# Preparation, Characterization, and Properties of Poly(aryl ether sulfone) Systems with Double-Decker Silsesquioxane in the Main Chains by Reactive Blending

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ABSTRACT: A series of copoly(aryl ether sulfone)s containing double-decker-shaped silsesquioxane (DDSQ) in the main chain was prepared. Toward this end, a novel diphenol polyhedral oligomeric silsesquioxane macromer was synthesized by hydrosilylation between 3,13-dihydro octaphenyl double-decker silsesquioxane (denoted dihydro DDSQ) and eugenol. The poly(aryl ether sulfone)s were synthesized from diphenol DDSQ, bisphenol A (BPA), and 4-fluorophenyl sulfone using a onestep high-temperature solution method. By adjusting the ratio of diphenol DDSQ to BPA, copolymers with variable DDSQ content in the main chains were obtained. With increased DDSQ content in the main chain, the glass transition temperature decreased based on differential scanning calorimetry, and

INTRODUCTION Organic-inorganic hybrid materials are attracting considerable interest because they offer the opportunity to develop high-performance materials that combine many desirable properties of conventional organic and inorganic components, such as thermal stability, solubility, and processability.<sup>1</sup> Silsesquioxanes exist in a variety of structures, from random polymers to more ordered arrangements,<sup>2,3</sup> In particular, polyhedral oligomeric silsesquioxanes (POSSs) are a class of nanoscale molecule having a welldefined cube-like inorganic core (Si<sub>8</sub>O<sub>12</sub>) with its corners connected to eight organic functional groups.<sup>4</sup> The  $Si_8O_{12}$ core can have a wide variety of functional groups attached to each vertex of the core, leading to the use of POSSs in various applications.<sup>5</sup> POSSs are cube-octameric molecules of nanoscale dimensions that may be functionalized with reactive groups suitable for the synthesis of new organic-inorganic hybrids, thereby providing the opportunity to design and build materials with extremely well-defined dimensions possessing and nanophase behavior.<sup>6</sup> The rigid inorganic core of POSSs provides the strength and oxidative stability of a ceramic, whereas synthesis control over the organic coronae (R) provides processability and compatibility with other

**KEYWORDS**: dielectric properties; double-decker-shaped silsesquioxane (DDSQ); high performance polymers; macromonomers; nanocomposites; polysiloxanes; surface hydrophobicity; WAXS

materials. Given that the number and type of functional groups on POSS cages can be readily varied, POSS molecules are excellent building blocks for preparing organic–inorganic hybrid nanocomposites with lots of structures, such as linear,<sup>7–9</sup> star-shaped,<sup>10–12</sup> as well as network types.<sup>13–17</sup> Moreover, using POSS derivatives as a monomer has proven to be an efficient method of designing nanocomposite material and side chains<sup>18</sup> or end groups<sup>19</sup> in hybrid polymers. Surface and interfacial properties lie at the heart of many potential POSS applications, but information on the surface properties of POSSs is limited.<sup>20–22</sup> Furthermore, POSSs have a low dielectric constant because of their porosity.<sup>23–25</sup> Incorporation of a POSS into a polymer can reduce the dielectric constant of a nanocomposite.<sup>26</sup>

Recently, POSS-containing polymers have become the focus of many studies because these hybrid materials possess the combined properties of organic and inorganic components with the inclusion of well-defined nanosized building blocks.<sup>27-34</sup> Chemical approaches have been demonstrated to be efficient in introducing POSSs into polymers by the formation of chemical linkages between POSS cages and

anti-degradation was enhanced based on thermogravimetric analysis. Moreover, the dielectric constant  $\kappa$  of pure polymer (3.19 at 1 MHz) initially increased to 4.04 (DDSQ molar ratio = 10%), and then decreased to 2.68 at 1 MHz (DDSQ molar ratio = 100%). Crystallization behavior, solubility, and surface hydrophobicity were also investigated. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 780–788

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polymer matrices.<sup>35</sup> In a majority of the previous studies, POSS macromers bearing single polymerizable (or reactive) groups were either grafted onto polymer chains by radical copolymerization (reactive grafting) or capped to the ends of polymer chains.<sup>36–39</sup> Given that the double-decker-shaped silsesquioxane (DDSQ) possesses precisely two reactive hydrosilane groups, linear organic–inorganic hybrid polymers should be obtainable without cross-linking.<sup>40–45</sup>

Poly(arylene ether sulfone)s (PAESs) are important engineering thermoplastics with excellent resistance to chlorinated disinfectants, hydrolysis, and oxidation, as well as excellent mechanical properties, such as thermal stability and toughness.<sup>46</sup> To the best of our knowledge, no previous reports exist on the modification of PAES using DDSQ in the main chain.

In this article, we synthesize of a novel DDSQ aromatic disphenol macromer by hydrosilylation of eugenol with dihydro-DDSQ and its subsequent reaction with difluorophenyl sulfones and bisphenol A (BPA) to produce a series of linear containing DDSQ in the main chain hybrid PAESs. However, previous reports about low dielectric constant ( $\kappa$ ) materials focused on macroscopic influence on  $\kappa$  of homopolymers with DDSQ in the main chain. In contrast, in this article, both the free volume of chain entanglement and free volume of POSS self-cage are discussed in terms of their microcosmic effects on the  $\kappa$  of hybrid copolymers. The thermal and surface properties as well as crystallization behavior were also investigated.

### EXPERIMENTAL

#### Materials

Phenyltrimethoxysilane was purchased from Energy-Chemical and used without further purification. Methyldichlorosilane (AR) and BPA (AR) were purchased from Aladdin Industrial Corporation. Anhydrous magnesium and anhydrous calcium chloride were purchased from Guangdong Xilong Chemical. Triethylamine (AR) was purchased from Tianjin Fuyu Fine Chemical. Tetrahydrofuran (THF) (AR) was purchased from Tianjin Tiantai Fine Chemicals. Toluene (AR), chloroform (AR), ethyl acetate (AR), sodium hydroxide (AR), potassium carbonate (AR), N,N-dimethylacetamide (DMAc; AR), dimethyl sulfoxideand (DMSO; AR), and 2propanol (AR) were purchased from Beijing Chemical Works. N-methyl-2-pyrrolidinone (NMP; AR) and potassium carbonate (AR) were purchased from Tianjin BODI chemicals. NMP was further purified by distillation under reduced pressure over calcium hydride. Before use, the THF was refluxed above sodium and then distilled.

#### Methods

Differential scanning calocalorimetry (DSC) analysis was performed using a Mettler-Toledo Instrument DSC  $821^{e}$ -modulated thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen purge of 200 mL min<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pryis 1 TGA analyzer at a heating rate of 10 °C min<sup>-1</sup> under a

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nitrogen or air purge of 100 mL min<sup>-1</sup>. Infrared (IR) spectra were recorded with a Nicolet Impact 410 FTIR spectrophotometer by KBr pellet with a measurement from 400 cm<sup>-1</sup> to 4000  $\text{cm}^{-1}$ . Gel permeation chromatography (GPC) analysis was carried out using Waters 410 instrument with dimethylformamide (DMF) as an eluent and polystyrene as the standard. Hydrogen-1 nuclear magnetic resonance (<sup>1</sup>H NMR) was performed on a Brüker Advance 300 spectrometer (300 MHz), and <sup>29</sup>Si NMR was performed on a Brüker 510 NMR spectrometer (500 MHz). The solutions were measured using tetramethylsilane as an internal reference. The MALDI-TOF-MS experiment was performed using a Shimadzu/AMIMA-CFR. The matrix 2,5-dihydroxybenzoic acid 98% was dissolved in THF (10 mg  $mL^{-1}$ ) and mixed with the sample solution (0.5 mg mL<sup>-1</sup>-1.0 mg mL<sup>-1</sup> in THF) at a v/v ratio of 1:1. The samples were dried in air for at least 30 min and the measurements were taken in linear mode with a UV laser (337 nm). The spectra were calibrated using bradykinin dissolved in THF (10 mg  $mL^{-1}$ ) and mixed with the sample solution 0.5 mg mL<sup>-1</sup>–1.0° mg mL<sup>-1</sup>. The  $\kappa$  of the thin films coated with silver by vacuum evaporation were obtained using a Hewlett-Packard 4285A apparatus at room temperature and at frequencies from  $10^3$  Hz to  $10^6$  Hz. The crystallization behaviors of the hybrid polymer and control PAES were examined using a Rigaku D/max-2500 X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 0.154$  nm) as the X-ray source. Contact angle measurements were performed at room temperature using a POWEREACH/JC2002C2 contact angle meter with pure water as probe liquid. The dispersion of the POSS clusters in the polymer matrix was observed from SSX-550 Shimadzu scanning electron microscope (SEM).

#### **Monomer Synthesis**

# Synthesis of 3,13-Di(2-methoxy-4-propylphenol)octaphenyl DDSQ

3,13-Di(2-methoxy-4-propylphenol)octaphenyl DDSQ (diphenol DDSQ) was synthesized by hydrosilylation reaction between 3,13-dihydrooctaphenylhexacyclodecasiloxane (dihydro-DDSQ) synthesized according to the method reported by Seino et al.<sup>1</sup> and eugenol, catalyzed by Karstedt's catalyst, as shown in Scheme 1. Typically, a 50 mL two-necked roundbottomed flask equipped with a magnetic stirrer, a nitrogen inlet, and an anhydrous calcium chloride drying tube were connected to a Schlenk line to degas by a repeated exhausting-refilling process using pure nitrogen. DDSQ (2.3 g, 2 mmol), eugenol (0.69 g, 4.2 mmol), and toluene (20 mL) were then added. With 30 min of vigorous stirring, the reaction was conducted with the catalysis of Karstedt's catalyst (5 drops of 0.2 mol %) in toluene at 95 °C for 24 h to yield diphenol DDSQ. The mixture was then held for 12 h at 105 °C with stirring to insure that the hydrosilylation reached completion. The solvent and excess eugenol were removed under reduced pressure to yield the nearly colorless solids with a yield of 92%. <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ ): 0.30 (s, 3H, Si-CH<sub>3</sub>), 0.77 (t, 2H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 1.67 (t, 2H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 2.42 (t, 2H, SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 3.52 (s, 3H, CH<sub>3</sub>-O), 6.32-6.35 (d, 1H, Ar H), 6.50-6.55 (m, 2H, AR H), 7.17–7.751 (m, 20H, AR H of Si-Ph), 8.62 (s,1H,-OH). <sup>13</sup>C



**SCHEME 1** Synthesis of 3,13-di(2-methoxy-4-propylphenol)oc-taphenyl DDSQ.

NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ ): 15.72, 24.58, 37.79, 55.24, 112.17, 115.15, 120.21, 128.14, 129.91, 131.00, 132.50, 133.24, 144.36, and 147.21. <sup>29</sup>Si NMR (500MHz; DMSO- $d_6$ ;  $\delta$ ): -17.33, -77.32, -78.56, -78.80, -78.88, and -79.48. MALDI-TOF-MASS spectroscopy [m/z (%)]: 1481.6 (M<sup>+</sup>, 43%); 1505.0 ([M + Na] <sup>+</sup>, 100), calculated: 1505.2 Da.

## Polymer Synthesis

### Synthesis of Hybrid Silicon PAESs

The novel poly(ether sulfones of bisphenol A) (PSF) copolymers with POSS in the main chains were synthesized by aromatic substituted reaction between diphenol [BPA and/or diphenol DDSQ] and 4-fluorophenyl sulfone as depicted in Scheme 2. By adjusting the molar ratio of diphenol DDSQ to BPA, a series of DDSQ/PSF copolymers was obtained. Typically, for the preparation of 50%-DDSQPSF copolymer, to a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap with a condenser were added BPA (1.140 g, 5 mmol), 4-Fluorophenyl sulfone (2.542 g, 10 mmol), diphenol DDSQ (0.7410 g, 5 mmol), anhydrous  $K_2CO_3$  (1.794 g, 13 mmol), DMSO (18 mL), and toluene (7 mL). The system was allowed to reflux for 3 h, and then a substantial amount of the resulting water and toluene were removed. The reaction mixture was heated to 180 °C-190 °C. After 6 h, another 10 mL of DMSO was added to the viscous reaction mixture. The polymerization was complete after another 2 h. The viscous solution was then poured into distilled water. The flexible threadlike polymer was pulverized into powder using a blender. The polymer was then refluxed in deionized water and ethanol several times to remove the salts and solvents and dried at 120 °C for 24 h to obtain a constant weight. The yield was 92%. All the organic-inorganic PSF with DDSQ in the main chains were subjected to GPC to measure their molecular weights. The GPC profiles were shown in Table 2. In all cases, highmolecular-weight products were obtained. In fact, the GPC result of 5%-DDSQPSF displayed longer elution time. This observation suggests that there could be some components that possessed lower molecular weights in the resulting polymers, which were not easy to grow into highermolecular-weight species. Similar results of polymerization have been reported in other organic-inorganic copolymers with POSS in the main chains.<sup>1,42,45,47</sup>

#### **Film Preparation**

A total of 1 g copolymer was dissolved into 10 mL DMAc, keeping under magnetic stirring for 24 h, and was then filtered. The filtrate was poured on a 8 cm  $\times$  8 cm glass plate. The programmed temperature was increased from 60 °C to 120 °C at a heating rate of 10 °C h<sup>-1</sup> and dried for 48 h to remove the solution completely. A series of novel PAES hybrid films were finally obtained. The blending films were prepared in a same procedure, with a mass content of 3,13-di(2-methoxy-4-propylphenol)octaphenyl DDSQ in polymer equal to that in hybrid films.

#### **RESULTS AND DISCUSSION**

#### **Structure Characterization**

In this article, direct polymerization between difluoromethyl sulfone and diphenol *via* nucleophilic substitution reaction catalyzed by Lewis bases (*e.g.*, potassium carbonate) was employed to afford PAES. The diphenol-functionalized POSS macromer (*viz.*, diphenol DDSQ) was synthesized *via* a three-step approach, as shown in Scheme 1. First, octaphenyldicycloocatasiloxane



SCHEME 2 Synthesis of hybrid poly(aryl ether sulfone)s.

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**FIGURE 1** <sup>1</sup>H NMR spectrum of 3,13-di(2-methoxy-4-propylphenol)octaphenyl DDSQ.

tetrasodium silanolate [Na<sub>4</sub>O<sub>14</sub>Si<sub>8</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>8</sub>] was synthesized by following the method reported by Seino et al.<sup>1</sup> Second, the silylation reaction between  $Na_4O_{14}Si_8(C_6H_5)_8$  and methyldichlorosilane (HSiCH<sub>3</sub>Cl<sub>2</sub>) was conducted obtain 3,13to dihydrooctaphenyl DDSQ (i.e., dihydro-DDSQ). Thereafter, the hydrosilylation reaction between dihydro-DDSQ and eugenol was performed to afford 3,13-di(2-methoxy-4-propylphenol)octaphenyl double-decker silsesquioxane (viz., diphenol DDSQ). The <sup>29</sup>Si NMR spectrum of di(2-methoxy-4-propylphenol)octaphenyl double-decked silsesquioxane (diphenol DDSQ) is shown in Figure 3. The resonance at -17.33 ppm was ascribed to the silicon nucleus connected to methyl group whereas the signals of resonance in the range -77.3 ppm to -79.4 ppm were ascribed to other silicon nuclei of the POSS cage. The resonance at -17.33 ppm, -77.32 ppm, and -78.8 ppm were ascribed to the silicon nucleus of the POSS cage in trans configuration and the resonance at -17.33 ppm, -77.32 ppm, -78.56 ppm, and -79.48 ppm were assigned to the silicon nucleus of the POSS cages in *cis* configuration.<sup>48</sup> The <sup>1</sup>H NMR spectra of di(2methoxy-4-propylphenol)octaphenyl DDSQ are shown in Figure 1. Signals of resonance appeared at 0.77 ppm, 1.67 ppm, 2.41 ppm, 3.52 ppm, 6.32-6.35 ppm, and 6.50-6.55 ppm, which were assigned to the protons of 2-methoxy-4-propylphenol groups. The ratio of the integration intensity of signals at 0.77 ppm, 1.67 ppm, and 2.41 ppm was 1:1:1, which well agreed with the value calculated according to the structural formula, suggesting that the hydrosilylation was complete. The 3,13-di(2-methoxy-4-propylphenol)octaphenyl DDSQ was subjected to MALDI-TOF-MS spectroscopy to measure its molecular weight and the mass spectrum is presented in Figure 2. The POSS macromer possessed the molecular weight of M = 1482.0 (viz., 1505.0–23), which perfectly matched the value calculated according to the structural formula (Fig. 3). The results of <sup>29</sup>Si NMR, <sup>1</sup>H NMR, and mass spectroscopy indicated that diphenol DDSQ was successfully obtained. The structure of the synthesized 50%-DDSQPSF polymer was confirmed by <sup>1</sup>H NMR and FTIR spectra. The <sup>1</sup>H NMR spectra obtained with a 500 MHz Bruker 510 spectrometer



**FIGURE 2** MALDI-TOF-MS spectrum of 3,13-di(2-methoxy-4-propylphenol)octaphenyl DDSQ.

and using deuterated dimethylsulfoxide as a solvent were displayed in Figure 4. The peaks from 6.5 ppm to 8.0 ppm were assigned to the protons of aromatic ring, the single peaks at 3.45 ppm and 0.64 ppm were assigned to alkyl in the main chain, and the single peaks at 0.15 ppm and 1.63 ppm were assigned to methyl.

IR (KBr) spectrum of pure PSF polymer is shown in Figure 5(a): 1013 cm<sup>-1</sup> (Ar), 1102 cm<sup>-1</sup>, and 1153 cm<sup>-1</sup> (O=S=O sym—), 1240 cm<sup>-1</sup> (C=O=C), 1296 cm<sup>-1</sup>, and 1320 cm<sup>-1</sup> (O=S=O asym—). The results of IR and <sup>1</sup>H NMR confirmed that the copolymer was synthesized successfully.

The structure of the prepared DDSQ/PSF hybrid films were confirmed by IR (KBr) spectra, as shown in Figure 5(b-f):  $1255 \text{ cm}^{-1}$  and  $830 \text{ cm}^{-1}$ could be assigned to Si—C band,



FIGURE 3 <sup>29</sup>Si NMR spectrum of 3,13-di(2-methoxy-4-propyl-phenol)octaphenyl DDSQ.



FIGURE 4 <sup>1</sup>H NMR spectrum of 50%-DDSQPSF copolymer in  $d_6$ -DMSO.

and 1071 cm<sup>-1</sup> and 480 cm<sup>-1</sup> could be attributed to Si-0 band of the DDSQ. From the comparison with IR spectrum of pure PSF polymer Figure 5(a), the typical absorption band at 1255 cm<sup>-1</sup>, 830 cm<sup>-1</sup> of Si-C band, and 1071 cm<sup>-1</sup>, 480 cm<sup>-1</sup> of Si-O band in the skeleton of DDSQ disappeared. In summary, Figure 5 confirms that DDSQ nanoparticles were successfully introduced into the main chains of the polymer by covalent bonds.

# Crystallization Behavior of Pure Dihydro-DDSQ and DDSQ/PSF Hybrids Films

In Figure 6, the solid state pure dihydro-DDSQ exhibited multiple sharp diffraction peaks at  $2\theta = 6.1^{\circ}$ ,  $7.0^{\circ}$ ,  $8.0^{\circ}$ ,  $8.7^{\circ}$ ,  $10.1^{\circ}$ ,  $11.4^{\circ}$ ,  $12.0^{\circ}$ ,  $16.6^{\circ}$ ,  $18.3^{\circ}$ ,  $19.1^{\circ}$ ,  $19.8^{\circ}$ ,  $20.5^{\circ}$ , and  $24.9^{\circ}$ , respectively, suggesting that the pure dihydro-DDSQ formed a crystalline structure. The pure 0%-DDSQPSF only exhibited a diffuse peak at  $2\theta = 18.3^{\circ}$ , and the rest of DDSQPSF hybrid films exhibited two diffuse peaks at  $2\theta = 18.3^{\circ}$  and  $2\theta = 7.3^{\circ}$ , respectively. The diffuse peak at



**FIGURE 5** IR spectra of (a) 0%-DDSQPSF, (b) 5%-DDSQPSF, (c) 10%-DDSQPSF, (d) 20%-DDSQPSF, (e) 50%-DDSQPSF, (f) 100%-DDSQPSF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 6** WAXD profiles of (a) pure 3,13-dihydrooctaphenyl DDSQ, (b) 0%-DDSQPSF, (c) 5%-DDSQPSF, (d) 10%-DDSQPSF, (e) 20%-DDSQPSF, (f) 50%-DDSQPSF, and (g) 100%-DDSQPSF hybrids films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 $2\theta = 7.3^{\circ}$  observed in the diffraction curve of hybrid films indicated that the DDSQ molecules still retained their nanoscale dimensions in the polymer main chain. The peak intensity of  $2\theta = 7.3^{\circ}$  increased as the amount of DDSQ in the polymer increased. A similar phenomenon is observed for hybrid films in other systems.<sup>49–52</sup> In addition, the disappearing crystalline structure also indicated the successful introduction of the POSSs into the main chain of the copolymer.

# Dielectric Constant of Pure PSF, DDSQ/PSF Hybrid Films, and Blending Films

Figure 7(a) presents the  $\kappa$  of pure PSF and DDSQ/PSF hybrid films at a frequency ranging from 1000 Hz to 1 MHz, and Figure 7(b) summarizes the variation of their  $\kappa$  along with the contents of POSSs at 1 MHz. Figure 7(a) shows that when the molar ratio of diphenol DDSQ to 4-fluorophenyl sulfone was 5:5 or higher,  $\kappa$  of organic–inorganic copolymers were lower than those of pure PSF. Nonetheless,  $\kappa$  values of the copolymers were higher than that of pure PSF. The content of POSSs in the main chain molar percent was 10%, and  $\kappa$  was the largest at nearly 4.04. This article proposed that the following opposite tendencies affect the  $\kappa$  of the organic-inorganic copolymers. On the one hand, the introduction of vacant cage-like structure of the POSS macromer into the main chains of copolymers simultaneously resulted in the increase in the free volume of the main chain in the copolymers, which reduced  $\kappa$ . On the other hand, the introduction of the bulky and vacant cage-like structure of the POSS macromer resulted in the polymer chains unable to undo chain entanglements because the POSSs existed in place of the phenoxy structural units in the main chains of the copolymers, causing the free volume of chain to decrease. This decrease resulted in the decreased of the amount of copolymers. Moreover, as the content of POSSs in



FIGURE 7 (a) Frequency dependence of dielectric constants of DDSQ/PSF hybrid films; (b) plot of dielectric constants at 1 MHz as a function of the content of POSS in the organic-inorganic copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 1 Dielectric Cons	tant of blending films
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Polymer

Samples	0%-DDSQPSF	Blending polymer 1	Blending polymer 2	Blending polymer 3	Blending polymer 4	Blending polymer 5
Dielectric constant	3.19	3.14	3.08	3.37	-	-

Dielectric constants were measured at 1 MHz.



FIGURE 8 SEM photographs of (a) blending polymer 1 film; (b) blending polymer 2 film; (c) blending polymer 3 film; and (d) the image of blending polymer 4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Samples	T <sub>g</sub> (°C) <sup>a</sup>	<i>T</i> d₅ (°C) <sup>b</sup>	Contact angle (°)	Dielectric constant ( $\kappa$ ) <sup>c</sup>	Residue (%) <sup>d</sup>	<i>M</i> <sub>n</sub>	$M_{\rm w}/M_{\rm n}$
0%-DDSQPSF	194	444.5	78.2	3.19	0.0	92,795	1.20
5%-DDSQPSF	184	430.2	81.3	3.32	5.2	48,107	4.18
10%-DDSQPSF	174	416.4	87.4	4.04	8.7	44,708	1.25
20%-DDSQPSF	167	398.6	91.5	3.56	15.6	31,586	1.84
50%-DDSQPSF	156	376.4	92.5	2.78	28.8	11,270	1.49
100%-DDSQPSF	130	377.3	97.5	2.68	36.6	9861	1.32

TABLE 2 Summary of the Properties of the POSS-PSF

<sup>a</sup> DSC at a heating rate of 10 °C min<sup>-1</sup> in nitrogen.

 $^{\rm b}$  Temperature at which 5% weight loss was recorded by thermogravimetry at a heating rate of 10  $^{\circ}{\rm C}$  min $^{-1}$  in air.

the main chain increased, the trend of chain entanglements worsened, and the trend of free volume of organic-inorganic POSS cage changed. When the POSS content in the main chain was low, the increased free volume of organic-inorganic POSS cage could not counteract the decreased free volume resulting from chain stretching. However, with the molar ratio content of POSSs in the main chain increasing by 10% or higher, the free volume of POSS cage was increased by POSS cage introduction, in which one part was used to counteract the decreased free volume of chain stretching and the other part was used to enhance the free volume of copolymer; thus, the decrease in  $\kappa$ . This article proposed that if the POSS content in the main chain is low, free volume formed by chain entanglements becomes dominant, whereas if the POSS content in the main chain is high, free volume of POSSs itself dominates.

The dielectric constant of blending of POSS and poly(aryl ether sulfone) with different contents at 1 MHz was summarized in Table 1. The mass percentage of POSS in blending polymer 1, 2, 3, 4, 5 was equal to that in 5%-DDSQPSF, 10%-DDSQPSF, 20%-DDSQPSF, 50%-DDSQPSF, 100%-DDSQPSF, respectively. Meanwhile, due to hydrogen bonding interactions of 3,13-di(2-methoxy-4-propylphenol)octaphenyl DDSQ in blending polymers, blending films occurred too obvious phase separation to form a film when the mass content of POSS was increasing to equal to that in 50%-DDSQPSF or more. Phase separation of blending polymer 4 was shown in Figure 8(d). The dielectric constant (at 1 MHz) of blending polymer 1 and blending polymer 2 was decreasing with the content of POSS increasing. It was mainly due to the POSS hollow cage introduction. However, the  $\kappa$  of blending polymer 3 was higher than blending polymer 1 and blending polymer 2. That was because of numerous phenolic hydroxyl groups of 3,13-di(2-methoxy-4propylphenol)octaphenyl DDSQ in blending polymer 3 settling to the surface of film, shown in Figure 8(c), while the POSS of blending polymer 1 and blending polymer 2 was uniformly dispersed in blending films, shown in Figure 8(a,b). Blending polymer films had lower  $\kappa$  than hybrid polymer films with the same mass content of POSS, due to chain entanglements caused by the POSS in hybrid polymer. However, when the mass content of POSS was high, hybrid poly<sup>c</sup> The dielectric constant was measured at 1 MHz.

 $^{\rm d}$  The yields of degradation residues were taken as the values at 800  $^\circ \rm C$  in air.

mer films had lower  $\kappa$  while blending polymer could not form a film.

#### Surface Properties and Solubility of PSF Copolymers

Organosilicon compound of the POSS moiety was introduced into the PSF copolymers, which was of low free energy. The surface hydrophobicity of the PSF copolymers is expected to improve compared with pure PSF. This effect can be readily examined by measuring contact angles. In this article, the static surface contact angles were measured with water as probe liquids, and the results are summarized in Table 2. The water contact angle of pure PSF was ca. 78.2°. For 100%-DDSQPSF, the water contact angle was as high as 97.5°, indicating that the hydrophobicity of the materials was significantly enhanced. Compared with pure PSF, the water contact angles of the PSF copolymers were dramatically enhanced. The water contact angles increased as the POSS content in the copolymers increased (Fig. 9). The water contact angles became almost impartial to the molar ratio of DDSQ, suggesting that the surfaces of the organic-inorganic copolymers were saturated by the organosilicon moieties (viz. POSSs).



**FIGURE 9** Plot of surface water contact angles as a function of the content of POSS in the organic–inorganic copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Samples	DMAc	DMSO	DMF	THF	Chloroform	Acetone	Methanol
0%-DDSQPSF	+	+-	+	+	+	-	-
5%-DDSQPSF	+	+-	+-	+-	+-	_	-
10%-DDSQPSF	+-	+-	+-	+-	+-	_	-
20%-DDSQPSF	+-	+-	+-	+-	+-	_	_
50%-DDSQPSF	+-	+-	+-	-	-	_	-
100%-DDSQPSF	+-	+-	+-	_	_	_	_

#### TABLE 3 Solubility of POSS-PSF

Solubility under a mass of liquid: 0.1 g mL<sup>-1</sup>; + soluble at room temperature; - insoluble even on heating; +- partially soluble or swelling on heating.

The solubility of PSF copolymers is shown in Table 3. With the introduction of nanoscale POSSs into the main chain of polymers, the solubility of copolymers worsened.

#### **Thermal Properties of PSF Copolymers**

The organic-inorganic PSF copolymers were subjected to DSC to measure their  $T_{\rm g}$ . The values of  $T_{\rm g}$  are summarized in Table 2. The data indicated that the  $T_{\rm g}$  values of the materials changed with the content of DDSQ in the main chain of copolymers. The  $T_{\rm g}$  of 0%-DDSQPSF was about 192 °C, and  $T_{\rm g}$  of 100%-DDSQPSF was about 130 °C. This article proposed that the following opposite tendencies affected the  $T_{g}$ of the organic-inorganic copolymers. On the one hand, the nanoreinforcement of POSS cages in the main chains resulted in the enhanced  $T_{\rm g}$ . On the other hand, the introduction of POSSs into the main chains of copolymers simultaneously resulted in the increase in free volume in the copolymers. The increased free volume was responsible for the introduction of the bulky and vacant cage-like Si-O structure of the POSS macromer, which resulted in the polymer chains being unable to densely pack in the glassy state because the bulky and cage-like POSSs exist in place of the phenoxy structural units in the main chains of the copolymers. Introducing the



**FIGURE 10** TGA curves of PSF and the POSS-containing PSF copolymers in air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

POSS structure and the straight chain alkyl led to a lower  $T_{\rm g}$ value. As a consequence, the  $T_{\rm g}$  values of the copolymers decreased. The thermal stability of the organic-inorganic copolymers was evaluated using TGA and the TGA curves are shown in Figure 10. All copolymers displayed two steps in the degradation progress. The first step originated from the degradation of active alkyl chain and the second step originated from the degradation of frameworks, such as the aromatic ring and POSS cage. The temperatures at the maximum rate of degradation of all the copolymers were significantly higher than those of pure PSF, suggesting that the presence of POSS moiety in the main chains retarded the random-chain scission. The organic-inorganic copolymers displayed higher residuals of degradation than pure PSF, and the yields of the degradation residues increased as the POSS content increased. The increased yields of degradation residues were ascribed to the ceramic formation from POSS moiety during thermal decomposition.

## CONCLUSIONS

In this article, a novel 3,13-di(2-methoxy-4-propylphenol)octaphenyl double-decker silsesquioxane, which is a difunctional POSS macromer, was successfully synthesized. The diphenol POSS macromere was used to prepare organicinorganic PSF copolymers with POSSs in the main chains via direct polymerization based on the nucleophilic substitution reaction. By adjusting the molar ratio of BPA to di(2methoxy-4-propylphenol)octaphenyl DDSQ, a series of PSF copolymers with variable POSS contents was successfully obtained. These PSF copolymers were characterized by NMR spectroscopy and GPC. DSC showed that the  $T_{g}$  of the organic-inorganic PSF copolymers was relatively dependent on the composition of the copolymers. TGA indicated that the stability of the copolymers was significantly improved in terms of the temperatures at the maximum rate of degradation and the yields of degradation residues. Owing to the presence of POSSs in the main chains, the surface hydrophobicity of the organic-inorganic copolymers was significantly improved compared with those of the pure PSF, which only related to the POSS amount in the main chain. Hybrid films could get a lower  $\kappa$  than blending films. Meanwhile, in hybrid films,  $\kappa$  was affected by the combined effects of free volume of chain entanglement and the POSS cavity of the

main chain. When the POSS content in main chain was low, the free volume produced by chain entanglements dominated, and  $\kappa$  was decided by the extent of chain entanglements. In contrast, when the POSS content in the main chain was high, the free volume of POSS cavity dominated, and  $\kappa$  was determined by the amount of POSS cavity. Moreover, with the nanoscale POSS introduction into main chain of polymer, the solubility worsened.

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