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Chlorinating cleavage of silicon–naphthyl bonds of polycarbosilane, and introduction of poly(ethylene glycol) graft copolymer micelles

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ABSTRACT

A new series of polycarbosilanes [$(PhCH_2)SiCH_3Cl$, Poly B] was designed by chlorinating cleavage reaction of silicon–naphthyl in polycarbosilane. The ^{1}H spectra of poly B revealed that the $SiCH_2$ and the $SiCH_3$ protons peak were up-field shifted compared with the type [$(PhCH_2)SiCH_3Np$, Poly A] polycarbosilane. Grafted polycarbosilane was synthesized with poly ethylene glycol (PEG) by nucleophilic substitution of the chloride substituents on the polycarbosilane. The aggregation behaviors of graft copolymers were investigated by dynamic light scattering and fluorescence at 25 °C in aqueous solutions of different polyethylene glycol (PEG) substituent.

1. Introduction

Polycarbosilane, consisting of a substituted inorganic backbone with organic side chain, has many advantages allowing unique applications in advanced materials [1–4]. Controlling the structure and molecular architecture of polycarbosilane has been intensively studied [5,6]. Kawakami and co-workers previously reported the stereoregularity of polycarbosilane and the highly stereoselective halogenating cleavage reaction of the silicon–naphthyl bond [7,8]. The transition metal-catalyzed, ring opening polymerization (ROP) of the optically pure monomer via the retention stereochemistry of the asymmetric silicon atom induces the well-controlled, stereoregular structure of the backbone and enables the effective control of the molecular weight in the presence of Et_3SiH [9,10].

Another typical way to functionalize organosilicon compounds is to introduce a reactive functional group such as Br or Cl by the cleavage of the silicon–naphthyl bond. This result demonstrates that the chlorinating cleavage reaction of the silicon–naphthyl bond proceeded with preference in inversion of configuration of the silicon atom. A convenient route to polycarbosilanes containing the Si–naphthyl functional group bond must be established as highly functionality materials. Functionalization via halogenation cleavage of the silicon–naphthyl bonds is one of the possible methods to achieve these objectives, thereby affording functionalized polycarbosilane exhibiting unique properties derived from the optical activity of the polymers.

The incorporation of PEG in polymer architectures such as star, block and graft polymers has become very important for industrial and commercial applications with amphiphilic assembly polymers. Amphiphilic graft copolymers consisting of a hydrophobic backbone and a hydrophilic function group have investigated not only as coating agents, water-leak sensors and packing materials, but also for biomedical applications [12]. The self-assembly of water-soluble polymers was achieved with the intermolecular and intramolecular interaction of the hydrophobic group attached to hydrophilic polymers while varying the surrounding conditions such as solvent composition, temperature and pH field [13,15,16].

In this paper, we describe the halogenating cleavage of silicon–naphthyl bonds of polycarbosilane with well controlled molecular weight. The synthesis of grafted polycarbosilanes was controlled by the degree of substitution (DS) via the incorporation of PEG on the hydrophobic polycarbosilane backbone. The micellar characteristics of the controlled degree of substituent (DS) of PEG per monomer unit-graft copolymers in an aqueous phase were investigated by using fluorescence and dynamic light scattering (DLS).

2. Experimental

2.1. Materials

Methyl-1-(naphthyl)2,3-benzosilacyclobut-2-ene was prepared according to the method previously reported in the literature [7]. Monomethoxy PEG (Mn 550) was purchased from Aldrich. All solvent were dried by standard procedures and distilled before use.

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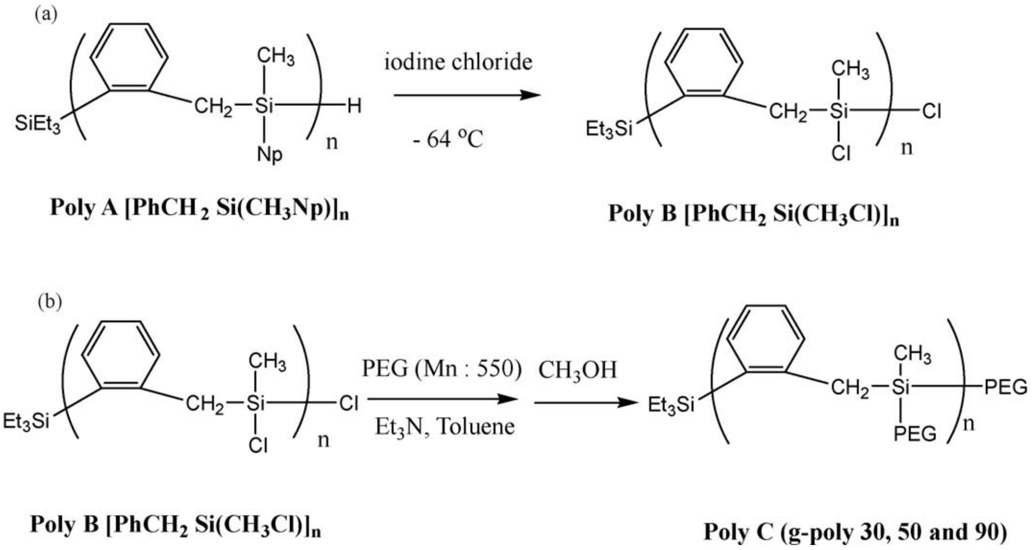

Scheme 1. Synthesis of the grafted polycarbosilane: (a) the chlorinating cleavage of poly A $[PhCH_2Si(CH_3Np)]_n$ to poly B $[PhCH_2Si(CH_3Cl)]_n$, and (b) the synthesis of polycarbosilane-g-polyethylene glycol (PEG).

2.2. Synthesis of poly A $[PhCH_2Si(CH_3Np)]_n$

The polymerization of monomer (0.26 g, 1 mmol) and Et_3SiH (0.03 mmol for monomer) in toluene (1 mL) with PDT catalyst (0.001 mmol) was carried out for 25 h. After removing the solvent, the residue was dissolved in THF and the product was precipitated into hexane.

Poly A; yield (65.7%), GPC (THF, polystyrene standards): Mn = 8200, PDI = 1.67.

^1H NMR ($CDCl_3$): δ = 7.46–7.7 (br), 6.76–7.28 (br), 6.13–6.34 (br), 2.26–2.54 (br, 2H), −0.03 to −0.52 (br, 3H).

2.3. Synthesis of poly B $[PhCH_2Si(CH_3Cl)]_n$; reaction of poly A $[PhCH_2Si(CH_3Np)]_n$ with iodine chloride (ICl)

A solution of iodine chloride (0.385 mmol) in $CHCl_3$ was added dropwise to a mixture of Poly A (0.385 mmol for unit of monomer in polymer) in $CHCl_3$ (15 mL) during 30 min at −64 °C. The reaction mixture was stirred at the same temperature for 2 h. The products were washed with hexane.

^1H NMR of poly B ($CDCl_3$): δ = 7.95.2–7.45 (br), 7.45–6.8 (br), 1.26–1.24 (br, 2H), 0.90–0.85 (t, 3H).

2.4. Synthesis of g-poly 30, 50 and 90

The poly B (0.385 mmol) was dissolved in toluene (15 mL) and Et_3N (3.85 mmol) was added to the mixture. A solution of PEG (Mn = 550, 0.115 mmol for g-poly C30, 0.193 mmol for g-poly C50, and 0.347 mmol for g-poly C90) in toluene (5 mL) was added, and the reaction mixture was stirred overnight, and an excess of methanol (0.5 mL) was added to the solution to produce terminally end-capped methoxy groups. After filtering, the excess methanol, triethylamine and toluene were removed in vacuum. The product was washed with hexane. The g-poly C30, 50 and 90 were recovered as amber, highly viscous materials.

^1H NMR of *g*-poly C30 ($CDCl_3$): δ = 8.09–8.07 (br), 7.82–6.7 (br), 6.79–6.77 (br), 3.75 (br, 2H, $SiOCH_2$), 3.66–3.54 (br, 44H, OCH_2CH_2 and 3H, $SiOCH_3$), 3.37 (s, 3H, OCH_3), 2.39–2.37 (br, 2H, backbone CH_2) 058–0.37, 0.13–0.06 (br, 3H, $SiCH_3$). ^1H NMR of *g*-poly C50 ($CDCl_3$): δ = 2.60–2.58 (br, 2H, backbone CH_2). ^1H NMR of *g*-poly C90 ($CDCl_3$): δ = 2.94–2.92 (br, 2H, backbone CH_2). ^1H NMR of grafted polycarbosilane (D_2O): δ = 3.57–3.5 (br, 44H, OCH_2CH_2), 3.24 (s, 3H, OCH_3).

Yield: *g*-poly C30 (92.7 wt%), *g*-poly C50 (91.6 wt%), and *g*-poly C90 (89.0 wt%).

3. Result and discussion

The starting material, 1-methyl-1-(naphthyl) 2,3-benzosilacyclobut-2-ene, was prepared following the reported procedure [7]. Pt-catalyzed ROP of monomer with Et_3SiH as the capping agent was carried out for 25 h. The polycarbosilane molecular weight was measured by SEC, and assigned in the ^1H NMR. Furthermore, a typical way to make the functionalized polycarbosilane is to introduce a reactive Si-Cl functional group by the cleavage of the silicon–naphthyl bonds of polycarbosilane. The reaction of iodine chloride with the poly A in chloroform results in the complete substitution of the Si-Cl group in poly B $[PhCH_2Si(CH_3Cl)]_n$ in Scheme 1. In Fig. 1, the methylene protons in poly B were observed at around 3.03–3.05 ppm as a down-field shifted signal, while the Si-CH_3 peak exhibited three shoulder signals at 0.07, 0.08 and 0.09 ppm that were down-field shifted compared with poly A due to the different diastereometric sequences formed by the splitting of the peaks of the nuclei and the $SiCH_3$. Poly B was synthesized under mild conditions in toluene with PEG (Mn: 550) via

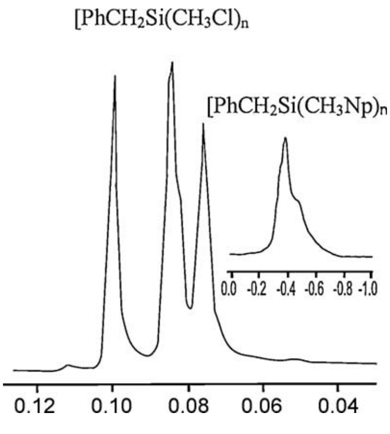

Fig. 1. ^1H NMR spectra of poly B $[(PhCH_2)SiCH_3Cl]_n$ in methyl region.