductive elimination of Ni(0) complex.[27] Less electron-rich characteristic of fluorene might be another reason for ease of reductive elimination.

Scheme 2. Proposed Polymerization Mechanism for the Synthesis of Poly(9,9-dioctylfluorene) by the Grignard Metathesis Method[a]



[a] $R = n\text{-}C_8H_{17}$; L_2 = 1,3-bis(diphenylphosphino) propane.

Similar to PThs, "Br/H"-ended polymer is yielded by quenching active polymer chain with acid.[13] Meanwhile, the presence of chain termination results in poly(9,9-dioctylfluorene)s with broader molecular weight distributions, while compared with those from chain-growth Suzuki polymerization as reported by Yokozawa et al.[19]

Summary

We have demonstrated that Grignard metathesis method is also applicable to the synthesis of polyfluorenes. Poly(9,9-dioctylfluorene) with M_n as high as 8.60×10^4 can be easily synthesized. The polymerization follows a chain-growth mechanism and includes chain termination. Further studies should lead to a fully controlled synthesis of polyfluorenes.

Acknowledgment. This work is supported by NSFC (Nos. 20423003 and 20521415), and Science Fund for Creative Research Groups of NSFC (20621401).

Supporting Information Available: Details for polymerization with 50 mol % $Ni(dppp)Cl_2$, and MALDI-TOF spectra of resulting oligomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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