



Synthesis of poly(siloxane/double-decker silsesquioxane) via dehydrocarbonative condensation reaction and its functionalization



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ABSTRACT

Chlorine-containing poly(siloxane/double-decker silsesquioxane) (**P-Cl**) was prepared in high yield at ambient room temperature via dehydrocarbonative polycondensation reaction between di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**DDSQ**) and hexamethyltrisiloxane. Particular attention for this polymer was also given to its functionalization through substitution reaction, especially due to nucleophilic substitution on the side-chain of polymer at silsesquioxane units. But more important, the use of halogen exchange method with bromine anion allows the formation of more reactive, bromine-containing poly(siloxane/double-decker silsesquioxane) (**P-Br**), which enables further post-substitution modification reactions in a POSS unit. The glass transition temperatures ($T_g \sim 15^\circ\text{C}$) of both halogenated polymers were significantly higher than poly(dimethylsiloxane) (PDMS). High transparency of polymers with hydrophobic surface could be found from solvent-casting thin film.

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1. Introduction

Polysiloxanes are considered as one type of synthetic hybrid polymers, widely used as lubricant, mold release, working media in automobile, and heat transferred oil [1]. The presence of Si–O–Si repeating units in its main chain makes polysiloxanes exhibit several outstanding properties such as high thermal stability, elasticity, and optical transparency [2]. Meanwhile, polyhedral oligomeric silsesquioxanes (POSS) are well-defined nano-sized organic-inorganic materials [3], which are commonly used as a reinforcement enhancer by blending them with polymers [4–6]. Therefore, silsesquioxane-based polymers are much interesting as they are expected to provide several useful properties, such as high thermal stability, enhanced toughness, and low dielectric constant [7–9]. However, as typical silsesquioxanes cages are highly symmetric (e.g. octameric T_8 cage), simply blending them with polymers usually leads to aggregation and poor dispersion of silsesquioxanes molecules in the material [4–6]. One way to overcome these problems is to covalently attach silsesquioxanes molecules to the backbone of polymeric nanocomposite [6,10–13].

Several chemical reactions including hydrosilylation [14–17], Heck [10,11,18], cross-metathesis [14,19], click [6,20], dehydrogenation [21], polycondensation, and ring-opening reaction [22] have been successfully employed to covalently linked POSS molecules into the polymer backbone, resulting in the composite materials with significantly increasing glass transition temperature [7,8,21–24]. Despite several application of dehydrocarbonative condensation in syntheses of siloxane polymers and copolymers [25–29], none has found for the syntheses of covalently linked POSS polymers in main chain. More importantly, the polymerization could be found at ambient temperature due to higher solubility of our starting monomer in organic solvents.

Double-decker silsesquioxane is one of POSS structures, considered to be a bifunctional monomer and applicable to prepare silsesquioxane-based polymer [15,16,19,20]. We have recently reported the synthesis of a novel double-decker silsesquioxane; named di[(3-chloropropyl)(isopropoxy)silyl]-bridged double-decker octaphenylsilsesquioxane (**DDSQ**) that has two different functional groups; (*i*-propoxy)silyl and chloropropyl groups [30]. In this report, we actually show that (*i*-propoxy)silyloxy groups can further react with hydrosilane via Piers–Rubinsztajn reaction using tris(pentafluorophenyl)borane; $\text{B}(\text{C}_6\text{F}_5)_3$ as a catalyst to form Si–O–Si linkages, leading to the formation of chlorine-containing

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poly(siloxane/double-decker silsesquioxane) (**P-Cl**). The Piers–Rubinsztajn reaction between hydrosilane and alkoxy silane is notably rapid and highly efficient [31,32,39]. Moreover, **P-Cl** bearing reactively chloropropyl groups on the side chains of polymer can be further functionalized through substitution reaction to obtain bromine-containing poly(siloxane/double-decker silsesquioxane) (**P-Br**). Our recent reports also suggest that a wide range of functional groups on silsesquioxane materials can be simply done through substitution reaction [33–38]. Herein, we introduce, for the first time, the method for modification on both main and side chains of poly(siloxane/double-decker silsesquioxane).

2. Experimental section

2.1. Materials and methods

If not stated, all chemicals were commercially available and used without additional purification. Hexamethyltrisiloxane, tris(pentafluorophenyl)borane, tetrabutylammonium bromide (TBAB), 1-bromopropane, anhydrous toluene were purchased from Sigma Aldrich, while **DDSQ** compound was freshly prepared according to our previous report [30]. Fourier transform nuclear magnetic resonance spectra were obtained using a Bruker-AscendTM 400 high-resolution magnetic resonance spectrometer for ^1H (400 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) and $^{29}\text{Si}\{^1\text{H}\}$ (79 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane (TMS), and residual solvents peaks were used as a reference. Gel permeation chromatography (GPC) analyses were performed on a Waters e2695 instrument equipped with Model 3580 refractive index detectors (Viscotek) and two 10 μm PL Gel columns with flow rate of 1.0 mL/min at 35 °C. Molecular weights and molecular weight distributions were also calibrated with polystyrene standards ranging from 500 to 10,000,000 amu. DSC measurements were carried out using a DSC Q200 (TA Instruments). Approximately, 15 mg of the samples were capsulated in aluminum pans. Each experiment was performed under nitrogen atmosphere at a heating rate of 10 °C/min over the temperature range from –50 to 200 °C. TGA experiments were carried out using a TGA/SDTA 851 (Mettler Toledo). Approximately, 8 mg of samples were heated from room temperature to 780 °C at a rate 10 °C/min under nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were obtained by using Bruker Hong Kong Limited, FT-IR spectrometer model ALPHA. The polymeric films were simply prepared by dropping the polymer solution (82 mg/ml in chloroform) on a glass slide (26 \times 26 mm²). The slide was then left at room temperature for 1 h, subsequently at 70 °C for an additional 1 h to completely remove the solvent. Finally, the solidification of the films was obtained by freezing the films in the refrigerator or freezer, while the thickness of **P-Cl** (22–38 μm) and **P-Br** (16–35 μm) films was measured by Bruker's Dektak XTTM stylus profiler. Contact angles of water on the film surfaces were measured by sessile drop method at 25 °C with the average of five measurements at different positions for one sample.

2.1.1. Synthesis of chlorine-containing poly(siloxane/double-decker silsesquioxane) (**P-Cl**)

The starting material of *cis*- and *trans*-**DDSQ** in 1:1 ratio was freshly prepared according to our previous report [30]. **DDSQ** (1.0 g, 0.863 mmol) and tris(pentafluorophenyl)borane (8.8 mg, 2% mol) were transferred into a vial under nitrogen atmosphere. 2.50 mL of anhydrous toluene was then added into a reaction mixture. The mixture was kept stirring at room temperature until the solid was completely dissolved. Then, an equivalent molar ratio of 1,1,3,3,5,5 hexamethyltrisiloxane (219 μL , 0.863 mmol) was slowly added into

the reaction solution at room temperature. The reaction was allowed to proceed at room temperature for 3 days. The reaction was stopped by adding it into methanol (10 mL) where polymeric gel was immediately formed. This polymeric gel was washed several times with methanol and finally dried under vacuum to obtain 1.06 g (96% yield) of dried **P-Cl**.

FT-IR (cm^{-1}) 3074, 2960, 1594, 1431, 1261, 1089, 1010, 842, 801, 726, 695, 577; ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ –0.097 to 0.077 (m, 18H, O–Si(CH_3)₂–O), 0.85 (m, 4H, –Si–CH₂–CH₂–), 1.90 (m, 4H, –CH₂–CH₂–CH₂–), 3.38 (m, 4H, –CH₂–CH₂–Cl) 7.12–7.59 (m, 40H, –C₆H₅) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ 0.96, 11.23, 26.61, 47.28, 127.60, 127.73, 127.86, 130.42, 130.59, 131.54, 134.01, 134.11 ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CDCl_3 , 25 °C, TMS): δ = –79.76, –79.43, –77.27, –79.10, –67.65, –19.84 ppm.

2.1.2. Synthesis of bromine-containing poly(siloxane/double-decker silsesquioxane) (**P-Br**)

0.50 g of **P-Cl**, sodium bromide (0.24 g, 2.3 mmol), and TBAB (0.038 g, 0.12 mmol) were transferred into thick-wall tube. Then, the mixture was evacuated under vacuum for 10 min and sealed properly. Then, 2.5 mL of acetone was added into the mixture via syringe. The solution mixture was stirred at 70 °C for 2 days. The solution mixture was then cooled down to ambient temperature, and was added with 0.7 mL of 1-bromopropane. The temperature was then elevated back to 70 °C and the reaction proceeded at this temperature for another 3 days. The solvent was then evaporated to yield a crude mixture, which was then washed with 25 mL deionized water to remove the soluble salt. And 25 mL of CH_2Cl_2 was additionally added to redissolve the crude product. Two phases separation between water and CH_2Cl_2 was used to further purify the product. Evaporation of CH_2Cl_2 layer yielded 0.53 g of **P-Br** as a yellow viscous gel (99% yields).

FT-IR (cm^{-1}) 3073, 3052, 2961, 1594, 1431, 1261, 1240, 1089, 1010, 843, 801, 726, 695, 577; ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ –0.093 to 0.151 (m, 18H, O–Si(CH_3)₂–O), 0.86 (m, 4H, Si–CH₂–CH₂–), 1.96 (m, 4H, –CH₂–CH₂–CH₂–), 3.25 (m, 4H, –CH₂–CH₂–Br) 7.14–7.59 (m, 40H, –C₆H₅) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 25 °C): δ 0.97, 12.72, 26.80, 36.35, 127.60, 127.74, 127.88, 128.02, 130.42, 130.54, 130.60, 131.51, 134.01, 134.12 ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, CDCl_3 , 25 °C, TMS): δ = –79.76, –79.43, –79.26, –79.10, –67.96, –19.84 ppm.

3. Results and discussion

Firstly, a mixture of *cis* and *trans*-**DDSQ** monomers in 1:1 ratio was freshly prepared according to our previous report by using a coupling reaction between tetrasiloxane salt of double-decker phenylsilsesquioxane (**DDONa**) and 3-chloropropyltrichlorosilane in the presence of sodium *i*-propoxide (***i*-PrONa**) [30]. Then, mixed isomers of **DDSQ** bearing a reactive function of di(*i*-propoxy) silyl groups were polymerized with hydrosilane groups at terminal chain of hexamethyltrisiloxane (**Scheme 1**) using $\text{B}(\text{C}_6\text{F}_5)_3$ as a Lewis acid catalyst through dehydrocarbonative condensation reaction at ambient temperature to obtain **P-Cl** in 96% yields. Previously, Kawakami et al. prepared the poly(siloxane/silsesquioxane) at higher temperature (60 °C) via dehydrocoupling condensation reaction between reactively silanol and hydrosilane groups [21,23], because of poorer solubility in organic solvents of their **DDSQ** monomer. Therefore, during the polymerization progress, their double-decker silsesquioxane monomer containing a higher polarity of silanol groups may need a higher temperature to be solubilized.

In contrast, our polymerization can be performed at ambient temperature due to the presence of highly soluble (*i*-propoxy)silyl groups in our **DDSQ** monomer. The evolution of bubbles was immediately observed upon the addition of hexamethyltrisiloxane

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