Macromolecules **2006,** *39,* 7793−7795

Synthesis of Well-Defined Polythiophene with Oxyethylene Side Chain: Effect of Phosphine Ligands on Catalyst-Transfer Polycondensation

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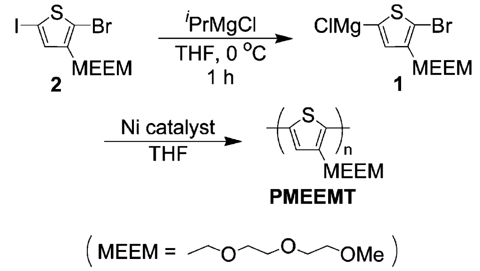
Received August 9, 2006
Revised Manuscript Received October 2, 2006

Poly(3-alkylthiophene)s[1] are well-known conductive polymers, and their regioselective synthesis was developed by McCullough et al.[2] and Rieke et al.[3] The polymerization had been believed to proceed via a step-growth polymerization mechanism, but we recently reported that the polycondensation of 2-bromo-5-chloromagnesio-3-hexylthiophene with Ni(dppp)Cl_2 (dppp = 1,3-bis(diphenylphosphino)propane) proceeds via a chain-growth polycondensation mechanism to yield head-to-tail poly(3-hexylthiophene) (HT-P3HT) with low polydispersity and controlled molecular weight.[4] Detailed studies of this polycondensation revealed that one end of the polymer is terminated by a bromine atom and the other end by a hydrogen atom in all the polymer molecules and that one Ni catalyst molecule forms one polymer chain. On the basis of these results, we have proposed catalyst-transfer polycondensation as a new mechanism of chain-growth polycondensation.[5,6] While regioregular poly(3-alkylthiophene)s have received much attention because of their useful electronic and optical properties, polythiophenes with etheric side chains showed unique and interesting characteristics.[7−11] For example, Walree and coworkers reported that a thin film of poly{3-[2-(2-methoxyethoxy)ethoxy]methylthiophene} (PMEEMT) on a ZnSe single-crystal surface exhibited suitable oxidative potentials for application in LEDs.[11] The regioselective synthesis of ether-functionalized polythiophenes was carried out under conditions similar to those used for poly(3-alkylthiophene),[8] but chain-growth polymerization has not been reported.

In this Communication, we describe the effect of the phosphine ligand of the Ni catalyst on the polymerization of 2-bromo-5-chloromagnesio-3-[2-(2-methoxyethoxy)ethoxy]methylthiophene (**1**). We found that ligand choice was critical for the chain-growth polymerization of **1** and that the best ligand for the chain-growth polymerization of **1** was 1,2-bis(diphenylphosphino)ethane (dppe), not dppp, which was used in the chain-growth polymerization for the synthesis of poly(3-hexylthiophene). McCullough and co-workers have examined the effects of metals and ligands on the regioselectivity for the synthesis of PHT,[12] but the influence of the ligand of the Ni catalyst on the chain-growth polymerization has not been reported.

Scheme 1. Synthesis of PMEEMT



Treatment of 2-bromo-5-iodo-3-[2-(2-methoxyethoxy)ethoxy]methylthiophene (**2**) with 1 equiv of isopropylmagnesium chloride at 0 °C for 1 h gave **1** via magnesium−iodine exchange reaction,[13] and the polymerization was carried out by the addition of Ni catalyst to the reaction mixture (Scheme 1). We first polymerized **1** with Ni(dppp)Cl_2 in THF at room temperature because polymerization of the 3-hexyl monomer under the same conditions proceeded via chain-growth polycondensation to give well-defined PHT. The polymerization of **1** was completed in 5 min, being much faster than that of the 3-hexyl monomer. The GPC profile of the obtained PMEEMT showed a unimodal peak,[14] but the polydispersity was rather broad (Table 1, entry 1). When 1,1′-bis(diphenylphosphino)ferrocene (dppf) was used as a ligand, the monomer **1** was not consumed completely within 30 min, and the polydispersity of PMEEMT became broader (entry 2).[14] Polymerization with 1,2-bis(diphenylphosphino)ethane (dppe) at room temperature resulted in almost complete consumption of **1** in 15 min to give PMEEMT with a low polydispersity (entry 3). However, prolongation of the polymerization time to 1 h resulted in an increase of M_w/M_n due to a small shoulder of the GPC chromatogram in the higher molecular weight region (entry 4). We speculated that, as in the case of quenching the polymerization of the 3-hexyl monomer with water,[4b] the small shoulder would have resulted from the disproportionation reaction between the chain ends of the polymers when the concentration of the monomer became low due to the instability of the propagating polymer−Ni−Br complex. Therefore, we next examined the effect of temperature on the polymerization using dppe as the ligand. The rate of the polymerization decreased as the polymerization temperature was lowered. When the polymerization was carried out at 0 °C, the shoulder peak at the late stage of polymerization did not appear, and the polymer showed narrower polydispersity than that obtained at room temperature (entry 5).[14] Further decrease of the polymerization temperature to −20 °C resulted in an increase of M_w/M_n (entry 6). On the basis of these results, we found that the polymerization of **1** at 0 °C using dppe as the ligand of the Ni catalyst gave PMEEMT with the narrowest polydispersity.

To demonstrate the chain-growth polymerization nature of this polycondensation, the correlation between the conversion of the monomer **1** and the molecular weight of the obtained polymer was investigated in the polymerization of **1** at 0 °C using dppe as the ligand of the Ni catalyst. The M_n and M_w/M_n values of the crude PMEEMT (without purification by precipitation or fractionation) at each conversion were analyzed by GPC relative to polystyrene standards. Conversion−M_n and conversion−M_w/M_n plots showed that the M_n values increased in proportion to the conversion of **1**, and the M_w/M_n ratios were 1.11−1.15 throughout the polymerization (Figure 1a). We next investigated the correlation between the feed ratio of monomer **1** to the Ni catalyst and the molecular weight of the obtained polymer. The molecular weight increased linearly in proportion to the feed ratio, and the molecular weight was controlled by the amount of catalyst (Figure 1b). These results suggest that the synthesis of PMEEMT by polymerization of **1** with Ni-

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10.1021/ma061809k CCC: $33.50

Table 1. Effect of Various Ligands on the Polymerization of 1[a]

entry	ligand	temp (°C)	time (min)	conv of **1** (%)[b]	M_n[c]	M_w/M_n[c]
1	dppp	rt	5	95	11600	1.42
2	dppf	rt	30	64	3400	1.53
3	dppe	rt	15	87	7800	1.20
4			60	93	7900	1.24
5		0	120	86	8600	1.15
6		−20	1680	94	6900	1.36

[a] Polymerization of **1** was carried out by treatment of **2** with 1.0 equiv of ^{i}PrMgCl, followed by 1.8 mol % of Ni(ligand)Cl$_2$ ([**2**]$_0$ = 0.10 M). [b] Determined by GC. [c] Estimated by GPC based on polystyrene standards (eluent: THF).

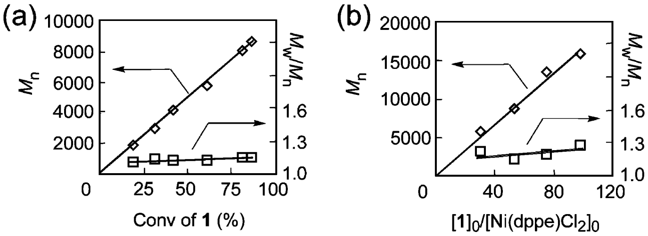

Figure 1. M_n and M_w/M_n values of PMEEMT as a function of (a) monomer conversion, obtained with **1** and 1.8 mol % of Ni(dppe)Cl$_2$ in THF at 0 °C, and (b) the feed ratio of **1** to Ni(dppe)Cl$_2$.

(dppe)Cl$_2$ proceeded via a chain-growth polymerization mechanism to yield polymer with a low polydispersity and a molecular weight that was determined by the feed ratio of **1** to the Ni catalyst.

The end groups of PMEEMT were analyzed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry with dithranol as a matrix in the presence of sodium trifluoroacetate. If the chain-growth polymerization of **1** proceeds via a catalyst-transfer polycondensation mechanism, the obtained PMEEMT would bear a bromine atom at one end and a hydrogen atom at the other end (designated as Br/H), as in the case of polymerization of the 3-hexyl monomer.[5] The polymerization of **1** was carried out in the presence of 1.7 mol % of Ni(dppe)Cl$_2$ in THF at 0 °C, and a small aliquot of the reaction mixture was withdrawn for analysis. The MALDI-TOF mass spectrum of PMEEMT obtained by polymerization for 30 min (conversion of **1** = 39%, M_n = 3000 (GPC), M_w/M_n = 1.15 (GPC)) contains two series of major peaks, which correspond to Br/H end polymers and their Na$^+$ adducts, accompanied by four series of minor peaks (Figure 2a). Two series of the minor peaks can be easily assigned to Br/Br end polymers and their Na$^+$ adducts, but the other two series show molecular weight values close to, but not identical with, those of H/H end polymers and their Na$^+$ adducts.[15] Prolongation of the polymerization time to 1.5 h converted 78% of **1** to PMEEMT with M_n = 6800 and M_w/M_n = 1.17 (GPC). While the GPC profile of the polymer shows a unimodal curve,[14] the MALDI-TOF mass spectrum of the PMEEMT contains two maxima in the lower and higher molecular weight regions (Figure 2b). The lower molecular weight region contains six series of peaks, which correspond to Br/Br, H/H, and Br/H end polymers, with intensities in this order, and their Na$^+$ adducts. The signals in the higher molecular weight region in Figure 2b are similar to those of the polymer obtained at 39% conversion of **1**: Na$^+$ adducts of Br/H end polymers are observed as major peaks, Br/H end polymers and Na$^+$ adducts of Br/Br end polymers are observed as minor peaks, and the mass/charge values of the other two series of minor peaks are close to, but not identical with, those of H/H end polymers and their Na$^+$ adducts.[15] Because the GPC profile of the polymer shows a unimodal elution curve with M_n = 6800, the intense peaks of Br/Br and H/H end polymers and their Na$^+$ adducts in the lower molecular weight region of Figure 2b would be exaggerated due to higher detection sensitivity. All the results mentioned above indicate that the polymerization of **1** with Ni(dppe)Cl$_2$ proceeds mainly via the *intramolecular* catalyst-transfer polycondensation mechanism, but *intermolecular* catalyst-transfer reaction also occurs as a minor side reaction to afford H/H and Br/Br end oligomers and polymers.

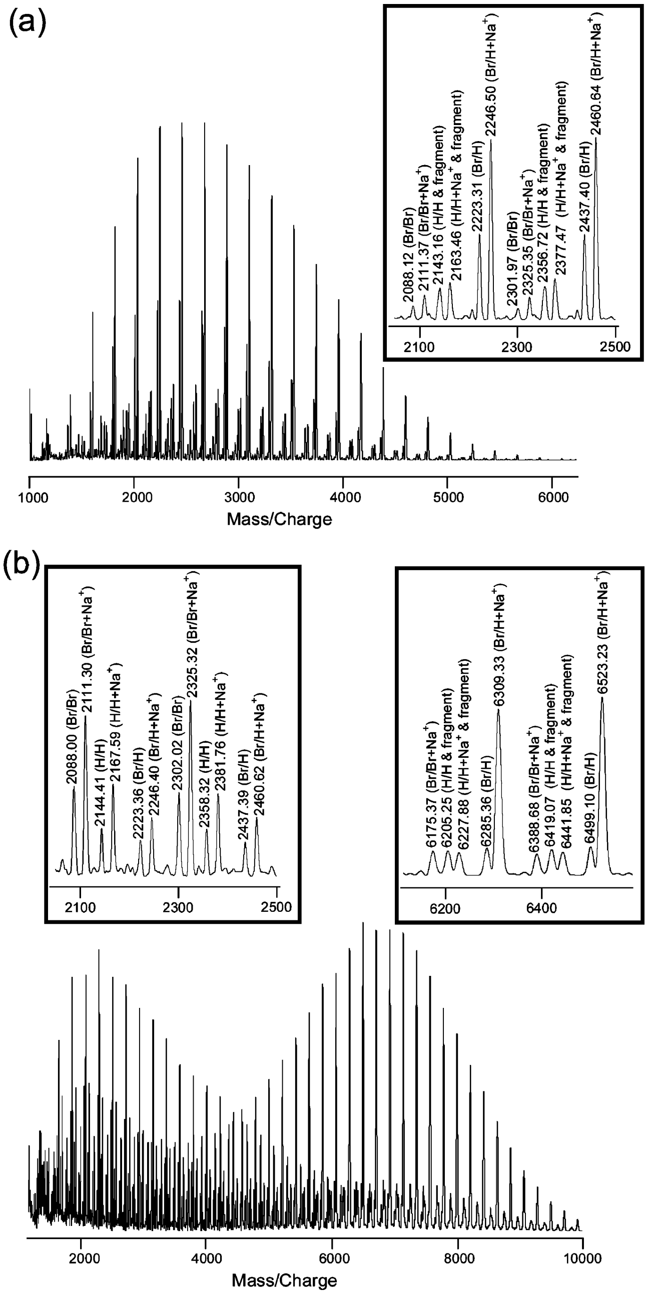

Figure 2. MALDI-TOF mass spectra of PMEEMT obtained with **1** and 1.7 mol % of Ni(dppe)Cl$_2$ at 0 °C. Conversion of **1** = (a) 39% and (b) 78%.

In conclusion, we have demonstrated that the chain-growth polymerization of **1** depends on the ligand of the Ni catalyst, and the polymerization at 0 °C using dppe as the ligand proceeded in a chain-growth polymerization manner to give PMEEMT with low polydispersity. Furthermore, the molecular weight of the polymer was controlled by the feed ratio of the Ni catalyst. Analysis of the polymers by means of MALDI-TOF mass spectroscopy indicated that the polymerization proceeds mainly via a metal-transfer polycondensation mechanism accompanied by disproportionation reaction between the polymer−Ni ends. Detailed analysis of the polymerization mechanism and studies aimed at tighter control of the polymerization are in progress.

Supporting Information Available: Synthesis and polymerization of the monomer and GPC profiles and MALDI-TOF mass spectra of PMEEMT. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The selective formation of **1** by the reaction of **2** with isopropylmagnesium chloride was confirmed by the detection of 2-bromo-3-[2-(2-methoxyethoxy)ethoxy]methylthiophene after hydrolysis of a small aliquot of the reaction mixture before addition of the Ni catalyst. The conversion of **2** to **1** was 89−99% determined by GC, and remaining **2** was recovered after the polymerization.

(14) GPC profiles are shown in the Supporting Information.

(15) When we compare the same molecular weight regions (mass/charge = 2100−2500) of Figure 2a and Figure 2b and the lower molecular weight region of Figure 2b with the higher one, the deviation occurs when Br/H end polymers are observed as major peaks in the region. Therefore, we speculate that the deviated minor peaks observed in Figure 2a,b are due to the signals of H/H end polymers and their Na^+ adducts, and the apparent deviation is caused by overlap with the peaks of fragmented Br/H end polymers.

MA061809K