# A Core-First Preparation of Poly(3-alkylthiophene) Stars

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**Summary:** A new and facile method for the preparation of mono- and hexa-functional Ni-bipyridyl-based initiators that mediate Kumada polycondensation of 2-bromo-5-chloromagnesio-3-hexylthiophene into head-to-tail regioregular poly(3-hexylthiophene), P3HT, has been developed. An important advantage of the catalytic system presented herein is the ease of the preparation of a number of Ar-Nibipy-Br initiators from readily available aryl halides. As an example, the ''core-first'' synthesis of 6-arm star-like P3HT having a hexaphenylbenzene core is demonstrated.

**Keywords:** atomic force microscopy; chain-growth; conjugated polymers; polycondensation; scanning tunneling microscopy; star polymers

## Introduction

Star-like polymers have received much attention due to their unique chemical and physical properties as well as due to potential applications in coatings, additives, and drug and gene delivery. Star-like polymers are also interesting nanoscale macromolecular building blocks that can be used for the construction of novel functional materials, such as well-defined polymer networks.[1] There are two general strategies to produce star-like polymers: the ''arm-first'' method and the ''core-first'' method.[2] The ''arm-first'' approach implies the coupling of end-functional, possibly ''living'' linear polymer chains onto a multi-functional core, whereas the ''core-first'' approach involves the simultaneous polymerization of several arms from appropriate multifunctional initiators. To date, both of these methods have been applied for the preparation of various star-like polymers. Different kinds of vinylic and cyclic monomers and various addition polymerization techniques (e.g. anionic,[3] controlled radical,[4] ring opening) have been employed. However, examples of the preparation of π-conjugated aromatic star-like polymers remains scarce.[5] This is due to the fact that the synthesis of most of the π-conjugated polymers involves a step-growth condensation polymerization that is itself not well-suited for the preparation of complex polymer architectures. Due to the inherent mechanistic features of step-growth polycondensation (random coupling of monomers and initial formation of oligomers rather than rapid formation of some high polymer from the beginning of the process taking place in chain-growth polymerization), this type of reaction has never been used for the ''core-first'' synthesis of conjugated star-like polymers. Although a decade ago Wang et. al reported the ''core-first'' synthesis of poly(3-alkylthiophene) star-like polymers via the coupling of the in-situ polymerizing poly(3-hexylthiophene) (P3HT) chains to a multifunctional core,[5] this process rather falls under the definition of the ''arm-first'' approach.

Although the synthesis of most conjugated polymers involves a step-growth polycondensation mechanism, it was recently recognized that Ni-mediated

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Kumada polycondensation into P3HT proceeds in a chain-growth manner and leads to polymers with narrow polydispersity indices (PDIs), controlled molecular weights (MWs) and well-defined end-groups.[6,7] In principle, this finding paves the way to various polymer architectures of conjugated polymers; however, the ''core-first'' synthesis of star-like conjugated polymers still remains a challenge. The critical step in the ''core-first'' preparation of polythiophene stars using the Kumada chain-growth polycondensation is the preparation of the multifunctional initiators with the general formula Z(-Ar-$NiL_2$-X)$_n$ from Z(-Ar-X)$_n$, where Z are any suitable core compounds, Ar are aryl groups, L are supporting ligands and X are halogen atoms. According to the ''classical'' performance of the Kumada polycondensation, the initiator forms *in situ* from $NiL_2Cl_2$ ($L_2 = Ph_2PCH_2CH_2PPh_2$, dppe; $Ph_2PCH_2CH_2CH_2PPh_2$; dppp) and *two* monomer molecules. Clearly, this procedure is barely suitable for the ''core-first'' synthesis of stars that would require preparation of initiators from a single source. Recently, we demonstrated that various initiators for Kumada polycondensation can be prepared by oxidative addition of aryl halides to $Ni(PPh_3)_4$: Ar-X + $Ni(PPh_3)_4 \rightarrow$ Ar-$Ni(PPh_3)_2$-X.[8–10] These initiators efficiently polymerize 2-bromo-5-chloromagnesio-3-hexylthiophene (1) into Ar-terminated regioregular head-to-tail (HT) P3HT. Furthermore, it was possible to grow P3HT selectively from photo-cross-linked poly(4-bromostyrene) films that were pre-activated with $Ni(PPh_3)_4$.[8,9] However, due to the monodentate nature of the $PPh_3$ supporting ligand, the performance of the polymerizations induced by $Ni(PPh_3)_4$-based initiators is much worse than the performance of the Nidppe$Cl_2$-mediated polymerizations. For example, high enough regioregularities with Ar-$Ni(PPh_3)_2$-X can be achieved only at decreased temperature, and chain-terminations are pronounced at any reaction conditions.

Our first attempts in the ''core-first'' synthesis of P3HT stars were focused on the employment of the $Ni(PPh_3)_4$ initiator precursor and hexaphenylbenzene, as the core compound. Hexaphenylbenzene derivatives were used, as they can be easily converted into hexabenzocoronene-discotics with interesting self-assembly properties (Figure 1).[11] Unfortunately, reaction

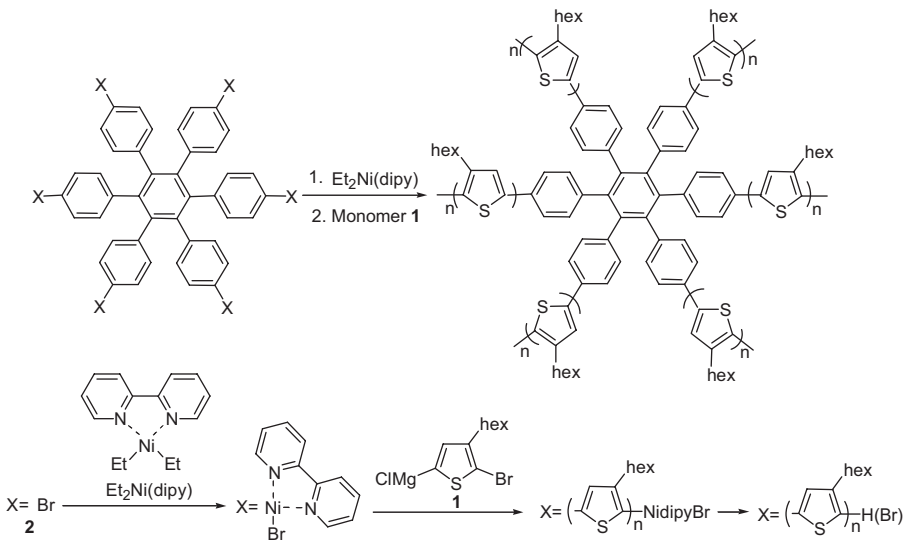


***Figure 1.***
A ''core-first'' synthesis of the 6-arm P3HT star *via* Kumada polycondensation mediated by Nibipy complexes.

 

of hexakis(4-bromophenyl)benzene (**2**) with $Ni(PPh_3)_4$ resulted in largely insoluble materials, most likely due to undesired homocoupling reactions leading to intermolecular cross-linking of hexaphenylbenzene. In this work, we explore the Kumada polycondensation mediated by Ni-bipyridyl complexes and use them in the synthesis of 6-arm P3HT stars.

## Experimental Part

### Materials

All reagents were purchased from Aldrich and used without further purification. $Et_2$Nibipy,[12] hexakis(4-bromophenyl)benzene (**2**), hexaphenylbenzene (**3**),[13] and 2-bromo-3-hexyl-5-iodothiophene (**4**)[6] were prepared as previously described.

### Instrumentation

$^1$H NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500.13 MHz for $^1$H using $CDCl_3$ as solvent. The spectra were referenced on the solvent peak ($\delta(1H) = 7.26$ ppm).

Size exclusion chromatography (SEC) measurements were carried out on an Agilent 1100 Series (Agilent, USA) normal-temperature chromatograph, equipped with refractive index (RI) detector and one column PL Gel MIXED-B (Polymer Laboratories, UK), and using chloroform as eluent, delivered at a flow rate of 1 mL min$^{-1}$. Calibration was based on polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

AFM. The Multimode atomic force microscope (AFM) (Digital Instruments, Santa Barbara) was operated with amplitude feedback and in a ''light'' tapping mode configuration. The amplitude setpoint was set to the maximum possible value. Silicon tips with a spring constant of 0.3 N m$^{-1}$ and a resonance frequency of 250–300 KHz were used after calibration with gold nanoparticles (of diameter ~2 nm) to evaluate the tip radius. Tips with a nominal radius 5 nm were used for the measurements. A series of chloroform solutions of star-like and linear P3HT samples with concentrations of 0.1, 0.01, 0.001, and 0.0001 g L$^{-1}$ were prepared by sequential dilution of 1 g L$^{-1}$ stock solutions. The solutions were stirred at least for one day before the next dilution or AFM experiments. To prepare AFM samples, a drop of the solution of the sample being investigated was placed onto the surface of mica and was allowed to stand until the solvent evaporated.

### Synthesis of $C_6$-[$C_6H_4$-Nibipy-Br]$_6$

All operations were performed under an argon atmosphere in a glovebox. To a solution of **2** (0.129 g, 0.1 mmol) in 20 mL of dry THF, the green solution of $Et_2$Nibipy (0.191 g, 0.7 mmol) in 10 mL of dry THF was added at room temperature. The mixture was stirred for 2 hours, and the resulting precipitate was separated by filtration, washed 2 times with dry ether, hexane and dried in vacuum to give 0.25 g (96% yield) of dark-red powder of $C_6$-[$C_6H_4$-Nibipy-Br]$_6$.

### Synthesis of P3HT stars

Compound **4** (373 mg, 1 mmol) was placed in a round-bottomed flask equipped with a magnetic stirring bar, and the atmosphere was replaced with argon. Dry THF (20 mL) was added via a syringe, and the mixture was cooled to 0 °C. Afterwards, *tert*-butylmagnesium chloride (2.0 M solution in THF, 0.50 mL, 1.0 mmol) was added via a syringe, and the mixture was stirred at 0 °C for 1 h. A suspension of $C_6$-[$C_6H_4$-Nibipy-Br]$_6$ in toluene (21.5 mg, 0.0083 mmol in 1 mL) was added via a syringe and then the mixture was stirred for 3 h at RT. The reaction mixture was quenched by 5 M HCl and the product was extracted with $CHCl_3$. The organic layers were washed with water, dried over anhydrous $MgSO_4$ and concentrated under a reduced pressure. Finally, MeOH was added to the residue, the insoluble material was washed with MeOH and collected by filtration under vacuum to give P3HT stars as a black solid (120 mg, 75%).

 

## Results and Discussion

4,4′-Bipyridine (bipy) complexes of nickel have attracted our attention as potentially viable alternative to phosphorous-containing catalysts for Kumada polycondensation. Such complexes are widely used in Yamamoto coupling polycondensation into various polyaromatics.[14] On the other hand, Ni-diimine bidentate complexes were recently employed by the McCoullogh group in the Kumada preparation of rrP3HT.[15] However, no reports exist in the literature describing utilization of nickel bipyridine in the Kumada polycondensations. An attractive feature of this polymerization approach originates from the availability of **Ar-Nibipy-X** complexes that potentially could act as initiators in the Kumada polycondensation. It is known that $Et_2$Nibipy[12] smoothly reacts with various arylhalides giving **Ar-Nibipy-X** adducts in high yields. In this work, we employed this process for the preparation of mono- and multifunctional initiators (Figure 1).

### Ph-Nibipy-Br-Mediated Polymerization

Ph-Nibipy-Br was prepared from $Et_2$Nibipy and a model aryl halide, Ph-Br: **$Et_2$Nibipy + Ar-Br→Ph-Nibipy-Br + $C_4H_{10}$**.[16] The reaction course was easily monitored by a change in the color of the reaction mixture from green to red. The room temperature (RT) Ph-Nibipy-Br-mediated RT-polycondensation of **1** resulted into near 100% regioregular HT P3HT. Although, in some cases, this polymerization gave a product with a bimodal molecular weight distribution (MWD), in optimized reaction conditions[17] it was possible to obtain P3HT with a monomodal and relatively narrow MWD with a PDI of about 1.6. The reaction showed clear signs of the chain-growth polymerization mechanism, and, most notably, the formation of high MW P3HT at low conversions of **1**).

### Synthesis of P3HT Stars

Addition of **2** to an excess of $Et_2$Nibipy solution resulted in a red precipitate, presumably $C_6$-[$C_6H_4$-Nibipy-Br]$_6$, that was isolated and washed from the excess of $Et_2$Nibipy. Since the resulting product was found to be poorly soluble and unstable in solvents suitable for NMR analysis, some amount of $C_6$-[$C_6H_4$-Nibipy-Br]$_6$ was quenched with acidic water, and the resulting product of yellowish color was isolated and analyzed by NMR. It was identified to be hexaphenylbenzene of, at least, 95% purity. This result indicated near complete course of the addition reaction that led to the desired hexa-functional initiator $C_6$-[$C_6H_4$-Nibipy-Br]$_6$. Aiming at the preparation of the 6-arm P3HT stars with a degree of polymerization (DP) of 20 in each P3HT arm, monomer **1** was added to the solution of $C_6$-[$C_6H_4$-Nibipy-Br]$_6$ at a **1** to $C_6$-[$C_6H_4$-Nibipy-Br]$_6$ ratio of 120/1. After polycondensation at room temperature, the reaction mixture was quenched with acidic water. $^1$H NMR confirmed the presence of the hexaphenylbenzene core coupled with P3HT chains (Figure 2a, b). SEC showed a monomodal MWD ($M_n = 8000\,g\,mol^{-1}$, PDI = 1.98, Figure 2c).[17]

A proof of the star-like structure of polymers in many cases is a highly challenging task. In this work, we found that many standard techniques were not suitable for verification of the architecture of our P3HT stars. One of the most frequently used methods to prove the branched architecture implies a measurement and comparison of the relative and absolute MWs for supposed branched and reference linear samples. Relative MWs can be determined by SEC with an RI detector, whereas absolute MWs can be measured by SEC combined with a static light-scattering detector (SEC-LS).[3] In this case, more compact branched polymers will show higher absolute MWs than samples with a linear architecture and of the same relative MW. We tried to apply this approach for the elucidation of the structure of our P3HT samples, but, unfortunately, without a noticeable success due to the formation of P3HT aggregates that strongly scattered light.

Investigation of individual polymer molecules with microscopic techniques is another powerful approach to directly

 

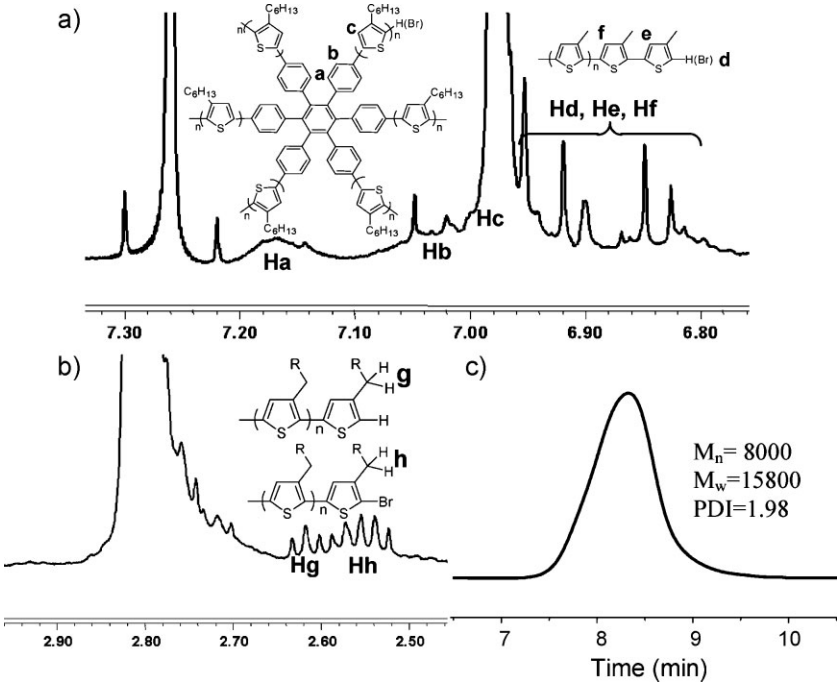


***Figure 2.***
Aromatic (a) and aliphatic (b) regions of the $^1$H NMR spectrum of 6-arm P3HT star prepared by the Kumada polycondensation route at a **1**/$C_6$-[$C_6H_4$-Nibipy-Br]$_6$ ratio of 120/1 (the per-arm seed ratio of 1/20). SEC trace of the star-like P3HT after purification in Soxlet apparatus (chloroform fraction) (c).

verify macromolecular architecture. Previously, linear oligo-alkylthiophenes and P3HT molecules adsorbed at the solution/highly ordered pyrolytic graphite (HOPG) interface were investigated using scanning tunneling microscopy (STM).[18,19] STM was also used to study the present star-like P3HT samples. However only very short chains, from 4 to 7 nm, were visualized (Figure 3). In these experiments, the contour length of most visualized molecules corresponded to a DP of less than 20, which was considerably less than what the SEC data indicated (MWs in the range from $\sim$8000 to $\sim$16000 g mol$^{-1}$ correspond to DPs from 48 to 95). Solid state UV-vis absorption spectra for the star-like P3HT ($\lambda_{max} = 555$ nm, shoulder $\lambda = 605$ nm, not shown) exhibited spectral features which also corresponded to rather high MW regioregular P3HTs.[20] The shorter chains in the STM may, therefore, be attributed to a fractionation at the solid-liquid interface, since upon adsorption the chains lost conformational entropy which increased with the chain length.[21] Alternatively, large and branched star molecules may adsorb only partly during the STM experiment, forming a kind of brushes in which only some locally crystallized parts of the stars can be visualized.

AFM is another powerful imaging technique previously used by us[22–27] for the investigation of single molecules. Although the resolution of AFM is not as high as that of STM, it is, nonetheless, sufficient for the investigation of macromolecules of many types, such as linear[22–24] and star-like macromolecules,[25,26] as well as dendrimers.[28] To ensure the detection of individual molecules, a series of solutions in chloroform with decreasing polymer concentration were prepared and spin-coated onto mica. At relatively high concentrations of P3HT stars, 1 g L$^{-1}$, films with nanofibrillar morphology were formed (Figure 4).

 

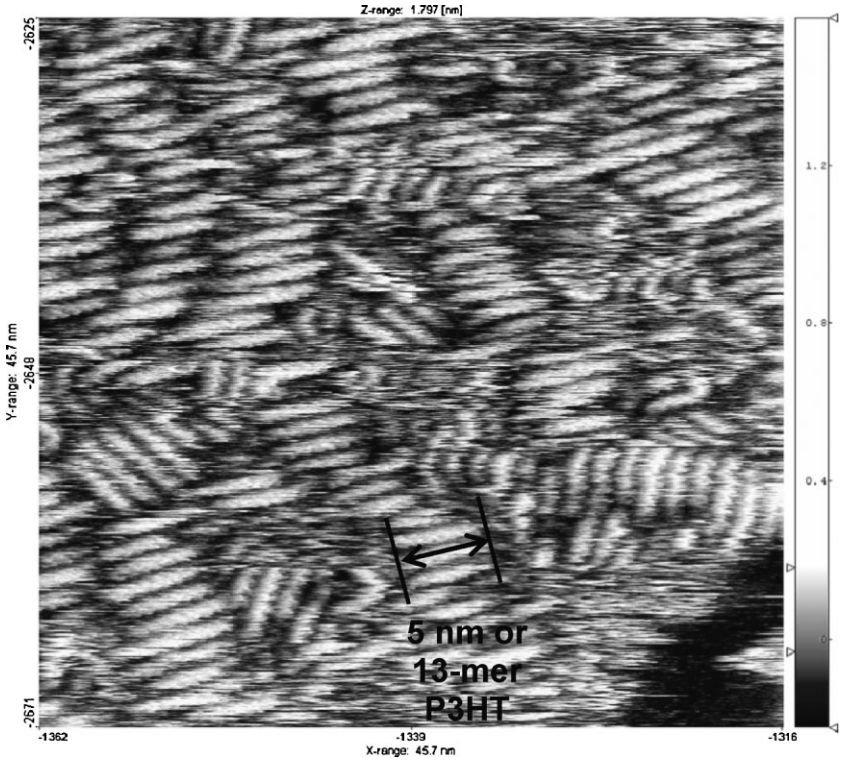


***Figure 3.***
An STM image (45.7 nm × 45.7 nm) of the star-like P3HT adsorbed at the phenyloctane/HOPG interface.

The mean diameter of the one-dimensional structures within the given sample was fairly uniform, but depended on the deposition conditions. When deposited from chloroform, the nanostructures exhibited a diameter of about 2 nm, whereas a diameter of about 4 nm was measured when the star-like P3HT was deposited from a chloroform-hexane mixture (1/1 v/v). The propensity of linear conjugated polymers[29] and, in particular, of regioregular

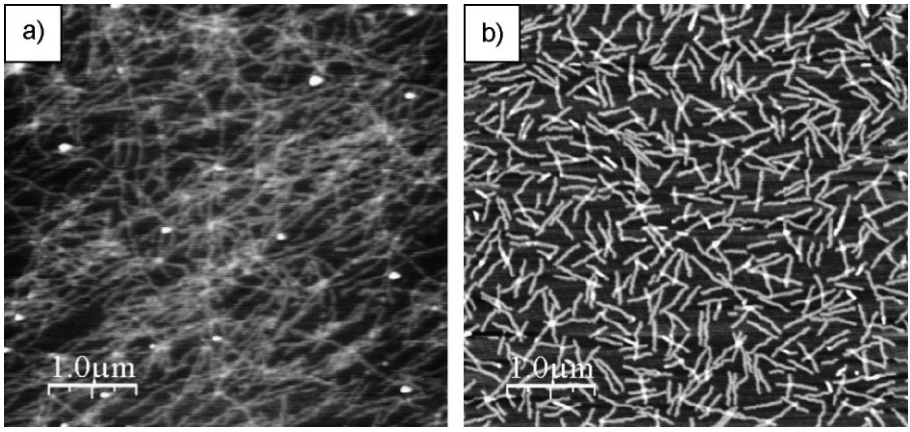


***Figure 4.***
AFM topography images of the star-like P3HT deposited onto mica from chloroform (left) and from a 1/1 v/v chloroform/hexane solution at a concentration of 1 g $L^{-1}$.

 

P3HT to form one-dimensional structures is well-documented in the literature and, therefore, the formation of such structures in our case could not be ascribed solely to the influence of the star-like architecture.[20,30] At concentrations below 0.01 g $L^{-1}$, the polymer films broke up into isolated islands representing clusters of P3HT molecules (Figure 5a). Further lowering of the polymer concentration resulted in a decrease of the size of islands and in an increase of the separation between them. It is important to note that further decrease of the concentration from 0.0001 g $L^{-1}$ down to 0.00001 g $L^{-1}$ did not affect the size of the structures and only reduced their surface concentration.

The structures visualized at these extremely low concentrations in the case of the star-like polymer appeared as 1–2 nm in the height dots and about 10–20 nm in diameter (Figure 5b,c). Since the structures are fairly uniform and keep their integrity even at very low concentrations, we suggest that they represent single molecules of the star-like P3HT. It is well-known that AFM gives always overestimated lateral dimensions for nanostructures due to the tip-broadening

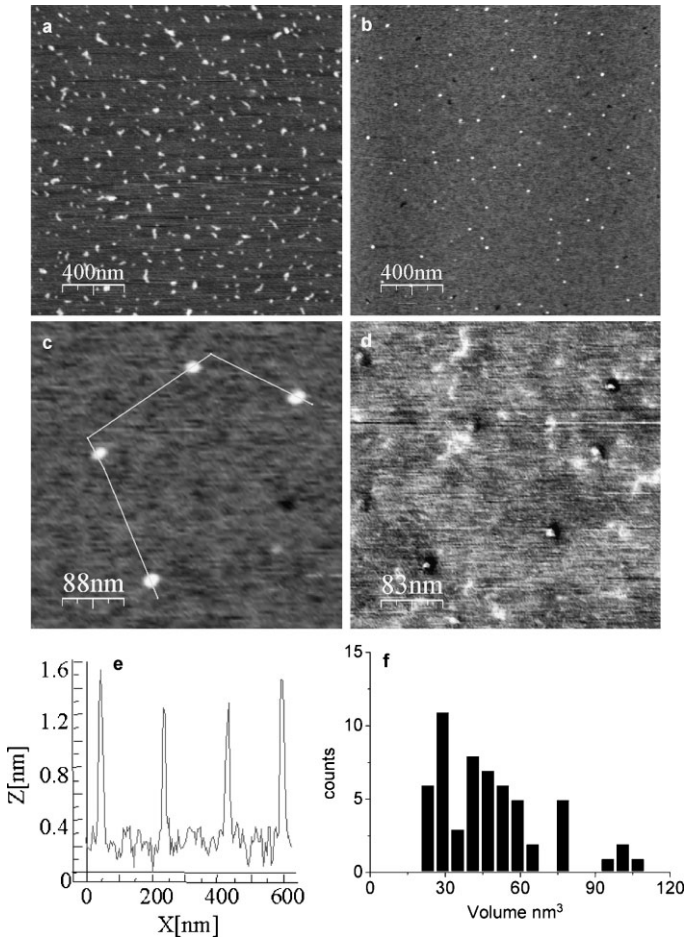


***Figure 5.***
(a-c) AFM topography images of the star-like P3HT deposited onto mica from a chloroform solution at a concentration of 0.01 g $L^{-1}$ (a) and 0.0001 g $L^{-1}$ (b,c). (d) AFM phase image of linear P3HT with $M_n \sim 8000$ g $mol^{-1}$ deposited from a 0.0001 g $L^{-1}$ chloroform solution. (e) Cross-section made as shown in image (c). (f) Histogram of the volume distribution of the structures in images (b) and (c).

 

effect. The tip-broadening contribution was estimated by the AFM-investigation on ~2 nm spherical gold nanoclusters. These data were further used for the deconvolution of the star-like P3HT images and the determination of their volumes, according to the previously described procedure.[26] A mean volume of the nanodot structures determined after statistical treatment of the AFM data was found to be equal to $V \sim 31\ nm^3$. This value corresponds to a ~170-mer of P3HT, or to the 6-arm P3HT stars with P3HT arms, each having a DP of ~27 (170/6). These data are consistent with the SEC data for the sample that corresponds to DP = 95. The DP measured by SEC could be somewhat underestimated due to the branched nature of the P3HT stars. On the other hand, the higher value obtained by AFM might be also due to the error of the AFM method. For comparison, the same visualization experiments were performed with a sample of linear P3HT of about the same MW. In particular, we found that nanodot structures did not form in this case. In contrast to the readily visualizable star-like P3HT molecules, the molecules of linear P3HT deposited from dilute solutions were very difficult to detect. Sometimes, they could be observed in phase images as shown in Figure 5d. Thus, the obtained results confirm that the formation of the nanodot structures is an inherent feature of the star-like architecture of P3HT.

## Conclusion

A novel and facile method for the preparation of mono- and hexa-functional Ni-bipyridyl-based initiators that mediate Kumada polycondensation of 2-bromo-5-chloromagnesio-3-hexylthiophene into head-to-tail regioregular poly(3-hexylthiophene) has been developed. An important advantage of the catalytic system presented herein is the ease of the preparation of a number of Ar-Nibipy-Br initiators from readily available aryl halides. As an example, the ''core-first'' synthesis of 6-arm star-like P3HT with a hexaphenylbenzene core is demonstrated. Individual molecules of P3HT stars could be imaged by AFM.

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