Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Synthesis of Low Dispersity Star-like Polyethylene: a Combination of Click Chemistry and Sol-gel Process

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Low dispersity star-like polyethylene with a "silica" core was synthesized via a simple yet efficient sol-gel process of trimethoxysilane-terminated polyethylene, which was prepared using radical-mediated thiol-ene click chemistry between low molecular weight vinyl-terminated polyethylene and (3-mercaptopropyl)trimethoxysilane.

Star polymers, the simplest complex architectures with several arms emanating from a central core, have drawn much attention due to their unique structures and properties. By utilizing living polymerization or click chemistry, star polymer can be synthesized via three general approaches: "core first", "arm first" and "coupling onto".[1-3] Though couples of fine contributions on star polyolefin have been reported[4], synthesis of star polyolefin actually lags behind. Ye et al. reported several sophisticated procedures, including "core first"[5-7] and "arm first"[8, 9] approaches, to prepare star polyethylene using living ethylene polymerization, in which specially designed Pd-diimine catalysts were employed. Alternatively, following a typical "coupling onto" approach, we synthesized well-defined 3-arm star isotactic polypropylene (iPP) by clicking azide-terminated iPP onto a tri-alkyne-functionalized compound.[10] Though the click feature of Cu-catalyzed azide alkyne cycloaddition secured the successful preparation of targeted star iPP, tedious multi-step syntheses involved in such a procedure make it labor-consuming and time-costing to prepare star iPP in a relatively large amount.

Likewise, three methods have been developed for the preparation of polymer/silica nanocomposites[11]: blending, sol-gel process (similar to "arm first" method), and surface-initiated

polymerization (similar to "core first" method); therefore, in a sense, nano silica in polymer nanocomposites share common feature with "cores" in star polymer. The past two decades witness dramatic growth of academic interest for sol−gel technology, which has a profound impact on a number of chemical domains, addressing disparate applications in advanced functional silica-based materials (including polymer/silica nanocomposites).[12] Star polystyrene (PS) with low dispersity $(Đ)$ via controlled sol-gel process of phenyltrimethoxyeilyl-terminated PS derived from living polymeric carbanions has been reported earlier, which, however, only draw limited attention[13]; since, firstly, more convenient ways to prepare star PS, via either living anionic polymerization[1] or controlled radical polymerization[2], are available, and, secondly, the efficiency of sol-gel chemistry in such report is relatively low for only four arms were formed in final products.

Chain end functionalized polyethylene (Cef-PE) is of great importance in constructing complex macromolecular architectures and preparation of nanocomposites.[14-19] Starting from Fe(II) diimine complex produced v-PE, we have been dedicated to synthesizing and utilizing Cef-PE.[20] Trimethoxysilane-terminated polyethylene (TMS-PE) was previously prepared via thiol-ene coupling reaction between vinyl-terminated polyethylene (v-PE) and (3-mercaptopropyl)trimethoxysilane. The click feature of thiol-ene chemistry guarantees efficient and simple preparation of TMS-PE.

Industrially, sol-gel process of grafted akloxysilane groups, usually catalyzed by organotin derivatives, is used to produce cross-linked polyolefins.[21] Recently, combining thiol-ene click

chemistry and subsequent sol-gel polymerization, robust aerogel was prepared via facile, low-cost preparation procedures.[22] Herein, we report our recent progress on low dispersity star-like PE (sPE) with a "silica" core via sol-gel process of TMS-PE. In the presence of (excessive) water, dibutyltin maleate (DBTM) catalyzed TMS-PE to "sol-gel" into sPE at elevated temperature in toluene solution, which lasted less than 1 day (Scheme 1).

Fistrly, TMS-PE1 (number average molecular weight (M_n)=644 g/mol, Đ=1.23) was prepared with v-PE1 (vinyl group selectivity>91%; 630 g/mol, estimated by ^{1}H NMR, for calculation procedure, see SI) as precursor according to our previous report.[20] Subsequently, TMS-PE1 underwent aforementioned sol-gel process to give sPE (labeled as sPE1). Sol-gel process includes two separated steps: hydrolysis of silica precursors (often alkoxysilanes) and subsequent condensation of resulted silanol. Figure 1 exhibits the proton NMR spectrums of TMS-PE1 and sPE1. Clearly, former terminal trimethoxysilane group in TMS-PE1 was hydrolyzed completely since the resonances at 3.5 ppm corresponding to Si-O-CH_3 vanished after the sol-gel process. Minor resonance peak at 0.20 ppm is identified to be the absorption of SiCH_3 derived from the chemical impurity of starting material. In addition, chemical shifts of hydrogen on methylene adjacent to the "silica" core systematically moved to downfield due to the electron-withdrawing character of silicon-oxygen framework.
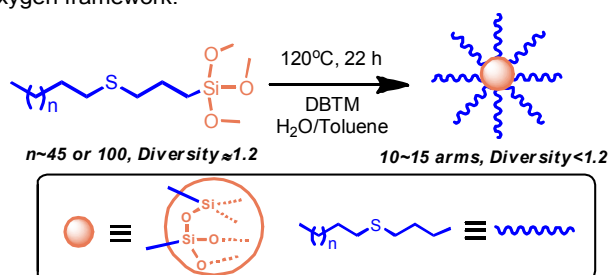
**Scheme 1** Synthesis of low dispersity sPE with a "silica" core via sol-gel process of TMS-PE
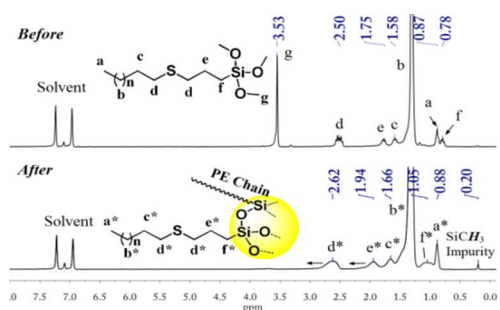
Figure 1 ^{1}H NMR spectrums (1,2-Dichlorobenzene-d4) of TMS-PE1 (upper) and sPE1 (below)

To determine the extent of condensation, solid Cross-Polarization Magic Angle Spinning (CP-MAS) ^{29}Si NMR of sPE1 was carried out. As depicted in Figure 2, absorption peaks at around -58.9/-55.4 ppm and -65.6 ppm in ^{29}Si NMR of sPE correspond to monohydroxy-substituted silica (T_2) and nonhydroxy-substituted silica (T_3), respectively.[23] The T_1

[C(SiO)(OH)2] absorption peak at around -50 ppm was almost undetected, revealing the high conversion of the condensation reaction of silanol groups and the formation of "silica" cores. In contrast, only T_1 and T_2 resonances were found in the former report on star PS via sol-gel process; the formation of T_3 was claimed to be difficult.[13] Therefore, higher arm number of sPE1 is expectable since higher extent of condensation is clearly evidenced.

sPE1, which can be viewed as a specific type of organic-inorganic hybrid materials, is still readily soluble in common hydrocarbon solvents at elevated temperature and thus amenable for high-temperature Gel Permeation Chromatography (GPC) characterization. GPC analysis provides direct proof for the successful synthesis of low dispersity sPE. The absolute weight average molecular weight (M_w) of sPE1, which was determined by multiple angle laser light scattering (MALLS) detector, reached to 13,853 g/mol while the dispersity value remained as low as 1.17. With the calculated molecular weight (MW) of v-PE1 and TMS-PE1 to be 630 g/mol and 830 g/mol, respectively, the estimated arm number of sPE1 is around 14. From the GPC curve (refractive index (RI) detector) of sPE1 (Figure 3), a minor peak at longer retention time (M_n=850 g/mol, Đ=1.11) was observed. The low dispersity feature of sPE1 makes it easy to separate the main peak from the impurity.

To identify the repeatability of such procedures, a duplicated experiment was conducted to prepare sPE (labeled as sPE1a) with TMS-PE1 as precursor. NMR analyses give similar results except that minor resonance at 3.55 ppm corresponding to Si-O-CH_3 in proton NMR and weak T_1 resonance at -49.9 ppm in ^{29}Si NMR were detected (see SI). Thus, the extents of hydrolysis and condensation reactions in preparing sPE1a were a little lower than in preparing sPE1. Nonetheless, the absolute M_w of sPE1a still shifted to beyond 11,400 g/mol (about 12 arms) while Đ remaining as low as 1.13 (for GPC traces, see SI). Therefore, the repeatability is believed to be quite good.
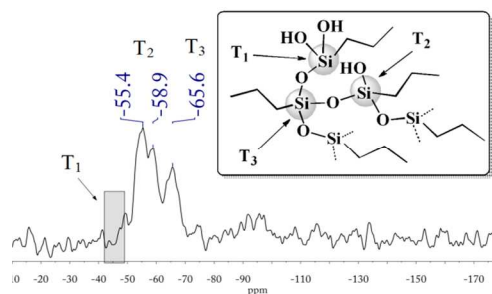
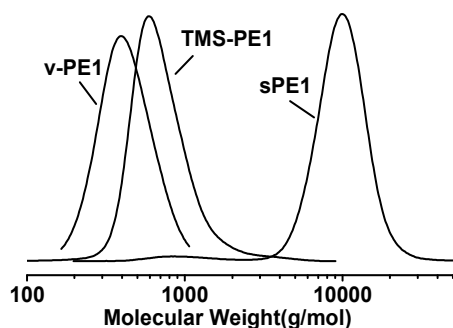**Figure 2.** CP-MAS solid ^{29}Si NMR spectrums of sPE1

Figure 3. GPC curves (RI detector) of v-PE1, TMS-PE1 and sPE1

Likewise, sPE with longer arm length (labeled as sPE2) was also successfully synthesized with v-PE2 (M_n=1,151 g/mol, Đ=1.24; vinyl group selectivity>87%; 1,400 g/mol, estimated by ^{1}H NMR; for calculation procedure, see SI). TMS-PE2 resulted from thiol-ene addition between v-PE2 and (3-mercaptopropyl)trimethoxysilane was unambiguously by ^{1}H and ^{13}C NMR (See SI). Subsequently, TMS-PE2 underwent similar sol-gel process to give sPE2. In proton NMR of sPE2, the resonances at 3.5 ppm became almost unseen, which evidences the complete hydrolysis of terminal trimethoxysilane groups. Solid CP-MAS ^{29}Si NMR of sPE2 (see SI), which shows little difference from that of sPE1, verifies that the silanol groups resulted from hydrolysis reaction of TMS-PE2 condensed into "silica" core at high conversion. The absolute M_w of sPE2 determined by MALLS is 17,670 g/mol and Đ is 1.16. The calculated arm number of sPE2 (around 10) is close to those of sPE1 and sPE1a even though the sol-gel process was conducted at a lower concentration (nearly half of TMS-PE1).
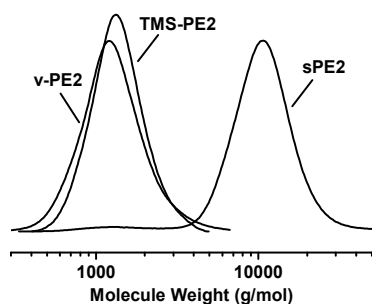

Figure 4. GPC curves (RI detector) of v-PE2, TMS-PE2 and sPE2

The intrinsic viscosity values of sPE are much lower than that of linear polyethylene[24](LPE, M_n=12,797 g/mol, Đ=1.85) at the same MW and show weak dependence on MW, which indicates low Mark-Houwink exponent (0-0.08) and highly compact architecture of sPE.[5, 6, 8] In contrast, the Mark-Houwink exponent of LPE is 0.67 (Table 1), which is a typical value for linear polymer in good solvent. Since MW of sPE roughly equals arm length multiplies arm number, longer arm length means lower

arm number (for LPE, arm number=1) and less compact architecture at a given MW. It explains that the intrinsic viscosity values at the same MW list in the following sequence: LPE>sPE2>sPE1(sPE1a) (Figure 5). In Ye's previous reports, the weight-average intrinsic viscosity ($[\eta]_w$) of star polyethylenes synthesized from the "arm-first" strategy is only about 1.15−1.5 times that of their constituting polyethylene arms despite the high MW of star polyethylenes[8, 9], whereas the star polyethylenes synthesized from the "core-first" strategy have their $[\eta]_w$ data about twice the value of the constituting arms[6]. However, the $[\eta]_w$ of sPEs is found to be about 2-3 times that of TMS-PEs (Table 1). Such difference between our finding and Ye's results may be due to the different core sizes of star polyethylenes prepared via similar but different "arm-first" approaches and the different arm length of constituting polyethylene arms.
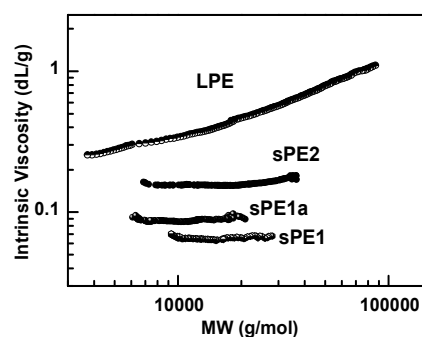

Figure 5. Polymer intrinsic viscosity as a function of MW from tri-detector GPC analysis in TCB at 150[o]C (MW determined by light scattering detector)

Star polymer represent model branched systems, in which the presence of branching points and restricted chains often cause crystalline imperfection, resulting in decreases in melting temperatures (T_m) and enthalpy values. Research on fusion of polyethylene and higher alkanes has shown that both MW and degree of branching have significant impacts on T_m.[25] Differential Scanning Calorimetry (DSC) results show that T_m of sPE1 and sPE1a are 20[o]C higher than that of v-PE1 due to increases in MW, but still much lower than that for linear PE with identical MW (over 130[o]C when MW>10,000 g/mol) due to their structural irregularity. T_m of sPE2 is close to v-PE2 since the effect of branched structures on lowering T_m may well compromise the effect of increase in MW on enhancing it. However, melting enthalpy (ΔH_m) of sPEs are systematically lowered compared to their parent v-PEs, which is a typical crystallization feature of star-branched polymer (Table 1).

Table 1. GPC, TGA, and DSC characterizations of v-PEs, TMS-PEs, sPEs and LPE
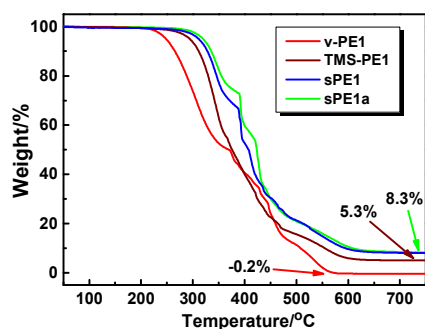
Figure 6. TGA curves of v-PE, TMS-PE and sPE in air (10°C/min)

Thermogravimetric analysis (TGA) (from 50 to 750°C at 10°C/min in air) show higher thermal stabilities of TMS-PE and sPE compared to their counterpart v-PE, due to the introduction of silicon-oxygen and thioether structure (Figure 6). Moreover, the residual weight of TMS-PE are close to their calculated values (7% and 4% for TMS-PE1 and TMS-PE2, respectively, assuming Si atom to form SiO_2 totally at 750°C[26]). Reasonable increases in residual weight of sPEs are observed since terminal TMS groups "condensed" into "silica" cores during the sol-gel process. Thus, TGA results reconfirm the successful preparation of sPE with TMS-PE as starting materials.
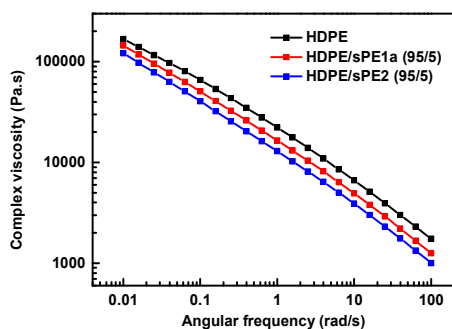

Figure 7. Complex viscosity of HDPE and sPE/HDPE blends

Starlike and hyperbranched polymers share common features both in highly branched chain structures and in many characteristic properties, such as crystallinity, crystalline melting temperature, solution viscosities and melt viscosities. Ye et al.[27] demonstrated that hyperbranched polyethylene (HBPE) can act as polymer processing aid in a metallocene linear-low-density polyethylene matrix due to its tendency to migrate to the surface and the subsequent formation a HBPE rich lubricating layer whereas the low-frequency (0.1 rad/s) viscosity of polymer blends was slightly reduced by HBPE. Figure 7 shows that sPE1a and sPE2 both caused a slight reduction in complex viscosity of blends of sPE and a commercial high-density polyethylene (HDPE) (DGDB-2480) in the frequency range from 0.01 to 100 rad/s at a concentration of 5 wt% compared to pure HDPE. The minor difference in the bulk complex viscosity of

HDPE/sPE1a and HDPE/sPE2 may relate to the different capabilities of two sPE additives in preventing chain entanglements, which is essential for effective polymer-based polymer processing aids. More work on rheological properties of such blends and exploration for the promising application of sPE will be done in the near future.

Conclusions

In conclusion, we present a simple yet efficient approach to prepare sPE with low dispersity via robust thoil-ene click chemistry and subsequent sol-gel chemistry. By doing so, the utility of TMS-PE is high-lightened, which may find appealing applications in nanoparticle surface modification, constructing complex architecture, and preparation of nanocomposites. Using such a "arm-first" method to prepare star polymer, the arm length of sPE is predetermined, yet the precise control of arm number, which may be achieved by adjusting experimental conditions of sol-gel process, still needs to be uncovered. Further study is going intensively in our lab.

Notes and references

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Table 1. GPC, TGA, and DSC characterizations of v-PEs, TMS-PEs, sPEs and LPE

Sample	$M_n{}^a$ (g/mol)	$Đ^a$	f^b	$α^c$	$[η]_w{}^d$ (dL/g)	Residual weight[e] (%)	T_m (°C)	$ΔH_m$ (J/g)
v-PE1	390	1.17	\	\	\	-0.2	74.4	203.3
TMS-PE1	644	1.23	\	\	0.032	5.3	79.8	160.3
sPE1	11,806	1.17	14	≈0	0.066	8.3	94.0	118.2
sPE1a	10,131	1.13	12	0.02	0.088	8.5	94.8	123.1
v-PE2	1,151	1.24	\	\	\	-0.2	116.2/104.4	232.3
TMS-PE2	1,274	1.15	\	\	0.051	3.6	113.8	170.7
sPE2	15,293	1.16	10	0.08	0.161	5.1	113.2	131.2
LPE	12,797	1.85	\	0.67	0.478	\	132.3	222.9

[a] The M_n and $Đ$ values for sPEs and LPE were determined with tri-detector. The M_n and $Đ$ values for v-PEs and TMS-PEs were determined with RI detector. [b] The number-average arm number (f) is calculated as (M_n of the star polymer)/(M_n of arm). The M_n of the arm (830 g/mol for TMS-PE1, 1,600 g/mol for TMS-PE2) is calculated from ^{1}H NMR of v-PEs (630 g/mol for v-PE1, 1,400 g/mol for v-PE2). [c] α is the Mark-Houwink exponent of sPEs and LPE, which calculated from the slope of Mark-Houwink plot of sPEs and LPE. [d] Weight-average intrinsic viscosity ($[η]_w$) of sPEs and LPE was determined with the viscosity detector. [e] Residual weight values at 750°C in TGA analyses.

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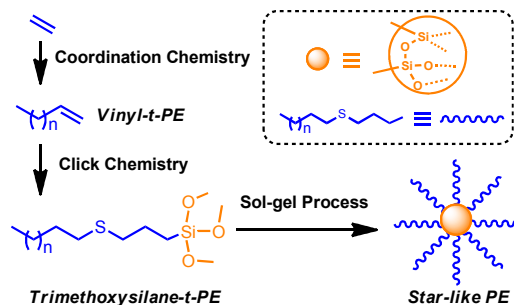
Low dispersity star-like polyethylene was synthesized via a facile sol-gel process of trimethoxysilane-terminated polyethylene derived from thiol-ene click chemistry.