Organic–Inorganic Copolymers with Double-Decker Silsesquioxane in the Main Chains by Polymerization via Click Chemistry

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ABSTRACT: A series of novel organic–inorganic copolymers with polyhedral oligomeric silsesquioxane (POSS) in the main chains were synthesized via the copper-catalyzed Huisgen 1,3-dipolar cycloaddition polymerization approach. Toward this end, we synthesized 3,13-azidopropyloctaphenyl double-decked silsesquioxane (DDSQ). This difunctional POSS macromer was used to copolymerize with α, ω -dialkynyl-terminated oligoethylenes with variable number of ethylene units. The organic–inorganic copolymers were obtained with the mass fraction of POSS up to 79%. Gel permeation chromatography showed that the high-molecular-weight copolymers were successfully obtained in all the cases. Differential scanning calorimetry showed that the amplitude of glass transitions for these copolymers was very feeble, suggesting that the segmental

INTRODUCTION Combining inorganic (or organometallic) with organic segments (or blocks) is an effective approach to obtain organic-inorganic hybrid materials with new and improved properties. Polyhedral oligomeric silsesquioxanes (POSS) are a class of interesting building blocks for organicinorganic hybrids. A typical POSS molecule is composed of a cage-like Si-O framework and several organic groups covalently bonded to each Si atom, one or more of which is reactive. Owing to the well-defined nanosized cage-like structure and organometallic features, POSS macromers together with POSS-containing organic-inorganic hybrids have been the focuses of a great number of studies in the past years.^{1–7} In terms of the functionality of POSS macromers, a variety of approaches can be designed and utilized to incorporate POSS cages into organic polymers. The POSS macromers bearing single polymerizable (or reactive) groups are introduced into organic polymers via either copolymerization or reactive grafting techniques. Alternatively, monofunctional POSS macromers can be bonded to the ends of organic polymer chains to obtain the so-called POSS-capped telechelics.⁸⁻¹⁵ In these organic-inorganic hybrids, POSS cages behave as either pendent side groups or end groups in polymers; the main

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motions responsible for the glass transitions was highly restricted with DDSQ cages in the main chains. Thermogravimetric analysis showed that the organic-inorganic hybrid copolymers displayed extremely high thermal stability. Contact angle measurements showed that these organic-inorganic copolymers are highly hydrophobic and possessed very low surface energy. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

KEYWORDS: click chemistry; double-decked silsesquioxane (DDSQ); high-performance polymers; inorganic polymers; nanocomposites; organic-inorganic copolymers; polyhedral oligomeric silsesquioxane (POSS); step-growth polymerization; structure-property relations; thermomechanical properties

chains of organic polymers remain unchanged. In addition to monofunctional POSS macromers, multifunctional POSS macromers have also been employed to access the POSScontaining nanocomposites.^{16–30} In this category of POSScontaining hybrids, POSS cages act as bulky nanocrosslinkers to participate in the formation of polymer networks. Owing to the formation of crosslinked networks, these POSScontaining hybrids are no longer soluble in organic solvents and cannot be processed as linear polymers.

It is desirable to prepare linear POSS-containing polymers with POSS in the main chains for many applications. The key to the organic-inorganic hybrids is efficiently to obtain welldefined difunctional POSS macromers, with which the organic-inorganic hybrids would be synthesized via stepgrowth polymerization approach. Nonetheless, such a study remained largely unexplored because the efficient and precise synthesis of difunctional POSS macromers is long a challenging task. Recently, there have been a few reports on the synthesis of several difunctional POSS macromers, which have been employed to prepare the organic-inorganic hybrids with POSS in the main chains of organic polymers.

1

In 2003, Wright and coworkers³¹ first reported the synthesis of a POSS framework bearing two anilino ligands; this difunctional POSS macromer was used as one of the copolymerization monomers to afford the organic-inorganic polyimides with POSS in the main chains. It was found that the glass transition temperatures $(T_{\rho s})$ and the curing kinetics of phenyl-ethynyl-terminated imide resins remained unaffected with the inclusion of POSS units in the main chains. Recently, Kakimoto and coworkers³²⁻³⁴ reported the synthesis of double-decker silsesquioxanes (DDSQ), a class of novel difunctional POSS macromers. These DDSQ macromers have been incorporated into the main chains of polyimide and polysiloxanes. By the use of two new DDSQ macromers, Zheng and coworkers^{35,36} synthesized the organic-inorganic poly(hydroxyether of bisphenol A) and polyurethane with DDSQ in the main chains. These organic-inorganic copolymers with DDSQ in the main chains displayed some excellent thermomechanical properties. More recently, Laine and coworkers^{37,38} reported the preparation of difunctional POSS macromers via fluorine ion-catalyzed rearrangement of octasilsesquioxanes bearing different functional groups and these difunctional POSS macromers can be used to prepare the soluble polymers called beads on a chain polymers. Owing to the nanoscaled size, these difunctional POSS macromers could exhibit relatively low mobility (or reactivity) in the polymerization compared to low-molecular organic monomers. Therefore, it is of interest to perform the polymerization of the nanoscaled POSS macromers via highly efficient reactions such as click chemistry.^{39,40} To the best of our knowledge, there has been no previous report yet.

In this contribution, we reported the synthesis of a class of novel organic-inorganic copolymers with DDSQ in the main chains via copper-catalyzed 1,3-dipolar cycloaddition polymerization (i.e., a polymerization via click chemistry). Toward this end, we first reported the synthesis of 3,13-azidopropyloctaphenyl DDSQ and several α, ω -dialkynyl-terminated oligoethylenes. Thereafter, the step-growth polymerization based on the click chemistry was carried out to afford the targeting copolymers. To the best of our knowledge, there has been no previous report on the synthesis of organic-inorganic hybrid copolymers with POSS in the main chains via click chemistry polymerization approach. The purpose of this study is twofold: (i) to examine the effect of a highly efficient polymerization approach on the polymerization behavior of the nanoscaled POSS macromers and (ii) to examine the thermomechanical properties of the organic-inorganic copolymers with POSS in the main chains with the high mass fraction of DDSQ up to 79%.

EXPERIMENTAL

Materials

Phenyltrimethoxysilane (98%) was obtained from Zhejiang Chemical Technology (China) and methyldichlorosilane was purchased from Aldrich Co. (USA) and they were used as received. Karstedt catalyst (viz. the complex of Platinum with divinyltetramethyldisiloxane dissolved in toluene at the concentration of 2 wt %) was prepared by following the method described in the previously published literature.⁴¹ Ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,10decanediol, allyl bromide, propargly bromide, sodium azide, and sodium hydride (60 wt %) were supplied by Shanghai Reagent (China). *N*,*N*,*N'*,*N'*,*N''*-pentamethyldiethylenetriamine (PMDETA) was purchased from Aldrich and used as received. Copper (I) bromide (CuBr) was purchased from Shanghai Reagent (China). Unless specially indicated, all other reagents were purchased from Shanghai Reagent (China). The solvents such as toluene, tetrahydrofuran (THF), isopropyl alcohol, triethylamine, methanol, N,N'-dimethylformamide (DMF), and 1,4-dioxane were of chemically pure grade, obtained from commercial sources. Before use, toluene, 1,4-dioxane, and THF were refluxed above sodium and then distilled and stored in the presence of a molecular sieve of 4 Å; triethylamine was refluxed over CaH2 and then was treated with ptoluenesulfonyl chloride, followed by distillation; DMF was distilled over calcium hydride (CaH₂) under decreased pressure and then stored in a sealed vessel with the molecular sieve of 4 Å. Before use, ethylene glycol and 1,4-butanediol were distilled under reduced pressure; 1,6-hexanediol, 1,8octanediol, and 1,10-decanediol were dried via azeotropic distillation with anhydrous toluene.

Synthesis of 3,13-Dihydrooctphenyl DDSQ

Typically, phenyltrimethoxysiloxane (31.7 g, 0.16 mol), isopropyl alcohol (160 mL), deionized water (3.33 g, 0.185 mol), and sodium hydroxide (4.267 g, 0.107 mol) were charged to a flask equipped with a condenser and a magnetic stirrer. After refluxed for 4 h, the reactive system was cooled to room temperature with vigorous stirring for additional 15 h. All the solvents and other volatile compounds were removed via rotary evaporation and the white solids were obtained. After dried at 60 °C in vacuo for 12 h, the product (i.e., $Na_4O_{14}Si_8(C_6H_5)_8^{42}$) (22.7 g) was obtained with the yield of 98%. The silvlation reaction between $Na_4O_{14}Si_8(C_6H_5)_8$ and methyldichlorosilane was carried out to afford 3,13-dihydrooctaphenylhexacyclodecasiloxane (denoted dihydro DDSQ). Typically, Na₄O₁₄ $Si_8(C_6H_5)_8$ (22.48 g, 19.4 mmol) and triethylamine (5.83 mL, 57.6 mmol) were charged to a flask equipped with a magnetic stirrer, 200 mL of anhydrous THF were added with vigorous stirring. The flask was immersed into an ice-water bath and purged with highly pure nitrogen for 1 h. Then, methyldichlorosilane (6.77 g, 57.6 mmol) dissolved in 10 mL of anhydorus THF was added dropwise within 30 min. The reaction was performed at 0 °C for 4 h and at room temperature for 20 h. The insoluable solids (i.e., sodium chloride and unreacted tetrasodium silanolate) were removed by centrifugation and the solvents together with other volatile compounds were eliminated via rotary evaporation to afford the white solids. The solids were washed three times with 100 mL of methanol and dried in vacuo at 40 °C for 24 h and the product (9.60 g) was obtained with the yield of 43%.

Fourier transform infrared spectra (FTIR) (cm⁻¹, KBr windows): 2175 (v_s , Si—H), 1131 (v_s , Si—O—Si). ¹H NMR (ppm, CDCl₃): 0.38 (*d*, 6.0H, C**H**₃—Si), 4.98 (*d*, 2.0H, Si**H**), 7.14–7.50

(*m*, 40H, protons of aromatic ring); ²⁹Si NMR (ppm, CDCl₃): -32.72, -77.73, -79.02, -79.21, and -79.42. MALDI-TOF-mass (product + Na⁺): 1176.1 Da.

Synthesis of 3,13-Dibrompropyloctaphenyl DDSQ

To a flask equipped with a magnetic stirrer, 1,13-dihydro DDSQ (5.44 g, 4.71 mmol), anhydrous toluene (50 mL) and allyl bromide (2.28 g, 18.84 mmol) were charged. The flask was connected to a Schlenk line to degas by a repeated exhausting-refilling process with highly pure nitrogen and the Karstedt catalyst was added with vigorous stirring. The hydrosilylation was performed at 95 °C for 36 h. The solvents were removed via rotary evaporation and a viscous liquid was afforded. The solids were washed with 100 mL of methanol twice. After dried *in vacuo* at 40 °C for 24 h, the product (5.73 g) was obtained with the yield of 87%.

FTIR (cm⁻¹, KBr windows):1131 (v_s , Si–O–Si), 571 (v_s , C–Br). ¹H NMR (ppm, CDCl₃): 7.14–7.50 (*m*, 40H, protons of aromatic ring), 0.32 [*s*, 3H, –OSiCH₃CH₂CH₂CH₂Br], 0.85 [*m*, 2H, –OSiCH₃CH₂CH₂CH₂Br], 1.94 [*m*, 2H, –OSiCH₃CH₂CH₂CH₂Br], et al. (CH₂Br], and 3.27 [*m*, 2H, –OSiCH₃CH₂CH₂CH₂CH₂Br]. ²⁹Si NMR (ppm, CDCl₃): –18.5, –78.3, and –79.5 ppm.

Synthesis of 3,13-Diazidopropyloctaphenyl DDSQ

To a flask equipped with a magnetic stirrer, 3,13-dibromopropyloctaphenyl DDSQ (5.0 g, 3.58 mmol), sodium azide (1.40 g, 21.48 mmol), and anhydrous THF (100 mL) were charged and 100 mL of anhydrous DMF was added at room temperature with vigorous stirring. The reaction was performed at room temperature for 24 h. The resultant mixture was dropped in 50 mL of the mixtures of methanol with water (volume, 50/50) to afford the precipitates. This procedure was repeated thrice to purify the product. After dried in a vacuum oven at 40 °C for 24 h, the product (3.93 g) was obtained with the yield of 83%.

FTIR (cm⁻¹, KBr windows): 2098 (v_s , $-N_3$), 1131 (v_s , Si-0-Si). ¹H NMR (ppm, CDCl₃): 7.14–7.50 (*m*, 40H, protons of aromatic ring), 0.32 (*s*, 3.1H, -0SiCH₃CH₂CH₂CH₂CH₂N₃), 0.77 [*m*, 2.0H, -0SiCH₃CH₂CH₂CH₂CH₂N₃, 1.68 [*m*, 2.2H, -0SiCH₃CH₂CH₂CH₂N₃], 3.13 [*t*, 2.0H, OSiCH₃CH₂CH₂CH₂CH₂N₃].

Synthesis of a, ω -Dialkynyl-terminated Oligoethylenes

To a 250-mL flask equipped with a magnetic stirrer, sodium hydride (2.03 g, 50.75 mmol) and anhydrous THF (100 mL) were changed and then one diol (12.69 mmol) dissolved in 50 mL of anhydrous THF was added to the flask. At room temperature, the mixture was stirred for 3 h and then 4.53 g (38.06 mmol) propargyl bromide dissolved in 30 mL of anhydrous THF was added dropwise within 30 min. After the reaction was performed at room temperature for 24 h, the salts (NaBr and excess NaH) were removed via filtration and the solution was concentrated with rotary evaporation. After the top oil layer was isolated and eliminated, the liquid product was obtained. The product was subjected to ¹H NMR spectroscopy:

1,2-Dipropargyloxyethane: 4.20 (*t*, 4H, CH≡CCH₂O−), 3.71 (*d*, 4H, −OC**H**₂C**H**₂O−), 2.43 (*t*, 2H, −C**H**≡CCH₂O−);

1,4-Dipropargyloxybutane: 4.12 (*d*, 4H, −CH≡CC**H**₂O−), 3.53 (*m*, 4H, −OC**H**₂CH₂CH₂CH₂O−), 2.41 (*t*, 2H, −CH≡CCH₂O−), 1.67 (*m*, 4H, −OCH₂C**H**₂C**H**₂CH₂CH₂O−);

1,6-Dipropargyloxyhexane: 4.12 (d, 4H, -CH \equiv CC H_2 0-), 3.50 (t, 4H, -OC H_2 CH₂CH₂CH₂CH₂CH₂CH₂O-), 2.41 (t, 2H, -C $H \equiv$ CCH₂O-), 1.60 (m, 4H, -OCH₂C H_2 CH₂CH₂CH₂CH₂CH₂O-), 1.38 (m, 4H, -OCH₂CH₂CH₂CH₂CH₂CH₂O-);

1,8-Dipropargyloxyoctane, 4.12 (d, 4H, -CH \equiv CCH₂O-), 3.50 [t, 4H, -OCH₂CH₂(CH₂CH₂)₂CH₂CH₂O-], 2.41 (t, 2H, -CH \equiv CCH₂O-), 1.58 [m, 4H, -OCH₂CH₂(CH₂CH₂)₂CH₂CH₂O-], 1.32 [m, 8H, -OCH₂CH₂(CH₂CH₂)₂CH₂CH₂O-];

1,10-Dipropargyloxydecane (dissolved in DMSO- d_6): 4.30 (t, 2H, –CH=CCH₂O–), 3.35 (q, 4H, –CH=CC H_2 O–), 1.38 [m, 4H, –OCH₂(CH₂CH₂)₄C H_2 O–], 1.22 [m, 12H, –OCH₂(C H_2 C H_2)₄ C H_2 O–].

Synthesis of Organic–Inorganic Copolymers via Click Polymerization

To a flask equipped with a magnetic stirrer, one α, ω -dialkynyl-terminated oligoethylene (1.0 mmol), 3,13-diazidopropyloctaphenyl DDSQ (1.32 g, 1.00 mmol), PMDETA (0.21 ml, 0.10 mmol), and 1,4-dioxane (10 mL) were charged. The system was purged with argon for 30 min and then CuBr (0.14g, 1.00 mmol) was added. Then, the system was purged with argon for additional 5 min. The polymerization was performed at 50 °C for at least 24 h. After cooled to room temperature, 20 mL of THF was added to the reacted mixture and the solution was passed through a basic alumina column to remove the catalyst and the solution was concentrated via rotary evaporation and dropped into 200 mL of nhexane to afford the precipitates. The resulting product was obtained after dried in vacuo at 30 °C for 24 h. The polymers were subjected to gel permeation chromatography (GPC) to measure the molecular weights and molecular weight distribution and the results of the polymerizations are summarized in Table 1.

Measurement and Techniques

Nuclear Magnetic Resonance Spectroscopy

The ¹H NMR measurements were carried out on a Varian Mercury Plus 400 MHz NMR spectrometer at 25 °C. The samples were dissolved with deuterated chloroform (CD₃Cl) or dimethylsulfone (DMSO- d_6) and the solutions were measured with tetramethylsilane as an internal reference.

Matrix-Assisted Ultraviolet Laser Desorption/Ionization Time-of-Flight Mass Spectroscopy

Gentisic acid (2,5-dihydroxybenzoic acid) was used as the matrix with dichloromethane as the solvent. The matrixassisted ultraviolet laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) experiment was carried out on an IonSpec HiResMALDI mass spectrometer equipped with a pulsed nitrogen laser ($\lambda = 337$ nm; pulse with = 3 ns). This instrument was operated at an accelerating potential of 20 kV in reflector mode. Sodium is used as the cationizing agent and all the data shown are for positive ions.



Samples	DDSQ (wt %)	Number of Ethylene Units ^a	M _n	$M_{\rm w}/M_{\rm n}$
Poly(DDSQ-C2)	79.0	1	15,800	1.45
Poly(DDSQ-C4)	77.6	2	16,500	1.37
Poly(DDSQ-C6)	76.1	3	13,600	1.37
Poly(DDSQ-C8)	74.7	4	19,400	1.34
Poly(DDSQ-C10)	73.4	5	16,300	1.33

TABLE 1 Results of Click Polymerizations of 3,13-Diazidopropyloctaphenyl DDSQ with a, w-Dialkynyl-Terminated oligoethylenes

^a Number of ethylene units in α, ω -dialkynyl-terminated oligoethylenes.

Gel Permeation Chromatography

The molecular weights and molecular weight distribution of polymers were determined on a Waters 1515 GPC system equipped with Waters RH columns, an Isocratic HPLC pump equipped with a RI detector. The measurements were carried out with *N*,*N*-dimethylformamide (DMF) as the eluent at the flow rate of 1.0 mL/min.

Differential Scanning Calorimetry

Calorimetric measurements were performed on a TA Instruments Q2000 differential scanning calorimeter in dry nitrogen atmosphere. The instrument was calibrated with a standard indium. To measure glass transition temperature ($T_{\rm g}$) a heating rate of 20 °C/min was used in all cases. $T_{\rm g}$ was taken as the midpoint of the heat capacity change.

Wide-Angle X-ray Diffraction

The wide-angle X-ray diffraction (XRD) experiments were carried out on a Shimadzu XRD-6000 X-ray diffractometer with CuK_{α} (λ = 0.154 nm) irradiation at 40 kV and 30 mA using a Ni filter. Data were recorded in the range of 2 θ = 5-50° at the scanning rate and step size of 5.0°/min and 0.02°, respectively.

Thermal Gravimetric Analysis

A TA Instruments Q5000 thermal gravimetric analyzer was used to investigate the thermal stability of the polymers. The measurements were conducted in nitrogen atmosphere from ambient temperature to 800 °C at the heating rate of 20 °C/ min. The temperature of initial degradation (T_d) was taken as the onset temperature at which 5 wt % of weight loss occurs.

Surface Contact Angle Analysis

The solutions (10 wt %) of the organic–inorganic alternating copolymer samples dissolved in THF were spin-coated onto the clean and flat surface of glass slides with the thickness of 20 μ m; the majority of solvent was evaporated at room temperature and the residual solvent was eliminated in a vacuum oven at 30 °C for 12 h. The film specimens were subjected to the measurement of static contract angles. The static contact angle measurements with ultrapure water and ethylene glycol as the probe liquid were carried out at room temperature on a DSA30 contact angle measurement apparatus (Krüss GmbH, Germany).

RESULTS AND DISCUSSION

Synthesis of 3,13-Diazidopropyloctaphenyl DDSQ

In a previous study, Kawakami and coworkers⁴³ reported the synthesis of 3,13-dichloropropyloctaphenyl DDSQ via the silvlation reaction of double-decker octasilsesquioxane tetraol tetrasodium salt [viz. Na₄O₁₄Si₈(C₆H₅)₈] with 3-chloro proplydichlorosilane. The 3,13-dichloropropyloctaphenyl DDSQ was then employed to perform the substitution reaction with sodium azide to afford 3,13-diazidopropyloctaphenyl DDSQ. In this study, a different approach was utilized to obtain this difunctional POSS macromer. The route of synthesis for 3,13-diazidopropyloctaphenyl DDSQ is shown in Scheme 1. First, the double-decker octasilsesquioxane tetraol tetrasodium salt [viz. Na₄O₁₄Si₈(C₆H₅)₈] was synthesized via hydrolysis and rearrangement of phenyltrimethoxysiloxane in the presence of isopropyl alcohol, water, and sodium hydroxide by following the approach reported by Seino et al.41 Thereafter, the silylation reaction of double-decker octasilsesquioxane tetraol tetrasodium salt [viz. Na₄O₁₄₋ $Si_8(C_6H_5)_8$ with dichlorosilane was carried out to obtain 3,13-dihydrooctphenyl DDSQ.³⁵ The ²⁹Si NMR spectroscopy indicated the formation of DDSQ cage containing two Si-H bonds.³⁵ This compound was subjected to MS to measure its molecular weight and the MALDI-TOF-MS spectrum is shown in Figure 1. It is seen that the POSS macromer possessed the molecular weight of M = 1153.1 (viz. 11,176.1-23), which is in accordance with the value calculated according to the structural formulation (Scheme 1). The hydrosilylation reaction between 3,13-dihydrooctphenyl DDSQ and allyl bromide was carried out to obtain 3,13-dibrompropyloctphenyl DDSQ. Figure 2 shows the ²⁹Si NMR spectrum of 3,13-dibrompropyloctphenyl DDSQ. For comparison, the ²⁹Si NMR spectrum is also incorporated into this figure. It is noted that with the occurrence of the hydrosilylation reaction, the signal of resonance at -32.7 ppm assignable to the silicon nucleus connected to Si-H bond fully shifted to -18.2 ppm, whereas the resonance at -79.3 and -77.8 ppm remained almost invariant. The ²⁹Si NMR spectroscopy indicates that the hydrosilylation reaction between 3,13-dihydrooctphenyl DDSQ and allyl bromide was carried out to completion. With 3,13-dibrompropyloctphenyl DDSQ, 3,13-diazidopropyloctphenyl DDSQ can be obtained via the substitution reaction between 3,13-dibromopropyloctphenyl DDSQ and sodium



SCHEME 1 Synthesis of 3,13-diazidopropyloctaphenyl DDSQ and α , ω -dialkynyl-terminated oligoethylenes.



FIGURE 1 MALDI-TOF mass spectrum of 3,13-dihydrooctphenyl DDSQ.





FIGURE 2 ²⁹Si NMR spectra of 3,13-dihydrophenyl, 3,13-dibromopropyloctphenyl DDSQ.

azide (NaN₃) (Scheme 1). The ¹H NMR spectra of 3,13-dihydrooctphenyl, 3,13-dibromopropyloctphenyl, and 3,13-diazidopropyloctphenyl DDSQ are shown in Figure 3. With the occurrence of 3,13-dihydrooctphenyl DDSQ with allyl bromide, the resonance of silicon nucleus at 5.0 ppm, which is assignable to the proton of Si-H bond fully disappeared, suggesting that the hydrosilylation reaction has been performed to completion. Concurrently, there appeared several signals of resonance at 0.86, 1.95, and 3.3 ppm, respectively, which are assignable to the protons of the methylene connected to corner silicon atom, the middle methylene, and the methylene connected to bromine atom in 3-bromoproply group. It is worth noticing that the signal of resonance at about 1.4 ppm assignable to protons of methyl groups was hardly discernible. This observation suggests that the under the present condition the hydrosilylation was carried out almost in the α -addition manner. With the occurrence of the substitution between 3,13-dibrompropyloctphenyl DDSQ and sodium azide (NaN₃), the signals of resonance at 1.95 and 3.30 ppm fully shifted to 1.66 and 3.10 ppm, respectively. This observation indicates that the substitution reaction underwent to completion. The ¹H, ²⁹Si, and MALDI-TOF-MS spectroscopy indicates that 3,13-diazidopropyloctphenyl DDSQ (viz. the difunctional POSS monomer) was successfully obtained.

Synthesis of α,ω-Dialkynyl-terminated Oligoethylenes

The α,ω -dialkynyl-terminated oligoethylenes with the number of ethylene units up to five were synthesized with the substitution reactions of the corresponding diols with propargly bromide in the presence of sodium hydride (NaH). Figure 4 shows the ¹H NMR spectra of α,ω -dialkynyl-terminated oligoethylenes with variable number of ethylene units. In all the cases, the signals of resonance at 2.41 ppm were displayed in the ¹H NMR spectra, which are assignable to the protons of alkynyl groups. According to the ratio of the integral intensity of the proton resonance at this position to those of other methylene protons, it is judged that all the terminal hydroxyl groups of these diols were capped with propargly groups, that is, α,ω -dialkynyl-terminated oligoethylenes with variable number of ethylene units were successfully obtained.

Polymerization via Click Chemistry

With 3,13-diazidopropyloctaphenyl DDSQ and α,ω -dialkynylterminated oligoethylenes, the polymerizations based on the copper-catalyzed Huisgen 1,3-dipolar cycloaddition were carried out to obtain the organic–inorganic hybrid polymers with DDSQ in the main chains as shown in Scheme 2. In all the cases, the molar ratio of 3,13-diazidopropyloctaphenyl DDSQ and α,ω -dialkynyl-terminated oligoethylenes was



FIGURE 3 ¹H NMR spectra of 3,13-dihydro, 3,13-dibromopropyl, and 3,13-diazidopropyloctaphenyl DDSQ.

controlled to be 1:1. The viscosity of the systems increased with the reaction proceeding, implying the occurrence of the polymerizations. All the organic-inorganic copolymers were homogenous and transparent. These polymers were soluble in common solvents such as dichloromethane, chloroform, THF, and *N*,*N*'-dimethylformamide. Representatively shown in Figure 5 are the FTIR spectra of 3,13-diazidopropyloctaphenyl DDSQ, 1,6-dipropargyloxyhexane and their copolymer [viz. Poly(DDSQ-C6)]. For 3,13-diazidopropyloctaphenyl DDSQ, two intense bands at 2098 and 1131 cm⁻¹ were displayed. The former is characteristic of the stretching vibration of azido group $(-N_3)$, whereas the letter is assignable to Si-O-Si linkage in silsesquioxane cage. For 1,6-dipropargyloxyhexane, the band characteristic of the stretching vibration of alkynyl groups was detected at 2118 cm⁻¹. For Poly(DDSQ-C6), the two bands at 2098 and 2118 cm^{-1} were indiscernible, suggesting the occurrence of polymerization between 3,13-diazidopropyloctaphenyl DDSQ and 1,6-dipropargyloxyhexane. The organic-inorganic copolymers were subjected to ¹H NMR spectroscopy. Representatively shown in Figure 6 are the ¹H NMR spectra of poly(DDSQ-C2) and poly(DDSQ-C6). The organic-inorganic copolymers are characteristic of the signals of proton resonance at 0-2.5, 3.0-5.0, and 6.0-8.0 ppm, which are assignable to the protons of methyl, methylene, and phenyl groups as shown in Figure 6. For poly(DDSQ-C6), the signal of resonance at 7.75 ppm is discernible, assignable to the proton of methine groups in triazole structures which resulted from the copper-catalyzed



FIGURE 4 ¹H NMR spectra of 1,2-dipropargyloxyethane, 1,4dipropargyloxybutane, 1,6-dipropargyloxyhexane, 1,8-dipropargyloxybutane, and 1,10-dipropargyloxydecane (dissolved in DMSO- d_6).

Huisgen 1,3-dipolar cycloaddition reaction. Notably, with the occurrence of click polymerization, the signals of resonance assignable to the protons of methyl group connected to the corner Si atom of DDSQ were split into two components at 0.17 and 0.31 ppm, respectively. The similar result was also obtained for the resonance of methylene protons connected to this Si atom. The splitting of resonance signals could be associated with the formation of the bead-like polymer chain. It is plausible to propose that the shielding environment of the proton nucleus could be affected owing to the formation of the macromolecular chains. The ¹H NMR spectroscopy indicates that the resulting products combined the structural features from oligoethylenes and DDSQ. All the organic-inorganic copolymers were subjected to GPC to measure the molecular weights. The GPC profiles are shown in Figure 7 and the results of polymerization are summarized in Table 1. In all the cases, the high-molecular-weight products were obtained and the polydispersity indices of these organicinorganic copolymers were in the range of 1.33-1.45, suggesting that the polymerizations have been successfully carried out. It is noted that all these GPC profiles displayed the shoulder peaks at the longer retention times. These peaks at the low retention time did not disappear although we have prolonged the time of polymerizations. According to the values of retention time, the two separate peaks at the retention times of t = 19.9 and 20.8 min corresponded to the species with the molecular weights to be $M_{\rm n} = 5200$ and



SCHEME 2 Synthesis of organic-inorganic copolymers with DDSQ in the main chains.

3400, respectively (Fig. 7), which could be some oligomers (e.g., pentamer and trimer) typical of step-growth polymerizations.⁴⁴ It is noteworthy that the peaks of oligomers were more pronounced for the polymers, resulting from 3,13-diazidopropyloctaphenyl DDSQ with 1,2-dipropargyloxyethane and/or 1,4-dipropargyloxybutane. This observation could be related to the higher steric hindrance of reactions between the POSS macromer and the smaller dialkynyl monomers, which resulted that the step-growth polymerizations were not easy to grow into the higher-molecular-weight species although the highly efficient polymerization approach was employed.^{33,35} The results of ¹H NMR and GPC indicate that the organic-inorganic copolymers with DDSQ in the main chains were successfully obtained.

Characterization of Organic–Inorganic Copolymers Wide-angle X-ray Diffraction

The organic-inorganic copolymers were subjected to wideangle XRD. Figure 8 shows the XRD profiles of 3,13-diazidopropyloctaphenyl DDSQ and the organic-inorganic copolymers. In the diffraction curve of the POSS macromer, there were some sharp diffraction peaks, suggesting that this compound was crystallizable. For the organic-inorganic copolymers, the XRD curves displayed two broad amorphous halos at about $2\theta = 7.1$ and 19.8° , respectively, and no sharp diffraction peaks were detected. The results of XRD indicate that the organic-inorganic copolymers were no longer crystalline. It is seen that the diffraction peak at $2\theta = 7.1^\circ$ was



FIGURE 5 FTIR spectra of 3,13-diazidopropyloctaphenyl DDSQ, 3,13-diazidopropyloctaphenyl DDSQ, and poly(DDSQ-C6).



FIGURE 6 ¹H NMR spectra of poly(DDSQ-C2) and poly(DDSQ-C6).



FIGURE 7 GPC curves of organic–inorganic copolymers with DDSQ in the main chains.

detected in all the copolymers as in 3,13-diazidopropyloctaphenyl DDSQ. The diffraction peak is attributable to the aggregation of DDSQ moiety. It is proposed that there could be POSS aggregation in the organic–inorganic copolymers, that is, the copolymers could be microphase-separated. The similar observation was previously found in other POSScontaining polymers.^{8,45–47}



FIGURE 8 XRD profiles of 3,13-diazidopropyloctaphenyl DDSQ and the organic–inorganic copolymers with DDSQ in the main chains.

Differential Scanning Calorimetry

The organic-inorganic copolymers with DDSQ in the main chains were subjected to DSC and the DSC curves are shown in Figure 9. It is noted that in the range from -60 to 180 °C, the plots of heat flow as functions of temperature displayed the broad ramps and the amplitude of glass transitions was feeble. The DSC curves are in marked contrast to those of organic amorphous polymers, which is attributable to the formation of the organic-inorganic copolymers with POSS in the main chains. It is proposed that the amplitude of segmental motions responsible for glass transitions was significantly reduced with the POSS cages in the main chains. In other words, the macromolecular chains become highly rigid owing to the inclusion of DDSQ in the main chains.

Thermogravimetric Analysis

TGA was used to evaluate the thermal stability of the organic-inorganic copolymers and the TGA curves are shown in Figure 10. For comparison, both 3,13-diazidopropyloctaphenyl DDSQ and 1,6-dipropargyloxyhexane were also measured under the identical condition and their GPC profiles are also included in this figure. The initial slight degradation of 3,13-diazidopropyloctaphenyl DDSQ occurred at about 250 °C, whereas that of 1,6-dipropargyloxyhexane about 130 °C. It is proposed that the slight degradations of both the monomers resulted from the azido and alkynyl groups of some oligomers, respectively. All the organic-inorganic copolymers displayed the quite similar TGA profiles, suggesting that their mechanisms of thermal degradations were quite close. Notably, these organic-inorganic copolymers underwent the slight degradations at about 200 °C. It is proposed that the slight



FIGURE 9 DSC curves of the organic-inorganic copolymers with DDSQ in the main chains.

9



 $\ensuremath{\textit{FIGURE}}$ 10 TGA curves of the organic–inorganic copolymers with DDSQ in the main chains.

degradations result from the terminal groups of the copolymers (i.e., azido and/or alkynyl groups). After the initial slight degradations at about 200 °C, these organic-inorganic copolymers remained stable until 410 °C. For poly(DDSQ-C2), poly(DDSQ-C8), and poly(DDSQ-C10), the large weight loss occurred at about 510, 472, and 410 °C, respectively. For poly(DDSQ-C6) and poly(DDSQ-C4), the large weight loss started at the temperatures even as high as 568 and 550 $^\circ$ C, respectively. It is worth noticing that the large degradation temperatures (denoted T_2) of these organic-inorganic copolymers did not monotonously increase with increasing the mass fraction of DDSQ in the copolymers. Poly(DDSQ-C6) displayed the highest T_2 among all these copolymers. It is proposed that the following factors could affect the thermal stability of the organic-inorganic copolymers: (i) the mass fraction of DDSQ in the main chains and (ii) the number of ethylene units together with the molar percentage of triazole structural units in the main chains, which equals that of DDSQ. The inorganic component (viz. DDSQ) possessed the thermal stability much higher than that of the organic portions (i.e., ethylene units and triazole structural units). For poly(DDSQ-C2), the highest content of triazole structural units gave rise to its low thermal stability although the content of DDSQ was also the highest among all these organicinorganic copolymers. The low thermal stability could result from the thermal scission of the chains at triazole structural units. For the copolymers with longer ethylene units (e.g., poly(DDSQ-C8) and poly(DDSQ-C10)), the relatively low thermal stability is attributable to the lower contents of DDSQ. In addition, these organic-inorganic copolymers also displayed the high yields of degradation residues. In all the cases, the yields of degradation residues were as high as

Analysis of Surface Contact Angles

It is of interest to investigate the surface hydrophobicity of the organic-inorganic copolymers with DDSQ in the main chains. This surface dewettability was examined in terms of the measurement of contact angles. The static surface contact angles were measured with water and ethylene glycol as probe liquids, respectively; the results of measurements are summarized in Table 2. The values of water contact angles of all these copolymers were higher than 103° (Fig. 11), indicating that these copolymers were quite hydrophobic. It is of interest to note that the water contact angles increased with increasing the mass fraction of DDSQ in the main chains. The surface-free energies of the organic-inorganic copolymers were calculated according to the geometric mean model^{48–50}:

$$\cos\theta = \frac{2}{\gamma_{\rm L}} \left[(\gamma_{\rm L}^{\rm d} \gamma_{\rm s}^{\rm d})^{\frac{1}{2}} + (\gamma_{\rm L}^{\rm p} \gamma_{\rm s}^{\rm p})^{\frac{1}{2}} \right] - 1 \tag{1}$$

$$\gamma_{\rm s} = \gamma_{\rm s}^{\rm d} + \gamma_{\rm s}^{\rm p} \tag{2}$$

where θ is the contact angle and γ_L is the liquid surface tension; γ_s^{d} and γ_s^{p} are the dispersive and polar components of $\gamma_{\rm L}$ respectively. The total surface free energies of for all the organic-inorganic copolymers were calculated to be in the range of 9.3-11.5 mN/m. It is worth noticing that the polar component (γ_s^{p}) increased with increasing the number of ethylene units, whereas the dispersive component (γ_s^d) decreased with increasing the number of ethylene units in the organic-inorganic copolymers. This observation suggests that the percentage of DDSQ at the surface of the materials increased with increasing the number of ethylene units and the content of ethylene units at the surface of the copolymers decreased with increasing the number of ethylene unit. In other words, the DDSQ cages with the lower surface energy were enriched at the surface of the organicinorganic copolymers to minimize the polymer-air surface tension.51-54 The very low surface energy could endow the linear organic-inorganic hybrid copolymers with potential application as the highly hydrophobic coating materials.

TABLE 2 Static Contact Angles and Surface-free Energy of

 Organic–Inorganic Copolymers with DDSQ in the Main Chains

	Static Con	Surface Free Energy (mN/m)			
Sample	$\theta_{\rm H2O}$	$\theta_{\mathrm{ethylene}}$ glycol	γ^d_s	γ ^p s	γs
Poly(DDSQ-C2)	114.8 ± 0.36	99.5 ± 0.56	8.04	1.22	9.26
Poly(DDSQ-C4)	110.6 ± 0.44	96.2 ± 0.21	7.77	2.19	9.96
Poly(DDSQ-C6)	106.0 ± 0.99	93.4 ± 0.18	6.69	4.01	10.69
Poly(DDSQ-C8)	103.9 ± 0.72	92.1 ± 0.35	6.21	5.03	11.24
Poly(DDSQ-C10)	103.0 ± 0.11	91.6 ± 0.77	5.96	5.54	11.50



FIGURE 11 Plot of surface water contact angles as a function of mass fraction of DDSQ for the organic–inorganic copolymers.

CONCLUSIONS

In this study, we successfully synthesized 3,13-azidopropyloctaphenyl DDSQ. This difunctional POSS macromer was employed to copolymerize with α, ω -dialkynyl-terminated oligoethylenes with variable number of oligoethylene units by polymerization via the copper-catalyzed Huisgen 1,3-dipolar cycloaddition (viz. click chemistry). A series of novel organicinorganic copolymers were obtained with the mass fraction of POSS up to 79%. GPC showed that the high-molecularweight copolymers were successfully obtained in all the cases. Owing to the presence of DDSQ cages in the main chains, the macromolecular chains of these organic-inorganic copolymers were highly rigid. TGA showed that the organicinorganic hybrid copolymers displayed extremely high thermal stability. Contact angle measurements showed that these organic-inorganic copolymers are highly hydrophobic and possessed very low surface energy.

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The synthesis of a series of novel organic-inorganic copolymers with polyhedral oligomeric silsesquioxane (POSS) in the main chains is reported by polymerization via the copper-catalyzed Huisgen 1,3-dipolar cycloaddition. These organic-inorganic copolymers are highly rigid and display extremely high thermal stability. Contact angle measurements show that the copolymers are highly hydrophobic and possess very low surface energy.