Bulk and Surface Assembly of Branched Amphiphilic Polyhedral Oligomer Silsesquioxane Compounds

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This study probes the behavior of two series of organic-functionalized core—shell silsesquioxane (POSS-M)p-(x/y) derivatives with various hydrophobic—hydrophilic terminal group compositions in the bulk state and within monoand multilayered films at the air—water interface and on solid surface. POSS-M refers to mixed silsesquioxane cores, in contrast to the geometrically specific POSS compounds. It is composed of polyhedra, incompletely condensed polyhedra, ladder-type structures, linear structures, and all the possible combinations thereof and attracts great interest because of its facile preparation, low polydispersity, high yield, and low cost. The two series of (POSS-M)p-(x/y) molecules are different in hydrophobic—hydrophilic balance of their terminal groups, with x and y respectively referring to the molar percent of $-OCONH-C_{18}H_{37}$ tails and -OH for p = 1 and the percent of $-OCONH-C_{18}H_{37}$ tails and $-OCO-C_6H_4COOH$ terminal groups for p = 2. In the bulk state, the presence of aromatic rings in (POSS-M)p-(x/y) molecules that contain a sufficient amount of $-OCONH-C_{18}H_{37}$ tails exhibit double endothermic transition, which attributed to the melting of alkyl chains followed by the melting of the unit cells of (POSS-M) cores. The surface morphologies for the various hydrophobic—hydrophilic combinations at surface pressure p = 0.5 mN/m are similar to that observed for the classical amphiphilic star polymers. However, at higher surface pressure ($p \ge 5$ mN/m), the POSS-M compounds with lower content of hydrophilic groups form a uniform monolayer.

Introduction

Polyhedral oligomeric silsesquioxane (POSS) class is a recent intriguing example of nanostructured organic—inorganic building blocks having inorganic nanoscale cores surrounded by multiple terminal functionalities to be exploited for the fabrication of hybrid reinforced nanomaterials. Their well-defined geometric shapes resemble polyhedral nanoparticles with a general formula (R-SiO_{1.5})_n, where R represents any peripheral chemical functional groups.¹ Central cores (SiO_{1.5})_n are inert, stiff, and optically transparent.² Facile chemical modifications of POSS derivatives yield organic inorganic hybrid materials that are composed of highly dispersed soft-rigid aggregates. In their bulk state, POSS molecules containing multiple functional groups were found to crystallize into rhombohedral (trigonal) or hexagonal unit cells.^{3,4}

Numerous studies have shown that chemical functional groups can be covalently introduced at the periphery of POSS molecules, and the resulting core—shell structures could be incorporated into a polymer matrix as a reinforcing agent. This reinforcement affects their overall bulk-properties, including thermal and mechanical properties.^{5,6} POSS molecules blended with polymer matrices can either function as mechanical reinforcers or plasticizers, depending on the interactions between the polymer matrix and the POSS molecules.⁷ Mechanical strengthening in POSS-based composites

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- Schwab, J. J.; Lichtenhan, J. D. Appl. Organomet. Chem. 1998, 12, 707.
 Pescarmona, P. P.; Maschmeyer, T. Aust. J. Chem. 2001, 54, 583.
- (2) Pescalinona, F. F., Maschineyer, T. Aust. J. Chem. 2001, 54, 585. (3) Zheng, L.; Waddon, A. J.; Farris, J. R.; Coughlin, E. B. Macromolecules

(4) Waddon, A. J.; Coughlin, E. B. Chem. Mater. 2003, 15, 4555.

is due to the incorporation of stiff inorganic cores and their ability to restrict polymer chain mobility because of the relatively large size and cage-like structure.7 For example, an improved tensile and dynamic mechanical modulus was observed in trisilanolphenyl-POSS-polycarbonate composites.8 For improved mechanical properties in composite structures, matrix-filler compatibility at the interface is necessary.9 The high compatibility at the interface is due to its ease of functionalization to incorporate a suitable functional group on POSS peripheries for certain targeted application. Molecular dynamics calculations estimated the bulk modulus of octacyclopentyl polyhedral oligomeric silsesquioxane (CpPOSS) to be 7.5 GPa, which is significantly higher than that of conventional polymers (1-3 GPa)in glassy state).¹⁰ Monte Carlo calculations indicated that all polyhedral-shaped oligomer silsesquioxanes, including the incompletely condensed systems, are rigid, except for the two-dimensional ladder-shaped molecules.¹¹ In addition, the presence of POSSoctaphenyl in acrylate-based dental adhesive can reduce shrinkage of the acrylate system upon polymerization.¹² Furthermore, anhydridecured POSS/epoxy composites show high storage moduli and low coefficient of thermal expansion, and they are stable at high temperatures, making them suitable for applications in high temperature and temperature variable environment.¹³

While the synthesis of geometrically specific POSS moieties is plagued by relatively low yields of multistage syntheses, one alternative to exploit them for practical applications is to employ a more easily accessible mixture of POSS moieties, POSS-M, which

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^{2002, 35, 2375}

⁽⁵⁾ Carroll, J. B.; Waddon, A. J.; Nakade, H.; Rotello, V. M. *Macromolecules* **2003**, *36*, 6289.

⁽⁶⁾ Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W., Jr. *Macromolecules* 2007, 40, 9517.

⁽⁷⁾ Kopesky, E.; Haddad, T. S.; McKinley, G. H.; Cohen, R. E. *Polymer* **2005**, *46*, 4743.

⁽⁸⁾ Zhao, Y.; Schiraldi, D. A. Polymer 2005, 46, 11640.

⁽⁹⁾ Barbero, E. J. in *Introduction to Composite Materials Design*; Taylor & Francis Group: New York, 1999.

⁽¹⁰⁾ Capaldi, F. M.; Boyce, M. C.; Rutledge, G. C. J. Chem. Phys. 2006, 124, 214709.

⁽¹¹⁾ Hillson, S. D.; Smith, E.; Zeldin, M.; Parish, C. A. J. Phys. Chem. A 2005, 109, 8371.

⁽¹²⁾ Dodiuk-Kenig, H.; Maoz, Y.; Lizenboim, K.; Eppelbaum, I.; Zalsman, B.; Kenig, S. J. Adhesion Sci. Technol. 2006, 20, 1401.

⁽¹³⁾ Xiao, F.; Sun, Y.; Xiu, Y.; Wong, C. P. J. Appl. Polym. Sci. 2007, 104, 2113.



Figure 1. POSS-M composition, where Tn refers to the number of silicon corners for the three-dimensional cage-like POSS structures, where n is any integer. It denotes a completely condensed silsesquioxane structure. Figures are not drawn to scale.

can be prepared by short-synthetic steps with high yield.¹⁴⁻¹⁷ Such POSS-M compounds are composed of a mixture of polyhedra, incompletely condensed polyhedra, ladder type structures, open structures, linear structures, and all the possible combinations thereof (Figure 1).¹⁸ As it is well-known, the POSS-M cores are estimated to have a degree of condensation, n, varying between 12 and 18.¹⁵ Transmission electron microscopy shows the polyhedral POSS-M as highly dispersed round nanoparticles with an average particle size of 2.7 nm, which is much larger than the more common fully condensed hexahedral oligomeric silsesquioxanes (Figure 1).¹⁵ Asprepared POSS-M molecules are decorated with hydroxyl and tertiary amine groups at their periphery, onto which various functional groups can be attached, and has a general formula [(HOCH2CH(OH)-CH₂)₂N(CH₂)₃SiO_{1.5}]_n. Moreover, a high density of chemically bonded peripheral functional groups allows POSS molecules to disperse in common organic solvents. The presence of these functional groups can lead to the assembly of organized structures via specific interactions, e.g., hydrogen-bonding, acid-base interactions, electrostatic interactions, or chemical cross-linking.19,20

The surface behavior of functionalized POSS molecules is interesting from the point of view of the interfacial assembly process directed by the multifunctionalized nature of these molecules.²¹⁻²³ This class of compound has unique, well-defined organic-inorganic core-shell architecture, which gives it a rigid-soft character, while at the same time, it resembles hyperbranched molecules because of its highly functionalized character with multiple branches growing from a single center.²⁴ From this perspective, highly branched

- (18) Agaskar, P. A.; Klemperer, W. G. Inorg. Chim. Acta 1995, 229, 355. (19) Mori, H.; Müller, A. H. E.; Klee, J. E. J. Am. Chem. Soc. 2003, 125, 3712. (20) Mu, J.; Liu, Y.; Zheng, S. Polymer 2007, 48, 1176.
- (21) Mitsuishi, M.; Zhao, F.; Kim, Y.; Watanabe, A.; Miyashita, T. Chem. Mater. 2008, 20, 4310.
- (22) Deng, J.; Hottle, J. R.; Polidan, J. T.; Kim, H.-J.; Farmer-Creely, C. E.; Viers, B. D.; Esker, A. R. Langmuir 2004, 20, 109.
- (23) Deng, J.; Farmer-Creely, C. E.; Viers, B. D.; Esker, A. R. Langmuir 2004, 20. 2527.
- (24) Ornatska, M.; Peleshanko, S.; Genson, K. L.; Rybak, B.; Bergman, K. N.; Tsukruk, V. V. J. Am. Chem. Soc. 2004, 126, 9675.

POSS-M molecules are similar to hyperbranched and dendrimer molecules. For instance, similar to these highly branched molecules, POSS-based compounds exhibit higher solubility in organic solvents, easier processability, and lower viscosity than their linear analogues as a result of lower entanglements.²⁵ Recently, Tuteja et al. demonstrated that adding mixed -CF3 and -CF2 terminal groups onto POSS cores can create a superoleophobic surface with contact angles greater than 150°.26

It is not uncommon to observe long-range assemblies that are composed of unique macrostructures with well-defined shape and dimensions from highly branched amphiphilic species.^{27,28} For example, a systematic study of hyperbranched polyester containing variable compositions of alkyl tails, amino, and carboxyl groups showed that terminal groups can be responsible for the formation of monodispersed nanofibrillar morphology at a certain composition.^{29,30} Other forms of rigid nanoparticles combined with multiple terminal groups to control their aggregations have been widely demonstrated in the form of gold nanoparticles functionalized with amphiphilic polybutadiene-poly(ethylene glycol) (PB-PEG) V-shaped arms,³¹ polyethyleneoxide-functionalized buckyballs,³¹ polystyrene-functionalized gold nanorods,³³ silver-gold nanocobs³⁴ and CdTe quantum rods capped with a mixture of alkylphosphines.35 However, to date, unlike these fully organic branched amphiphilic compounds, the surface behavior of highly branched POSS-M compounds has been rarely addressed.

In this work, we investigate the role of the chemical composition of functionalized mixed POSS derivatives (POSS-M) that contain various molar ratios of hydrophobic and hydrophilic (hydroxilic and carboxylic) terminal groups on the bulk structure and on their surface

- (25) Seino, M.; Hayakawa, T.; Ishida, Y.; Kakimoto, M. Macromolecules 2006. 39. 8892.
- (26) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, H. H.; Cohen, R. E. Science 2007, 318, 1618. (27) Peleshanko, S.; Tsukruk, V. V. Prog. Polym. Sci. 2008, 33, 523.
- (28) Jiang, G.; Wang, L.; Chen, T.; Dong, X.; Yu, H.; Wang, J.; Chen, C. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 5554.
- (29) Ornatska, M.; Bergman, K. N.; Rybak, B.; Peleshanko, S.; Tsukruk, V. V. Angew. Chem., Int. Ed. 2004, 43, 5246.
- (30) Ornatska, M.; Bergman, K. N.; Goodman, M.; Peleshanko, S.; Shevchenko, V. V.; Tsukruk, V. V. Polymer 2006, 47, 8137
- (31) Genson, K. L.; Holzmueller, J.; Jiang, C.; Xu, J.; Gibson, J. D.; Zubarev, E. R.; Tsukruk, V. V. Langmuir 2006, 22, 7011.
- (32) Song, T.; Dai, S.; Tam, K. C.; Lee, S. Y.; Hoh, S. H. Langmuir 2003, 19 4798
- (33) Khanal, B. P.; Zubarev, E. R. Angew. Chem., Int. Ed. 2007, 46, 2195.

⁽¹⁴⁾ Bliznyuk, V. N.; Tereshchenko, T. A.; Gumenna, M. A.; Gomza, Yu. P.; Shevchuk, A. V.; Klimenko, N. S.; Shevchenko, V. V. Polymer 2008, 49, 2298. (15) Mori, H.; Lanzendörfer, M. G.; Muller, A. H. E.; Klee, J. E. Macromolecules

^{2004. 37. 5228.} (16) Muthukrishnan, S.; Plamper, F.; Mori, H.; Muller, A. H. E. Macromolecules 2005. 38, 10631.

⁽¹⁷⁾ Tereshchenko, T. A.; Shevchuk, A. V.; Shevchenko, V. V.; Snegir, S. V.; Pokrovskii, V. A. Polym. Sci. Ser. A 2006, 48, 1248.



Figure 2. Molecular models for mixed compositions and their corresponding chemical structure for equal amounts of hydrophilic/hydrophobic groups for (a) first series, (POSS-M)1-(x/y): $x = -OCO-NH-C_{18}H_{37}$ (hydrophobic) and y = -OH (hydrophilic); (b) second series, (POSS-M)2-(x/y): $x = -OCO-NH-C_{18}H_{37}$ (hydrophobic) and $y = -OCO-NH-C_{18}H_{37}$ (hydrophobic) for T16 cores. (x/y) is the hydrophobic/hydrophilic terminal group compositions.

behavior. The two sets of compounds studied here are abbreviated as (POSS-M)p(x/y), where x and y refer to the molar percent composition of hydrophobic and hydrophilic terminal groups, respectively. Specifically, x and y refer to $-OCONH-C_{18}H_{37}$ hydrophobic tails and -OH hydrophilic groups, respectively, for p = 1 and $-OCONH-C_{18}H_{37}$ hydrophobic tails and -OCO- C_6H_4COOH hydrophilic groups, respectively, for p = 2 (Figure 2). In these schematics, it is assumed that each corner contains four terminal groups, and the average core is presented by a T16 core, as suggested in the literature and confirmed from gel permeation chromatography (GPC) measurement (Figures 1 and 2). GPC measurement of the (POSS-M)1-(0/100) compound yields a polydispersity index of 1.1, and the number average molecular mass, $M_{\rm n}$ = 4040 g/mol, that corresponds to the molecular formula $[(HOCH_2CH(OH)CH_2)_2N(CH_2)_3SiO_{1.5}]_n$, with *n* approximately equal to 16 (see Supporting Information).¹⁴ Therefore, throughout this manuscript, we utilize the molecular model of the POSS-M derivatives as having a value of n = 16 Si corners (a T16 core). Also, it should be noted that, in this work, each of the 16 corners of the (POSS-M)1-(0/100) core contains four terminal groups (Figure 2). Hence, each of the POSS-M molecules contains a total of 64 terminal groups. The complete list of all compounds studied here is presented in Table 1.

Materials and Methods

Materials. POSS-M cores with different compositions of hydroxyl and *tert*-amine groups at their peripherals were synthesized with hydrolytic condensation of the product of the reaction between 3-aminopropyl triethoxysilane with a 2-fold molar excess of glycidol, according to the procedures well-described in the literature.^{15,17,19} The two series of samples were prepared by reaction of the hydroxyl POSS-M core with certain molar ratios of *n*-octadecylisocyanate for the first series, (POSS-M)1-(*x*/*y*): *x* = $-OCONH-C_{18}H_{37}$, *y* = -OH, and reaction with *n*-octadecylisocyanate and phthalic anhydride for the second series, (POSS-M)2-(*x*/*y*): *x* = $-OCONH-C_{18}H_{37}$, *y* =

Table 1. Molecular Weights and Silica-Core Composition of (POSS-M)p-(x/y) Molecules for p = 1 and p = 2.

sample names	solubility	$M_{ m n,theoret}$	core	$\% M_{\rm n}$, core ^a	% char
(POSS-M)1-(0/100)	H ₂ O, MeOH, DMF, DMSO	4128	832	20.2	30.5
(POSS-M)1-(25/75)	DMF, boiling DMF/toluene	8848	832	9.4	10.6
(POSS-M)1-(50/50)	boiling DMF	13 568	832	6.1	8.4
(POSS-M)1-(75/25)	boiling toluene	18 288	832	4.5	6.6
(POSS-M)2-(25/75)	boiling DMF	15 952	832	5.2	9.4
(POSS-M)2-(50/50)	DMF/toluene	18 304	832	4.5	6.6
(POSS-M)2-(75/25)	toluene	20 656	832	4.0	5.9
(POSS-M)2-(100/0)	boiling toluene	23 008	832	3.6	5.4

^a Estimated for T16 core composition (Figure 1).





^a (1) (POSS-M)1-(25/75); (2) (POSS-M)1-(50/50); (3) (POSS-M)1-(75/ 25); (4) (POSS-M)2-(100/0).

 $-OCO-C_6H_4$ -COOH ($M_n = 4128-23\ 008\ g/mol$), as described in detail earlier (Figure 2).³⁶ A brief description of its synthesis is presented below.

Synthesis of (POSS-M)1-(x/y). POSS-M and n-octadecylisocyanate were reacted with calculated ratios of OH/NCO equal to 4:1 (POSS-M)1-(25/75), 2:1 (POSS-M)1-(50/50), 4:3 (POSS-M)1-(75/25), and 1:1 (POSS-M)2-(100/0) (Scheme 1). For the synthesis of POSS1-(50/50), a solution of 5.73 g of n-octadecylisocyanate in 10 mL of benzene was added to a solution of 3 g of POSS-M in 8 mL of dimethylformamide (DMF). The mixture was stirred for 8 h at 80 °C. Upon cooling to ambient temperature, the product precipitated from solution. It was filtered and dried in vacuum at 60 °C until a constant mass was achieved. Yield was 86%. (POSS-M)1-(25/75) (yield was 90%), (POSS-M)1-(75/25) (yield was 91%), and (POSS-M)2-(100/0) (yield was 86%) were prepared in a similar way.

Synthesis of (POSS-M)2-(x/y). The corresponding (POSS-M)1-(x/y) were reacted with a calculated ratio of phthalic anhydride (Scheme 2). For the synthesis of POSS2-(50/50), a solution of 1.49 g of phthalic anhydride was added to a solution of 4.69 g of POSS1-(50/50) in a mixture of 5 mL of DMF and 5 mL of benzene with stirring at 80 °C. The synthesis was carried out for 8 h at 90 °C. At the ambient temperature, the product formed precipitate. It was filtered and dried in vacuum at 60 °C until a constant mass was achieved. Yield was 65%. (POSS-M)2-(25/75) (yield was 60%) and (POSS-M)2-(75/25) (yield was 71%) were prepared in a similar way.

Methods. Molecular models were built with Materials Studio 3.1. Langmuir and Langmuir-Blodgett (LB) monolayers were fabricated and studied with a KSV-2000 minitrough according to a standard procedure.37,38 The solution prepared for deposition consisted of a dilute (POSS-M)p-(x/y) dissolved in a methanol-

Scheme 2. The Synthesis of (POSS-M)2-(x/y)^a



^a (1) (POSS-M)1-(25/75); (2) (POSS-M)1-(50/50); (3) (POSS-M)1-(75/ 25); (5) (POSS-M)2-(25/75); (6) (POSS-M)2-(50/50); (7) (POSS-M)2-(75/ 25).

chloroform solvent mixture (1:10 ratio, HPLC grade). The volume of the solution ranged from 40 to 120 μ L, and the concentration ranged between 0.5 and 1.2 mg/mL. Higher concentration of (POSS-M)p-(x/y) require DMF or dimethyl sulfoxide (DMSO) solvents, or mixed solvents to dissolve into a transparent and homogeneous solution, sometimes with assisted heating (Table 1). Silicon wafers (Semiconductor Processing Co.) used for the deposition of LB films were cleaned according to well-established techniques in our laboratory.39 This preparation allowed for wafer decontamination of both organic and inorganic substances. The silicon wafers were first cut into rectangular pieces $(1.5 \times 3.0 \text{ cm})$ and submerged into Nanopure water (Nanopure, $18.2 \text{ M}\Omega$ cm). Next, they were sonicated at room temperature for 10 min and then treated with piranha solution (30% hydrogen peroxide, 70% concentrated sulfuric acid, hazardous solution) for 1 h. Lastly, these substrates were rinsed with Nanopure water and dried with a nitrogen stream. These substrates were prepared in a clean room environment. While dipping, the wafers moved at 2 mm/min and were allotted 30 s between each dip for multilayer deposition. Quartz slide preparation was similar. The minitrough was filled with Nanopure water, and the solution was then uniformly deposited in several droplets and subsequently left alone for 30 min to allow complete evaporation of the chloroform. The monolayers were then compressed at a rate of 5 mm/min before deposition. The value of the limiting cross-sectional area in condensed state, A_0 , was

⁽³⁴⁾ Gunawidjaja, R.; Peleshanko, S.; Ko, H.; Tsukruk, V. V. Adv. Mater. 2008, 20, 1544

⁽³⁵⁾ Zimnitsky, D.; Xu, J.; Lin, Z.; Tsukruk, V. V. Nanotechnology 2008, 10, 215606.

⁽³⁶⁾ Shevchenko, V. V.; Gumenna, M. A.; Shevchuk, A. V.; Gomza, Yu. P.; Klimenko, N. S.; Boichuk, V. V. Polym. Sci. Ser. A., in press.

⁽³⁷⁾ Small, D. M. The Physical Chemistry of Lipids; Plenum Press: New York, 1986.

⁽³⁸⁾ Ulman, A. An Introduction to Ultrathin Organic Films: From Langmuir Blodgett to Self Assembly; Academic Press: Boston, MA, 1991.

⁽³⁹⁾ Tsukruk, V. V.; Bliznyuk, V. N. Langmuir 1998, 14, 446.



Figure 3. FTIR spectra of (a) (POSS-M)1-(x/y) and (b) (POSS-M)2-(x/y).

derived from pressure—area isotherms by using the tangent line corresponding to the first steep rise in the surface pressure.³⁷

The effective thickness of LB monolayers was determined with a Woolam M2000U spectroscopic ellipsometer equipped with WVASE32 modeling software at three incident angles of 65° , 70° , and 75° , and within a wavelength range from 245 to 1000 nm. The effective thickness was determined by applying a multilayered model initially using the optical constants of the SiO₂ surface layer, followed by numerical fit of the refractive index (*n*), the absorption coefficient (*k*), and the thickness (*t*) at the three incident angles.

Surface morphologies were studied with a Dimension-3000 atomic force microscope (AFM) in the light tapping mode in the accordance with the usual procedure adapted in our laboratory.^{40,41} AFM images were captured at several random locations with surface areas ranging from $40 \times 40 \,\mu\text{m}^2$ to $1 \times 1 \,\mu\text{m}^2$. X-ray diffraction data were obtained with an Alpha1-Philips Analytical Instrument. Analysis of X-ray diffraction data was performed with MDI Jade 7 X-ray diffraction software. The TREOR90 algorithm was used for space group determination and peak assignments. Water contact angle values were acquired using a CAM100 System (KSV Instruments). UV– visible spectra were collected with a UV-2450 spectrophotometer (Shimadzu).

GPC measurements were carried out in a DMF solution using a Waters Breeze 1500 system with application of polystyrene calibrating standards. It is equipped with two sequentially joint Waters Styragel HR 3 THF columns with bore diameter of 4.6 mm and length of 300 mm, charged by polystyrene gel with a medial size of particles of 5 μ m. The temperature of the measurements was 35 °C, and the flow rate of the eluent was 0.3 mL/min. For the analysis, we used a 0.25% solution of polymer in DMF, with an inlet volume of 75 μ L. Infrared spectra were obtained on a "Tensor 37" Fourier transform infrared (FTIR) spectrometer (Bruker Optics). ¹H NMR spectra were obtained with a Bruker AMX400 nuclear magnetic resonance spectrometer. All samples, except (POSS-M)1-(0/100) were measured at 55 °C to get them completely dissolved in solution. (POSS-M)1-(0/100) and (POSS-M)2-(25/75) were dissolved in $(CD_3)_2SO$, and all others were dissolved in $(CD_3)_2SO/CDCl_3$ 2:8 solvent mixture at 10-15 mg/mL concentration.

Thermal analysis measurements were conducted on a TG-DTA/ DSC apparatus model STA 449 C Jupiter (Netzsch Instruments, Inc.) and differential scanning calorimetry (DSC) data on Q100 (TA Instruments). The scanning rate for thermogravimetric analysis (TGA) measurement was 5 °C/min. For multiple heating—cooling cycle measurements, the cooling rate for DSC measurement was 5 °C/ min, and the heating rate was 20 °C/min. Both experiments were performed under inert N₂ atmosphere. Two-heating—cooling cycles were utilized to eliminate thermal history.

Results and Discussions

Chemical Characterizations of (POSS-M)p(x/y). The chemical compositions of the two series of compounds that were synthesized from a common POSS-M core, i.e., (POSS-M)1-(0/100), were monitored with FTIR spectroscopy (Figure 3). The following peaks that represent the silsesquioxane core are observed in all eight samples: $1000-1180 \text{ cm}^{-1}$ (v Si-O-Si); $1240-1280 \text{ cm}^{-1}(v \text{ Si}-\text{CH}_2)$; and $2840 \text{ and } 2940 \text{ cm}^{-1}(v \text{ C}-\text{H})$. The broad peak within $3110-3650 \text{ cm}^{-1}$ (v OH) is evidence of the hydroxyl groups. The formation of urethane bond in all (POSS-M)1-(x/y) and (POSS-M)2-(x/y) samples, except for (POSS-M)1-(0/100) is observed upon introduction of $-OCO-NH-C_{18}H_{37}$ group by the appearance of a peak within $1695-1750 \text{ cm}^{-1}$ (v C=O) and $3232-3450 \text{ cm}^{-1}$ (v N-H). These peaks are absent in (POSS-M)1-(0/100). Furthermore, its relative intensities increase linearly with molar percent of the -OCO-NH-C₁₈H₃₇ group, indicating proper chemical composition changes. Subsequent reaction of (POSS-1)1-(x/y) with phthalic anhydride was utilized to form (POSS-M)2-(x/y) with x/y = 25/75, 50/50, and 75/25, as reflected by the broad peak within $2400-3600 \text{ cm}^{-1}$ (v OH) that is characteristic of -COOH group (compare panels a and b of Figure 3). This broad peak is in fact absent for (POSS-M)2-(100/0). However, the extent of complete transformation of the -OH group into -OCO-C₄H₄-COOH cannot be verified from the FTIR spectrum because the stretching vibrations of -COOH, -OH, and -NH occur within the same regions.

The chemical structure of the (POSS-M)p-(x/y) molecules can be further verified with ¹H NMR spectra. The presence of benzoic acid in (POSS-M)2-(x/y) samples can be seen from the appearance of ¹H NMR peaks in the 7.5–7.8 ppm range, indicative of a phenyl ring. The phenyl ring peaks are absent in ¹H NMR spectrum of (POSS-M)1-(x/y) samples. The extent of estertification reaction of phthalic anhydride onto hydroxyl groups can be seen from the peak at 4.2–4.8 ppm.⁴² The presence of small peaks within this region for the (POSS-M)2-(x/y) compounds suggests that some amount of -OH did not react with phthalic anhydride as a result of steric hindrance from the bulky -OCO-NH-C₁₈H₃₇ groups. This peak is very distinctive in (POSS-M)1-(0/100) (Figure S1a). Traces of solvents: DMSO (2.49 ppm) and CHCl₃ (7.62 ppm). Significant shift in CHCl3 peak maybe due to the mixed (CD₃)₂SO-CDCl₃ solvent environment and elevated temperature measurement.43

⁽⁴⁰⁾ Magonov, S. N.; Elings, V.; Whangbo, M. H. Surf. Sci. 1997, 375, L385.
(41) (a) Tsukruk, V. V.; Reneker, D. H. Polymer 1995, 36, 1791. (b) Tsukruk, V. V. Rubber Chem. Technol. 1997, 70, 430.

⁽⁴²⁾ Sharma, B.; Keul, H.; Höcker, H.; Loontjens, T.; van Benthem, R. Polymer 2005, 46, 1775.

⁽⁴³⁾ Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. J. Org. Chem. 1997, 62, 7512.

Table 2. Thermal Properties of (POSS-M)p-(x/y) for p = 1 and p = 2

sample names	$T_{\rm d}$ (°C)	$T_{m,1}$ (°C)	$\Delta H_{\rm f,1}$ (10 ⁵ J/mol)	$T_{m,2}$ (°C)	$\Delta H_{\rm f,2}$ (10 ⁵ J/mol)
(POSS-M)1-(0/100)	99	N/A	N/A	N/A	N/A
(POSS-M)1-(25/75)	285.3	58.2	1.6	107.6	5.2
(POSS-M)1-(50/50)	288.4	54	3.9	114.2	5.7
(POSS-M)1-(75/25)	287.4	57.4	7.3	112.7	4.4
(POSS-M)2-(25/75)	127	34.8	1.2	N/A	N/A
(POSS-M)2-(50/50)	150	43.4	4.5	109.9	3.3
(POSS-M)2-(75/25)	150	47.7	7.3	108.2	3.1
(POSS-M)2-(100/0)	297.2	56.1	6.8	114.5	12

Bulk Properties of (POSS-M)*p*-(*x*/*y*). The molecular weight and terminal group composition for all eights samples, (POSS-M)*p*-(*x*/*y*) for *p* = 1 and *p* = 2 ($M_{n,theor}$ = 4160–23 040 g/mol), is clearly reflected in their bulk behavior (Tables 1 and 2). The samples with few or no alkyl groups, (POSS-M)1-(0/100) and (POSS-M)2-(25/75) are viscous oils, whereas the rest of materials from these series are brittle solids. The difference in bulk properties between the two series, i.e., hydroxyl- (–OH) and benzoic acid-containing (–OCO–C₆H₄–COOH) terminal groups, respectively, can be seen from the physical appearance for (POSS-M)1-(25/75) and (POSS-M)2-(25/75). Despite the fact that these compounds from each group have equal amounts of alkyl chains, (POSS-M)1-(25/75) is a brittle solid, while (POSS-M)2-(25/75) is a viscous oil.

The presence of sharp X-ray diffraction peaks as well as a diffuse halo indicates partial crystallinity of all compounds studied here (Figure 4). Only a few sharp crystalline peaks are seen for (POSS-M)1-(0/100) and (POSS-M)2-(25/75), which indicates the predominantly amorphous nature of these compounds. There are not enough resolved peaks in (POSS-M)1-(100/0) and (POSS-M)2-(25/75) to draw any conclusions about the molecular packing, and thus they were excluded from further analysis.

Exhaustive peak indexing was successfully performed only for samples that have sufficient number of crystalline peaks, namely, samples (POSS-M)1-(25/75) and (POSS-M)2-(50/50) (Figure 4). The most probable space group solution was designated as $R3m^{160}$ for the former and $P321^{150}$ for the latter.⁴⁴ The positions of some peaks visible for (POSS-M)2-(75/25) coincide with (POSS-M)2-(50/50), while all other samples have peaks that coincide with (POSS-M)1-(25/75), indicating similar crystal structures for these compounds within each group. Hence, we suggest that all the samples belong to the rhombohedral (trigonal)/ hexagonal crystal systems.^{3,4} It is worth noting that the crystalline peak positions detected here closely resemble those of octasubstituted POSS molecules, which contain low molecular-weight terminal groups indicating that the mixed nature of POSS-M does not critically affect the ordering of these compounds.⁴⁵

Figure 5 shows the unit cells obtained from X-ray analysis for (POSS-M)1-(25/75) and (POSS-M)2-(50/50) that corresponds to a rhombohedral-centered hexagonal and a primitive hexagonal lattice, respectively. The former has the unit cell parameters a = b = 2.4 nm, c = 1.8 nm (yielding a c/a ratio of 0.75), $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$, and the latter has the unit cell parameters a = b = 1.4 nm, c = 1.9 nm (yielding c/a ratio of 1.36), $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$ (Figure 5). These unit cell dimensions are similar to those of the alkyl-substituted POSS molecules with different chain length studied earlier indicating the critical role of the POSS cores and the minor role of the peripheral

chains.^{46–51} Indeed, all alkyl-substituted POSS with different tails, i.e., (H-SiO_{1.5})₈, (CH₃SiO_{1.5})₈, (C₂H₅SiO_{1.5})₈, (nC₃H₇SiO_{1.5})₈, and (*i*C₃H₇SiO_{1.5})₈ reported to date showed similar unit cell symmetries and dimensions. Nevertheless, the presence of a nonalkyl terminal groups on the POSS-periphery may cause the POSS molecules to crystallize into a unit cell that deviates from a hexagonal geometry.^{46,52}

The unit cell parameters reported here are significantly smaller than the unperturbed molecular dimensions for isolated branched POSS-cores derived from molecular models (Figures 2 and 5). Packing of these branched cores within such unit cells suggests that the alkyl tails must interdigitate to a great extent, as presented in corresponding molecular models (Figure 5). Overall, it can be concluded that all molecules in the first series, (POSS-M)1-(x/y), form more close-packed structures than representatives of the second series, (POSS-M)2-(x/y). We can suggest that steric constraints caused by the bulky benzene groups acting as linkers in the second series may have reduced the ability for the alkyl tails to efficiently pack. This difference in molecular packing defines the diversity in the microstructure of LB monolayers, as will be discussed below.

Comparison of the onset temperature of decomposition from TGA shows that (POSS-M)1-(x/y) compounds are generally more stable than (POSS-M)2-(x/y) (Figure 6, Table 2). The fully hydroxylated (POSS-M)1-(0/100) compound is the least thermally stable (it begins to decompose under N₂ atmosphere at 99 °C), and, in contrast, the fully alkyl-functionalized (POSS-M)2-(100/ 0) compound is the most thermally stable (it begins to decompose at 297 °C) (Figure 6).

Table 1 shows the mass of the residue for all samples, (POSS-M)p-(x/y), following heat treatment of up to 600 °C. The "core" content represents the mass of silica core char after complete removal of organic shells. The compositional data obtained from TGA shows a trend similar to that estimated from theoretical calculations assuming a T16 cage structure of silica cores (Table 1). Since the mixed POSS compounds studied here are composed of a low degree of condensation, incompletely condensed polyhedra, and open structures, the mechanism of its degradation may be similar to the two-stage degradation mechanism for POSScontaining SiOH end groups, as proposed by Liu et al.⁵³ This author suggested that, above 200 °C, the SiOH end-groups became dehydrated and transformed into OCH₃ end-groups. Upon subsequent heating, CH₃OH is released as another volatile product. In addition, isolated cage-like structures $(CH_3SiO_{3/2})_n$ and lowcondensation structures might sublimate. Finally, SiCH₃ groups undergo oxidation to release CO2 and H2O at a temperature between 400–500 °C with the final product being the SiO₂ char.

As seen from Figure 6a,c, (POSS-M)1-(0/100) is stable up to 99 °C, and, within the -60 to 100 °C range, neither DSC nor TGA curves show transition peaks for the fully hydroxylated (POSS-M)1-(0/100) material (Figure 6). This implies very little crystallinity that corresponds to our former conclusion made from X-ray analysis. However, the fully alkyl-functionalized (POSS-M)2-(100/0) compound exhibits two distinct endothermic peaks, which were assumed to be melting (Figure 6). When

(52) Feher, F. J.; Buzichowski, T. A. J. Organomet. Chem. 1989, 373, 153.
 (53) Liu, Y. R.; Huang, Y. D.; Liu, L. Polym. Degrad. Stab. 2006, 91, 2731.

⁽⁴⁴⁾ Pecharsky, V. K.; Zavalij, P. Y. In Fundamentals of Powder Diffraction and Structural Characterization of Materials; Kluwer Academic Publishers: Norwell, MA, 2003.

⁽⁴⁵⁾ Miao, J.; Cui, L.; Lau, H. P.; Mather, P. T.; Zhu, L. Macromolecules 2007, 40, 5460.

⁽⁴⁶⁾ Larsson, K. Ark. Kemi 1960, 16, 203.

⁽⁴⁷⁾ Larsson, K. Ark. Kemi 1960, 16, 209.

⁽⁴⁸⁾ Larsson, K. Ark. Kemi 1960, 16, 215.

⁽⁴⁹⁾ Fu, B. X.; Zhang, W. H.; Hsiao, B. S.; Rafailovich, M.; Sokolov, J.; Johansson, G.; Sauer, B. B.; Philips, S.; Blanski, R. *High Perform. Polym.* **2000**, *12*, 565.

⁽⁵⁰⁾ Zheng, L.; Waddon, A.;J.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2002**, *35*, 2375.

⁽⁵¹⁾ Waddon, A. J.; Zheng, L.; Farris, R. J.; Coughlin, E. B. Nano Lett. 2002, 2, 1149.



Figure 4. X-ray diffraction patterns of different series: (a) (POSS-M)1-(x/y) for x/y = 0/100, 25/75, 50/50, and 75/25 and (b) (POSS-M)2-(x/y) for x/y = 25/75, 50/50, 75/25, and 100/0.



 $\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$

Figure 5. Unit cell and molecular packing of (a) (POSS-M)1-(25/75) and (b) (POSS-M)2-(50/50).

cooled, corresponding exothermic peaks, indicating crystallization, are observed as well (not shown). TGA curves confirmed that no significant mass-loss ($\leq 2\%$ mass) occurred within the range where these endothermic and exothermic peaks were observed. Moreover, for (POSS-M)2-(25/75), which has the lowest amount of C₁₈H₃₇ groups and the highest amount of benzoic acid groups, only one endothermic (melting) transition is observed. Generally, benzoic-acid-containing POSS-M molecules showed slightly lower melting points and lower enthalpy than the hydroxyl-containing POSS-M materials (Table 2). In agreement with the proposed X-ray diffraction analysis, the above combination implies that molecules in the second group are less ordered as a result of the bulky benzene rings that retard the alkyl chains from forming highly crystalline phase (Figure 2).

The presence of two thermal transitions such as observed here is not a rare event for branched compounds (Figure 6).⁵⁶ Generally, it is considered that, for fine core—shell structures, the microphase separation of core and shell fragments should result in two independent phase transitions associated with each of these distinct groups. Sunder et al. also reported double melting transitions for $C_{16}H_{33}$ - and $C_{18}H_{37}$ -functionalized hyperbranched polyether polyols, which were attributed to the formation of ordered mesophases before crystallization⁵⁶ or the presence of different types of crystallites.⁵⁴ DSC measurements on similar alkylfunctionalized hyperbranched polyesters were reported to exhibit two distinct transitions related to independent behavior of peripheral tail and cores.^{55,56} The first transition at 40–60 °C was assigned to the melting of $C_{18}H_{37}$ alkyl tails, and the other transition was assigned to a glass transition of the polyester core.⁵⁵

For compounds studied here, two thermal transitions were consistently observed for both series (Figure 6, Table 2). Similarly for other branched compounds, here we suggest that the two endothermic peaks may be assigned to the energy that was needed to overcome alkyl-alkyl peripheral chain interactions on the POSS-M surface for $T_{m,1}$ (between 43 and 58 °C), and the energy needed to disassemble the unit cell of POSS cores for $T_{m,2}$, (between 103 and 114 °C) (Table 2). The trend observed here corresponds to the results on a homologous series of octak-is(hydrridosilsesquioxane),⁵⁷ [CH₃(CH₂)_nSiO_{3/2}]₈, for *n* increasing from 1 to 9, that showed the overall decreasing in the melting point caused by diminishing electrostatic interaction between the silsesquioxanes cores as the alkyl length increases.

The enthalpies of the first melting transition for each group showed an increase with increasing numbers of alkyl tails in the organic shell (Table 2). If normalized with respect to the number of alkyl tails, the values are on par with hyperbranched polyglycerol with mixed $C_{16}H_{33}/OH$ functionalization, and the

 ⁽⁵⁴⁾ Wei, H.-Y.; Shi, W.-F.; Nie, K.-M.; Shen, X.-F. Polymer 2002, 1969.
 (55) Zhai, X.; Peleshanko, S.; Klimenko, N. S.; Genson, K. L.; Vaknin, D.;
 Ya, M.; Shevchenko, V. V.; Tsukruk, V. V. Macromolecules 2003, 36, 3101.

 ⁽⁵⁶⁾ Sunder, A.; Bauer, T.; Mulhaupt, R.; Frey, H. *Macromolecules* 2005, 50, 5101.
 (53) Sunder, A.; Bauer, T.; Mulhaupt, R.; Frey, H. *Macromolecules* 2000, 33, 1330.

⁽⁵⁷⁾ Bolln, C.; Tsuchida, A.; Frey, H.; Mülhaupt, R. Chem. Mater. 1997, 9, 1475.



Figure 6. TGA and DSC data for (a) (POSS-M)1-(x/y) for x/y = 0/100, 25/75, 50/50, and 75/25 and (b) (POSS-M)2-(x/y) for x/y = 25/75, 50/50, 75/25, and 100/0.

normalized enthalpies of melting for P(G23C16_{0.6}), P(G23C16_{0.6}), and P(G83C16_{0.6}) per alkyl tail are 10 kJ/mol, 8 kJ/mol, and 10 kJ/mol, respectively.⁵⁶ For general abbreviation P(G_xR_z), P is poly, G_x is the degree of polymerization for the glycerol core, and R_z is the fraction of C₁₆H₃₃ alkyl substitutent with respect to hydroxyl substituent. The enthalpies of melting in each group do not differ much with varying the percent of alkyl/hydroxyl or alkyl/benzoic acid compositions between 3.1 × 10⁵ kJ/mol and 5.7 × 10⁵ kJ/mol (Table 2). High *T*_{m,2} energy is seen for the first group and is most notable for the fully alkyl-functionalized (POSS-M)2-(100/0), 12 × 10⁵ kJ/mol. The high enthalpy for *T*_{m,2} melting may be associated with hydrogen bonding due to the urethane group that links the alkyl chain to the POSS-M core. The effect is diminished in the second series due to the presence of the bulky benzene rings.

Our suggestion for the nature of thermal transitions is supported by recent computer modeling. Molecular dynamics simulation of monofunctionalized polyhedral silsesquioxane, $C_6H_{13}(H_7Si_8-O_{12})$, suggested preferential core—core and hydrocarbon hydrocarbon chain aggregation during crystallization as a result of microphase separation.⁵⁸ Such an aggregation leads to a bilayer structure with separately packed cores and peripheral chains. Although the simulation shows a single melting point, there is evidence of two-stage events: first, the partial melting of the hydrocarbon chain domain and, second, the disintegration of the lattice of POSS core order. Considering that the alkyl chains in our POSS-M compounds are much longer than those in this study ($C_{18}H_{37}$ vs C_6H_7), their trend toward phase separation from cores should be higher and, thus, provide a higher chance for the appearance of two independent phase transformations. Finally, multiple transitions were observed for dendritic polyetheramide with different percentages of alkyl/hydroxyl terminal groups.⁵⁴

Surface Behavior of (POSS-M)p-(x/y) at the Air–Water and Solid-Air Interfaces. The composition of mixed hydrophobic-hydrophilic terminal groups defines the molecular packing and monolayer stability at the air-water interface, as can be concluded from stark differences in the pressure-area isotherms as well as the area per molecule and the collapse surface pressure for two series of POSS-M compounds (Figure 7, Table 3). From the Langmuir isotherms, the area per molecule was determined to be either very low (3.8 nm²) for (POSS-M)1-(50/50) or high (13.5 nm²) for (POSS-M)2-(100/0) (Table 3). Molecular models overestimate the surface area per a single molecule for fully expanded molecules. It ranges from 5.9 nm² (diameter = 2.75 nm) for fully hydroxylated POSS-M compounds and 35.7 nm^2 (diameter = 6.74 nm) for POSS-M compounds that are fully functionalized with alkyl tails (Figure 2). These values correspond to the circular area of the smallest molecule, (POSS-M)1-(0/100), and the largest molecule, (POSS-M)2-(100/ 0), respectively. While the fully hydrophilic molecule, (POSS-M)1-(0/100), does not show much resistance with increasing surface pressure, the fully hydrophobic (POSS-M)2-(100/0) shows the largest area per molecule (Figure 7).

Since the experimental surface areas per molecule are systematically lower than the theoretical values, the POSS-M molecules must be in their condensed state under compression within Langmuir monolayers. Indeed, because the hydrophobic

⁽⁵⁸⁾ Zhou, J.; Kieffer, J. J. Phys. Chem. C. 2008, 112, 3473.



Figure 7. Pressure–area isotherms and repeated compression–decompression cycles for (POSS-M)1-(x/y) for x/y = 25/75, 50/50, and 75/25 (top row) and (POSS-M)2-(x/y) for x/y = 25/75, 50/50, 75/25, and 100/0 (bottom row).

Table	3.	Data	Derived	from	Langmuir	Isotherms	and	Contact	Angles

	effective thickness (nm)/domain height (nm)						Anara	An theorem		
sample names	$P_1 = 2 \text{ mN/m}$ $P_2 = 10 \text{ mN/m}$		$P_3 = 25^{\rm a} \text{ mN/m or } 40^{\rm b} \text{ mN/m}$		(nm^2)	(nm^2)	TR^a at P_3	CA, ^{<i>b</i>} θ at P_3		
(POSS-M)1-(25/75)	1.6 ± 0.1	1.5 ± 0.1	2.4 ± 0.1	1.8 ± 0.2	$3.4\pm0.1^{\text{b}}$	1.1 ± 0.1^{b}	4.9	6.6	1	99 ± 2
(POSS-M)1-(50/50)	2.6 ± 0.1	1.6 ± 0.1	2.7 ± 0.1	1.8 ± 0.1	3.2 ± 0.1^{b}	$1.7 \pm 0.2^{\circ}$	3.8	7.5	1	99 ± 3
(POSS-M)1-(75/25)	1.6 ± 0.1	2.7 ± 0.3	0.2 ± 0.1	1.8 ± 0.3	0.3 ± 0.1^{b}	$1.4\pm0.2^{\circ}$	10	8.6	0.2	95 ± 4
(POSS-M)2-(25/75)	2.1 ± 0.1	1.2 ± 0.4	4.1 ± 0.1	1.5 ± 0.3	$3.4\pm0.1^{\mathrm{a}}$	1.4 ± 0.2^{a}	4.4	7.5	1	96 ± 3
(POSS-M)2-(50/50)	2.6 ± 0.1	1.5 ± 0.2	2.7 ± 0.1	1.6 ± 0.5	3.2 ± 0.1^{b}	$1.3 \pm 0.2^{\circ}$	7.3	8.6	1	100 ± 2
(POSS-M)2-(75/25)	1.1 ± 0.1	2.1 ± 0.3	2.3 ± 0.1	2.4 ± 0.3	2.1 ± 0.1^{a}	$2.2\pm0.3^{\mathrm{a}}$	7.1	9.6	0.8	92 ± 1
(POSS-M)2-(100/0)	1.2 ± 0.1	2.0 ± 0.2	0.8 ± 0.1	2.0 ± 0.3	$0.8\pm0.1^{\mathrm{a}}$	$2.0\pm0.4^{\mathrm{a}}$	13.5	10.8	0.4	100 ± 3

^a TR is transfer ratio. ^b CA is water contact angle.

groups tend to stretch away from the water subphase, increasing the amount of hydrophobic groups naturally increases the area per molecule.⁵⁵ As known, amphiphilic branched compounds comprising polar core and hydrophobic alkyl tails placed at the air—water interface reorganize themselves in such a way that the hydrophobic alkyl tails align perpendicular to the water surface and the polar core forms pancakes on the water surface.^{59,60} Contact angle measurements for monolayers at the highest surface pressure confirmed that the topmost layer is in fact hydrophobic with similar values (92–100°) for all monolayers studied here (Table 3, Figures 8 and 9). The contact angle value for POSS-M monolayers is close to that known for octadecyltriethoxysilane self-assembling monolayers (SAMs) with densely packed, vertically oriented alkyl tails (102°).^{38,39,61}

The level of reorganization of POSS-M molecules under compression is controlled by the content of alkyl peripheral chains (Table 3). The absence of hydrophobic groups in (POSS-M)1-(0/100) cores resulted in their unstable behavior at the air-water interface. The pressure-area isotherm does not show an increase in surface pressure, even if the molecules are compressed below the theoretical area per molecule, 5.9 nm², indicating gradual dissolution into the water subphase (Figure 7a). On the other hand, the presence of hydrophobic alkyl chains in the fully hydrophobic (POSS-M)2-(100/0) molecule prevents their dissolution into the water subphase. The steady increase in surface pressure implies molecular incompressibility and resistance to compression (Figure 7b). The presence of some polar ester and urethane groups in the molecule must provide the necessary amphiphilic character for the molecules to form a stable monolayer at the air-water interface when subjected to surface compression.

Area per molecule estimation from molecular model predicts that the values will increase linearly as the amount of alkyl tails increases (Table 2). Such a proportional increase in the area per molecule is experimentally observed for similar alkyl/hydroxylfunctionalized hyperbranched polyester systems from the mol-

⁽⁵⁹⁾ Schenning, A. P. H. J.; Elissen-Roman, C.; Weener, J.-W.; Baars, M. W. P. L.; Van der Gaast, S. J.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 8199.

^{(60) (}a) Johnson, M. A.; Santini, C. M.; Iyer, J.; Satija, S.; Ivkov, R.; Hammond, P. T. *Macromolecules* **2002**, *35*, 231. (b) Genson, K. L.; Vaknin, D.; Villavicencio, O.; McGrath, D.; Tsukruk, V. V. J. Phys. Chem. **2002**, *106*, 11277.

⁽⁶¹⁾ Ornatska, M.; Jones, S. E.; Naik, R. R.; Stone, M.; Tsukruk, V. V. J. Am. Chem. Soc. 2003, 125, 12722.



Figure 8. AFM images of LB monolayers at low (p = 2 mN/m), intermediate (p = 10 mN/m), and high surface pressures (40 mN/m) for (a) (POSS-M)1-(25/75), (b) (POSS-M)1-(50/50), and (c) (POSS-M)1-(75/25). 5 μ m × 5 μ m, Z scale is 10 nm. Insets are photographs of water droplets.

ecules with the smallest amount of alkyl content to those with the highest amount of alkyl content.³⁵ However, in the case of (POSS-M)p-(x/y), the smallest area per molecule, apart from (POSS-M)1-(0/100), which failed to form a stable monolayer at the air—water interface, was seen for (POSS-M)p-(50/50) in each series, rather than (POSS-M)p-(25/75), which has the smallest amount of hydrophobic tails (Table 3). At low hydrophobic content, similar to that of the alkyl/hydroxyl hyperbranched polyester systems studied by Zhai et al.,⁵⁵ the hyperbranched core adopted a cylindrical or prolate shape. The crowding of the alkyl chains, on the other hand, caused an oblate and squashed shape.

Thickness measurements revealed that the smaller area per molecule (POSS-M)p-(50/50) is indeed thicker than (POSS-M)p-(25/75) (see Table 3). Both the area per molecule and thickness comparison, therefore, showed that (POSS-M)p-(50/50) adopts a cylindrical or prolate structure, whereas (POSS-M)p-(25/75) adopts an oblate or squashed shape. The prolate structure in (POSS-M)p-(50/50) may be the result of an efficient hydrophobic/hydrophilic phase-separation within the mixed peripheral. On the other hand, the few alkyl tails in (POSS-M)p-(25/75) means that, during compression, the vertically aligned hydrophobic tails are mixed with the hydrophilic interactions prevents dense packing and results in a lower compressibility, and hence the oblate shape and a larger area per molecule.

Monolayer reversibility can give information about intermolecular interaction and elasticity of the monolayers (Figure 7b,c). There are several possible mechanisms for monolayer reversibility-irreversibility, i.e., monolayer dissolution into the subphase, monolayer cracking for brittle monolayers, and monolayer buckling for ductile monolayers.⁶² Monolayer dissolution and cracking are irreversible, such that the collapsed materials do not reincorporate into the monolayer upon expanding the film. The Langmuir isotherms for the compounds with the lowest content of hydrophobic groups, (POSS-M)p-(25/75), show that the area per molecule gradually shrinks during the compression-decompression cycles. On the other hand, minimal hysteresis is seen for samples with equal amounts of hydrophobic and hydrophilic terminal groups, (POSS-M)p-(50/50), for both series. The hysteresis observed implies irreversible creep caused by spontaneous aggregation, formation of multilayers, or partial sinking of the POSS-M molecules.²² It is worth noting that (POSS-M)2-(75/25) at P = 25 mN/m above a slope-change transition underwent buckling instability, which explains the large hysteresis and indicates a mechanically robust monolayer with high stiffness due to the presence of silica POSS-M cores (see below). A similar phenomenon has been reported for a monolayer of ligated gold nanoparticles at the air-water interface, and it seems to be common for monolayers containing inorganic nanoparticles.63,64

Figures 8 and 9 show the surface morphologies of (POSS-M)p-(x/y) at low, intermediate, and high surface pressures (ranging

⁽⁶²⁾ Yee, K.; Lee, C. Annu. Phys. Chem. 2008, 59, 771.

⁽⁶³⁾ Schultz, D. G.; Lin, X.-M.; Li, D.; Gebhardt, J.; Meron, M.; Viccaro, P. J.; Lin, B. J. Phys. Chem. B. 2006, 110, 24529.

⁽⁶⁴⁾ Lin, B.; Schultz, D. G.; Lin, X.-M.; Li, D.; Gebhardt, J.; Meron, M.; Viccaro, P. J. *Thin Solid Films* **2007**, *515*, 5669.



Figure 9. AFM images of LB monolayers at low (p = 2 mN/m), intermediate (p = 10 mN/m), and high surface pressures (p = 25 or 40 mN/m) for (a) (POSS-M)2-(25/75), (b) (POSS-M)2-(50/50) (c) (POSS-M)2-(75/25), and (d) (POSS-M)2-(100/0). 5 μ m × 5 μ m, Z scale is 10 nm. Insets are photographs of water droplets.

from 2 to 40 mN/m). Overall, the molecules formed three distinct geometries: one-dimensional, circular, and planar aggregates. The lengths of the one-dimensional and diameters of the circular aggregates are in the micron range (Figure 8a and Figure 9a). From one-dimensional to planar aggregates, the geometrical curvature increases as the amount of the hydrophobic content is gradually increased.²⁷ Such a phenomenon is consistently observed and governed especially by the hydrophobic—hydrophilic balance, but the stability is affected by other external variables, e.g., temperature, architecture, and terminal groups.^{65–69} Branched, mainly star-shaped, polymers differ from linear polymers in terms of aggregation number in their surface aggregates.⁶⁵ A highly

curved morphology is thermodynamically more favorable for star-shaped polymers because of the chain crowding at a single junction point at its core, as theoretically predicted by Milner.⁷⁰

In the first series, (POSS-M)1-(25/75), which has the lowest hydrophobic content, aggregates into one-dimensional aggregates. For equal amounts of hydrophobic content, (POSS-M)2-(25/75) in the second series, which contains an additional hydrophobic benzene ring, exhibits circular aggregates (compare Figures 8a and 9a). Except for the (POSS-M)1-(25/75), all other compounds eventually formed a uniform LB monolayer at a high surface pressure (Figures 8 and 9). At the highest surface pressure, the overall morphology is eventually dominated by the crowding of the POSS-M cores and alkyl tails.

⁽⁶⁵⁾ Gunawidjaja, R.; Peleshanko, S.; Tsukruk, V. V. Macromolecules 2005, 38, 8765.

⁽⁶⁶⁾ Peleshanko, S.; Jeong, J.; Gunawidjaja, R.; Tsukruk, V. V. *Macromolecules* **2004**, *37*, 6511.

^{(67) (}a) Li, S.; Clarke, C. J.; Eisenberg, A.; Lennox, R. B. *Thin Solid Films* **1999**, *354*, 136. (b) Zhu, J.; Lennox, R. B.; Eisenberg, A. J. Phys. Chem. **1992**, *96*, 4121.

⁽⁶⁸⁾ Gunawidjaja, R.; Peleshanko, S.; Genson, K. L.; Tsitsilianis, C.; Tsukruk, V. V. Langmuir **2006**, 22, 6168.

^{(69) (}a) Matmour, R.; Francis, R.; Duran, R. S.; Gnanou, Y. *Macromolecules* **2005**, *38*, 7754. (b) Francis, R.; Skolnik, A. M.; Carino, S. R.; Logan, J. L.; Underhill, R. S.; Angot, S.; Taton, D.; Gnanou, Y.; Duran, R. S. *Macromolecules* **2002**, *35*, 6483. (c) Logan, J. L.; Masse, P.; Dorvel, B.; Skolnik, A. M.; Sheiko, S. S.; Francis, R.; Taton, D.; Gnanou, Y.; Duran, R. S. *Langmuir* **2005**, *21*, 3424.

⁽⁷⁰⁾ Milner, S. T. Macromolecules 1994, 27, 2333.

Table 4. Variation in Thickness and Optical Absorbance at 210 nm of (POSS-M)p-(50/50) Multilayer Film for p = 1 and p = 2

	1 layer		5 layer	rs	11 layers		
sample name	$t \text{ (rms)}^a$, nm	abs ^b	t (rms), nm	abs	t (rms), nm	abs	
(POSS-M)1-(50/50)	2.7 (0.5)	0.004	13.7 (2.4)	0.004	33.5 (3.0)	0.019	
(POSS-M)2-(50/50)	2.7 (0.4)	0.014	13.7 (2.1)	0.023	26.6 (3.4)	0.034	

^a t is effective thickness, and rms is mean square roughness. ^b abs is absorbance.



Figure 10. UV-vis absorbance of LB monolayers of (POSS-M)p-(50/50), p = 1 (a) and p = 2 (b) with increasing number of layers.

Ellipsometry allows for the estimation of the effective monolayer thickness. Complementary information can be obtained from the AFM image with regards to the individual domain morphologies (Table 3). If taking into account the domain area coverage, the effective thickness obtained from ellipsometry should match closely with AFM height measurements. For the molecules that are predominantly hydrophilic and contain 25% and 50% hydrophobic content [(POSS-M)p-(25/75) and (POSS-M)p-(50/50) for p = 1 and p = 2], a complete monolayer transfer is achieved (Table 3). In this case, the effective thickness measured from ellipsometry is representative of the average monolayer thickness. This value is up to 4.1 nm in the fully condensed state, which is expected for a single (POSS-M)p-(x/y) molecule with vertically aligned alkyl tails. Between the domains for (POSS-M)p-(25/75) and (POSS-M)p-(50/50) for p = 1 and p = 2, there is a thin underlying monolayer. Such mixed morphologies may be ascribed to the two-phase solid-liquid state, which was previously reported for alkyl-containing hyperbranched systems.⁷¹ In a two-phase solid-liquid state, each of the coexisting twophases belongs to different types of molecular packing.^{31,72} The solid-phase is more densely packed and has a higher thickness than the liquid phase.

The higher domains cannot be attributed to a bilayered structure, since the theoretical height of a vertically aligned (POSS-M)p-(x/y) molecules is within 2–5 nm (Figure 2), whereas the height of these domains may be as low as 1 nm (Table 3). All other molecules with 75% and 100% hydrophobic content formed planar morphologies, and the height of these planar domains, which is measurable from AFM image, represents the true monolayer height. However, in these cases, the effective thickness determined from ellipsometry is not trustworthy, because of the low transfer ratio (Table 3). The value measured from AFM images is, on average, lower for the lower hydrophobic content; it is only up to 2.4 nm (Table 3). This is in agreement with the molecules adopting an oblate shape due to the crowding of alkyl chains, in contrast to the prolate shape that is more likely adopted

by the molecules with lower alkyl content, as discussed previously.

Finally, multilayered LB films were fabricated for two POSS-M molecules that have equal hydrophilic—hydrophobic content in each series at an intermediate surface pressure, P = 10 mN/m (Table 4). UV absorbance is detected for both series despite that silsesquioxane cores are transparent as a result of the presence of organic linkers (Figure 10). The absorption peak around 210 nm is due to the ester and urethane groups. The additional presence of benzene ring in the second series, (POSS-M)2-(*x*/*y*), absorbs at 250 nm (Figure 10).^{27,73} The optical absorbance shows an increase with the number of monolayers deposited, indicating consistent multilayered deposition with linear increase in the amount of POSS-M material transferred (Table 4 and Figure 10).

The thickness of the LB films obtained from AFM images (Figure 11) increased linearly with a number of depositions as well (Table 4 and Figure 12). Moreover, the surface roughness of the LB films is leveled off with increasing number of layers as a result of the "healing" of defects and voids with subsequently deposited layers, a common effect for LB films (Figure 11, Table 4).⁷⁴ The slope of the total thickness versus number of layers yields a incremental value of 3.1 nm/layer for (POSS-M)1-(50/ 50) and 2.4 nm for (POSS-M)1-(50/50) (Figure 12). Such a large increment per monolayer is close to but larger than the spacing observed for the bulk packing (Figure 5) and implies preferential vertical orientation of hydrophobic tails in compressed POSS-M molecules, such as depicted in Figure 13. The multilayer LB films contain alternating hydrophilic-hydrophobic portions of POSS-M molecules, as expected and known for the Y-type deposition applied in this work (Figure 13).³⁷ Since the theoretical height of (POSS-M)p-(50/50) molecules with vertically aligned alkyl tails reaches 5 nm (Figure 13), some interdigitation of the peripheral alkyl tails must be suggested for the multilayered LB films similarly to that suggested for bulk structures (Figure 5).

^{(71) (}a) Kaganer, V. V.; Möhwald, H.; Dutta, P. *Rev. Mod. Phys.* **1999**, *71*, 779. (b) Peterson, I. R. *J. Phys. D: Appl. Phys.* **1990**, *23*, 379.

⁽⁷²⁾ Gaines, G. L., Jr. Insoluble Monolayers at Liquid-Gas Interfaces; Interscience: New York, 1996.

^{(73) (}a) Crews, P.; Rodríguez, J.; Jaspars, M. Organic Structure Analysis; Oxford: New York, 1998. (b) Pretsch, E.; Bühlmann, P.; Affolter, C. Structure Determination of Organic Compounds: Tables of Spectral Data; Springer-Verlag: Berlin Heidelberg, 2000.

⁽⁷⁴⁾ Tsukruk, V. V.; Bliznyuk, V. N. Prog. Polym. Sci. 1997, 22, 1089.



Figure 11. AFM images of LB multilayers deposited at an intermediate surface pressure, p = 10 mN/m, for (a) (POSS-M)1-(50/50) and (b) (POSS-M)2-(50/50) for monolayer, 5 layers, and 11 layers. 5 μ m × 5 μ m, Z scale is 50 nm.



Figure 12. An effective thickness versus number of layers for LB films of (a) (POSS-M)1-(50/50) and (b) (POSS-M)2-(50/50).

Conclusions

In conclusion, the collective properties of mixed POSS derivatives (POSS-M) have been studied due to their facile preparation in contrast with the geometrically specific POSS. The two series of (POSS-M)p-(x/y), p = 1 and p = 2, compounds with variable composition of the hydrophobic—hydrophilic peripheral groups studied here showed the presence of the crystalline phase with the unit cell dimensions suggesting the molecular packing with interdigitated peripheral tails of POSS cores. The presence of aromatic rings as linkers in the second series, (POSS-M)2-(x/y), yields a lower-symmetry crystal structure than for the first series, (POSS-M)1-(x/y). DSC measurement shows two distinct endothermic transitions for (POSS-M)p-(x/y) compounds that may be assigned to independent melting of alkyl chains followed by the disassembly of the POSS-M cores.

Stable LB monolayers of the amphiphilic (POSS-M)p-(x/y) compounds were observed for a range of terminal group compositions, for both combinations studied here $-C_{18}H_{37}/-OH$ or $-C_{18}H_{37}/-OCO-C_{6}H_{4}$ -COOH. And the absence of hydrophobic groups in a fully hydroxylated (POSS-M)1-(0/100) compromised the ability to form a stable monolayer. The influence of functional terminal group composition on morphologies is conspicuous only at a low-surface pressure. The variation of



Figure 13. (a) Multilayered LB film composed of amphiphilic POSS-M cores with alternating hydrophilic and hydrophobic peripheral groups. Models of (b) (POSS-M)1-(50/50) and (c) (POSS-M)2-(50/50) with the alkyl tails stretched in the vertical direction, away from the hydrophilic surface.

terminal group composition led to diverse morphologies that ranged from one-dimensional and curved domains for low

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hydrophobic content to planar aggregates with increasing hydrophobic alkyl chain contents. The surface morphologies, especially for 25% and 50% alkyl content resembled the two-phase solid–liquid state that is common for alkyl-containing hyperbranched systems. At high surface pressure, all of the (POSS-M)p-(x/y) molecules eventually aggregated into a uniform monolayer film. Finally, a uniform formation of multilayered structures and high transfer ratio was observed for a series of (POSS-M)p-(50/50) molecules with equal content of hydrophilic–hydrophobic terminal groups.

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Supporting Information Available: GPC and ¹H NMR spectra of (POSS-M)1-(x/y) and (POSS-M)2-(x/y) for x/y = 0/100, 25/75, 50/ 50, 75/25/, and 100/0. This material is available free of charge via the Internet at http://pubs.acs.org.

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