

# Polysiloxanes containing polyhedral oligomeric silsesquioxane groups in the side chains; synthesis and properties

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## ABSTRACT

Linear polysiloxanes having different amounts of polyhedral oligomeric silsesquioxane (POSS) side groups were prepared from the hydrosilylation reaction of poly(ethylhydrosiloxane) with different amount of POSS and 1-octene using platinum(0)-divinyl tetramethyldisiloxane as a catalyst. 1-Octene and platinum(0)-divinyl tetramethyldisiloxane were found to be very important for the preparation of the linear polymer without any cross-linked structures. The linear polysiloxanes with POSS side groups are soluble in various organic solvents. When the content of POSS-containing monomeric unit is larger than 10 mol%, free standing films can be prepared from a routine solution casting method, although this polysiloxane is not cross-linked.

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## 1. Introduction

Polysiloxane derivatives have long been used widely in many applications including elastomers, silicone oils, sealing agents, adhesives, low dielectric materials, and biomedical materials, because of their unique properties such as heat resistance, high oxygen permeability, low toxicity, poor wettability, extremely low surface tension, outstanding electrical isolating properties, chemical resistance, and biocompatibility [1–6]. Because linear polysiloxane derivatives have poor thermal/mechanical properties and low dimensional stability, cross-linked polysiloxanes or copolymers having siloxane units were prepared to improve their thermal/mechanical properties [7–11]. As an alternative approach to improve their thermal/mechanical properties, polysiloxane composites can be prepared by mixing linear polysiloxanes with metal oxide fillers such as zinc oxide, aluminum oxide, and ferric oxide, etc. or polyhedral oligomeric silsesquioxane (POSS) nanoparticles, but phase separation of these inorganic materials in the polymer matrix was found to be major problem to improve their physical properties [12–19]. POSS/polymer blend systems were also studied to improve the polymers' properties. However, POSS molecules were also phase-separated and aggregated in polymer matrix. So the polymer membranes are not fully transparent and have optical defects even at low POSS loading levels [14]. Therefore bulky groups such as phenyl, biphenyl, triphenyl, naphthalene, carbohydrate, cholesteric, and cyclohexyl groups also have been attached to the polysiloxanes

through covalent bonding to improve their thermal/mechanical properties [20–29].

In this work, POSS nanoparticles were covalently bonded to polysiloxanes to obtain organic/inorganic hybrid polymeric materials with improved thermal/mechanical properties. These materials were synthesized from hydrosilylation reactions of silane groups (Si–H) in poly(ethylhydrosiloxane) (PEHS) with allyl-cyclohexylPOSS (allyl-CyPOSS)/1-octene using platinum(0)-divinyl tetramethyldisiloxane as a catalyst. The detailed synthetic procedures and characterization of these polymers using instrumental methods such as nuclear magnetic resonance, Fourier transform infrared, gel-permeation chromatography, wide-angle X-ray scattering, differential scanning calorimetry, thermogravimetry analysis, rheometry, dynamic mechanical thermal analysis, and universal testing machine are discussed in this paper.

## 2. Experimental

### 2.1. Materials

1,3,5,7,9,11,14-Heptacyclohexyltricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane-endo-3,7,14-triol (trisilanol-CyPOSS) was obtained from Hybrid Plastics Inc. and used without further purification. Allyltrichlorosilane, 1-octene, and Platinum(0)-divinyl tetramethyldisiloxane, Pt<sub>2</sub>[(CH<sub>2</sub>=CH)SiMe<sub>2</sub>OSiMe<sub>2</sub>(CH=CH<sub>2</sub>)<sub>3</sub>], (Pt<sub>2</sub>(dvs)<sub>3</sub>, 2 wt% Pt solution in xylene) were used as received from Aldrich. Toluene and tetrahydrofuran were distilled from Na/benzophenone and stored under dry nitrogen. All other reagents and solvents were

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used as received from commercial sources, unless otherwise mentioned. Trimethyl-terminated poly(ethylhydrosiloxane) (PEHS, viscosity at 25 °C is 100 cSt on average.) was purchased from Gelest. The degree of polymerization of PEHS was estimated from the  $^1\text{H}$  NMR spectrum of PEHS by comparing the intensities of peaks from 18 protons of the methyl groups at the chain end and that from one proton of the hydrosilane (Si–H) group in the backbone. The degree of polymerization was about 370.

## 2.2. Measurements

$^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded using 2 wt% samples in  $\text{CDCl}_3$  on a Jeol (JNM-LA 300) (300 MHz). The Fourier transform infrared (FT-IR) measurements were performed on a Perkin Elmer Spectrum 2000 FT-IR spectrometer in combination with a deuterated triglycine sulfate (DTGS) detector using KBr pellets. In all cases, 16 scans at a resolution of  $4\text{ cm}^{-1}$  were used to record the spectra. Weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and molecular weight distributions were measured by conventional gel-permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR2 and HR4,  $7.8\text{ mm} \times 300\text{ mm}$ ). GPC measurements were carried out at 30 °C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with against ten known polystyrene standards. The absolute molecular weights of some polymers were determined by GPC equipped with a multi-angle light scattering detector (GPC/MALS). THF was used as eluent with a flow rate of 1.0 mL/min. Detectors: Wyatt OPTILAB DSP interferometric refractive index detector and Wyatt miniDAWN light scattering detector with a 20 mW semiconductor laser operating at 690 nm. The glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) were determined using a TA Instruments differential scanning calorimeter (DSC 2920) equipped with a DSC Cooling Can, which is allowed to cool down using liquid nitrogen, under a continuous nitrogen purge (60 mL/min). The heating rate was 10 °C/min. Pure indium was used to calibrate the instrument. The glass transition temperatures were taken as the inflection point in the change in heat capacity with temperature in the DSC curves. The thermal stability of the polymers was analyzed by thermogravimetry analysis (TGA) using a TA Instruments TGA 2050 under a continuous nitrogen purge of 60 mL/min. The samples were heated from room temperature to 700 °C with a uniform heating rate of 10 °C/min. The residual char yield was taken as the weight percentage remaining at  $T = 700\text{ °C}$ . Wide-angle X-ray scattering was used to analyze the chemical structures of polymer samples. The measurements were carried out using the bending magnet beam line 3C2 at the Pohang Light Source, Korea. X-rays of wavelength  $\lambda = 1.5406\text{ \AA}$  monochromatized by a Si(111) double-crystal monochromator were focused at the sample position by a toroidal premirror. For high resolution – transmission electron microscopy (HR-TEM) measurement, the 0.5 wt% solution of polymers in THF was dropped onto carbon-coated copper grid. Just after vacuum evaporation of the solvent, thin polymer films formed between copper grid lines were observed from the transmittance for 300 keV using TEM (JEM-3010, JEOL). The linear viscoelastic properties were measured with an ARES rheometer (TA Instruments). All of the measurements were performed within the linear viscoelastic range, using rotation rates of  $0.1\text{--}500\text{ rad s}^{-1}$ , where the dynamic shear storage ( $G'$ ) and shear loss modulus ( $G''$ ) are independent of strain. Apparent shear viscosity [ $\eta$  (Pa s)], storage modulus [ $G'$  (Pa)], and loss modulus [ $G''$  (Pa)] were measured as a function of frequency in the dynamic oscillatory mode. All of the rheological characterizations were performed using a cone and plate with 25 mm diameter and with the gap between cone and plate being controlled precisely,

with a typical value of 1.0 mm. Dynamic mechanical thermal analysis (DMTA) was carried out in a nitrogen atmosphere with a Rheometric Scientific analyzer (MARK IV). Measurement of the tensile storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of samples were performed at a frequency of 1 Hz and working in single cantilever in the temperature range from  $-70$  to  $100\text{ °C}$ . The heating rate was  $3\text{ °C/min}$ . The testing was performed using rectangular samples measuring approximately  $35 \times 5.0 \times 0.2\text{ mm}^3$ . The exact dimensions of each sample were measured before the scan. The tensile strength of the polymer film was measured with dumbbell specimens according to the ASTM D638 Type V. The value for each sample was taken as the median value of five specimens. These tests were carried out at room temperature on a universal tensile testing machine (Lloyd instruments LR 10K) with a crosshead speed of 50 mm/min.

## 2.3. Synthesis of 1-allyl-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]-octasiloxane (allyl-CyPOSS)

Allyl-CyPOSS was prepared using the method described by Lichtenhan et al. as shown in Fig. 1 [30]. 1,3,5,7,9,11,14-Heptacyclohexyltricyclo[7.3.3.1<sup>5,11</sup>]heptasiloxane-endo-3,7,14-triol (trisilanol-CyPOSS) (24.34 g, 25 mmol) and triethylamine (8.348 g, 82.5 mmol) were dissolved in distilled THF (200 mL) and cooled in an ice bath. A solution of allyl trichlorosilane (4.875 g, 27.5 mmol) in THF (25 mL) was added using an addition funnel to the cooled solution. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Afterwards the reaction mixture was filtered to remove the  $\text{Et}_3\text{N}\cdot\text{HCl}$  byproduct. Volatiles were removed under reduced pressure at ambient temperature, and obtained yellow solid was subsequently dissolved in a minimum amount of benzene and precipitated into acetonitrile (5-fold excess) to eliminate the remaining byproduct completely. After filtration and drying under vacuum at room temperature, the yield of the obtained white powder was 97%.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 5.78 (m, 1H,  $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 5.00–4.90 (s, 2H,  $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 1.75 (m, 35H, cyclohexyl- $\text{CH}_2$ ), 1.61 (d, 2H,  $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 1.25 (m, 35H, cyclohexyl- $\text{CH}_2$ ), 0.76 (m, 7H, cyclohexyl- $\text{CH}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm): 132.6 ( $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 114.7 ( $\text{SiCH}_2\text{CH}=\text{CH}_2$ ), 27.5–26.6 (cyclohexyl- $\text{CH}_2$ ), 23.2–23.1 (cyclohexyl- $\text{CH}$ ), 19.7 ( $\text{SiCH}_2\text{CH}=\text{CH}_2$ ). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3077 ( $\nu$ , allyl- $\text{CH}$ ), 3000–2800 ( $\nu$ ,  $\text{CH}_2$ ), 1646 ( $\nu$ ,  $\text{C}=\text{C}$ ), 1447 ( $\delta$ ,  $\text{CH}_2$ ), 1108 ( $\nu$ , T-type Si–O–Si),  $\nu$ : stretching mode;  $\delta$ : bending mode.

## 2.4. Synthesis of poly(ethylsiloxane)s containing CyPOSS and *n*-octyl side groups (PES#: # = 0, 1, 4, 7, 10, 20, 25)

The abbreviation of poly(ethylsiloxane)s containing CyPOSS and *n*-octyl in the side groups is PES#, where # is the mol-% of allyl-CyPOSS groups with respect to the Si–H groups in PEHS used in the synthesis. Fig. 1 shows the synthetic routes for the preparation of PES#s and the synthetic procedure is exemplified in the case of PES20 as follows. Allyl-CyPOSS (1.14 g, 1.096 mmol, 20 mol% versus the Si–H groups in PEHS) and PEHS (0.406 g, 5.480 mmol) were dissolved in freshly distilled toluene (5.5 mL). The reaction mixture was stirred at room temperature for 5 min to obtain a homogeneous solution, and then 0.05 mL solution of  $\text{Pt}_2(\text{dvs})_3$  in xylene (2 wt% Pt solution) was added to the reaction mixture. After 1 h of stirring, 1-octene (0.590 g, 5.261 mmol, 1.2 equiv. versus the remaining Si–H groups) was added to the reaction mixture and the reaction solution was stirred at room temperature for 5 days. The reaction was monitored by  $^1\text{H}$  NMR and FT-IR. The disappearance of chemical shift ( $\delta = 4.7\text{ ppm}$ ) and stretching vibration ( $\nu = 2160\text{ cm}^{-1}$ ) contributed by the hydrosilane (Si–H) group confirmed 100% conversion of Si–H groups through the

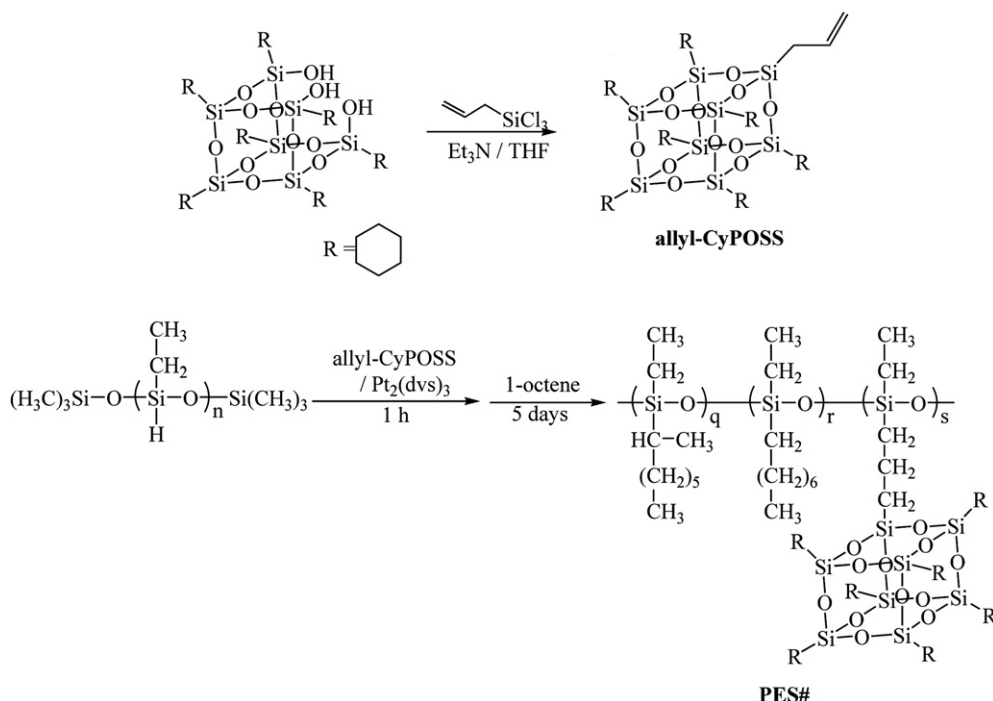


Fig. 1. Synthetic routes for allyl-CyPOSS and polysiloxanes having POSS side groups (PES#s), where the # is molar ratio of CyPOSS fed. (# = 0, 1, 4, 7, 10, 20, and 25).

hydrosilylation reactions. The resulting polymer was obtained on precipitation in methanol three times and washed several times with methanol. The final product was obtained after drying in a vacuum oven at room temperature for 2 days. Other PES#s (# = 0, 1, 4, 7, 10, 25) were obtained with the same procedure, except for the amount of allyl-CyPOSS and 1-octene used (Table 1). The yields were always above 70% and 100% conversions from PEHS to PES#s were confirmed by <sup>1</sup>H NMR and FT-IR. The octyl and POSS content in polymers were calculated by comparing the intensity of the peak at 1.88 ppm from the cyclohexyl group attached to the POSS cage (k in Fig. 2) and that of the peak at 0.55 ppm from the two methylene groups covalently bonded at the silicone atom substituted with 1-octene (a and c in Fig. 2). The POSS content in the polymer was similar to the allyl-CyPOSS used in the hydrosilylation reactions (Table 1). The physical appearance of the isolated products changed from viscous liquid at 0–7 mol% of POSS to powders at 20 mol% or greater POSS content. A flexible transparent film about 200 μm thickness could be obtained by casting from the THF solution of PES20 (Fig. 3(a)). The weight-average molecular weight ( $M_w$ ) of the polymers measured from GPC using polystyrene standards are in the range of 111000–157000

(Table 1), high enough to ignore the effect of molecular weight on the thermal properties of the polymers.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.75 (cyclohexyl-CH<sub>2</sub>), 1.46 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiO<sub>3</sub>), 1.25 (SiCHCH<sub>3</sub>CH<sub>2</sub>, SiCHCH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>, SiCH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>, cyclohexyl-CH<sub>2</sub>), 0.94 (SiCH<sub>2</sub>CH<sub>3</sub>, SiCHCH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.72 (cyclohexyl-CH), 0.65 (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiO<sub>3</sub>), 0.51 (CH<sub>3</sub>CH<sub>2</sub>SiO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 34.0 (SiCH<sub>2</sub>CH<sub>2</sub>), 32.3 and 29.8 (SiCHCH<sub>3</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>, SiCH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>), 27.7–26.8 (cyclohexyl-CH<sub>2</sub>), 23.5–23.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, cyclohexyl-CH), 17.1 (Si(CH<sub>2</sub>)<sub>3</sub>SiO<sub>3</sub>), 16.3 (SiCH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 14.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 8.4–8.1 (SiCH<sub>2</sub>CH<sub>3</sub>, SiCHCH<sub>3</sub>CH<sub>2</sub>), 6.8 (SiCH<sub>2</sub>CH<sub>3</sub>). FT-IR (KBr, cm<sup>-1</sup>): 3000–2800 (ν, CH<sub>2</sub>), 1462 (δ, CH<sub>2</sub>), 1108 (ν, T-type Si-O-Si), ν: stretching mode; δ: bending mode.

### 3. Results and discussion

#### 3.1. Synthesis

A series of polysiloxanes containing *n*-octyl and POSS side groups (PES#) were prepared from hydrosilylation reactions of

Table 1  
Compositions of poly(ethylhydrosiloxane)s containing POSS and *n*-octyl side groups.

	POSS (mol%)		<i>n</i> -octyl content (mol%) <sup>a</sup>		$M_n^b (\times 10^{-3})$	$(M_w/M_n)^c (\times 10^{-3})$	PDI
	Feeding	In polymer <sup>d</sup>	Anti-Markovnikov addition	Markovnikov addition			
PEHS					27.4	35/8.7	4.00
PES0	0	0	94.2 (94.2 <sup>d</sup> )	5.8 (5.8 <sup>d</sup> )	69.0	140/23	5.97
PES1	1	1.2	91.6 (92.7 <sup>d</sup> )	7.2 (7.3 <sup>d</sup> )	73.1	157/24	5.88
PES4	4	4.3	90.8 (94.9 <sup>d</sup> )	4.9 (5.1 <sup>d</sup> )	83.7	144/25	5.69
PES7	7	7.5	87.0 (94.1 <sup>d</sup> )	5.5 (5.9 <sup>d</sup> )	94.7	134/22	6.03
PES10	10	11.0	81.9 (92.0 <sup>d</sup> )	7.1 (8.0 <sup>d</sup> )	106.7	154/24	6.50
PES20	20	22.1	70.3 (90.2 <sup>d</sup> )	7.6 (9.8 <sup>d</sup> )	144.8	151/31	4.94
PES25	25	26.4	66.8 (90.8 <sup>d</sup> )	6.8 (9.2 <sup>d</sup> )	160.0	110/26	4.19

<sup>a</sup> Calculated from <sup>1</sup>H NMR.

<sup>b</sup> Theoretical molecular weights from PEHS having 370 degree of polymerization.

<sup>c</sup> Obtained from GPC using THF as solvent with respect to monodisperse polystyrene as standards.

<sup>d</sup> The numbers in parentheses are mol% among the octyl side groups.

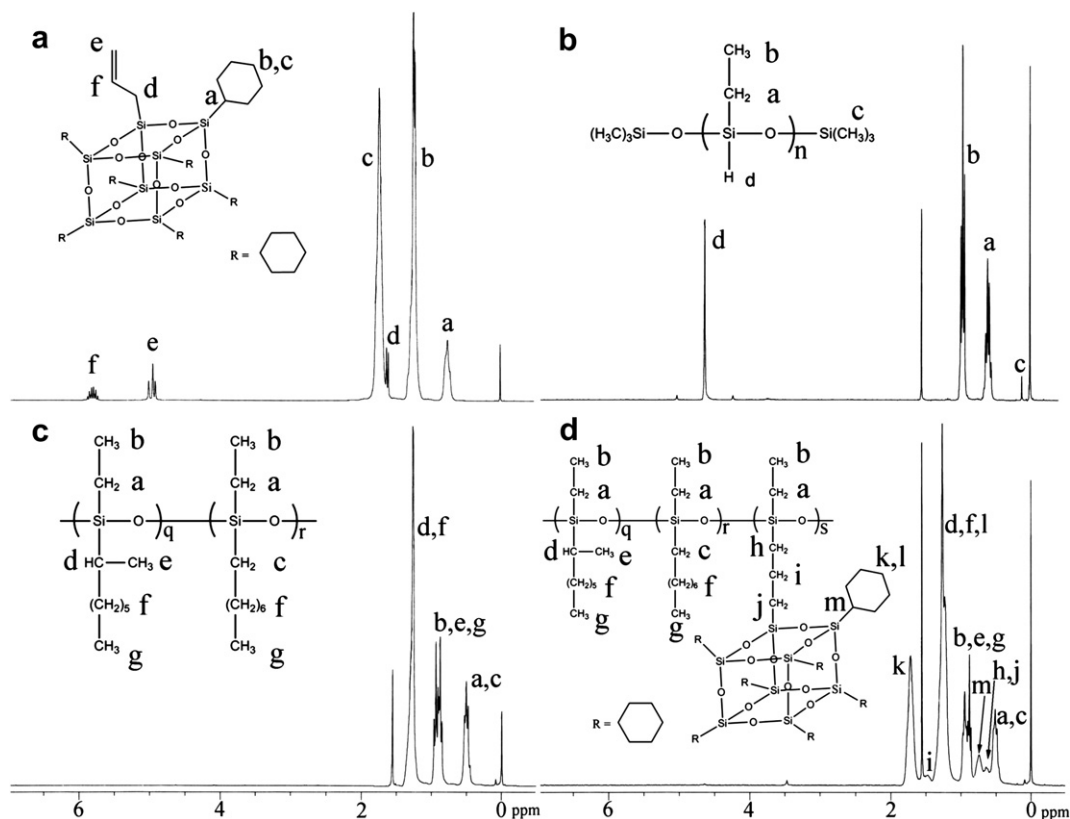


Fig. 2.  $^1\text{H}$  NMR spectra of starting compounds and polysiloxanes having POSS side groups; (a) allyl-CyPOSS, (b) PEHS, (c) PES0, and (d) PES20.

PEHS with different amounts of 1-octene and allyl-CyPOSS (Table 1) using the platinum catalyst,  $\text{Pt}_2(\text{dvs})_3$ , as shown in Fig. 1. Poly(ethylhydrosiloxane) (PEHS) was used as the parent polymer instead of poly(methylhydrosiloxane) (PMHS), which is more commonly used to obtain polysiloxane derivatives from hydrosilylation reactions [21,23,25,31]. Because the maximum degree of polymerization (DP) of commercially available PMHS is about 40, polysiloxanes with POSS content under 10 mol% could not be easily prepared. For example if 4 mol% of allyl-CyPOSS is reacted with PMHS with DP 40, the average number of POSS groups per each polymer chain would be about 1.6, then there should be quite large

content of polymer products that do not have any POSS side groups at all. Those products would not be pure polysiloxanes containing POSS side groups, but a mixture of polysiloxanes containing only *n*-octyl side groups and polysiloxanes containing both *n*-octyl and POSS side groups. Therefore, the chemical and physical properties of these products would reflect these mixtures. When PMHS was reacted with a small amount of allyl-CyPOSS, less than 4 mol%, the POSS content in the product was always much larger than the amount of allyl-CyPOSS used in the reaction. Some of the polymer products without POSS side groups could have been removed during the purification procedures because of different physical



Fig. 3. Photo images of free standing polymer films, (a) PES20 and (b) PES25, obtained by casting from THF solution.

properties, including polymer viscosity. Since the DP of PEHS used in this study is larger, about 370, all the polymer chains may contain POSS side groups, even with a small amount of allyl-CyPOSS in the hydrosilylation reactions. Even PES1 and PES4, which have POSS mol% of 1 and 4, respectively, prepared from the hydrosilylation reactions show reproducible chemical and physical properties.

1-Octene was intentionally reacted with the remaining Si-H groups in the polysiloxane backbone after the hydrosilylation reactions of PEHS and allyl-CyPOSS to prevent any possible reactions of Si-H in the polymer backbone with hydroxyl groups in alcohols (or water), known as O-silylation [32,33]. Alkoxysilane (Si-OR) or hydroxysilane (Si-OH) groups in the polymer backbone produced from the O-silylation reactions can undergo condensation reactions to produce cross-linked polymers. We obtained insoluble cross-linked polymers when Si-H groups were not fully substituted with *n*-octyl group reactions. 1-Octene not other 1-alkenes was intentionally used to produce *n*-octyl side groups for the reactions because (1) it is not easy to handle shorter gaseous alkenes such as 1-butene, (2) using longer 1-alkenes, such as 1-dodecene, could produce side chain crystalline phases where both the alkyl side chains and the POSS groups work as filler to increase the thermal properties [34]. Because the Si-H groups in PEHS are fully substituted by allyl-CyPOSS and 1-octene groups, the increase in POSS content is caused by decreased *n*-octyl content. The effect of *n*-octyl groups on thermal properties is discussed below.

Karstedt's catalyst,  $\text{Pt}_2(\text{dvs})_3$ , was used as a catalyst in the hydrosilylation, although acidic Speier's catalyst, a solution of platinum hydrochloric acid ( $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ) in isopropyl alcohol, was used for hydrosilylation reactions for poly(methylhydrosiloxane) by others [31,35]. Speier's catalyst produced O-silylation reactions of Si-H groups with isopropanol in the solution of the catalyst and with other alcohols and water used during the purification process, then the cross-linked polymers (insoluble polymer gels) were produced through condensation reactions between the alkoxysilane (or hydroxysilane) groups produced when we dried the products in a vacuum oven. On the contrary when we used Karstedt's catalyst,  $\text{Pt}_2(\text{dvs})_3$  in xylene, as the catalyst known for a hydrosilylation reaction, linear soluble polymers could be obtained; since isopropanol is not included in Karstedt's catalyst, O-silylation additions should not occur. The conversion of hydride groups to POSS and *n*-octyl groups was confirmed from  $^1\text{H}$  NMR and FT-IR spectrum. For example, an absorption band at  $2160\text{ cm}^{-1}$  from the Si-H group is not observed in the FT-IR spectrum of PES0 and PES20 (Fig. 4), and the proton peak at 4.7 ppm from Si-H is not observed in the  $^1\text{H}$  NMR spectrum of PES0 and PES20 (Fig. 2).

Anti-Markovnikov addition is a major reaction in the hydrosilylation of poly(alkylhydrosiloxane) using platinum catalysts [36–38], and both Markovnikov and anti-Markovnikov products can be produced with subtle changes of reaction conditions such as the types of alkenes and catalyst [33,39,40]. In our case, only Markovnikov products were obtained from the hydrosilylation reactions of allyl-CyPOSS, while both anti-Markovnikov and Markovnikov additions of Si-H groups into the double bond of 1-octene were observed. 2-Dimensional heterogeneous NMR spectroscopy was used to identify the proton peak positions of anti-Markovnikov and Markovnikov products from 1-octene (Fig. 5), and the integration of the peaks at 0.55 ppm from anti-Markovnikov addition (a and c in Fig. 2(d)) and that of the peak at 1.25 ppm from Markovnikov addition (d, f, and l in Fig. 2(d)) were compared to calculate the composition. The compositions of POSS and octyl groups in polymers were calculated from the integration of the NMR peaks in Fig. 2(d). The details for the calculation are listed in the Supporting Information. The mol% of *n*-octyl groups produced from the anti-Markovnikov ( $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ) and Markovnikov additions ( $-\text{Si}-\text{CH}(\text{CH}_3)-\text{CH}_2-$ ) is between 90.2–94.9 and 5.1–9.8,

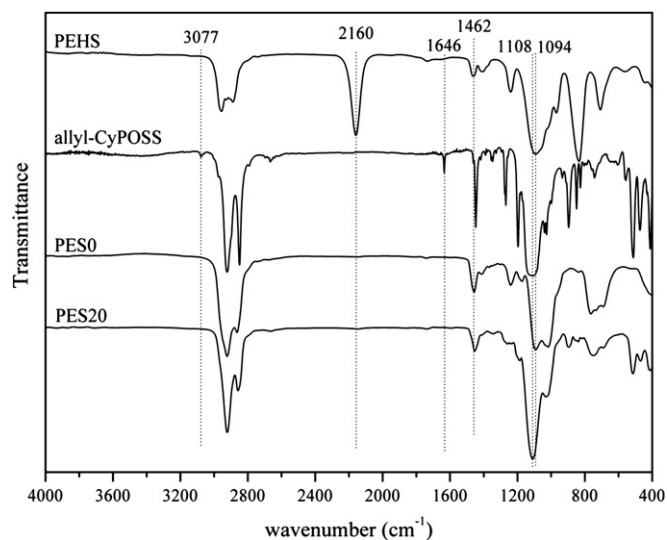


Fig. 4. FT-IR spectra of starting compounds (PEHS and allyl-CyPOSS) and polysiloxanes having POSS side groups (PES0 and PES20).

respectively (Table 1). Therefore, anti-Markovnikov addition is the major reaction, with a probability of 92% on average.

The weight-average molecular weight ( $M_w$ ) of the polymers measured from GPC are in the range of 111000–157000 (Table 1). There was not a strong correlation between the molecular weight and the POSS content, although the molecular weight of PES25 with the largest POSS content seems to be smaller than those of other PES#s. For comparison, we performed a SEC analysis with a light scattering detector. The molecular weight ( $M_w/M_n$ ) values of PES0, PES7, and PES25 obtained from the light scattering detector are 264100/66500, 568700/115900, and 295500/88800, respectively; the molecular weight of PES25 is slightly larger than that of PES0. Since these polymers were prepared by substitution reactions of

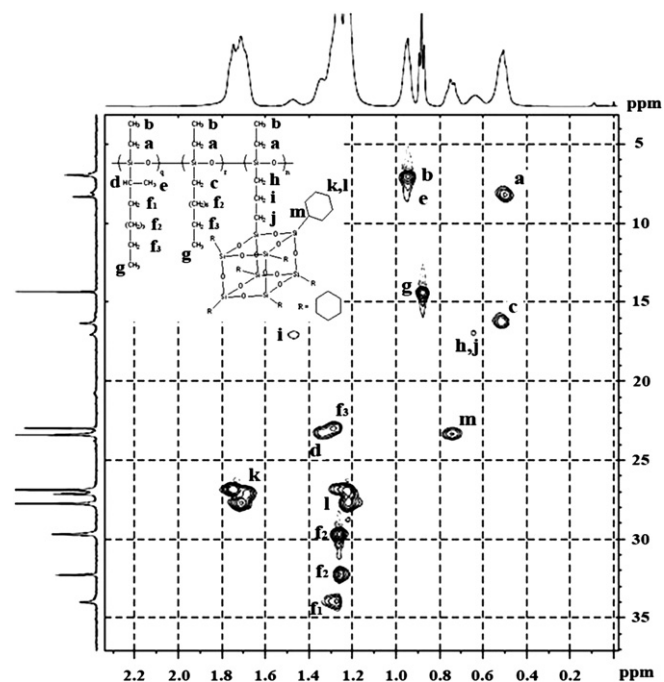


Fig. 5. 2-Dimensional heterogeneous NMR spectra of PES20.

PEHS, the molecular weight measured from light scattering detector should increase with the increase of the POSS content in the polymer because these polymers were made by substitution reactions of PEHS. Therefore, slight backbone cleavage may occur during the substitution reactions. We still don't know well the mechanism of the backbone cleavage because we have only limited information from NMR.

### 3.2. Thermal analysis

Fig. 6 shows DSC curves obtained from the second heating scans at a heating rate of 10 °C/min. Only glass transition temperatures ( $T_g$ ) were obtained when the samples were heated from –150 °C. Because the side chain melting transition of alkyl side groups occurs below 100 °C, our polymers do not have any side chain crystalline phases from the *n*-octyl side group that can affect the physical properties as fillers in the polysiloxane chain [41]. Still, the *n*-octyl side group increased the  $T_g$  of the polysiloxane; when the silane group in PEHS was 100% substituted with a *n*-octyl side group,  $T_g$  increased from –127 °C for PEHS to –97.3 °C for PES0. The medium-length *n*-alkyl side groups such as *n*-octyl decrease  $T_g$  because they act as a plasticizer to increase the free volume of the polymers by pushing the polymer backbones apart. Therefore, the  $T_g$  values of poly(*n*-alkyl methacrylate)s, poly(*n*-alkyl styrene)s, and poly(*n*-alkyl vinyl ether)s are lower than those polymers without corresponding *n*-alkyl side groups [42,43]. However, in our case, the *n*-octyl side group decreases the flexibility of the polysiloxane backbone by increasing the steric hindrance to the segmental motion of the flexible siloxane backbones. Therefore, the *n*-octyl side group can decrease  $T_g$  when attached to relatively stiff backbone such as poly(acrylate), poly(styrene), and poly(vinyl ether), but increases  $T_g$  for the flexible polysiloxanes as ours. Similarly, the  $T_g$  of polysiloxane derivatives with long *n*-alkyl groups are higher than that of poly(dimethyl siloxane) with small side groups [44,45]. The POSS side groups increased  $T_g$  further; as the content of POSS side groups increased,  $T_g$  increased. For example,  $T_g$  values of PES1, PES4, PES7 and PES10 were –95.5, –92.4, –87.3, and –77.3 °C, respectively. We could not observe a glass transition from DSC curves of PES20 and PES25 with larger POSS content, even when we quenched the sample from 150 °C to –150 °C using liquid nitrogen, possibly due to the very high POSS content; although the mol% of POSS side groups in PES20 and PES25 are 20 and 25, respectively, the weight percents of these polymers are 55.3% and 61.4%, respectively. Therefore it is not easy to detect the changes in heat capacity upon heating from the small portions of polymer chains in these polymers [46]. The increase of  $T_g$

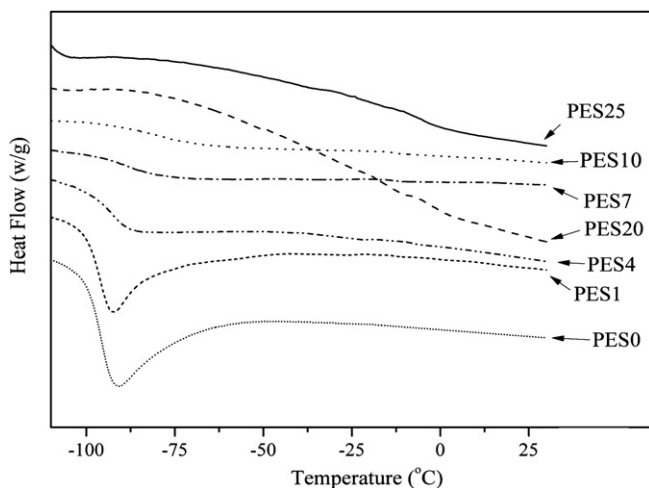


Fig. 6. DSC curves of polymers.

upon the incorporation of POSS groups into the polymer chains were also observed from other polymers such as polyfluorenes, poly(4-methylstyrene)s, poly(norbornyl)s, and poly(acrylate)s [47–51]. In addition, the PES0 and PES1 have very flexible backbones because of low POSS content and therefore show good enthalpy relaxation behavior. For these polymers, increasing POSS content increased  $T_g$ , indicating that the flexible domain of polymers decreases with increasing POSS content [46,52–54]. Although we could not measure  $T_g$  values of PES20 and PES25, these values would probably be lower than 0 °C based on other PES#s in this study. Still, non-sticky free standing films could be prepared as shown in Fig. 3(a) for PES20 at 200 μm thickness and in Fig. 3(b) for PES25 at 340 μm thickness.

Fig. 7 shows the TGA thermograms of POSS-containing polysiloxanes (PES#s), the starting polysiloxane (PEHS), and pure allyl-CyPOSS. The decomposition temperatures of 10% weight loss ( $T_{d,10\%}$ ) and the char yield data obtained from the TGA measurements are listed in Table 2. As shown in Fig. 7, all the polymers with POSS side groups exhibit good thermal stability above 400 °C. PEHS was thermally decomposed below 300 °C similar to PDMS by depolymerization [55], whereas thermal decomposition process of PES0 with only octyl side groups was different [see DTGA curves in the Supporting Information]. The *n*-octyl side groups in PES#s may interfere with the back-biting process for depolymerization [55,56]. Within the experimental temperature range, the TGA curves of all the polymers showed one-step decomposition behavior, suggesting that the incorporation of the CyPOSS nanoparticles changed the decomposition mechanism of the polymers, since the allyl-CyPOSS nanoparticle shows two-step decomposition behavior. The first derivative peak of CyPOSS nanoparticles is attributable to decomposition of the organic cyclohexyl ring at the POSS vertices, and the second peak is attributed to the inorganic POSS framework [57,58]. The incorporation of POSS groups into the side chain of polysiloxane increases the thermal stability, resulting in a retarded weight loss rate and char yield. For example, the incorporation of 1 mol% POSS groups increased the decomposition temperature by 47 °C. The enhanced thermal stability of POSS-containing polymers also occurs in other polymers [59–65].

### 3.3. Morphological characterization

Fig. 8 shows the wide-angle X-ray scattering (WAXS) patterns of the polymers and allyl-CyPOSS. The *d*-spacings of the samples were calculated using the Bragg equation. The WAXS pattern of PES0

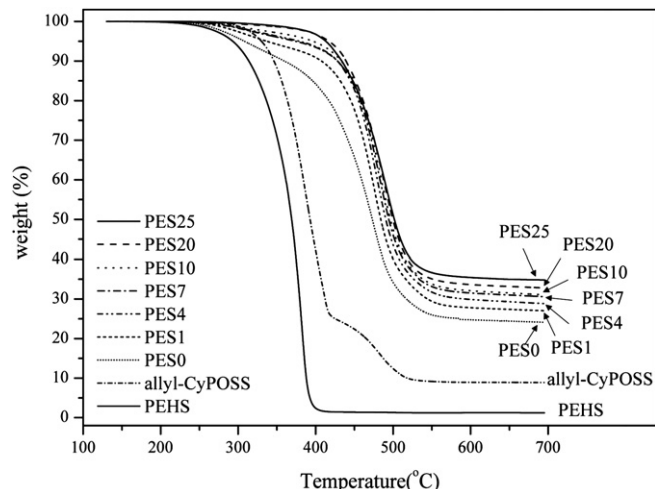


Fig. 7. TGA thermograms of PEHS, allyl-CyPOSS, and polymers.

**Table 2**  
Thermal and mechanical properties of the polymers.

	$T_g$ (°C)	$T_{d,10\%}$ (°C) <sup>a</sup>	Char yield (%) <sup>b</sup>	$G'/G''$ (Pa) <sup>c</sup>	viscosity (Pa s) <sup>d</sup>	$E'/E''$ (MPa) <sup>e</sup>	$\sigma$ (MPa) <sup>f</sup>
CyPOSS	–	346	8.91	–	–	–	–
PEHS	–127 <sup>g</sup>	314	1.21	–	1.0 <sup>h</sup>	–	–
PES0	–97.3	359	24.1	2.2/74.5	8.3	–	–
PES1	–95.8	407	27.0	9.2/140.6	14.2	–	–
PES4	–92.4	427	28.8	22.2/270.5	26.0	–	–
PES7	–87.3	428	30.6	79.0/582.4	70.9	–	–
PES10	–77.3	432	31.1	–	–	–	–
PES20	– <sup>i</sup>	439	32.8	–	–	5.6/1.7	2.1
PES25	– <sup>i</sup>	436	34.8	–	–	–	–

<sup>a</sup> The decomposition temperature ( $T_{d,10\%}$ ) is defined as 10 wt% loss.

<sup>b</sup> The char yield at 700 °C.

<sup>c</sup> Shear moduli obtained from rheometer at 10 rad s<sup>−1</sup>.

<sup>d</sup> Zero-shear viscosity was obtained at lowest shear rate, 0.1 s<sup>−1</sup>.

<sup>e</sup> Tensile moduli obtained from DMTA at 25 °C.

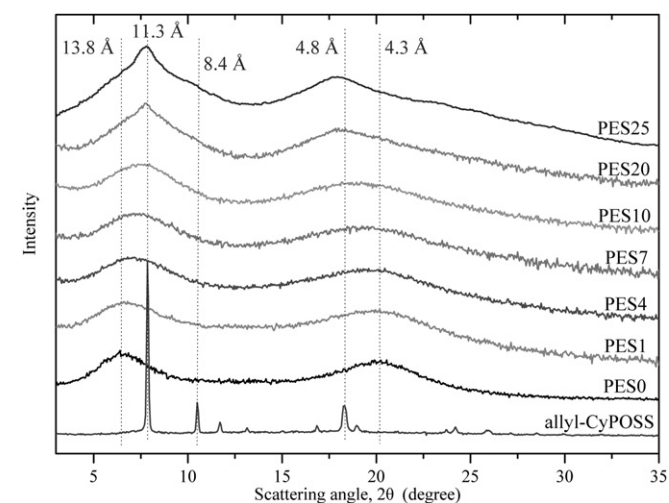
<sup>f</sup> Tensile strength obtained from UTM at 25 °C.

<sup>g</sup> Literature value of poly(dimethylsiloxane) in Polymer Handbook 4th edition.

<sup>h</sup> The value of PEHS from supplier, Gelest.

<sup>i</sup>  $T_g$ s were not detected.

shows two amorphous halos: one is centered at a  $d$ -spacing of 4.3 Å and the other one is at 13.8 Å. These two broad peaks are associated with correlations between the polysiloxane backbones ( $d = 13.8$  Å) and between  $n$ -octyl side groups ( $d = 4.3$  Å), respectively. When the POSS content increases in PES#s, the  $d$ -spacing of the backbone peak decreases, while that of the side chain peak increases. The incorporation of the POSS groups in the polymer may increase the distance between the  $n$ -octyl side groups, which in turn decreases the distance between the polymer backbones (see Supporting Information). The pure allyl-CyPOSS is a crystalline substance and features several diffraction peaks. The diffractogram of allyl-CyPOSS exhibits strong reflections at  $d$ -spacing of 11.3 Å ( $2\theta = 7.85^\circ$ ), 8.4 Å ( $10.5^\circ$ ), and 4.8 Å ( $18.3^\circ$ ), suggestive of a rhombohedral unit cell and nearly identical to the pattern for an octacyclohexyl-POSS studied by J. Schwab and co-workers [66]. In particular, there is a very intense and sharp diffraction peak at 11.3 Å ( $2\theta = 7.85^\circ$ ) associated with the 101  $hkl$  reflection of a lattice. These sharp peaks of allyl-CyPOSS become broad when incorporated in the side chain of polysiloxane, although they become a little sharper as the POSS content increases. If the POSS groups aggregate in the polymer matrix, relatively sharp peaks from the

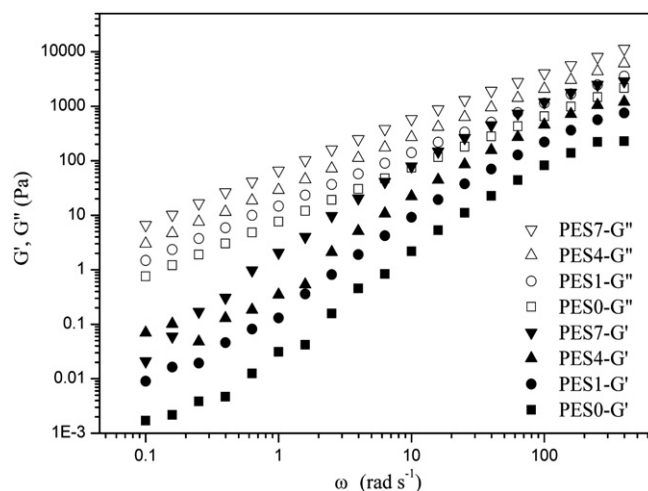


**Fig. 8.** Line profiles of WAXS diffractograms of polysiloxanes having POSS side groups.

POSS groups should appear, as previously reported [67–73]. Therefore, peak broadness and/or disappearance in PES#s indicates that the POSS groups are well-dispersed in the polymer matrix and/or ethyl  $n$ -octyl siloxane repeating units and ethyl POSS siloxane repeating units are randomly distributed in the polymer backbone. The films of PES25 have sharper peaks and are quite brittle, possibly due to the aggregation of POSS groups in the polymer due to high POSS content of 61.4 wt%.

### 3.4. Rheological and mechanical properties

Small-amplitude dynamic oscillatory measurements were conducted to investigate the effects of the POSS groups on rheological properties. These measurements were all performed in the linear viscoelastic regions of the polymer melts at 25 °C. Rheological results were obtained on the four polymers from PES0 to PES7, but PES10, PES20, and PES25 were too viscous at 25 °C to measure the rheological properties. Fig. 9 shows the shear storage modulus ( $G'$ ) and loss modulus ( $G''$ ) curves obtained by frequency sweep tests at 25 °C. Both  $G'$  and  $G''$  increase with increased POSS content, and  $G''$  is dominant over  $G'$ , with no crossover, indicating the polymers show predominantly viscous flow [67]. Fig. 10 shows shear viscosities ( $\eta$ ) versus shear rates (s<sup>−1</sup>) of the polymers. The zero-shear viscosity values of the polymers are quite low, but increase with higher POSS content, from 8.3, 12.2, 26.0, and 70.9 Pa s for PES0, PES1, PES4, and PES7, respectively, at 0.1 shear rate. Since these polymers were prepared by polymer modification reactions through hydrosilylation under very mild reaction conditions, backbone cleavage to decrease the degree of polymerization should not occur, and backbone length should be consistent [74]. Since the molecular weight values measured from the GPC of these polymers are not very different ( $M_n$  values of PES0, PES1, PES4, and PES7 are in the range of 69,000 to 94,700), the large differences of the shear viscosity value should not be caused by the hydrodynamic volume differences of these polymers [75]. Although the solubility of polymers in THF may be different with different POSS content, the differences of the shear viscosity values seems to be much larger than the molecular weight differences. Higher POSS content could increase the shear viscosity by bulkiness, which can increase the hydrodynamic volume of the polymers in the melt state and/or increase the entanglements between side chains [76–80]. The polymer with higher POSS content shows shear-thinning behavior at a lower shear rate; for



**Fig. 9.** Dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) curves for polymers (PES#s, # = 0, 1, 4, 7); (■) PES0, (●) PES1, (▲) PES4, and (▼) PES7. Filled and open symbols stand for  $G'$  and  $G''$ , respectively.

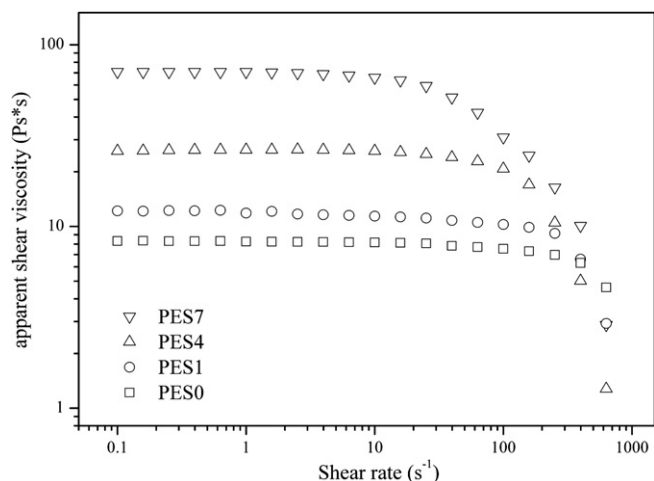


Fig. 10. Apparent shear viscosity curves for the polymers (PES#, # = 0, 1, 4, 7); ( $\square$ ) PES0, ( $\circ$ ) PES1, ( $\triangle$ ) PES4, and ( $\nabla$ ) PES7.

example, the decrease in shear viscosity with the increase of the shear rate (the shear-thinning behavior) starts at about  $40\text{ s}^{-1}$  and  $400\text{ s}^{-1}$  for PES7 and PES0, respectively. Similarly, more concentrated polymer solutions and polymer melts with higher molecular weight show increased shear viscosity and shear-thinning behavior at lower shear rates due to increased entanglements of the polymer chains [81–83].

Dynamic mechanical thermal analysis (DMTA) was performed to measure tensile storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of the polymer films. Although free standing films could be prepared from PES10, PES20, and PES25, the measurement was only possible from PES20 because PES10 is sticky and PES25 is too brittle to make rectangular samples for the measurement. The tensile storage modulus and loss modulus values of PES20 are 5.6 MPa and 1.7 MPa at  $25\text{ }^\circ\text{C}$ , respectively, and its tensile strength was in the range of 1.9–2.1 MPa, which is in the lower range of cross-linked silicone polymers for practical applications; tensile strength values of cross-linked silicone polymers are 0.5–12.0 MPa [84–86]. This lower tensile strength value of PES20 compared with those of cross-linked silicone polymers implies that the increased physical interactions through the incorporation of POSS groups into the silicone polymers are still lower than those obtained through cross-linking reactions. However, linear polysiloxanes with POSS side groups synthesized in this study are soluble in many organic solvents, so they can be used for silicon coating materials with good chemical and mechanical stability. Transparent coating materials having high chemical and mechanical properties could be prepared if some cross-linkable moieties such as acryl groups are included in the polysiloxanes with POSS groups during the post-curing process using heating or UV irradiation. Such work is in progress.

#### 4. Conclusion

A series of polysiloxane derivatives with different amounts of POSS groups in the side chain were prepared for the first time. Poly(ethylhydrosiloxane) was used as starting polymer because it has high enough molecular weight to prepare reproducible polymer products with small amounts of POSS groups. Platinum(0)-divinyl tetramethyldisiloxane was used as a catalyst for the hydrosilylation reaction of poly(ethylhydrosiloxane) to prevent the formation of hydroxyl and alkoxy side groups which can cause the cross-linking of the polymers. 1-Octene was used to protect the Si–H groups in the side chains to prevent the reactions of Si–H in

the polymer backbone with hydroxyl groups. As the POSS content increases, glass transition temperature, decomposition temperature, char yield, modulus, and viscosity increase. For example when the content of POSS-containing monomeric units increased from 0 to 7 mol%, the zero-shear viscosity values at 0.1 shear rate increase from 8.3 to 70.9 Pa s. Even free standing films could be prepared from the polysiloxanes with POSS monomeric units of more than 10 mol%.

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#### Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2010.01.066.

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