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Communications to the Editor

Chain-Growth Polymerization for Poly(3-hexylthiophene) with a Defined Molecular Weight and a Low Polydispersity

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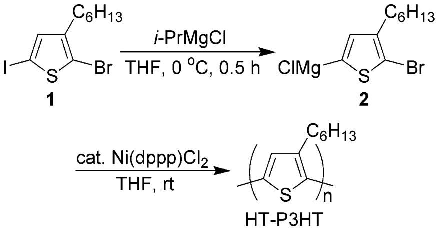
Regioregular poly(3-alkylthiophene) (P3AT) has received much attention in recent years because of its small band gap, high electrical conductivity,[1] and interesting properties such as light emitting ability[2] and high field effect mobility.[3] Regiocontrolled synthesis of almost completely head-to-tail P3AT (HT-P3AT)[4] has been developed by McCullough[5,6] and Rieke[7,8] using Ni-catalyzed dehalogenative polymerization, and the physical properties of HT-P3AT are superior to those of the regiorandom one. Their synthetic methods are very valuable and the dominant methods for the synthesis of HT-P3AT. To examine and refine the properties of HT-P3AT, synthesis of the polymer having a desired molecular weight with a low polydispersity is important and crucial. Such a controlled polymerization, however, has not been reported. Because the Ni-catalyzed dehalogenative polymerization is formally a polycondensation and gives polymer with a high polydispersity and an uncontrolled molecular weight, this polymerization is generally believed to proceed via a step-growth mechanism. Indeed, the reported polydispersities (M_w/M_n's) of crude HT-P3AT (without fractionation) obtained by the regiocontrolled polymerization were high such as 1.94[9] and 3.63;[8] HT-P3AT's with low polydispersities can be obtained only after fractionation by Soxhlet extraction of the crude product.[5−10]

In the course of our work to synthesize condensation polymers having controlled molecular weights and low polydispersities,[11] we took an interest in controlling the molecular weight and polydispersity in the synthesis of HT-P3AT. The Ni-catalyzed polymerizations of 3-alkyl-2-bromo-5-metalothiophene derivatives for HT-P3AT presumably proceed via oxidative addition of the carbon−halogen linkage of monomer or polymer propagating end to the Ni catalyst. As we proposed in Pd-catalyzed CO-insertion polycondensation,[12] an electron-donating carbon−metal bond in the monomer would suppress its oxidative addition. This should result in selective oxidative addition of the polymer propagating end to the Ni catalyst and a chain-growth polymerization as in our previous work.[11] In this Communication, we demonstrate that the Ni-catalyzed polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene, which is obtained by reaction of 2-bromo-3-hexyl-5-iodothiophene (**1**) with alkylmagnesium chloride, proceeds by a chain-growth mechanism to give HT-poly(3-hexylthiophene) (HT-P3HT) with a narrow molecular weight distribution and that the molecular weight of HT-P3HT is controlled by the feed ratio of monomer to the Ni catalyst. Previous polymerization using 2-bromo-3-dodecyl-5-iodothiophene and methylmagnesium chloride gave HT-poly(3-dodecylthiophene) with $M_n = 21\,000$ and $M_w/M_n = 1.36$ after $CHCl_3$ fractionation,[6] but the chain-growth nature of this polymerization has not been reported.[13]

Scheme 1. Synthesis of HT-P3HT



Treatment of 2-bromo-3-hexyl-5-iodothiophene (**1**) with 1 equiv of isopropylmagnesium chloride at 0 °C gave **2** via magnesium−iodine exchange (Scheme 1). Addition of 0.4 mol % of $Ni(dppp)Cl_2$ (dppp = 1,3-bis(diphenylphosphino)propane) to the reaction mixture and stirring at room temperature led to HT-P3HT. As shown in Figure 1a, the polymerization proceeded smoothly at room temperature, and the conversion of **2** was 50% in 15 min, 75% in 1 h, and 93% in 24 h. The M_n and M_w/M_n values of the crude HT-P3HT (without purification by precipitation or fractionation) at each conversion were analyzed by GPC relative to polystyrene standers. Conversion−M_n and conversion−M_w/M_n plots demonstrate that monomer **2** polymerized in a chain-growth polymerization manner: the M_n values increased in proportion to the conversion of **2**, and the M_w/M_n ratios were 1.30−1.39 throughout the polymerization (Figure 1b).

The above results indicate that an initiator species existed from which polymerization was propagated. We assumed that the initiators would be formed by the reaction of **2** with $Ni(dppp)Cl_2$ in the first step of polymerization and that the M_n values of HT-P3HT might be determined by the ratio of **2** to the initiators, whose amount would be affected by the amount of $Ni(dppp)Cl_2$ added. To test our assumption, the polymerization was carried out with varying the feed ratios of **2** to $Ni(dppp)Cl_2$. The M_n increased *linearly* in proportion to the feed ratio when $[\mathbf{2}]_0/[Ni(dppp)Cl_2]_0$ was between 10 and 108 (Figure 2). When $[\mathbf{2}]_0/[Ni(dppp)Cl_2]_0$ was more than 200, the M_w/M_n ratio of HT-P3HT

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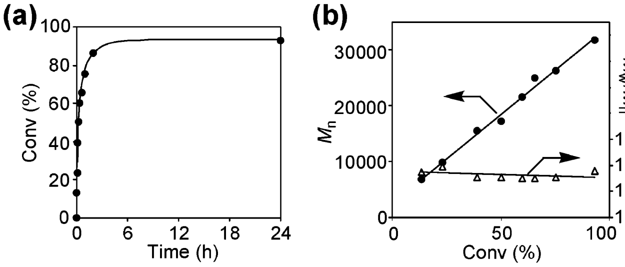

Figure 1. Polymerization of **2** with 0.4 mol % of Ni(dppp)Cl_2 in THF at room temperature ($[\mathbf{2}]_0$ = 0.12 M): (a) time−conversion curve; (b) M_n and M_w/M_n values of HT-P3HT as a function of monomer conversion.

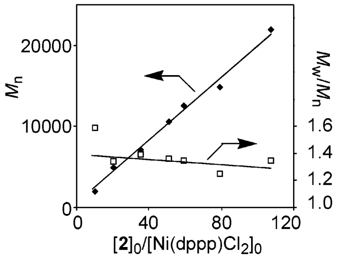

Figure 2. M_n and M_w/M_n values of HT-P3HT, obtained with **2** and Ni(dppp)Cl_2 in THF at room temperature, as a function of the feed ratio of **2** to Ni(dppp)Cl_2: $[\mathbf{2}]_0$ = 0.12 M; $[\text{Ni(dppp)Cl}_2]_0$ = 1.1−11.8 mM; conversion = 86−93%.

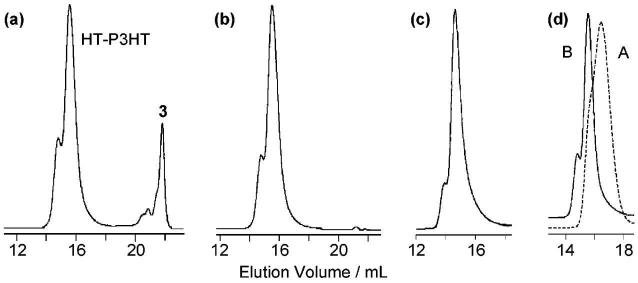

Figure 3. GPC profiles of HT-P3HT synthesized in THF at room temperature: (a) crude product obtained by the polymerization of **2** with 1.2 mol % of Ni(dppp)Cl_2 in 1 day; (b) after purification of the crude product by precipitation into MeOH; (c) polymerization with 0.4 mol % of Ni(dppp)Cl_2 after 1 day; (d) prepolymer (A, $[\mathbf{2}]_0/[\text{Ni(dppp)Cl}_2]_0$ = 53, reaction time = 1 h, conversion = 90%) and postpolymer (B, [added $\mathbf{2}]_0/[\text{Ni(dppp)Cl}_2]_0$ = 53, reaction time = 1 day conversion = 93%) from monomer addition experiment (fresh feed of **2** was added to the reaction mixture after prepolymerization was carried out for 1 h). $[\mathbf{2}]_0$ = 0.095 M [(a) and (b)] or 0.12 M [(c) and (d)].

obtained was less than 1.4, but the M_n value was not reproducibile because of the difficulty of weighing certain milligrams of Ni(dppp)Cl_2 exactly and charging it completely into a reaction vessel.

Typical GPC profiles of synthesized HT-P3HT are shown in Figure 3. Crude product obtained by the polymerization of **2** with 1.2 mol % of Ni(dppp)Cl_2 (conversion = 86%) showed two major peaks (Figure 3a): the one was HT-P3HT (M_n = 17 000, M_w/M_n = 1.31) accompanied by a shoulder in the higher molecular weight region (peak molecular weight = 37 400), and the other was 2-bromo-3-hexylthiophene (**3**) formed by the quenching of **2**. Washing the crude products with MeOH removed the low molecular weight fractions to give pure HT-P3HT in 78% yield (M_n = 17 000, M_w/M_n = 1.28) (Figure 3b). ^{1}H NMR spectroscopy ($CDCl_3$, 600 MHz) demonstrated that the precipitated HT-P3HT had more than 98% head-to-tail couplings.[14,15] When **2** was polymerized with 0.4 mol % of Ni(dppp)Cl_2 to afford HT-P3HT with higher M_n (M_n = 31 700, M_w/M_n = 1.36), the shoulder (peak molecular weight = 77 800) of GPC profile still remained (Figure 3c); the cause for this shoulder is unclear at the present time.

The absorption maxima in solution UV−vis spectra ($CHCl_3$) of HT-P3HT with M_n = 21 900 (M_w/M_n = 1.35) was 451 nm, which was almost identical with the reported value (λ_{max} was 456 nm when M_n = 25 500 and M_w/M_n = 1.48).[8] In accordance with Trznadel's results,[10] the λ_{max} of HT-P3HT increased as the M_n of HT-P3HT increased.[14]

The chain-growth nature of the polymerization was also examined by a "monomer-addition" experiment, in which a fresh feed of **2** ([added $\mathbf{2}]_0/[\text{Ni(dppp)Cl}_2]_0$ = 53) was added to the prepolymer ($[\mathbf{2}]_0/[\text{Ni(dppp)Cl}_2]_0$ = 53, conversion = 90%, M_n = 8900, M_w/M_n = 1.34) in the reaction mixture. As shown in Figure 3d, GPC chromatogram of the product clearly shifted toward the higher molecular weight region (conversion = 93%, M_n = 17 200, M_w/M_n = 1.34). This result indicates that the added **2** was polymerized from the polymer end group of the prepolymer due to chain-growth nature of this polymerization.

We tentatively propose two possible mechanisms accounting for the chain-growth nature of this polymerization. One is based on the difference in substituent effects between monomer and polymer propagating end as mentioned above. The other mechanism is explained by the behavior of active Ni catalyst: if the catalyst always existed around the polymer propagating end without diffusion, the coupling reaction would occur only at the polymer propagating end, resulting in a chain-growth polymerization. Such a situation would occur by the coordination of Ni catalyst to the π-bond or the nonbonding electron pair of the propagating thiophene moiety. Further studies by isolation of a Ni complex that directly initiates the polymerization will be essential to achieving a detailed understanding of the mechanism of this chain-growth polymerization.

In conclusion, we have demonstrated that the polymerization of **2** with Ni(dppp)Cl_2 proceeded in a chain-growth polymerization manner to give HT-P3HT with low polydispersities and that the M_n of the polymer increased linearly in proportion to the feed ratio of **2** to Ni(dppp)Cl_2. Our results will open a new scope to synthesize conjugated polymers by transition-metal-catalyzed coupling reactions, and well-defined HT-P3HT having a requisite molecular weight will contribute to the development of electrical and optical devices. We are now examining chain-growth polymerization for other conjugated polymers. Investigation of adequate initiators is also under way in order to synthesize HT-P3HT with a lower polydispersity and controlled end structures.

Supporting Information Available: Synthesis and polymerization of monomer and NMR and UV−vis spectra of polymer. This material is available free of charge via Internet at http://pubs.acs.org.

References and Notes

(1) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173−205. (b) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93−116.

(2) Chen, F.; Mehta, P. G.; Takiff, L.; McCullough, R. D. *J. Mater. Chem.* **1996**, *6*, 1763−1766.

(3) (a) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741−1744. (b) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B.

M. W.; Spiering, A. J. H.; Jansscen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature (London)* **1999**, *401*, 685−688.

(4) For a review of synthesis of polythiophenes, see: Yamamoto, T. *Macromol. Rapid Commun.* **2002**, *23*, 583−606. See also ref 1b.

(5) (a) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70−72. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904−912. (c) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250−253. (d) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329−332. (e) Liu, J.; McCullough, R. D. *Macromolecules* **2002**, *35*, 9882−9889.

(6) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324−4333.

(7) (a) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087−10088. (b) Chen, T.-A.; O'Brien, R. A.; Rieke, R. D. *Macromolecules* **1993**, *26*, 3462−3463.

(8) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233−244.

(9) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777−5785.

(10) Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules* **1998**, *31*, 5051−5058.

(11) (a) Yokozawa, T.; Asai, T.; Sugi, R.; Ishigooka, S.; Hiraoka, S. *J. Am. Chem. Soc.* **2000**, *122*, 8313−8314. (b) Yokozawa, T.; Suzuki, Y.; Hiraoka, S. *J. Am. Chem. Soc.* **2001**, *123*, 9902−9903. (c) Yokozawa, T.; Taniguchi, T.; Suzuki, Y.; Yokoyama, A. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3460−3464. (d) Yokoyama, A.; Iwashita, K.; Hirabayashi, K.; Aiyama, K.; Yokozawa, T. *Macromolecules* **2003**, *36*, 4328−4336.

(12) Yokozawa, T.; Shimura, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2607−2618.

(13) McCullough et al. mentioned in ref 6 that Ni-catalyzed dehalogenative polymerization for head-to-tail poly(3-alkylthiophene)s could proceed "by either a step growth or a chain growth polymerization mechanism" and that they "have observed that more highly conjugated intermediates react faster with the catalyst than the monomer". However, they have not shown the experimental data.

(14) See Supporting Information for details.

(15) (a) Sato, M.; Morii, H. *Polym. Commun.* **1991**, *32*, 42−44. (b) Sato, M.; Morii, H. *Macromolecules* **1991**, *24*, 1196−1200. (c) Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039−3045.

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