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Synthesis and Characteristics of Succinic Anhydride- and Disodium Succinate-Terminated Low Molecular Weight Polyethylenes

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The addition of functionality to a polyolefin that is otherwise nonpolar may widen the field to which polyolefinic materials may be applied. The added functional groups should influence the orientation of the polymer chains and thus are expected to provide ways of altering polymers to modify dyeability, adhesion, melt and solution rheology, etc.

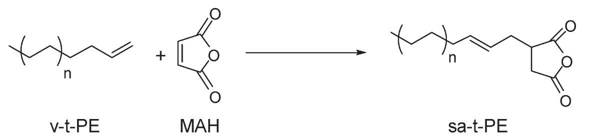
Therefore, a number of methods have been investigated for producing functionalized polyolefins.[1−5] One promising method is the functionalization of polyolefins having a high degree of vinyl unsaturation at one of the two polymer chain ends (vinyl-terminated polyolefins) made with single-site olefin polymerization catalysts, resulting in the formation of well-defined terminally functionalized polyolefins. These well-defined materials can act as reactive polyolefinic materials and are useful intermediates for graft and block copolymers containing polyolefin and polar polymer segments.[5] The selective synthesis of vinyl-terminated polyolefins, however, is normally difficult.[6]

In the course of ligand-oriented catalyst design research, we have discovered that the bis(phenoxyimine) and bis(phenoxyketimine) group 4 transition metal complexes (a.k.a. FI catalysts) can be used to undertake controlled olefin polymerization with high efficiency.[7] FI catalysts combined with appropriate activators can achieve precise control over chain transfers, leading to the production of unique polyolefinic materials, including selective vinyl- or Al-terminated polyethylenes (PEs), telechelic syndiotactic polypropylenes, and a wide variety of monodisperse (co)polymers and block copolymers derived from ethylene, propylene, and higher α-olefins.[7,8] We herein report on the synthesis and properties of succinic anhydride-terminated low molecular weight PE from a vinyl-terminated PE formed with an FI catalyst. Additionally, we present the unique self-assembled morphology of the corresponding disodium succinate-terminated PE in water dispersion.

The vinyl-terminated low molecular weight PE (v-t-PE; M_w 1400, M_w/M_n 2.0, vinyl selectivity 95%) employed in this study was prepared using bis[*N*-(3-cumyl-5-chlorosalicylidene)methylaminato]$ZrCl_2$ with modified methylaluminoxane. Since such v-t-PEs are rare materials, little is known about their transformation by chain-end functionalization to form end-functionalized PEs.[5,8a] First, therefore, we aimed at developing a method for converting this v-t-PE to the corresponding succinic anhydride-terminated PE (sa-t-PE) using the Alder−ene reaction, which is generally promoted by a Lewis acid (Scheme 1).[9]

The treatment of the v-t-PE with maleic anhydride (MAH) using $SnCl_2 \cdot 2H_2O$ or $RuCl_3 \cdot xH_2O$ as a catalyst resulted in the predominant formation of the isomerized products of the v-t-PE. Additionally, the reaction of the v-t-PE and MAH in the absence of a Lewis acid afforded the corresponding sa-t-PE with moderate selectivity (51%) together with the formation of two v-t-PE chains coupled with one MAH molecule through a radical reaction. We therefore conducted the reaction in the presence of a radical quencher [i.e., hydroquinone, *p*-cresol, or 2,6-di-*tert*-butyl-4-methylphenol (DTBMP)] without using a catalyst and found that the addition of DTBMP (6.0 equiv) is highly effective for achieving a high selectivity reaction in order to yield sa-t-PE (selectivity 97%) (Table 1, entry 7).

Scheme 1. Preparation of sa-t-PE by the Reaction of v-t-PE with MAH



With the above results in hand, the successful synthesis of sa-t-PE was achieved by the reaction of the v-t-PE and MAH in the presence of DTBMP (6.0 equiv) at 195 °C for 16 h. The product [MAH content 102 mol % (^{1}H NMR), M_w 1700, M_w/M_n 1.7][10] exhibited characteristic absorptions of the succinic anhydride moiety in its FT-IR spectrum; 1864 cm^{-1} (asymmetric stretching of C=O) and 920 cm^{-1} (ring stretching vibration of saturated five membered-ring anhydride), indicative of the production of PE with succinic anhydride functionality. The ^{1}H and ^{13}C NMR analyses showed the formation of sa-t-PE (v-t-PE conversion 97%, sa-t-PE selectivity 95%) (see Supporting Information). The sa-t-PE displayed a T_m of 117 °C (melting enthalpy ΔH 217 J/g), which is about the same as that of the parent v-t-PE (T_m 116 °C, melting enthalpy ΔH 226 J/g), suggesting that the sa-t-PE maintains the crystallinity of the parent v-t-PE, as expected.

The well-defined sa-t-PE described above is a new material that exhibits unique characteristics due to the presence of the chain-end succinic anhydride group. The melt viscosity of the sa-t-PE (86 mPa·s, which corresponds to the value of PE with a M_w of ca. 2800) is ∼4 times higher than that of the parent v-t-PE (22 mPa·s). The interactions between sa-t-PE molecules through the chain-end succinic anhydride moieties are probably responsible for this observation. We infer that the chain-end functionality plays a crucial role in achieving an effective interaction between sa-t-PEs. Interestingly, the sa-t-PE displays enhanced thermal stability compared to the v-t-PE under both nitrogen and air (see Supporting Information) though the origin of this unusual behavior is unclear at this time. The above results provide a clear demonstration that the introduction of only one succinic anhydride moiety at one of the two PE chain ends significantly affects material properties. The sa-t-PE possesses a high potential as a dispersant of hydrophilic materials (e.g., pigment) and as a modifier for polar polymers, in particular, engineering plastics.

We were interested in the behavior of the corresponding disodium succinate-terminated PE (Na_2-s-t-PE) in water, since this salt contains both hydrophobic (PE) and hydrophilic [$Na_2(COO)_2R$] parts in the same molecule. We thus prepared a water dispersion of Na_2-s-t-PE (1 wt %) according to the procedures shown in Scheme 2. The formation of the Na_2-s-t-PE was supported by ^{1}H/^{13}C NMR and FT-IR analyses (see Supporting Information).

No visible particles are present in the Na_2-s-t-PE water dispersion, thus highlighting the unique features of the Na_2-s-t-PE. Figure 1 displays particle size distribution (a) and a

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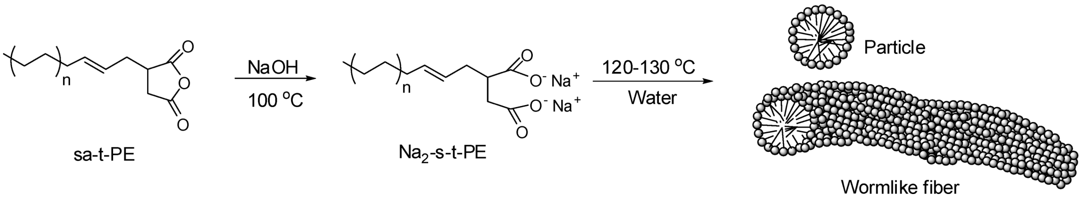
Table 1. Results for the Reaction of v-t-PE with MAH[a]

entry	radical quencher (equiv)[c]	v-t-PE conversion[b] (mol %)	sa-t-PE selectivity[b] (mol %)
1	none	63	51
2	hydroquinone (1.0)	35	71
3	hydroquinone (6.0)	21	48
4	*p*-cresol (1.0)	64	52
5	*p*-cresol (6.0)	60	77
6	DTBMP (1.0)	52	77
7	DTBMP (6.0)	69	97

[a] Conditions: MAH/v-t-PE = 10 (molar ratio), temperature = 195 °C, time = 8 h. [b] Determined by ^{1}H NMR. [c] Molar ratio of radical quencher/v-t-PE.

Scheme 2. Preparation of Na_2-s-t-PE and Its Self-Assembled Aggregates in Water



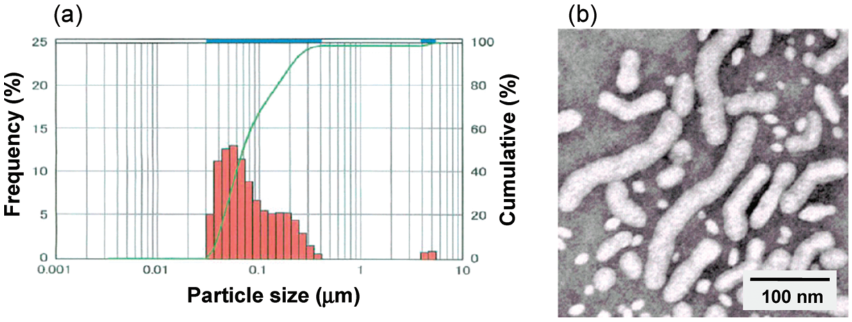


Figure 1. (a) Particle size distribution and (b) TEM image of Na_2-s-t-PE water dispersion.

transmission electron microscopy (TEM) image (b) of the Na_2-s-t-PE water dispersion, which demonstrates that the Na_2-s-t-PE forms nanosized particles (diameter 10−30 nm) and wormlike fibers (fiber diameter 20−30 nm, length 60−270 nm).

The nanosized particles and fibers are probably produced as a result of the self-assembly of the nonpolar PE chain ends as cores and also of the chain-end polar functionality [$Na_2(COO)_2R$] at the surface of the particles or fibers. While wormlike micelles composed of ionic low molecular weight surfactants are already known,[11] this is the first example of the formation of wormlike fibers containing PE segment supramolecular assembled aggregates. We are currently investigating the properties of the above-described sa-t-PE and Na_2-s-t-PE, and the results will be reported in due course.

In summary, we have succeeded in the selective synthesis of sa-t-PE by the reaction of v-t-PE with MAH in the presence of DTBMP. The resultant end-functionalized PE retains the natures of both the parent PE and of succinic anhydride, which can allow this material to act as a reactive PE or a distinctive intermediate. The sa-t-PE displayed higher melt viscosity and higher thermal stability than the parent v-t-PE, probably because of the presence of the chain-end succinic anhydride group. Additionally, the corresponding Na_2-s-t-PE forms nanosized particles and wormlike fibers as self-assemblies in water, demonstrating the unique behavior of well-defined end-functionalized polyolefins.

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Supporting Information Available: (1) General comments, (2) preparation of v-t-PE, (3) reaction of v-t-PE and MAH, (4) preparation of Na_2-s-t-PE and its water dispersion, (5) $^1H/^{13}C$ NMR spectra, (6) FT-IR spectra, and (7) TGA curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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