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Synthesis and characterization of fluorinated PEO-*b*-PDMS-*b*-fluorinated PEO by free radical addition

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Abstract

Fluorinated poly(ethylene oxide) propyl-*b*-polydimethylsiloxane-*b*-propyl fluorinated poly(ethylene oxide) (FPEO-*b*-PDMS-*b*-FPEO) was synthesized by a free radical addition of carbon–hydrogen of polyether segments of poly(ethylene oxide) propyl-*b*-polydimethylsiloxane-*b*-propyl poly(ethylene oxide) (PEO-*b*-PDMS-*b*-PEO) to hexafluoropropylene (HFP) using *tert*-butyl peroxypivalate as an initiator. In order to reduce the possibility of side reaction, the protection and deprotection *via* silylation were used for the end-hydroxyls in PEO-*b*-PDMS-*b*-PEO chain. The structure of Intermediates and FPEO-*b*-PDMS-*b*-FPEO was confirmed by means of Fourier transform infrared and ^{1}H NMR spectroscopy. The effects of amount of initiator, reaction temperature and time on free radical addition were investigated in detail.

Keywords: Fluorinated; Hexafluoropropylene; Polydimethylsiloxane; Free radical addition; Silylation

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Hydroxypolyether blocked polydimethylsiloxane, poly(ethylene oxide) propyl-*b*-polydimethylsiloxane-*b*-propyl poly(ethylene oxide) (PEO-*b*-PDMS-*b*-PEO) is an interestingly starting material for the preparation of a wide variety of segmented copolymers duo to its stability and reactivity [1]. However, oil resistance and mechanical property of siloxane-modified polymers need to be improved further. It has been proved recently that polymers containing both fluorine and siloxane had good oil resistance and mechanical properties [2–4]. A telechelic fluorinated siloxane oligomer with end-hydroxyls might be a good choice for the synthesis of polymers containing fluorine and siloxane.

Polyether segments of PEO-*b*-PDMS-*b*-PEO readily form radicals, especially at sites attached to oxygen, and the orientation of free radical addition of ether to unsaturated compounds such as hexafluoropropylene (HFP) has been established in principle [5,6]. In this letter, we report a novel fluorinated poly(ethylene oxide) propyl-*b*-polydimethylsiloxane-*b*-propyl fluorinated poly(ethylene oxide) (FPEO-*b*-PDMS-*b*-FPEO), prepared by a free radical addition of carbon–hydrogen in polyether segments of PEO-*b*-PDMS-*b*-PEO to HFP. *Tert*-butyl peroxypivalate (TBPV) was chosen as an initiator because of low decomposition energy and convenient half-life. To reduce the possibility of side reaction, the end-hydroxyls of PEO-*b*-PDMS-*b*-PEO were protected *via* silylation before free radical addition reaction.

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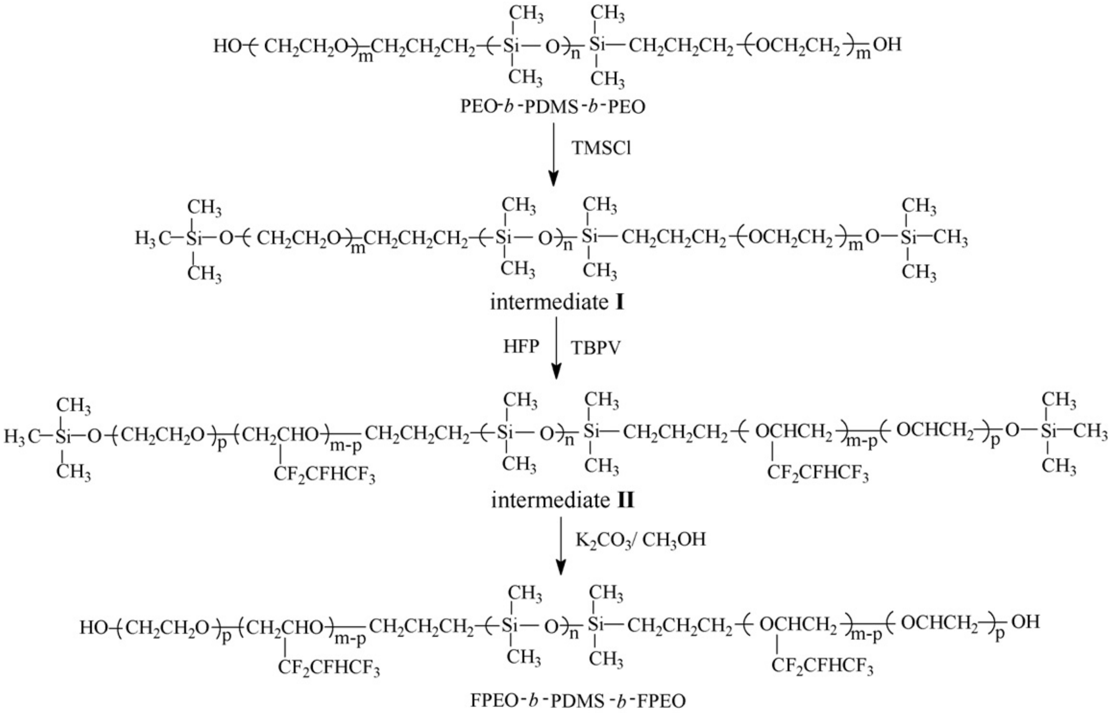

Scheme 1. Synthesis of FPEO-*b*-PDMS-*b*-FPEO.

PEO-*b*-PDMS-*b*-PEO was prepared using the method provided by Ref. [1]. FPEO-*b*-PDMS-*b*-FPEO was synthesized through the processes of silylation of end-hydroxyls, free radical addition and deprotection of protected end-hydroxyls, as shown in Scheme 1. Silylation of PEO-*b*-PDMS-*b*-PEO ($M_n = 2100$) with trimethylchlorosilane (TMSCl) in dimethyl sulfoxide was first carried out in a rockered flask. The silylated product intermediate **I** (220 g, 0.1 mol) and TBPV (1.8 mL, 0.009 mol) were then added into an autoclave (1000 mL) equipped with a stirrer, pressure gauge, bursting disc and inlet/outlet value. After introducing dried N_2 to drive the air for reducing side reaction, another reactant HFP (240 g, 1.6 mol) was added by the inlet value. Fluorination was realized at 100 °C for 9 h. After the reactor was cooled down to room temperature, fluorinated product intermediate **II** was obtained. Finally, the deprotection of the intermediate **II** was operated at 80 °C for 4 h with the deprotection reagent of K_2CO_3/CH_3OH as Ref. [7]. Synthesized product FPEO-*b*-PDMS-*b*-FPEO is a weak yellow liquid with a slight scent. GPC curves revealed there is only one mono-model distribution, showing that molecular chains of PEO-*b*-PDMS-*b*-PEO and FPEO-*b*-PDMS-*b*-FPEO are very stable in the grafting reaction under established reactive conditions. Based on the need of chain length, a series of FPEO-*b*-PDMS-*b*-FPEO with different molecular weight (M_n = 1500–7000) could be synthesized easily only through the choosing of PEO-*b*-PDMS-*b*-PEO with suitable molecular weight.

The occurrence of free radical addition, the structure of Intermediates and final product could be evidenced by Fourier transform infrared (FTIR) spectroscopy. There was new absorption originated from the vibration absorption of C–F bond except all the characteristic absorption bands of PEO-*b*-PDMS-*b*-PEO in the FTIR spectrum of FPEO-*b*-PDMS-*b*-FPEO, indicating that the expect free radical addition of C–H bonds to HFP occurred. The stronger characteristic absorption bands locating at 1191 and 1286 cm^{-1} could be attributed to stretching vibrations of C–F. Moreover, the absorption band at 684 cm^{-1} showed the deformation vibration of C–F. The protective and deprotective reactions of end-hydroxyls could also be evidenced by FTIR. Compared with the spectrum of PEO-*b*-PDMS-*b*-PEO, it could be seen apparently from the spectrum of intermediate **I** that the hydroxyl absorption at 3477 cm^{-1} disappeared, which indicated the hydroxyl groups of PEO-*b*-PDMS-*b*-PEO had been substituted completely, while the hydroxyl absorption observed again in the spectrum of FPEO-*b*-PDMS-*b*-FPEO proving to be the deprotection of intermediate **II** through the deprotective reaction.

Analysis of ^1H NMR spectra further supported chemical structure of FPEO-*b*-PDMS-*b*-FPEO. Compared with the spectrum of PEO-*b*-PDMS-*b*-PEO, two new broad peaks appeared at 4.12–3.73 ppm and 5.47–4.94 ppm in the