Chain-Growth Polymerization of Unusual Anion-Radical Monomers Based on Naphthalene Diimide: A New Route to Well-Defined n-Type Conjugated Copolymers

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Ⓢ Supporting Information

ABSTRACT: Strongly electron-deficient (n-type) main-chain π-conjugated polymers are commonly prepared via well-established step-growth polycondensation protocols which enable limited control over polymerization. Here we demonstrate that activated Zn and electron-deficient brominated thiophene-naphthalene diimide oligomers form anion-radical complexes instead of conventional Zn—organic derivatives. These highly unusual zinc complexes undergo Ni-catalyzed chain-growth polymerization leading to n-type conjugated polymers with controlled molecular weight, relatively narrow polydispersities, and specific end-functions.
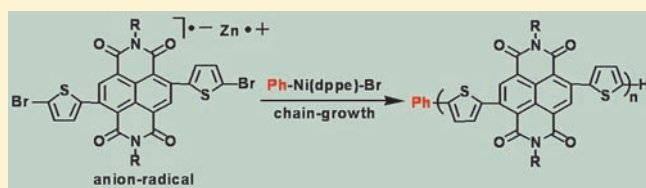
Conjugated polymers are ideal candidates for printed organic electronics, as they combine solution-processability with film-forming properties.[1] N-Type (or electron-conducting) polymers are essential components in organic devices such as ambipolar and n-channel field-effect transistors or organic photovoltaics.[2] In contrast to p-type (or hole-conducting) conjugated polymers, where a large variety of chemical structures has been presented,[3] a considerably smaller number of n-type polymers is known to date. Within the limited number of reports on n-type polymers,[4] rylene diimide alternating main chain copolymers are currently evolving as an intriguing class of electron-conducting materials. Especially π-conjugated polymers based on naphthalene diimide[5,6] and perylene diimide[7,8] have demonstrated impressive progress in n-channel OFETs and all-polymer OPV devices. For example, a bithiophene-naphthalene diimide copolymer was reported to yield high electron mobilities up to 0.85 cm^2/(V s) under ambient conditions.[5] Extending the length of the rylene diimide aromatic core at the peri-positions thus progressing from naphthalene diimide to perylene diimide seems to be beneficial for all-polymer solar cells. Very recently, Hashimoto et al. reported a record power conversion efficiency of 2.2% for a polythiophene/carbazole-perylene diimide copolymer blend.[8] Although all these materials have shown outstanding electronic properties, drawbacks with respect to control over polymer architecture remain. Typically, conventional step-growth polycondensations are used to synthesize rylene diimide-based alternating copolymers, which result in broad polydispersities (approximately 2—5) and limited control over polymer molecular weight. Moreover, the often used Stille-coupling method utilizes highly toxic organostannyl derivatives. New synthetic protocols that allow high performance n-type conjugated polymers to be reproducibly prepared from nontoxic monomers via controlled polymerization methods are therefore highly desirable.

We report here a novel nickel-catalyzed chain-growth polymerization of an unusual anion-radical monomer based on the symmetric building block 2,6-bis(2-bromothien-5-yl)naphthalene-1, 4,5,8-tetracarboxylic-N,N'-bis(2-octyldodecyl) diimide (Br-TNDIT-Br), polymerization of which leads to the corresponding bithiophene-naphthalene diimide conjugated polymer P(TNDT) with low polydispersity and specific end-functions (Scheme 1). Our initial intention was to extend the scope of the chain-growth Kumada catalyst transfer polycondensation (KCTP)[9] toward electron-acceptor monomers. This requires the design and preparation of asymmetric AB-type monomers with a Grignard- and a halide-function in the same molecule. Such monomers are commonly prepared via magnesium—halogen exchange from the corresponding dihalide precursors and alkyl magnesium halides. Although electron-deficient aryl halides are usually more reactive in halogen—magnesium exchange reactions than electron-rich ones,[10] we found that this method fails to give the Grignard monomer Br-TNDIT-MgBr upon the reaction of Br-TNDIT-Br with Grignard compounds. Another method to prepare monomers for the chain-growth polymerization of regioregular poly-(3-alkylthiophene)s is Negishi polymerization (also referred to as the "Rieke method").[11] Especially its variation which utilizes

Scheme 1. Preparation of the Br-TNDIT-Br/Zn Radical-Anion Monomer and Its Catalyst-Transfer Polymerization to Ph/H P(TNDT)
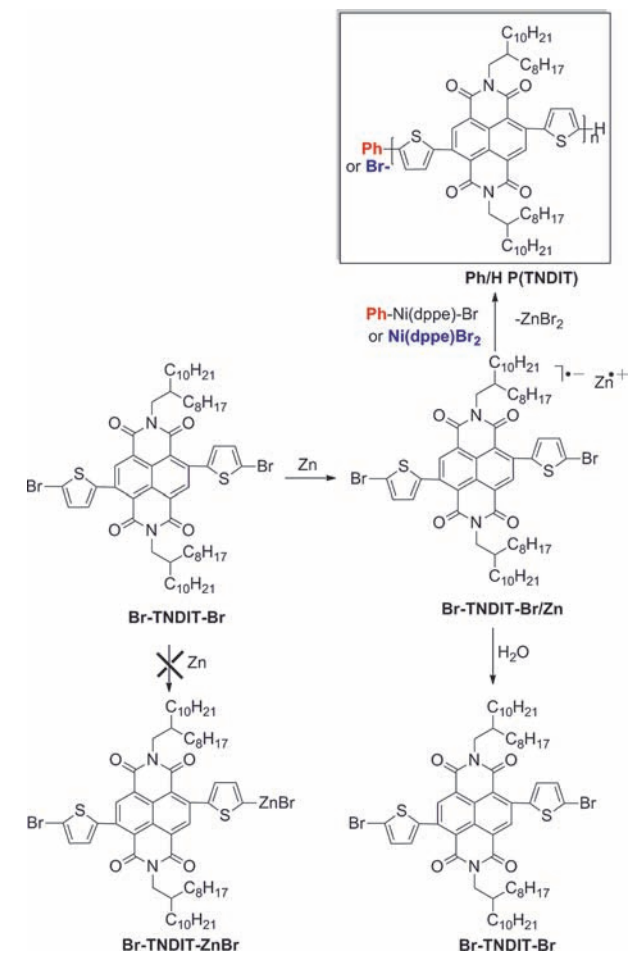
activated Zn for the generation of organozinc monomers from aryl dihalides (i.e., Br−Ar−ZnX) is interesting here and was applied in order to generate polymers from Br-TNDIT-Br. Reacting Br-TNDIT-Br with equimolar amounts of activated Zn prepared by the reduction of $ZnCl_2$ with sodium naphthalenide resulted in an immediate color change from red-orange (inherent to Br-TNDIT-Br) to deep-green, accompanied by the immediate disappearance of the solid phase. The resulting Br-TNDIT-Br/Zn complex was completely soluble in THF (it passed through a 200 nm membrane filter whereas active Zn suspension did not). It is remarkable that the acidic workup of the thus-prepared Br-TNDIT-Br/Zn complex resulted in quantitative recovering of Br-TNDIT-Br but not of Br-TNDIT-H. This indicates that the organo-zinc compound Br-TNDIT-ZnBr was not formed under these conditions because otherwise hydrolysis of Br-TNDIT-ZnBr should lead to Br-TNDIT-H. Thus, the reaction of Br-TNDIT-Br with active Zn did not lead to the usual monomer for Negishi/Rieke polymerizations. The green Br-TNDIT-Br/Zn complex remained stable under oxygen- and moisture-free conditions at least for several days at room temperature and during prolonged heating (at 60 °C); neither insertion of Zn into the C−Br bond nor the reduction of the imide groups occurred under these conditions. We propose that single electron transfer from Zn to the electron-

deficient Br-TNDIT-Br occurs which leads to a radical-anion (Scheme 1).

Electron paramagnetic resonance (EPR) measurements of the Br-TNDIT-Br/Zn complex confirmed our hypothesis. The presence of the intense electron paramagnetic resonance signal at around $g = 2.0035$ corroborated the formation of the Br-TNDIT-Br anion-radical (Figure S3, Supporting Information).[12] The fine-structure of the EPR spectrum showed features consistent with the coupling of the unpaired electron and the naphthalene diimide nitrogen. The formation of a paramagnetic species also corroborates the fact that addition of Zn to Br-TNDIT-Br leads to the complete disappearance of the aromatic signals in the ^{1}H NMR spectrum, while the signals corresponding to the alkyl chains are still observed (not shown).

Titration experiments with iodine confirmed the 1/1 stoichiometry of the Br-TNDIT-Br/Zn complex, irrespective of whether an equimolar amount or an excess of Zn was added. Such a stoichiometry is highly surprising since it formally corresponds to the unusual oxidation state +1 of Zn. Unlike mercury, which has an extensive +1 oxidation state chemistry, zinc usually adopts +2. We found only a single report in the literature describing decamethyldizincocene, $Zn_2(\eta^5\text{-}C_5Me_5)_2$, in which Zn formally adopts +1 due to the formation of zinc−zinc bonds.[13] By analogy, we hypothesize that the Br-TNDIT-Br/Zn complex dimerizes to form a zinc−zinc bond, which yields $[(\text{Br-TNDIT-Br})^{1-}]_2[\text{Zn}-\text{Zn}]^{2+}$. More studies are necessary to investigate the structure and properties of this highly unusual complex. It is also worthy to mention that the preparation of the charge-transfer complex Br-TNDIT-Br/Zn via mixing Br-TNDIT-Br with an excess of active Zn followed by filtration is very convenient because it eliminates the need to adjust the precise 1/1 stoichiometry, which otherwise is experimentally difficult.[14]

The polymerization of the Br-TNDIT-Br/Zn complex was attempted next using various nickel complexes. Surprisingly enough, the addition of $Ni(dppe)Br_2$ or Ph-Ni(dppe)Br to Br-TNDIT-Br/Zn resulted in its rapid polymerization (a few hours until complete conversion) at room temperature. The resulting dark-blue polymer (for UV−vis, see Figure S4, Supporting Information) was readily soluble in chloroform. Detailed analysis of ^{1}H and ^{13}C NMR spectra revealed a perfectly regioregular connection of the monomer units in the polymer structure via the 2-position of the thiophene rings (Figures S5,6, Supporting Information).[5] To clarify whether this polymerization involves the step-growth or the chain-growth mechanism, several experiments were performed at different initiator/monomer ratios. It was found that the polymerization allows a satisfactory control over molecular weight (MW) in a broad range of the feed ratio (i.e., from 1/10 to 1/70 (Figure 1). Although an accurate determination of MW for rigid-rod, yet prone to aggregation, polymers is challenging, it is obvious from Figure 1 that lowering of the $Ni(dppe)Br_2$/monomer ratio leads to a substantial increase of MW of the resulting polymer. Thus, polymers with $M_{n\text{ GPC}} = 25$ kg/mol and 104 kg/mol and polydispersities of ∼1.3 and 1.7 were obtained for feed ratios of 1/10 and 1/50, respectively. A small shoulder on the main polymeric peaks in GPC elution curves can be explained either by a slow initiation process or by concurrent chain-termination/reinitiation processes. The polydispersity could be further narrowed by washing the raw products with acetone and hexane.

The successful polymerization with high conversion further corroborates the 1/1 Br-TNDIT-Br/Zn stoichiometry, because
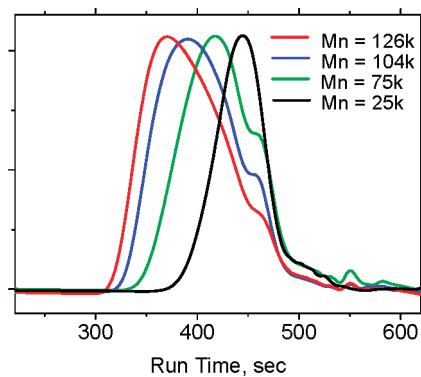
Figure 1. GPC elution curves of crude P(TNDT)s obtained upon polymerization of Br-TNDIT-Br/Zn in the presence Ni(dppe)Br$_2$ at the following ratios: [initiator]/[monomer] = 1/10 (black); 1/30 (green); 1/50 (blue); 1/70 (red).

ZnBr$_2$ is formed as leaving group.[15] As no insertion of Zn into the thiophene–bromine bond of Br-TNDIT-Br was observed, the discovered chain-growth polycondensation cannot be classified as Negishi/Rieke-type.

^{1}H NMR end-group analysis revealed the presence of a Ph-starting group in P(TNDT) for polymerization initiated by Ph-Ni(dppe)-Br (Figure S7, Supporting Information). Control experiments demonstrated that the Ph-moiety is not incorporated into the polymer structure in Ni(dppe)Br$_2$-initiated polymerizations, if Ph-Ni(dppe)Br is added after monomer consumption. Thus, the presence of the Ph-moiety in the polymer structure is an indication of the chain-growth polymerization mechanism. It is also worthy to note that polymeric products with relatively high MW are formed early in the polymerization reaction (at low monomer conversion)[16] which further supports the chain-growth mechanism.[17]

In situ ^{31}P and ^{1}H NMR studies are a powerful tool in the investigation of KCTP.[18] Such experiments were performed in this work in order to get insight into the mechanism of polymerization in more detail. Figure 2a depicts the ^{31}P spectrum after the addition of 1 equiv Br-TNDIT-Br/Zn to a solution of Ni(dppe)Br$_2$ in THF-d_8. Two doublets at 61.3 and 45.8 ppm ($J_{PP} \sim$ 33 Hz) are characteristic for monoaryl Ni(dppe) complexes.[18,19] Obviously, the complex Br-TNDIT-Ni(dppe)-Br, which is typical for the initiation of KCTP, was formed. Further evidence is given by the comparison of the ^{1}H NMR spectra of the reaction product and the reactants (Figure 2b–d). While the reactants could not be observed any more, the product showed two proton signals for the NDI moiety (H$_c$, H$_d$), indicating its nonsymmetric substitution. The two doublets at 7.13 and 7.04 ppm (H$_a$, H$_b$) correspond to the bromine-substituted thiophene moiety. The second thiophene moiety results in two signals at 7.22 and 6.50 ppm (H$_e$, H$_f$) as approved by a COSY spectrum (Figure S8a, Supporting Information). The signal at 6.50 ppm appears as a triplet, which is caused by P–H coupling as confirmed by a correlation peak in the ^{31}P–^{1}H heterocorrelated spectrum (Figure S8b). Assuming that $^4J_{PH} > {}^5J_{PH}$ in this complex, we assign this signal to H$_f$.

Adding several equivalents of Br-TNDIT-Br/Zn to Ni-(dppe)Br$_2$ resulted in the formation of closely located signals in the ^{31}P NMR spectrum between 49 and 46 ppm (Figure S9a, Supporting Information). The intensity of these signals decreased with polymerization time at the expense of two new distal
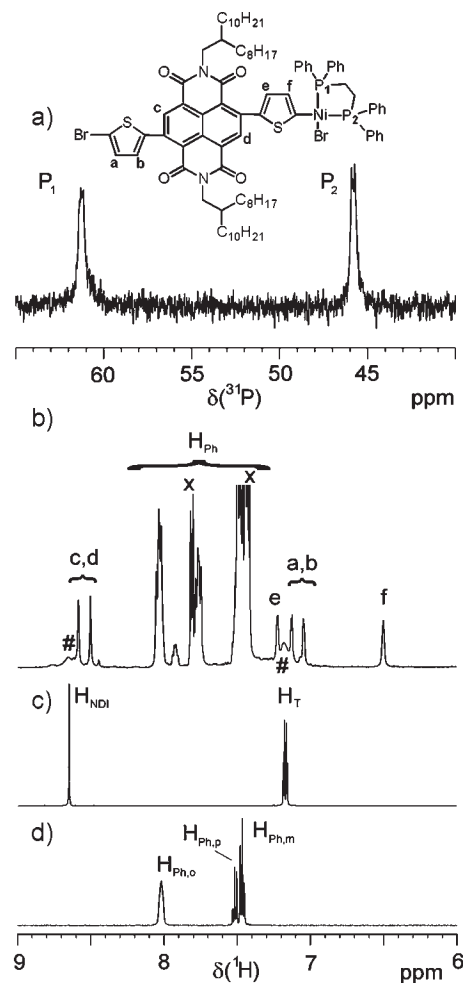

Figure 2. (a) ^{31}P NMR and (b) ^{1}H NMR spectrum (aromatic region) of the initiating Br-TNDIT-Ni(dppe)-Br complex (#, P(TNDIT) signals; ×, naphthalene from Zn monomer synthesis; see Figure S8, for 2D spectra). (c) ^{1}H NMR spectra of the reactants Br-TNDIT-Br and (d) Ni(dppe)Br$_2$ (solvent: THF-d_8).

doublets at 61 and 46 ppm (Figure S9b). As the latter doublets were the only signals after the full consumption of Br-TNDIT-Br/Zn, and because they appeared in the same region as the structurally similar Br-TNDIT-Ni(dppe)-Br initiator complex, we assign the doublets at 61 and 46 ppm to the propagating chain end P(TNDT)-Ni(dppe)-Br. Signals at 49–46 ppm may be attributed to either the Ni(0) complex between P(TNDT)-Br and Ni(dppe) species or to P(TNDT)-Ni(dppe)-TNDIT-Br; both are usual intermediates in catalyst-transfer polycondensations formed before and after the OA step, respectively. Further identification efforts are still needed, and they are under way in our lab.

A possible mechanism of the Ni(dppe)Br$_2$-initiated polymerization of Br-TNDIT-Br/Zn is given in Scheme 2. A catalytic cycle includes oxidative addition (OA) and reductive elimination (RE) elementary steps, the usual for metal-catalyzed coupling reactions.[20] Because the polymerization displays chain-growth behavior, we propose that most of the Ni(0) species undergo *intra*molecular OA (IV→V, Scheme 2), i.e., catalyst-transfer previously observed in polycondensations of electron-rich monomers.[9,21] In catalyst-transfer polycondensations, transmetalation (TM) is an important step of the catalytic cycle

Scheme 2. A Plausible Mechanism of Ni-Initiated Catalyst-Transfer Polymerization of Br-TNDIT-Br/Zn (dppe ligand is omitted)
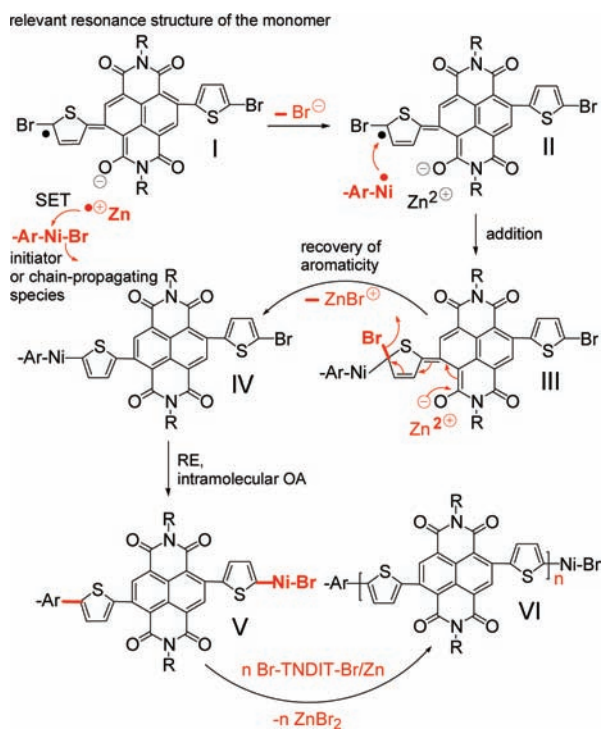
responsible for the addition of monomers to the growing polymer chain. Usually, TM involves a nucleophilic attack of the carbanionic center of the monomer onto electrophilic Ni along with elimination of $ZnBr_2$. Because there is no well-defined carbanionic center in the Br-TNDIT-Br/Zn, the TM here cannot follow the usual mechanism. We tentatively propose that the first step of a "quasi-transmetalation" process operative here involves a single electron transfer (SET) from Zn^+ to Ni(II) with a concomitant elimination of Br^- leading to Ni(I) species (I→II, Scheme 2). Ni(I) complexes are known as possible intermediates in the Kumada coupling.[22] The next step is an addition of Ar—Ni(I) to the terminal carbon of the monomer (II→III). Finally, the aromaticity of the system is recovered by elimination of Br^- and Zn^{2+} (III→IV). Taking into account that one Br^- was eliminated in a preceding step, the last elimination completes the formation of $ZnBr_2$, a usual byproduct in Negishi coupling. However so far, we have no solid experimental evidence of the proposed mechanism, and this is a subject of ongoing works in our lab.[23]

In conclusion, we have presented a highly unusual Ni-catalyzed chain-growth polymerization of NDI-based anion-radical monomers leading to high-performance n-type conjugated polymers P(TNDIT) with controlled molecular weight, relatively narrow polydispersity, and specific end-functions. To the best of our knowledge, this is the first report on the controlled chain-growth polymerization of highly electron-deficient monomers leading to high-performance n-type conjugated polymers. This result is outstanding, taking into account the large length of the monomer (approx 1.5 nm) and its highly polarized structure. Intuitively, one could expect that both these factors hamper the intramolecular catalyst-transfer process, which obviously is not

the case here. The structure of the NDI-based anion-radical monomer formed upon mixing Br-TNDIT-Br and active Zn is equally intriguing, as it involves Zn in the highly unusual +1 oxidation state and because any unreacted complex monomer can be recovered as the starting precursor Br-TNDIT-Br. Further efforts will be directed to investigate the exact structure of the anion-radical monomer and the details of the mechanism of polymerization, the fine-tuning of which we expect to lead to a plethora of novel and multifunctional conjugated polymer topologies when combined with additional other monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Description of instrumentation and materials used, experimental details for preparation of the monomer and polymerization procedure, NMR spectroscopic data, and discussion of the polymerization mechanism. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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(14) Active Zn is available as an unstable colloidal suspension; isolation of Zn powder in dry form is difficult and undesirable because it leads to partial deactivation of Zn; hence, it is practically very difficult to dose exact amounts of Zn. An excess of Zn generally leads to overmetalation (formation of XZn-Ar-ZnX instead of X-Ar-ZnX).

(15) The monomer conversion should approach 50% (and not 100%), if the reaction of Br-TNDIT-Br and active Zn results in $[(\text{Br-TNDIT-Br})^{-1}]_2\text{Zn}^{2+}$.

(16) Detailed kinetics of this polymerization will be published elsewhere.

(17) Step-growth polycondensations result in high MW polymers only at monomer conversions approaching 100%:Carothers, W. H. *J. Am. Chem. Soc.* **1929**, *51*, 2548–2559.

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(20) One of the key intermediates in coupling polymerizations, P(TNDIT)-Ni(dppe)Br, was identified in situ by NMR spectroscopy that supports the proposed general mechanism.

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(23) To monitor possible electron transfer processes and formation of paramagnetic species, the polymerization was conducted while measuring EPR spectra. However, no paramagnetic species other than the starting anion-radical monomer were found. Alternative mechanisms can also be proposed, such as discussed in Supporting Information, S12—14.