

## Polysiloxane graft polyethylene synthesized by a novel heterofunctional condensation approach

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### ABSTRACT

Polysiloxane/polyethylene graft copolymers can synergistically combine the distinguished properties obtained separately in polyethylene (PE) and polysiloxane and therefore attract considerable attentions from both academia and industry. Herein, we introduce a novel and efficient heterofunctional condensation approach to synthesize well-defined polydimethylsiloxane graft PE (PDMS-g-PE) under mild conditions. The chemical structures of PDMS-g-PE are characterized unambiguously, and the correlation between reaction conditions and the structural parameters of PDMS-g-PE is established. Scanning electron microscope images show that the obtained graft copolymer PDMS-g-PE can compatibilize the immiscible PE/silicone oil system.

### 1. Introduction

Polyethylene (PE) is a carbon-based crystalline thermoplastic polymer with distinctive properties and of low cost. To date, PE accounts for nearly 40% volume of plastics consumed worldwide. PE materials are used for making plastic bags, bulletproof vests, water pipes, medical materials, etc. With the aim of developing high-performance value-added polyolefin-based materials, researchers from both academia and industry are keen on seeking efficient ways to functionalize polyolefins (mostly PE and polypropylene) under mild conditions [1–3]. Polyolefin graft segmented copolymer, which is a fundamental class of functional polyolefin, has attracted considerable attention during the past few decades because graft copolymers containing crystalline polyolefin grafts promise high-performance polyolefin-based materials [4–8]. The backbone of polysiloxane (also called siloxane polymer or silicone) is made up by repeating “inorganic” siloxane bond linkage, while the substituents attached to each silicon atom are typically organic radicals. Due to the dual nature of its repeating units, i.e., the simultaneous presence of “organic” groups attached to an “inorganic” backbone, polysiloxane therefore “naturally” shows many distinguished and attractive physicochemical properties, such as high thermal stability, low surface energy, high electrical resistance and excellent biocompatibility, making it the material of choice for many special applications. When some silicon atoms in the backbone of polysiloxane are substituted by polymer chains, a polysiloxane-based

graft copolymer is formed [9,10].

Polysiloxane/PE graft copolymers can synergistically combine these disparate properties obtained separately in PE and polysiloxane and therefore show great potential in preparing high-performance polymeric materials. The last decades have witnessed great advances in the synthesis of PE- and/or polysiloxane-segmented graft copolymers. However, reports concerning the synthesis of polysiloxane/PE graft copolymers are rare. Moreover, existing approaches to synthesize polysiloxane/PE graft copolymers often suffer from distinct drawbacks, including the ill-defined structures of graft copolymers and/or tedious and labor-consuming procedures. Graft copolymers are generally prepared by one of the three synthetic approaches: “grafting-from”, “grafting-through”, and “grafting-onto” [11]. Following a typical “grafting-from” approach, Li et al. [12] synthesized PE-g-PDMS with lithiated ethylene/p-allyltoluene copolymers as the macroinitiator. However, the multistep syntheses involved in such a sophisticated procedure may restrict its potential real-world applications. The copolymerization of ethylene and  $\omega$ -vinyl polydimethylsiloxane (PDMS) macromonomer had been studied using either vanadium-based Ziegler-Natta or metallocene catalyst, thus attempting to synthesize PE-g-PDMS with PE as the main chain via a graft-through approach [13]. Unfortunately, poisoning of both catalysts was observed due to the  $\sigma$ -coordination between oxygen and early transition metal catalyst center, thus resulting in low catalytic activities and low degree of grafting density of the PDMS macromonomer. Alternatively, Villar et al. [14]

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synthesized PE-g-PDMS by successive hydrosilylation reactions between polybutadiene (PB) and  $\omega$ -silane PDMS and catalytic hydrogenation of resultant PB-g-PDMS. Fan et al. [15] also studied the hydrosilylation reactions between vinyl-terminated PE and polymethylhydrosiloxane, aiming to prepare PDMS-g-PE by a grafting-onto approach. Suffering from the low efficiency of hydrosilylation reactions (between two long chain polymers), the chemical structures of graft copolymers obtained by hydrosilylation were ill-defined.

The heterofunctional condensation (HFC) between silanol groups and other silyl-functional groups (mainly Si-OR and Si-Cl) is the fundamental reaction often exploited in the manufacturing of various silicone resins. Chemists are skilled in preparing silicone-containing block copolymers using  $\alpha,\omega$ -reactive difunctionally terminated (telechelic) silicone oligomers as starting materials [9,16]. We therefore assume that the successful implementation of HFC reactions between  $\alpha,\omega$ -disilanol siloxane oligomer and dimethoxysilane-terminated capped polymer may afford polysiloxane-based graft copolymers. The proposed approach, which can be classified as a “grafting-through” approach, may enjoy the advantage of not only high efficiency of HFC reactions but also the high availability of inexpensive starting materials. However, to the best of our knowledge, no report has been published elsewhere dealing with the synthesis of silicone-based graft copolymer taking advantage of the HFC reactions.

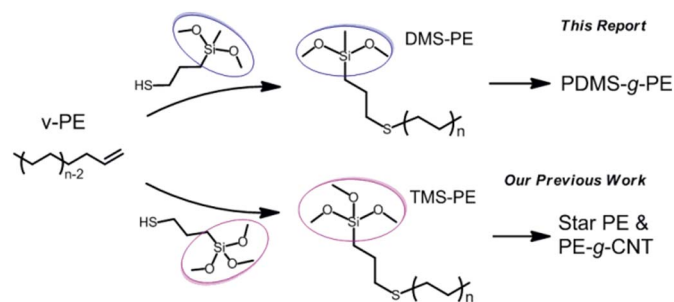
In our previous study, we developed convenient routes to synthesize chain-end functionalized PE with vinyl-terminated PE (v-PE) as starting materials. A group of chain-end functionalized PEs, including hydroxyl-, amino-, carboxyl-, sulfo-, chloro-, azide-, and trimethoxysilane-terminated PEs, have been synthesized highly efficiently and selectively via robust epoxide ring-opening or thiol-ene click chemistry [17]. In particular, we demonstrated that trimethoxysilane-terminated PE (TMS-PE), which is quite stable and can be easily stored under a routine condition, shows high activity in the presence of organotin catalyst and that the hydrolytic condensation of TMS-PE could be utilized for preparing star PE and PE-grafted carbon nanotubes (Scheme 1) [18,19]. This inspires us to test the HFC reactions between  $\alpha,\omega$ -disilanol siloxane oligomers and dimethoxysilane terminated PE (DMS-PE), since DMS-PE bearing terminal dimethoxysilane group actually can be viewed as a macromonomer and is likely to undergo HFC reactions with  $\alpha,\omega$ -disilanol siloxane oligomers.

The objective of this investigation is to synthesize PDMS-g-PE by HFC reactions between DMS-PE and  $\alpha,\omega$ -silanol terminated siloxane oligomers (Schemes 1 and 2). A special attempt was made to establish the correlation between reaction conditions and microstructures of generated graft copolymers.

## 2. Experimental section

### 2.1. Materials

Dibutyltin maleate (DBTM, 95%), 1,1'-Azobis(cyclohexanecarbonitrile) (ABCN, 98%), and silicone oil (PDMS, viscosity  $350 \pm 35$  mPa s)



**Scheme 1.** Synthesis routes and applications of DMS-PE and TMS-PE (Star PE [19]: starlike PE with a Si-O-Si network as the “core”; PE-g-CNT [18]: PE covalently grafted multiwall carbon nanotube).

from Aladdin Industrial Inc.; 3-mercaptopropylmethyldimethoxysilane (MPDMS) ( $> 95\%$ ) and disilanol-terminated dimethylsiloxane oligomer ( $M \sim 550$  g mol $^{-1}$ ) from Sigma; chlorobenzene (AR) and ethylether (AR) from Sinopharm Chemical Reagent; and high-purity nitrogen from Dalian Special Gases Co., Ltd., were used as received. Commercial low-density PE (LDPE, 1C7A) was purchased from SINOPEC Beijing Yanshan Company. 1C7A (MFR = 10 g/10 min) is a LDPE for extrusion coating produced by a 180-kta autoclave process plant without any additives. Toluene was dried over CaH $_2$  and distilled before use. v-PE was synthesized as described before [17].

### 2.2. Synthesis

#### 2.2.1. Synthesis of DMS-PE

All procedures in Section 2.2 with air-sensitive compounds were performed under inert gas atmosphere using a glovebox, syringe, or standard Schlenk techniques.

DMS-PE was prepared according to a procedure adapted from reference [19]. To a solution of v-PE (5 g, 0.79 mmol, 1 eq.) in 100 mL dry toluene, MPDMS (10 g, 7.0 eq.) and ABCN (1.5 g, 0.78 eq.) were added. The mixture was then heated to 85 °C. After stirring for 10 h, the reaction mixture was precipitated in methanol and filtered, and the product was washed with methanol and dried under vacuum at 40 °C to produce DMS-PE.

#### 2.2.2. Synthesis of PDMS-g-PE

In a typical procedure, to a solution of DMS-PE (0.3 g, 0.37 mmol, 1 eq.) in 40 mL chlorobenzene, DBTM (20 mg, 0.15 eq.), given amounts of PDMS-diol and deionized water (0.1 mL, 55 mmol, 150 eq.), if needed, were added. The mixture was then heated to 135 °C. After stirring for 30 h, the reaction mixture was precipitated in methanol and filtered. The collected white powder was further purified by centrifugation for 5 times. Ethylether was chosen as the solvent during the purification process, and the amount of solvent each time was nearly 45 mL. After purification, the final product was dried under vacuum at 40 °C to give PDMS-g-PE. The yields of isolated PDMS-g-PE are shown in Table 1.

#### 2.2.3. Preparation of LDPE/silicone oil blends

Binary LDPE/silicone oil blend was prepared via solution mixing method in chlorobenzene with 100 wt% LDPE and 5 wt% silicone oil. For the compatibilized blend, 1 wt% PDMS-g-PE was further added. The mixture was stirred vigorously at 130 °C for 1 h and subsequently cooled to ambient temperature, precipitated in methanol, filtered, washed with methanol, and dried thoroughly under vacuum. The blends were then extruded using a miniature parallel twin screw extruder (WLG10G, Xinshuo, Shanghai, 10 g capacity) and cooled to room temperature. The final extrudates of the blends were used for scanning electron microscope (SEM) tests.

### 2.3. Characterization

High-temperature  $^1\text{H}$  NMR spectra were recorded on Bruker DMX 300 instruments. The melting temperature of the polymers was measured by differential scanning calorimetry (DSC) using a TA Instrument Q2000 with a heating rate of 10 °C min $^{-1}$ . The molecular weight (MW) and dispersity ( $\mathcal{D}$ ) values of polymers were determined by gel permeation chromatography (GPC) using an Alliance PL-GPC 220 instrument equipped with a refractive index detector (890 nm), a PL-GPC 220 viscometer (four-bridge capillary viscometer), a PL-GPC 220 light scattering detector (Rayleigh scattering angles, 15° and 90°; laser wavelength, 658 nm), and three PLgel 10  $\mu\text{m}$  MIXED-B columns. The measurement was performed at 150 °C with 1,2,4-trichlorobenzene as the eluent at a flow rate of 1.0 mL/min. Narrow-molecular-weight-distribution polystyrene samples were used as standards for calibration ( $M_p$  ranging from 580 to 6,870,000 g mol $^{-1}$ ). Fourier transform

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