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A Trinuclear Pd−Diimine Catalyst for “Core-First” Synthesis of Three-Arm Star Polyethylenes via Ethylene “Living” Polymerization

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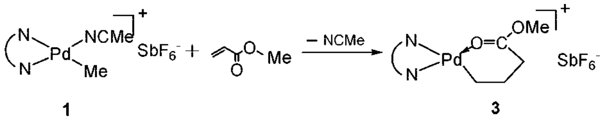
Star polymers containing multiple arms joined at a central core have received extensive research attention in the past decade due to their compact branching structures, spherical shape, and resulting superior properties.[1] Synthesis of star polymers, particularly those of well-defined arm length and number, is often accomplished with the use of “living” polymerization techniques, including the traditional “living” anionic[2] and cationic[3] polymerization techniques, and the recently developed “living”/controlled radical polymerization techniques.[4] Three synthetic strategies—“arm-first”, “core-first”, and “coupling-onto” —have often been employed for polymerization.[1−4] In particular, the “core-first” strategy requires the use of multifunctional initiators capable of initiating simultaneously multidirectional “living” growth of polymer arms emanating from multiple initiating sites bound on a central core. A variety of multifunctional initiators have been successfully developed in each of the above “living” polymerization techniques for “core-first” synthesis of star polymers from various monomer stocks including styrenics, conjugated dienes, methacrylates, and acrylates.

Synthesis of star polyolefins from olefin monomers like ethylene using catalytic “living” olefin coordination polymerization technique somehow has been very difficult compared to the great success with other “living” polymerization techniques. This “living” polymerization technique has not yet been reported for “core-first” synthesis of star polyolefins though it has advanced significantly in the past decades with the development of a great number of well-behaved transition metal catalysts.[5] The primary challenge lies in the overwhelming difficulty of finding versatile multinuclear metal catalysts that possess multiple metal centers capable of catalyzing and initiating multidirectional “living” chain growth from a common central core.

As a new class of late transition metal catalysts of some outstanding features, Pd−diimine series of catalysts, first discovered by Brookhart et al., enables unprecedented synthesis of novel polyolefins of unique chain structures and superior properties.[6] These catalysts can furthermore catalyze olefin “living” polymerization under prescribed conditions for tailored synthesis of narrow-distributed polyolefins, their block copolymers, and telechelic polymers.[7,8] Utilizing their unique synthetic and polymerization chemistry, we report herein the synthesis a novel trinuclear Pd−diimine catalyst (**2** in Scheme 1) that enables the first “core-first” synthesis of three-arm star polyethylenes via ethylene trifunctional “living” polymerization.

Complex **2** contains three identical cationic 6-membered Pd chelate centers bound together at the triester core. It was synthesized conveniently in one step by reacting an acetonitrile Pd−diimine complex **1** (ca. 3.3 equiv) with a triacrylate monomer, trimethylolpropane triacrylate (Scheme 1). This synthesis is based on the characteristic reaction of **1** with acrylate functionality (such as methyl acrylate in eq 1), wherein the acrylate double bond is inserted into the Pd−Me bond of **1** via 2,1-insertion followed by rearrangement resulting in a stable 6-membered chelate structure.[6b,c,8]



(1)

With **1** in excess in the synthesis herein, all three acryloyl groups of the triacrylate can be reacted, rendering the trinuclear complex with each cationic Pd center bound to the triester core via a 6-membered chelate structure. Compared to **1**, trinuclear complex **2** was found to exhibit reduced solubility in CH_2Cl_2/Et_2O mixture, thus facilitating its purification by removing unreacted residue of **1** through a dissolution−precipitation procedure. The trinuclear structure and purity of complex **2** were confirmed by characterizations using electrospray ionization mass spectrometry, nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis (see Supporting Information). X-ray diffraction characterization of a single crystal of **2** indicates that the three Pd centers are all chelated by the diimine nitrogens in a distorted square-planar fashion with the sterically bulky isopropyl-substituted aryl rings all nearly perpendicular to the plane of the butandiimino moiety (see Figure S.3 in Supporting Information), resembling mononuclear Pd−diimine catalysts.[9]

Mononuclear Pd−diimine chelate complexes such as **3** have been well demonstrated to readily initiate and catalyze ethylene “living” polymerization and enable the synthesis of telechelic polyethylenes end-capped with the ester moiety from the catalysts.[7,8] In the polymerization, chain initiation starts with the dissociation of the Pd−carbonyl coordination followed with subsequent ethylene insertion into the resulting $Pd-CH_2$ bond, which serves as the initiating site for chain growth.[7,8] When trinuclear complex **2** is employed for ethylene “living” polymerization, this unique polymerization chemistry ought to lead to three-arm symmetrical star polyethylenes through the three-directional simultaneous chain growth from the three initiating sites bound on the triester core, provided with the complete chain initiation and the absence of active center deactivation and chain transfer during chain growth (Scheme 1).

Ethylene polymerization with **2** was carried out in chlorobenzene for 5 h at an ethylene pressure of 400 psi and 5 °C, a typical condition for ethylene “living” polymerization with cationic Pd−diimine catalysts.[7,8] During the polymerization, prescribed amounts of polymerization solution were sampled every 1 h and quenched with Et_3SiH to obtain the as-produced star polymers. For the purpose of comparison, a control polymerization was also carried out using the mononuclear chelate catalyst **3** at the same condition, which led to well-demonstrated monofunctional “living” growth of narrow-distributed polymers of linear topology.[7]

^{1}H NMR analysis confirms the presence of the triester core in as-produced star polymers on the basis of the resonances at 2.30 and 4.02 ppm attributable respectively to methylene protons of the $-\mathrm{C}H_2\mathrm{C(O)OC}H_2-$ groups at the core.[10] A portion of each as-produced polymer was cleaved at the core

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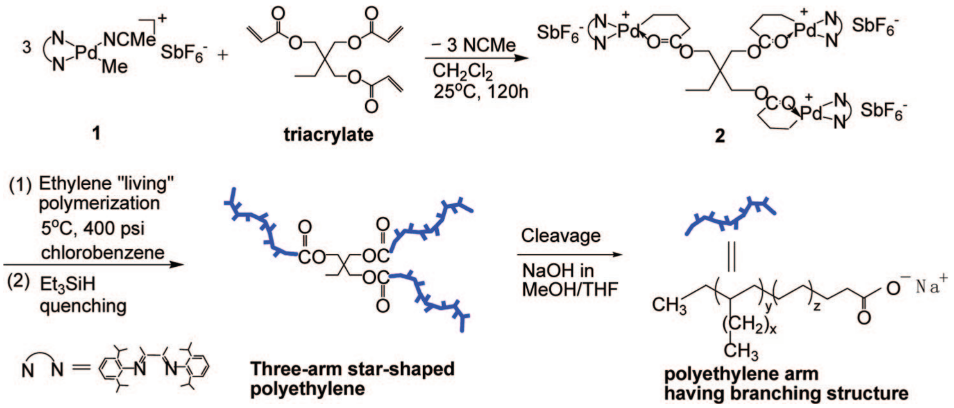
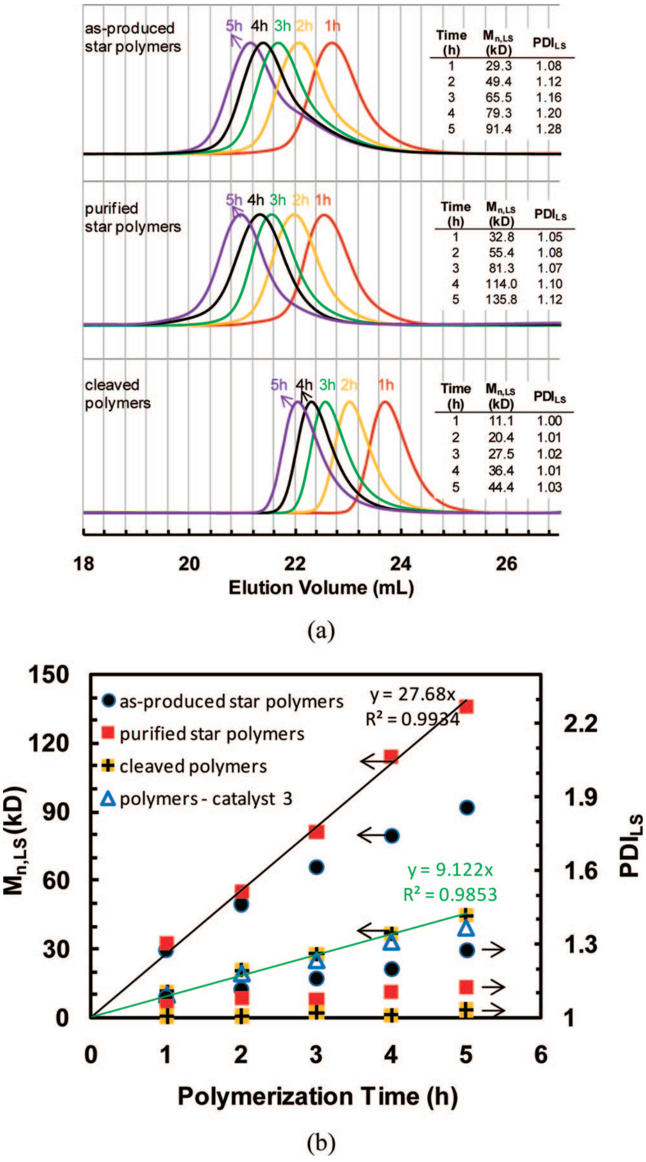
Scheme 1. Synthesis of Trinuclear Pd−Diimine Complex (2) and Three-Arm Star Polyethylenes



by alkaline hydrolysis of the ester groups to obtain the corresponding cleaved polymer, which represents the arms of the as-produced star polymer. From ^{1}H NMR spectra, the arms contain branching structures with a branching density of ca. 85 branches per 1000 carbons, resulting from chain walking of each Pd metal center during "living" polymerization.[7,8] However, these branches should be primarily short ones and the arms should have a linear topology given the polymerization condition, i.e., high ethylene pressure (400 psi) and low temperature (5 °C).[6h] The as-produced star polymers and their cleaved polymers were characterized using triple-detection gel permeation chromatography (GPC) equipped with an online refractive index (RI), three-angle light scattering (LS), and viscosity detector array. Figure 1a shows the GPC elution curves obtained from the RI detector, and Figure 1b plots the dependencies of number-average molecular weight ($M_{\mathrm{n,LS}}$) and polydispersity index ($\mathrm{PDI_{LS}}$), which are absolute values determined with the LS detector, on polymerization time.



(a)

(b)

Figure 1. (a) GPC elution traces (from RI detector) of as-produced, purified, and cleaved polymers obtained by ethylene polymerization with trinuclear catalyst **2** at different polymerization times. (b) Plot of $M_{\mathrm{n,LS}}$ and $\mathrm{PDI_{LS}}$ determined with LS detector vs polymerization time.

With the increase of polymerization time, the $M_{\mathrm{n,LS}}$ values of the as-produced polymers show a nearly linear increase within the first 2 h of polymerization and then the increase levels off afterward (Figure 1b). Their $\mathrm{PDI_{LS}}$ values increase significantly from 1.08 at 1 h to 1.28 at 5 h, with an increasingly pronounced low-molecular-weight shoulder found in the GPC elution curves (Figure 1a). The cleaved polymers, however, are all narrow distributed ($\mathrm{PDI_{LS}}$: 1.00−1.03) with a linear increase of $M_{\mathrm{n,LS}}$ with polymerization time even though increasingly observable low-molecular-weight tailing is found in their GPC elution curves with a marginal increase in $\mathrm{PDI_{LS}}$. The cleaved polymers have very similar $M_{\mathrm{n,LS}}$ and $\mathrm{PDI_{LS}}$ values compared to the corresponding control polymers synthesized with mononuclear catalyst **3** at the same polymerization time (Figure 1b), given the identical metal center structures in both **2** and **3**. The average arm number, calculated from the ratio of $(M_{\mathrm{n,LS}})_{\text{as-produced}}/(M_{\mathrm{n,LS}})_{\text{cleaved}}$, decreases from 2.7 at 1 h to 2.0 at 5 h. This deviates increasingly from the theoretical number of 3 for three-arm symmetrical star polymers with the increase of polymerization time. These GPC results suggest the trifunctional "living" polymerization behavior in the beginning of the polymerization and the presence of undesired active site deactivation and/or chain transfer, which become progressively severe with the increase of polymerization time. Such side reactions yielding low-molecular-weight polymer tails have been observed in "living" polymerization with mononuclear catalysts.[8] Herein, they terminated the growth of one or more arms in some star polymers during polymerization, yielded the undesired low-molecular-weight polymer shoulder portions shown in the GPC elution traces, and led to average arm numbers lower than expected.

Successful purification of the as-produced star polymers was achieved by fractional precipitation to obtain purified star

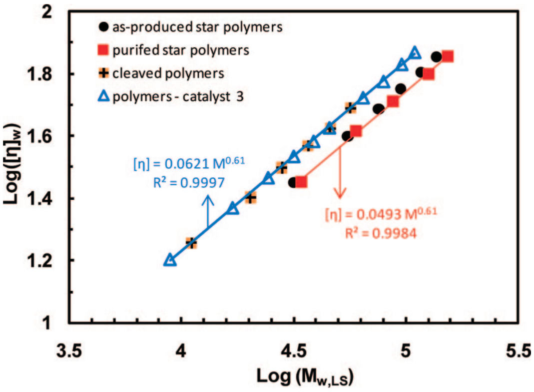


Figure 2. Mark−Houwink plot of the polymers synthesized with catalysts **2** and **3**.

polymers of narrower distribution with removed/reduced low-molecular-weight shoulder fractions. In this fractionation procedure, methanol was added slowly to a dilute solution of an as-produced star polymer (with a concentration about 3 mg/mL) in tetrahydrofuran (THF) under stirring. When the solution appeared cloudy, several more drops of methanol were added and stirring was stopped. The mixture was then left undisturbed for 2 or 3 days, and the polymer precipitate was collected and washed with methanol. After drying, the precipitate was characterized with GPC to monitor the relative intensity of low-molecular-weight shoulder. If still containing significant low-molecular-weight shoulder, the precipitate was then subject to further fractional precipitation until shoulder fractions were negligible. Because of the close proximity in molecular weight between the star polymers and the low-molecular-weight shoulder fractions, their complete separation is thus very difficult, and the yield of purified star polymers obtained herein with this fractionation method is generally low, within 10−50%. On the basis of GPC measurements, the supernatant polymer solutions resulted after the fractionation still possess a significant quantity of unseparated star polymers, whose intensity relative to the low-molecular-weight shoulder is, however, lower compared to the corresponding as-produced polymer (see Figure S.5 in Supporting Information). The GPC results of the purified star polymers are also shown in Figure 1. They possess a linear increase of $M_{n,LS}$ with polymerization time along with reduced PDI_{LS} values in the range of 1.05−1.12. Their average arm numbers, calculated from the ratio of $(M_{n,LS})_{purified}/(M_{n,LS})_{cleaved}$, are all about 3, indicating they are indeed three-arm star polymers with narrow arm length distribution.

Intrinsic viscosity data ($[\eta]$) of the polymers in THF at 33 °C were measured using the viscosity detector of the triple-detection GPC and were correlated to polymer molecular weight (Figure 2). The intrinsic viscosity of the narrow-distributed polymers of linear topology (including the cleaved polymer arms and the control polymers synthesized with **3**) follows $[\eta] = 0.0621M^{0.61}$ (mL/g) and that of the narrow-distributed purified star polymers follows $[\eta] = 0.0493M^{0.61}$ (mL/g) (Figure 2), demonstrating more compact chain conformation of the star polymers. The contraction factor (g'), defined as the ratio of intrinsic viscosity of star polymer to that of linear polymer of equal molecular weight, was determined to be about 0.81 for all five purified star polymers of different arm lengths in THF as a good solvent.[11] This is in good agreement with the values (0.82−0.84) found with several other three-arm star polymers in good solvent[1] and the predicated value of 0.83 for three-arm star polymers in good solvent following a semiempirical correlation by Douglas and Freed.[12] These intrinsic viscosity data thus provide further evidence of the symmetrical three-arm star topology of the purified star polymers. Compared to the purified star polymers of equal weight-average molecular weight ($M_{w,LS}$), the as-produced star polymers show slightly higher intrinsic viscosity due to the presence of undesired low-molecular-weight polymer portions without symmetrical three-arm star topology resulting from side reactions.

In conclusion, we have demonstrated the synthesis of a novel trinuclear Pd−diimine complex (**2**) and its enabled ethylene trifunctional "living" polymerization for "core-first" synthesis of star polyethylenes. Well-defined narrow-distributed three-arm star polyethylenes of controllable arm lengths have been obtained by purifying the as-produced polymers. The arms of these star polymers contain a backbone of linear topology with short branching structures.

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Supporting Information Available: Experimental details, including catalyst synthesis and characterization, detailed polymerization procedure and data, and triple-detection GPC characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) See Figure S.4 in Supporting Informationfor typical polymer NMR spectra.

(11) See Table S.1 in Supporting Information.

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