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## COMMUNICATION

# Controlled Synthesis of High Molecular Weight Poly(3-hexylthiophene)s via Kumada Catalyst Transfer Polycondensation with Ni(IPr)(acac)<sub>2</sub> as the Catalyst

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**The controlled synthesis of poly(3-hexylthiophene)s (P3HTs) with number-average molecular weights ( $M_n$ s) up to 350 kg/mol has been realized with Ni(IPr)(acac)<sub>2</sub> as the catalyst.**

Kumada catalyst transfer polycondensation (KCTP) is a new and rapidly developing method for the controlled synthesis of conjugated polymers (CPs).<sup>1</sup> This type of polycondensation involves an intramolecular catalyst transfer process, which leads to a chain-growth polymerization mechanism, making the control of molecular weight as well as chain ends and the one-pot synthesis of fully conjugated block copolymers possible.<sup>2,3</sup>

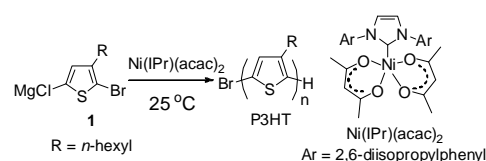
In the past several years, the monomer scope of KCTP has been greatly expanded, and various conjugated polymers have been synthesized in a controlled way.<sup>1b</sup> However, there are still a number of issues remaining to be solved before it becomes a versatile protocol for the controlled synthesis of CPs. For instance, number-average molecular weight ( $M_n$ ) can only be controlled at medium molecular weight range (< 70 kg/mol),<sup>4</sup> and the controlled synthesis of CPs with high molecular weights and low polydispersity indices (PDIs) is still a challenge. Even for poly(3-hexylthiophene) (P3HT), the most studied CP prepared from KCTP,  $M_n$  could only be well controlled at ≤ 40 kg/mol (the highest  $M_n$  was limited to be 91 kg/mol).<sup>4a</sup> Although P3HTs with  $M_n$ s up to 234 kg/mol were obtained using [CpNiCl(SIPr)] as the catalyst, the polymerization could not be controlled and PDIs of the polymers were rather large.<sup>5</sup> The difficult synthesis of high molecular weight CPs in a controlled manner is also a common issue for Suzuki and Nigeshi catalyst transfer polycondensations.<sup>6</sup>

Reductive elimination of the catalyst from propagating chains to the polymerization solution and disproportionation of active chain ends are two primary factors responsible for chain termination and therefore the low control of KCTP.<sup>7-10</sup> We think that the inefficient intramolecular catalyst transfer should

be more harmful in terms of the controlled synthesis of high molecular weight CPs since the disproportionation should be significantly suppressed by lowering the catalyst loading or increasing propagation rate. Therefore, exploring new catalyst to enhance the stability of metal-polymer  $\pi$ -complex and the propagation rate should be crucial to improve KCTP in terms of the controlled synthesis of high molecular weight CPs.

*N*-heterocyclic carbenes (NHCs) are stronger  $\sigma$ -donors than phosphines and their steric properties can be easily tuned by altering *N*-substituted groups. Some Pd- and Ni-complexes with NHCs as ligands exhibited superior performance in C-C cross-couplings.<sup>11,12</sup> In the current paper, we reported that Ni(IPr)(acac)<sub>2</sub> (IPr = bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) is a great catalyst for the controlled synthesis of high molecular weight P3HT. When the catalyst loading was tuned in 8.00–0.05 mol%, P3HTs with  $M_n$ s of 4.90–416 kg/mol were obtained. Especially, with 4.00–0.10 mol % catalyst,  $M_n$ s (9.90–350 kg/mol) were linearly correlated to [converted monomer]/[Ni(II)].

**Scheme 1. Synthesis of P3HT with Ni(IPr)(acac)<sub>2</sub> as the catalyst.**



The complex Ni(IPr)(acac)<sub>2</sub> was synthesized according to literature<sup>13</sup> and its structure was confirmed by elemental analysis and X-ray crystallographic analysis (Figure S1, Table S1 and S2 in ESI). IPr was selected as the ligand since it is readily accessible and was well-studied. The polymerization was carried out as shown in Scheme 1, and the data are listed in Table 1. LiCl was added to promote the polymerization.<sup>14</sup> Even with 0.05 mol % catalyst, the yield could reach up to 85% in 30 min. As shown in Figure 1b and Table 1, with decreasing

catalyst loading from 8.00 to 0.07 mol%, GPC profiles gradually shifted toward shorter elution time, and  $M_n$ s increased from 4.90 to 400 kg/mol (entries 1-10). No obvious enhancement of  $M_n$  was observed when further decreasing the catalyst loading to 0.05 mol%.  $M_n$ s were linearly correlated to [converted monomer]/[Ni(II)] along with PDIs  $\leq 1.50$  with catalyst loading in the range of 4.00-0.10 mol% (Figure 1a). As shown in Figure 1c, logarithm plot of monomer concentration versus time is linear, with 0.15 mol% Ni(IPr)(acac)<sub>2</sub> as an example. All these indicate that the polymerization followed the catalyst transfer mechanism proposed by Yokozawa et al.<sup>15</sup> Control polymerizations with 0.10 mol% Ni(dppp)Cl<sub>2</sub>, Ni(dppp)(acac)<sub>2</sub> or Ni(acac)<sub>2</sub> as the catalyst were also conducted in the same condition. Ni(dppp)Cl<sub>2</sub> and Ni(dppp)(acac)<sub>2</sub> could only afford P3HTs with  $M_n$ s of 94.0 and 92.0 kg/mol, respectively (entries 12 and 14). When Ni(acac)<sub>2</sub> was used, no polymer was obtained.

Table 1. Polymerization Results of **1** with Ni(IPr)(acac)<sub>2</sub> as the Catalyst.<sup>a</sup>

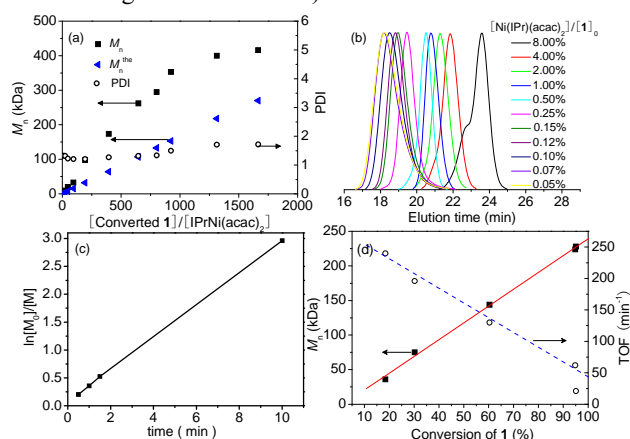
Entry	Cat (mol%)	$M_n^b$ (kg/mol)	PDI <sup>b</sup>	$M_n^{SLS,c}$ (kg/mol)	$M_n^{the,d}$ (kg/mol)	Yield <sup>e</sup> (%)
1	8.00	4.90	1.33		2.00	75
2	4.00	9.90	1.32		3.90	88
3	2.00	19.9	1.23		7.80	77
4	1.00	33.2	1.21		15.7	76
5	0.50	98.0	1.21	120	32.2	89
6	0.25	174	1.27	216	64.5	90
7	0.15	262	1.32	398	107	88
8	0.12	295	1.34	308	133	85
9	0.10	353	1.50	361	153	82
10	0.07	400	1.71	408	218	85
11	0.05	416	1.72	465	270	85
12 <sup>f</sup>	0.10	94.0	1.62		67.3	39
13 <sup>g</sup>	0.10	-	-		-	-
14 <sup>h</sup>	0.10	92.0	1.62		47.8	26

<sup>a</sup>All polymerizations were carried out at 25 °C for 30 min in the presence of 1 equiv LiCl with [1]<sub>0</sub> = 0.10 mol/L; <sup>b</sup>Measured by GPC at 150 °C in 1,2,4-C<sub>6</sub>Cl<sub>3</sub>H<sub>3</sub> with polystyrene as standard; <sup>c</sup>Measured with static light scattering at 150 °C in 1,2,4-C<sub>6</sub>Cl<sub>3</sub>H<sub>3</sub>; <sup>d</sup>Calculated according to monomer conversion by assuming the polymerization was living; <sup>e</sup>Yield after precipitation; <sup>f</sup>Using Ni(dppp)Cl<sub>2</sub> as catalyst; <sup>g</sup>Using Ni(acac)<sub>2</sub> as catalyst, and no polymer obtained; <sup>h</sup>Using Ni(dppp)(acac)<sub>2</sub> as catalyst.

It is well-known that GPC measurements overestimate the molecular weights of CPs when polystyrene is used as standard due to the more rigid chain structures of CPs. According to McCullough's report,  $M_n$  of P3HT measured by GPC is 1.2-2.3 times of real molecular weight ( $M_n$  range: 4-23 kg/mol).<sup>16</sup> We calculated theoretical  $M_n$ s ( $M_n^{the}$ s) according to the conversions by assuming the polymerizations were living according to GC measurement.  $M_n$ s of P3HTs prepared with high catalyst loadings were about 2.5 times of  $M_n^{the}$ s (entries 1 and 2). This large deviation can be attributed to the overestimation of molecular weights by GPC, but also to the noticeable disproportionation as evidenced by the presence of a pronounced shoulder peak in GPC profile (Figure 1b). At lower catalyst loadings (entries 3-11), this peak was almost invisible, indicating negligible occurrence of this side reaction. When the catalyst loading was below 0.10 mol%, PDIs increased to  $\sim 1.7$ .

This can be attributed to the precipitation of the high molecular weight polymers or the presence of the side reactions such as reductive elimination, which can cause chain termination.

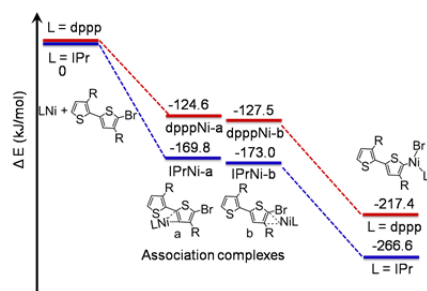
The molecular weights of P3HTs with  $M_n$ s higher than 90 kg/mol (entries 5-11, Table 1) were also measured with static light scattering technique. Consistent with the trend of  $M_n$ , obtained molecular weights ( $M_n^{SLS}$ ) increased from 120 to 465 kg/mol. Figure S3 in the ESI depicted <sup>1</sup>H NMR spectra of P3HTs with  $M_n$ s of 19.9, 98.0 and 262 kg/mol. The signals at  $\sim 2.83$  ppm decreased dramatically with an increase of  $M_n$  and became invisible for P3HT with  $M_n$  of 262 kg/mol, indicating that the regioregularity of the polymer was approaching 100%. All these results further confirm the successful synthesis of high molecular weight P3HT in a controlled manner. In order to further confirm the "quasi-living" nature of the polymerization, the synthesis of poly(3-(2-ethylhexyl)thiophene)-*b*-P3HT (P3EHT-*b*-P3HT) was also tested with 0.50 mol% Ni(IPr)(acac)<sub>2</sub> to **2** (**2**/**1** = 1:1), as shown in Scheme S1. After workup, the block copolymer P3EHT-*b*-P3HT with  $M_n$  of 176 kg/mol and PDI of 1.19 was obtained (GPC and <sup>1</sup>H NMR data please see Figure S4 in the ESI).



**Figure 1.** Number-average molecular weight ( $M_n$ ), theoretic number-average molecular weight ( $M_n^{the}$ ) and PDI versus [converted **1**]/[Ni(IPr)(acac)<sub>2</sub>] (a); GPC elution curves of P3HTs prepared with different Ni(IPr)(acac)<sub>2</sub> loadings (b); Logarithm plot of monomer concentration versus time (c) and  $M_n$  and TOF versus conversion of **1** (d) for the polymerization with 0.15 mol% Ni(IPr)(acac)<sub>2</sub>.

Above polymerizations proceeded much faster than those catalyzed by Ni-complexes based on dppp, the best catalysts for the controlled synthesis of P3HT via KCTP in literature. A typical polymerization of **1** with 4 mol% Ni(dppp)Cl<sub>2</sub> as the catalyst was complete in  $\sim 10$  min.<sup>14</sup> Table S3 shows the polymerization results with 0.15 mol% Ni(IPr)(acac)<sub>2</sub> at different polymerization time. After 3.5 min, the conversion of **1** reached 60.9%, and the polymerization was complete in 10 min with a conversion of 94.8%.  $M_n$  was linear to the monomer conversion along with PDI kept at  $\sim 1.30$  (Figure 1d and Table S3). The turnover frequency (TOF) of the catalyst was up to 240 min<sup>-1</sup> and decreased from 240 to 62 min<sup>-1</sup> when the monomer conversion increased from 18.4 to 94.8% (Figure 1d). This indicates that Ni(IPr)(acac)<sub>2</sub> is a very efficient catalyst.

In order to understand the above results, density functional theory (DFT) calculations were performed on Ni(0)-complex bearing IPr or dppp ligand by setting the energies of dissociated



**Figure 2.** Free energy diagram of association and oxidative addition complexes obtained from DFT calculations.

LNi(0) and 2-bromo-3,3'-dihexyl-5,2'-bithiophene as zero.<sup>17</sup> The structures of possible  $\eta^2$  complexes and HT-HT-Ni(L)Br are shown in Figure 2 along with their stabilization energies. After associated, the stabilization energies of two IPrNi(0)-complexes (IPrNi-a and IPrNi-b) and HT-HT-Ni(IPr)Br are 169.8, 173.0 and 266.6 kJ/mol, respectively. These energies are much higher than those of corresponding dpppNi(0)-complexes, which are 124.6, 127.5 and 217.4 kJ/mol for dpppNi-a, dpppNi-b and HT-HT-Ni(dppp)Br, respectively. This implies that IPrNi(0) should have stronger coordination interaction with conjugated backbone and the oxidative addition of IPrNi(0) to the C-Br bond at the chain-end is more feasible, resulting in the more efficient intramolecular catalyst transfer and thereby allowing the controlled synthesis of high molecular weight polymer.

In conclusion, we have demonstrated the controlled synthesis of P3HT with  $M_n$  up to 350 kg/mol using Ni(IPr)(acac)<sub>2</sub> as the catalyst. Particularly, with 4.00-0.10 mol% catalyst,  $M_n$ s of the resulting polymers were linearly correlated to [converted monomer]/[Ni(II)], indicating a "quasi-living" nature of the polymerization in a very wide range of catalyst loadings. This success can be attributed to the enhanced stability of the IPrNi(0)-polymer  $\pi$ -complex and the high activity of the catalyst.

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## Notes and references

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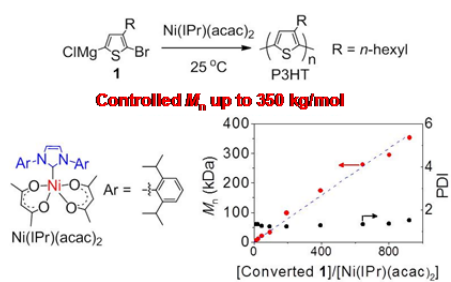
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Electronic Supplementary Information (ESI) available: [General procedures, data of the polymerizations, DFT calculations and X-ray single crystal analysis (CCDC1027838)]. See DOI: 10.1039/c000000x/

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