Controlled Synthesis of Fully π-Conjugated Donor−Acceptor Block Copolymers Using a Ni(II) Diimine Catalyst

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S *Supporting Information*

ABSTRACT: We use a Ni(II) diimine catalyst to prepare the first examples of the controlled synthesis of electron-rich/electron-deficient all-conjugated diblock copolymers. These catalysts are able to control polymerizations of both electron-rich and electron-deficient monomers, which we attribute to strong association to both monomer types. Block copolymers are prepared by controlled chain extension, and their structure is verified by gel permeation chromatography, ^{1}H NMR, electrochemistry, calorimetry, and atomic force microscopy.
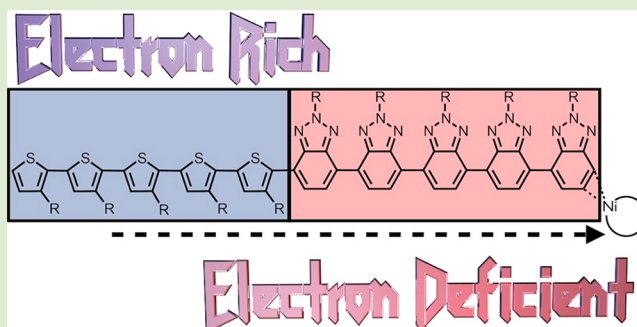
Block copolymers exhibit distinct and composition-dependent material properties compared to their respective polymer blends and have been under intense investigation for decades. More recently, studies on conjugated block copolymers have indicated they too can exhibit distinct morphological or optoelectronic properties compared to their respective blends, displaying favorable nanoscale morphologies, higher thermostabilities, and solvent-switchable properties.[1] Conjugated block copolymers are typically synthesized by chain extension of a different monomer from a polymer-based macroinitiator or by grafting two homopolymers together.[2] The so-called Kumada catalyst transfer polymerization (KCTP) is a controlled chain-growth route to conjugated polymers whereby a nickel catalyst remains coordinated to, and only allows monomer addition to, a single polymer chain during polymerization.[3] In this way KCTP allows for control over composition, sequence, and molecular weight and generally yields polymers with narrow dispersity. Using KCTP as a method for block copolymer synthesis has its limitations, however, which is mainly due to the types of monomers that are compatible with KCTP. To date, controlled KCTP has only been used to synthesize block copolymers consisting solely of electron-rich monomers such as thiophenes, selenophenes, pyrroles, fluorenes, and phenylenes.[4]

The affinity for catalyst association to the monomer is a critical aspect when considering the amount of control that can be achieved over KCTPs. Recent advances in catalyst design have extended KCTP to new monomers, affording scientists increasing control over material properties[5] and developing new applications for conjugated polymers by tailoring composition, sequence, end groups, and molecular weight. McNeil and co-workers have shown that electron-rich ancillary or reactive ligands will result in greater control over the

polymerization of thiophenes and phenylenes either through strengthening the catalyst association or by increasing initiation rates.[6,7a] We have used density functional theory (DFT) calculations to predict the strength of the association complex formed between the catalyst and monomer. More stable association complexes give greater control over the polymerization of electron-deficient monomers.[7a] This led us to consider Ni(II) diimine-type catalysts for KCTP, which allowed for the controlled preparation of polymers composed of solely electron-deficient heterocycles.

A catalyst that can bind strongly to both electron-rich and electron-deficient monomers is desirable, as it could act as a universal catalyst to allow for control over the polymerization of both monomer types. This could lead to simple, one-pot synthesis of electron-rich/electron-deficient π-conjugated diblock copolymers with control over molecular weight and composition. Herein we present a catalyst system that leads to the preparation of the first examples of these types of conjugated polymers.

For this study we chose poly-3-hexylthiophene (P3HT), synthesized from 2,5-dibromo-3-hexyl thiophene, and poly-benzotriazole (PBTz), synthesized from 4,7-dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3]triazole, as our electron-rich and electron-deficient blocks, respectively. Our candidate polymerization catalyst is [N,N′-dimesityl-2−3-(1,8-naphthyl)-1,4-diazabutadiene]dibromonickel (MesAn), a Ni(II) diimine catalyst with an electron-donating ligand (Figure 1). This system has been previously applied to the polymerization of
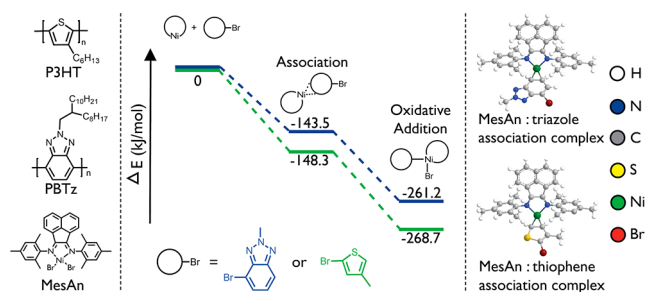
Figure 1. Polymer and catalyst structures, calculated reaction coordinate of catalyst association and oxidative addition to benzotriazole (green) and thiophene (blue), and optimized geometries of the coordination complexes.

Table 1. Molecular Weight and Dispersity for PBTz, P3HT, and P3HT-*b*-PBTz Block Copolymers

feed composition (P3HT:PBTz)	polymer composition (P3HT:PBTz)[a]	catalyst loading (mol %)	SEC M_n (kDa)[b]	Đ[b]
0:100	0:100	2	10.0	1.25
0:100	0:100	1	19.1	1.49
100:0	100:0	2	13.3	1.27
100:0	100:0	1	19.0	1.31
25:75	20:80	1	18.6	1.42
50:50	50:50	1	20.6	1.74
75:25	79:21[c]	1	21.2	1.39

[a]Determined using ^{1}H NMR. [b]Molecular weight and dispersity determined using SEC in 1,2,4-trichlorobenzene at 140 °C. [c]PBTz used as a macroinitiator.
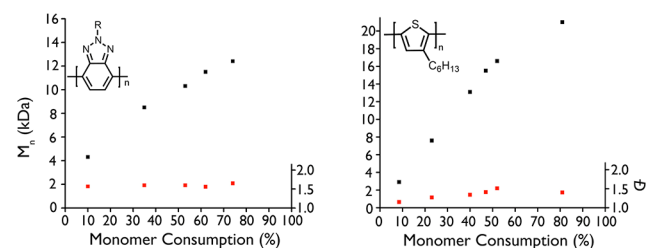

Figure 2. Number-average molecular weight (black) and dispersity (red) plotted as a function of monomer consumption for PBTz and P3HT prepared using 1 mol % MesAn.

polyolefins,[7b] but this is the first time that it has been tested for the preparation of π-conjugated diblock copolymers.

Gas-phase, single-point energy DFT calculations were used to create a reaction coordinate of the change in energy at each step in the catalytic cycle.[8] These calculations were conducted on the dissociated catalyst and monomer (all alkyl chains were replaced with methyl groups), the catalyst−monomer association complex, and the oxidative addition product to determine the association strength and estimate how favorable it is for the catalytic cycle to proceed. Stronger catalyst affinity to the monomer prevents chain termination or chain transfer reactions and will allow for more control over the polymerization. The MesAn catalyst association complex exhibits a stabilization of 148.3 and 143.8 kJ/mol for thiophene and triazole monomers, respectively. These complexes are more stable than other Ni(II) diimine catalyst−monomer systems,[7a] which suggests that MesAn will exhibit good control over both thiophene and benzotriazole polymerizations.

Controlled polymerizations are evidenced by narrow dispersity polymers with molecular weights that can be controlled by catalyst:monomer ratios. To test this, homopolymers of P3HT and PBTz were first synthesized from their respective monomers using optimized metathesis conditions (see Supporting Information). At 2 mol % MesAn produced P3HT with M_n = 13.3 kDa, Đ = 1.25 and PBTz with M_n = 10.0 kDa, Đ = 1.27. These M_n and dispersity values are very similar to previously reported values for controlled polymerizations of other conjugated polymers at this monomer:catalyst ratio.[3b,7a] Decreasing the catalyst:monomer ratio to 1 mol % resulted in the expected doubling of M_n to M_n = 19.0 kDa, Đ = 1.31 and M_n = 19.1 kDa, Đ = 1.49 for P3HT and PBTz, respectively (Table 1). These observations indicate that MesAn can control the polymerization of both electron-rich and electron-deficient monomers.

Ideal controlled polymerizations proceed without chain termination, chain coupling, or reinitiation such that the molecular weight should correlate linearly with monomer conversion, and the dispersity should remain constant throughout the polymerization. We therefore monitored the molecular weight and dispersity as a function of monomer consumption to better examine the amount of catalyst control exerted during these polymerizations. Using a 1 mol % catalyst loading we observe a near linear dependence of molecular weight on monomer consumption and that the dispersity remains below 1.6 and constant throughout the polymerization for both polymers (Figure 2). This indicates that chain termination and reinitiation events are suppressed, a hallmark of controlled polymerizations. The suppression of chain

termination reactions in both polymerizations is also supported by the linear semilogarithmic kinetic plots of monomer consumption as a function of time[3a] (see the Supporting Information).

Since MesAn can control the polymerization of both thiophene and benzotriazole, an electron-rich/electron-deficient block copolymer may be accessible using chain extension by sequential monomer addition. Block copolymer formation can be verified by comparing the size exclusion chromatography (SEC) elution curves of the polymer prior to the addition of the second monomer (the macroinitiator) to those of the final polymer. If the polymer distribution shifts entirely to a higher molecular weight while incorporating the second monomer (as determined by ^{1}H NMR), then there is strong evidence that a block copolymer has formed. While it has been shown that bidirectional growth (often referred to as ring walking) can occur in homopolymers that are not synthesized using external initiation,[9] catalyst ring walking is limited to roughly three monomer units.[10] We therefore allow our polymer chains to reach an expected length of at least 25 repeating units prior to addition of the second monomer by choosing a 1 mol % catalyst loading and feed ratios of 25:75, 50:50, and 75:25 for block copolymerization. We expect that it is unlikely that the catalyst can traverse the entire first block by ring walking and that chain extension is predominantly unidirectional when using long macroinitiators.[9]

Block copolymers were prepared by sequential monomer addition of benzotriazole and thiophene (Scheme 1). The composition of the block copolymer (as determined by ^{1}H NMR) closely resembles the feed ratio. In all block polymerization reactions, 1 mol % total catalyst loading resulted in the expected molecular weight (M_n ~ 20 kDa) as discussed above (Table 1). Importantly, in all cases the elution curve after the addition of the second monomer shifts to the expected lower

Scheme 1. Synthesis of P3HT-*b*-PBTz Block Copolymers
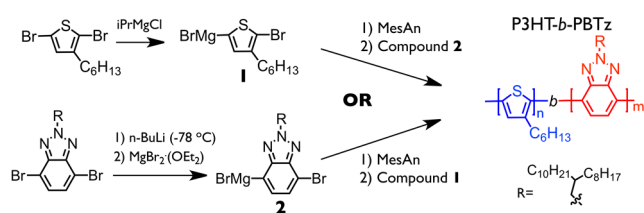
elution time (higher molecular weight) relative to the macroinitiator (Figure 3). This indicates that chain extension
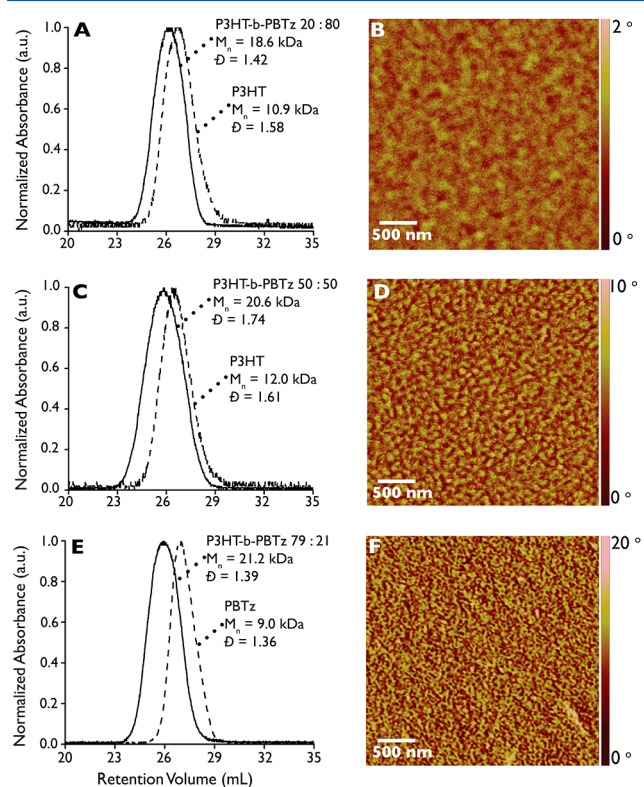

Figure 3. GPC elution curves of the macroinitiator (dashed line) and P3HT-*b*-PBTz copolymer (solid line) after chain extension. AFM phase images of a thin film of the corresponding polymers.

has occurred, and a block copolymer has been formed. Other evidence of block copolymer formation is provided by changes in polymer solubility as a function of composition. For example a polymer containing ~50% P3HT and ~50% PBTz with a M_n > 20 kDa is soluble in hexanes, whereas the P3HT macroinitiator is not. Here the P3HT block is rendered more soluble by chain extension with the more soluble PBTz block. It is also important to note that we are able to use either P3HT or PBTz as the macroinitiator (Table 1).

Differential scanning calorimetry (DSC) can help determine the difference between immiscible polymer blends or block copolymers. For reference, PBTz exhibits a weak melting transition at 135 °C, while P3HT exhibits a dominant melting transition at 220 °C, similar to previously reported values.[11] The 50:50 P3HT-*b*-PBTz copolymer has a broadened melting transition at 135 °C likely corresponding to the PBTz block, followed by a second broad melting transition at 150 °C, which is much lower than the value for P3HT. We hypothesize that this transition corresponds to the dissolution of the P3HT

block in the molten PBTz domains. The disappearance of the P3HT melting transition is therefore consistent with the structure of a block copolymer. DSC curves of block copolymers containing mostly P3HT or PBTz exhibited the same behavior as their respective homopolymers, as expected for block copolymers with high incorporation of a single monomer[12] (see the Supporting Information).

P3HT is a p-type polymer that is oxidized at relatively low potentials, while PBTz has a low reduction potential typical of electron-deficient n-type polymers. Cyclic voltammetry can be used to probe the redox properties of the block copolymer, which should exhibit both of these characteristics. P3HT-*b*-PBTz (50:50) exhibits prominent oxidation and reduction peaks that are nearly identical in potential and shape to the homopolymers (see the Supporting Information). For this to occur, oxidation must take place on the more easily oxidized P3HT block, while reduction must take place on the more easily reduced PBTz block. The potential difference between the reduction and oxidation peaks of the block copolymer (electrochemical band gap) is 1.60 eV, which is narrower than the value predicted by optical absorption (onset at 635 nm or 1.95 eV; see the Supporting Information). While this behavior is not direct proof of structure, it indicates that π-conjugated donor−block−acceptor copolymers are electronically distinct from donor−acceptor alternating copolymers, which have a nearly identical electrochemical and optical band gap.[13]

Another important feature of block copolymers is that even small differences in the interaction parameter (χ) will result in phase separation. Due to the covalent linkage between the blocks, phase separation typically occurs at the nanoscale. We conducted atomic force microscopy (AFM) on unannealed thin films of these block copolymers to better understand their nanoscale morphology. All block copolymers exhibit nanoscale structure. P3HT-*b*-PBTz 50:50 exhibits small domains of nanoscale lamella, indicating that ordered phase separation has occurred (Figure 3). While P3HT homopolymers also exhibit lamellar structure as a result of crystallization,[11,14] we do not believe that is occurring in P3HT-*b*-PBTz, due to the absence of the P3HT melting peak in the DSC experiments. As the composition changes to P3HT-*b*-PBTz 20:80 and P3HT-*b*-PBTz 79:21 the film morphology changes, all of which is indicative of well-defined block copolymers.

In conclusion we have demonstrated the controlled synthesis of all-conjugated donor−acceptor block copolymers. To accomplish this we use a Ni(diimine) catalyst system that has never been tested for KCTP and appears to overcome the limitations of polymerizing electron-deficient monomers while also achieving control over the polymerization of electron-rich monomers. With this MesAn catalyst it is possible to synthesize block copolymers using sequential monomer addition in either monomer order and control block composition and molecular weight. These new donor−block−acceptor copolymers have interesting phase separation and electrochemical properties. These results will be useful for designing future catalysts and future block copolymers that may exhibit interesting and useful morphological and optoelectronic properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and instrumentation. ^{1}H NMR, absorption spectroscopy, CV, and DSC on block copolymers. Polymerization kinetics for P3HT and PBTz. Stationary points

for the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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