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Self-Assembly of Organostannoxanes: Formation of Gels in Aromatic Solvents

Vadapalli Chandrasekhar,*[,†] Kandasamy Gopal,[†] Puja Singh,[†] Ramakirushnan Suriya Narayanan,[†] and Andrew Duthie[‡]

[†]*Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India, and* [‡]*School of Life and Environmental Sciences, Deakin University, Geelong Victoria 3217, Australia*

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Organostannoxane *drums* [*n*-BuSn(O)O_2C-C_6H_4-4-OR]$_6$ [R = $-CH_3$ (**1**); $-C_9H_{19}$ (**2**); $-C_{11}H_{23}$ (**3**)] and [*n*-BuSn(O)O_2C-C_6H_3-3,5-$(OR)_2]_6$ [R = $-CH_3$ (**4**); $-C_9H_{19}$ (**5**)] were synthesized by the reaction of *n*-BuSn(O)(OH) with the corresponding carboxylic acid in a 1:1 stoichiometry. Analogous reactions involving [*n*-Bu_2SnO]$_n$ in a 1:1 stoichiometry afforded the diorganostannoxane *ladders* $\{$[*n*-$Bu_2$$SnO_2$C-$C_6H_4$-4-$OR]_2O\}_2$ [R = $-CH_3$ (**6**); $-C_9H_{19}$ (**7**); $-C_{11}H_{23}$ (**8**)] and $\{$[*n*-$Bu_2$$SnO_2$C-$C_6H_3$-3,5-$(OR)_2]_2O\}_2$ [R = $-CH_3$ (**9**) and $-C_9H_{19}$ (**10**)]. Compounds **1**−**10** could also be prepared by a solventless methodology, which involved grinding the reactants together in a mortar and pestle at room temperature. Compounds **1**−**10** exhibit gelation behavior in aromatic solvents. In contrast, in aliphatic solvents gelation behavior was not observed. Among the organostannoxanes reported here, **2**, **3**, **5**, and **8** were found to be extremely efficient gelators based on their critical gelation concentration values. The microstructure of the organometallic gels, investigated by optical and scanning electron microscopy, reveals the presence of cross-linked network structures. The gels formed from **2** and **3** can be converted into xerogels by removal of solvent. The latter can be reconverted into the original gels by treatment with aromatic solvents.

Introduction

Organotin cages and clusters have been of interest because of the large structural diversity that is present in this family and also because of their importance in catalysis and other applications.[1−3] Most of these compounds are prepared, in general, by reactions involving organotin oxides, hydroxides, or oxide-hydroxides with protic acids. For example, the reaction of *n*-butylstannonic acid, [*n*-BuSn(O)OH]$_n$, with various carboxylic acids affords dendrimeric hexanuclear *drums*, [*n*-BuSn(O)O_2CR]$_6$, containing a [Sn_6O_6] core. Similarly, the reaction of protic acids with [*n*-Bu_2SnO]$_n$ affords tetranuclear *ladders*, $\{$[*n*-$Bu_2$$SnO_2$-CR]$_2O\}_2$. The reactions of organotin oxides/oxide-hydroxides with phosphorus-based acids are more complex and have been a rich source of structurally complex organotin cages. In spite of the complexity of the products, the current state-of-the art in *organostannoxane synthesis* is reasonably advanced and allows the assembly of desired organotin architectures. It is therefore possible to design organotin compounds and decorate the organostannoxane cores with suitable functional peripheries. Utilizing this strategy we have recently reported organooxotin-(*drum* and *ladder* core)-supported multiferrocene, -porphyrin, -fluorene, and pyrazolyl assemblies.[4−9] Similarly, Nierengarten and co-workers have reported the preparation of hexa- and dodecafullerene assemblies supported on a organotin *drum* core.[10]

We were interested in examining if the organostannoxane synthesis strategy can be extended to the preparation of organometallic gels. Recently, there has been a growing interest in the study of low molecular weight organogels and metallogels, owing to diverse applications in drug delivery, sensors, templates for synthesis of nanostructures, biomimetics, etc.[11] Although many gelators are polymers, there has also been a great deal of interest in

*To whom correspondence should be addressed. E-mail: vc@iitk.ac.in. Phone: (+91) 512-259-7259. Fax: (+91) 521-259-0007/7436.

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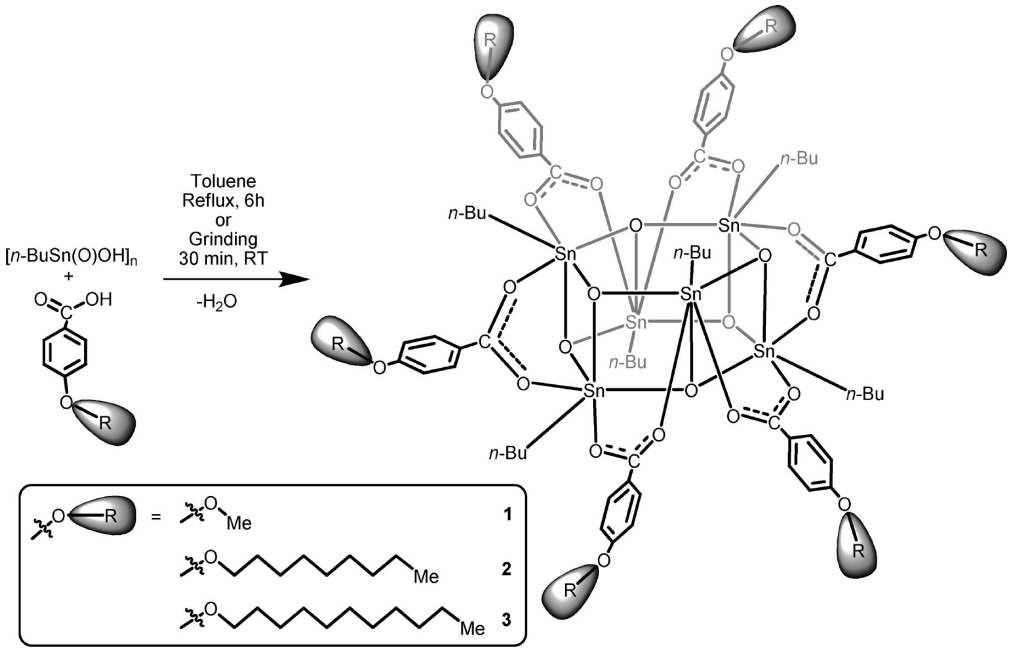
Scheme 1



recent years in discovering small molecules that can form gels in organic and aqueous solutions. Examples of nonpolymeric gelators reported in the literature include steroids, alkylamide derivatives, and fatty acids. The gelation property of these small-molecule gelators arises as a result of the utilization of noncovalent van der Waals forces, $\pi-\pi$ stacking, and hydrogen-bonding interactions.[12,13] We reasoned that reacting the organotin oxide-hydroxide [*n*-BuSn(O)(OH)]$_n$ or the organotin oxide with substituted benzoic acids 4-RO-C_6H_4-COOH or 3,5-$(OR)_2$-C_6H_3-COOH would afford organostannoxanes of defined *drum* or *ladder* structures. The intermolecular interactions among the substituents present in the periphery of these stannoxane cores would allow such molecules to self-assemble in solution, producing lamellar supramolecular structures containing large free volumes, which can trap solvent molecules and hence induce gelation. During the course of this work a preliminary communication was published by Nierengarten et al. on organotin gelators.[14] Herein, we describe the synthesis and characterization of organooxotin *drums*, [*n*-BuSn(O)O_2C-C_6H_4-4-OR]$_6$ [R = $-CH_3$ (**1**); $-C_9H_{19}$ (**2**); $-C_{11}H_{23}$ (**3**)] and [*n*-BuSn(O)O_2C-C_6H_3-3,5-$(OR)_2$]$_6$ [R = $-CH_3$ (**4**); $-C_9H_{19}$ (**5**)], and organooxotin *ladders*, {[*n*-Bu_2SnO_2C-C_6H_4-4-OR]$_2$O}$_2$ [R = $-CH_3$ (**6**); $-C_9H_{19}$ (7); $-C_{11}H_{23}$ (**8**)] and {[*n*-Bu_2SnO_2C-C_6H_3-3,5-$(OR)_2$]$_2$O}$_2$ [R = $-CH_3$ (**9**) and $-C_9H_{19}$ (**10**)]. These compounds induce gel formation in various aromatic solvents even at room temperature. We also report the microstructures of some representative examples of these new organostannoxane gels. These gels can also be transformed into xerogels by removal of solvent *in vacuo*.

Results and Discussion

Synthesis. The reaction of *n*-butylstannonic acid, [*n*-BuSn(O)OH]$_n$, with various alkoxy-substituted benzoic acids in a 1:1 stoichiometric ratio in refluxing toluene afforded hexanuclear organostannoxane *drums* **1**−**5** in quantitative yields (Schemes 1 and 2). Under similar conditions the reactions of the benzoic acids with [*n*-Bu_2SnO]$_n$ in a 1:1 ratio afforded the tetranuclear *ladder* compounds **6**−**10** (Schemes 3 and 4). A *solvent-free* methodology, which we have recently demonstrated,[15] also can be adopted for the preparation of **1**−**10**. In this latter technique the reactants are ground together followed by a workup to afford the final products (see Experimental Section).

The ^{119}Sn NMR spectra of **1**−**5** are characterized by the presence of a single resonance in a narrow chemical shift window (ranging from −484.9 to −486.1 ppm) (Table 1). These chemical shifts are the signature of the *drum* structure of organostannoxanes, which contain six equivalent tin atoms each with a 1C,5O coordination environment.[2,3] On the other hand, compounds **6**−**10** show two signals in their ^{119}Sn NMR spectra (ranging from −188 to −203 ppm), indicating the presence of two types of tin atoms in a tetranuclear *ladder* structure (Table S1).[2,3]

Gelation Properties of *Drums* and *Ladders*. Compounds **1**−**10** are not soluble in solvents such as *n*-hexane or diethyl ether. However, they are soluble in solvents such as dichloromethane, chloroform, acetone, benzene, toluene, methanol, and ethanol. We observed a viscous gel formation when the solutions of these compounds in aromatic solvents were allowed to age for about 48 h at room temperature. The solution turned viscous in about 10−12 h before becoming completely immobile (48 h). In contrast, gel formation is not observed in aliphatic solvents. This type of solvent

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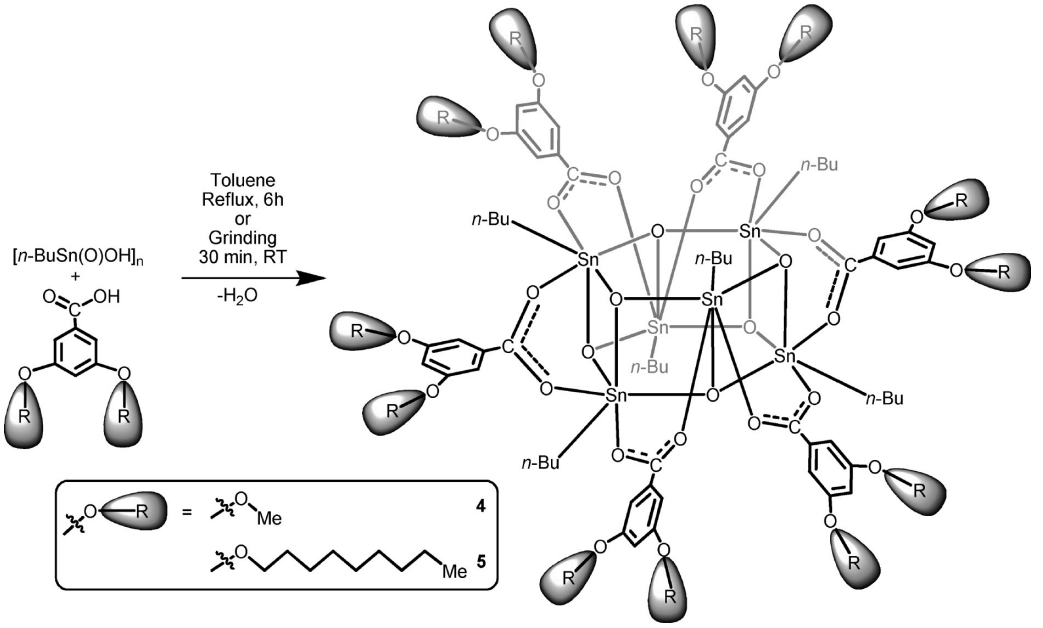
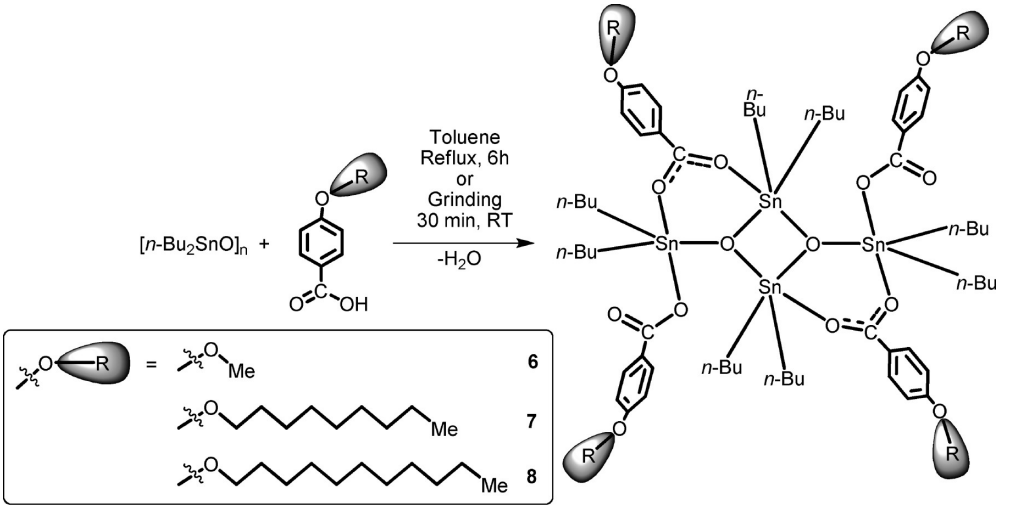
Scheme 2



Scheme 3



Scheme 4

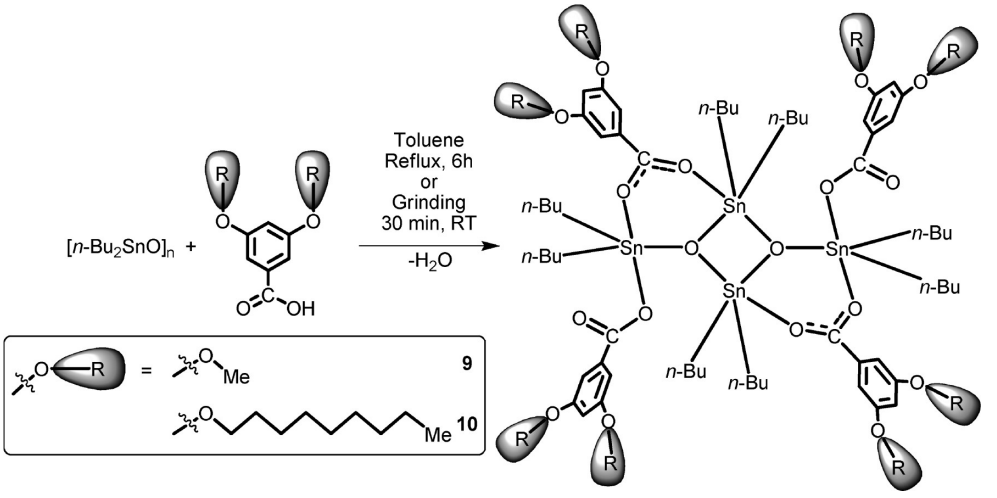


Table 1. Critical Gelation Concentration (CGC, wt %)[a] for Various Organostannoxanes in Different Aromatic Solvents

stannoxane	benzene	toluene	*p*-xylene	mesitylene	chlorobenzene
drum **1**	6.8	5.9	6.0	6.1	5.2
drum **2**	2.9	1.4	1.3	1.3	0.9
drum **3**	2.8	1.6	1.1	0.9	0.8
drum **4**	4.9	4.3	4.3	4.1	4.0
drum **5**	2.3	1.1	0.8	0.5	0.6
ladder **6**	7.2	6.8	6.7	6.8	6.8
ladder **7**	4.5	3.9	4.0	3.9	3.8
ladder **8**	3.2	2.8	2.1	2.0	2.4
ladder **9**	6.5	6.6	6.2	5.9	5.9
ladder **10**	4.1	3.4	3.2	2.0	2.3

[a] CGC measurements were performed in the concentration range from 30 to 100 mg/mL.

dependence on gel formation has been reported in some other systems also.[17,18] In the current system aromatic solvents appear to influence the self-assembly (aggregation) of drum molecules and the microstructure of the resultant sol−gels.

The gelation efficiency of the organostannoxane gelators was studied in terms of their critical gelation concentration (CGC) measurements (wt %). These data are summarized in Table 1. It can be seen that in general all the *drums* are more efficient than the corresponding *ladders* in inducing gelation.

This can be traced to the spherical Sn_6O_6 core in the former in comparison to the flat Sn_4O_2 structural motif present in the latter. The role of the peripheral substituents is also quite crucial. While even a simple methoxy substituent on the aromatic carboxylate ligand is able to induce gelation, the presence of long-chain alkylene spacers between the alkoxy and the aromatic groups dramatically improves the efficiency of gelation. For example, compounds **2**, **3**, and **5** have a CGC of < 1.5 wt % for toluene, *p*-xylene, mesitylene, and chlorobenzene. Among these, the CGC of **5** is the lowest (Table 1). These values suggest that **2**, **3**, and **5** can be considered as *supergelators*,[18] which require very low concentrations for inducing gelation. Among the *ladders*, compound **8** is the most efficient gelator followed closely by **10**. In order to understand the nature of the organostannoxanes (**1**−**10**) in solution during the process of gelation, their $^{119}Sn\{^1H\}$ NMR spectra were recorded in C_6D_6. Even after the solutions became sufficiently viscous (aging for 14 h) broad resonances, in the same chemical shift region as was observed in $CDCl_3$ solutions, could be detected (Table S1). After about 48 h the gels became completely immobile, and at this stage ^{119}Sn NMR signals could not be detected presumably because of large relaxation effects in the immobile gel phase.

The gel−sol transition temperatures (T_{gel}) of the *drum* and *ladder* gels **1**−**10** were determined by the tube inversion method (Figure 1). Gels obtained from benzene or toluene show T_{gel} at around 45−60 °C (Table 2).

Optical micrographs of the *drum* gels **1**−**3** formed from various aromatic solvents are indicative of the lamellar nature of these gels (Figure 1). The microstructure of the *drum* gels was studied by environmental scanning electron microscopy (ESEM). This technique allows the visualization of the morphology under low-vacuum conditions. An ESEM micrograph of the *drum* gel **2** (formed in toluene) reveals the formation of an intertwined fibrous network (Figure 2). Long chains with diameters of 5−10 μm consisting of intertwined fibers are generated, which aggregate to form fibrous networks. Such fibrous network formation is an indication for a typical sol−gel of low molecular mass gelators.[12,13] A similar pattern was also observed for the *drum* gels **3** and **5**. The microstructure of the *drum* gel **5** (formed from toluene) reveals that an intertwined tape network is formed with a diameter of 10−15 μm (Figure S1, Supporting Information). However, we were unable to study the microstructure of gels formed by **1** and **4** because even under ESEM conditions fast evaporation of the solvent occurred from the gel.

The gels formed with **2** and **3** (in toluene or mesitylene) do not suffer any shrinkage in volume upon removal of the solvent (sol) in vacuum (~3 Torr). We have studied this over a period of 2 days. The resulting material is a *xerogel* (Figures 3a,b).[19] These xerogels can be manually crushed in a mortar to obtain granules and are highly soluble in polar aliphatic solvents. The organostannoxane structure remains intact in the xerogels also. Evidence for this comes from the ^{119}Sn NMR of the dissolved granules of the xerogel. A single resonance at −484 ppm (in $CDCl_3$) was observed consistent with the *drum* structure (Table S1).[1−3] The CP MAS ^{119}Sn NMR of xerogels of **2** and **3** showed broad isotropic signals at −485 and −518 ppm, respectively, indicating that the stannoxane *drums* retain their structures in the xerogels. Thermal analysis of the xerogel of **2** (Figure S2a) revealed a gradual loss in weight percent (5.3%) until the onset of its decomposition at ~278 °C, while the thermogravimetric curve of the xerogel of **3** (Figure S2b) showed no significant weight loss prior to the onset of its decomposition at ~270 °C. The surface areas for xerogels of **2** and **3**, as obtained from nitrogen adsoption measurements, were found to be 0.26 and 1.17 m^2/g, respectively, indicating that the porosity of these xerogels is not significant.

It is also of interest to note that the xerogels **2** and **3** can be readily transformed to gels on the addition of aromatic solvents. These transformations are independent of the type of aromatic solvent. In case of compounds **1**, **4**, and **5** removal of solvent resulted in amorphous solids, which could be again transformed into gels upon treatment with the aromatic solvent.

The tetranuclear *ladder* compounds **6**−**10** also form gels in the presence of aromatic solvents (for optical micrograph of **7** and **10** see Figure S3 of the Supporting Information). Microstructures of *ladder* gels **7**, **8**, and **10** could be investigated by ESEM (Figure S4 of the Supporting Information shows an ESEM micrograph of **8**). These gels exist in a platelike morphology. *Ladder* gels form amorphous solids upon removal of solvent under reduced pressure. Similar to the *drum gel* **5**, the amorphous solid could be again transformed into a gel in the presence of aromatic solvent.

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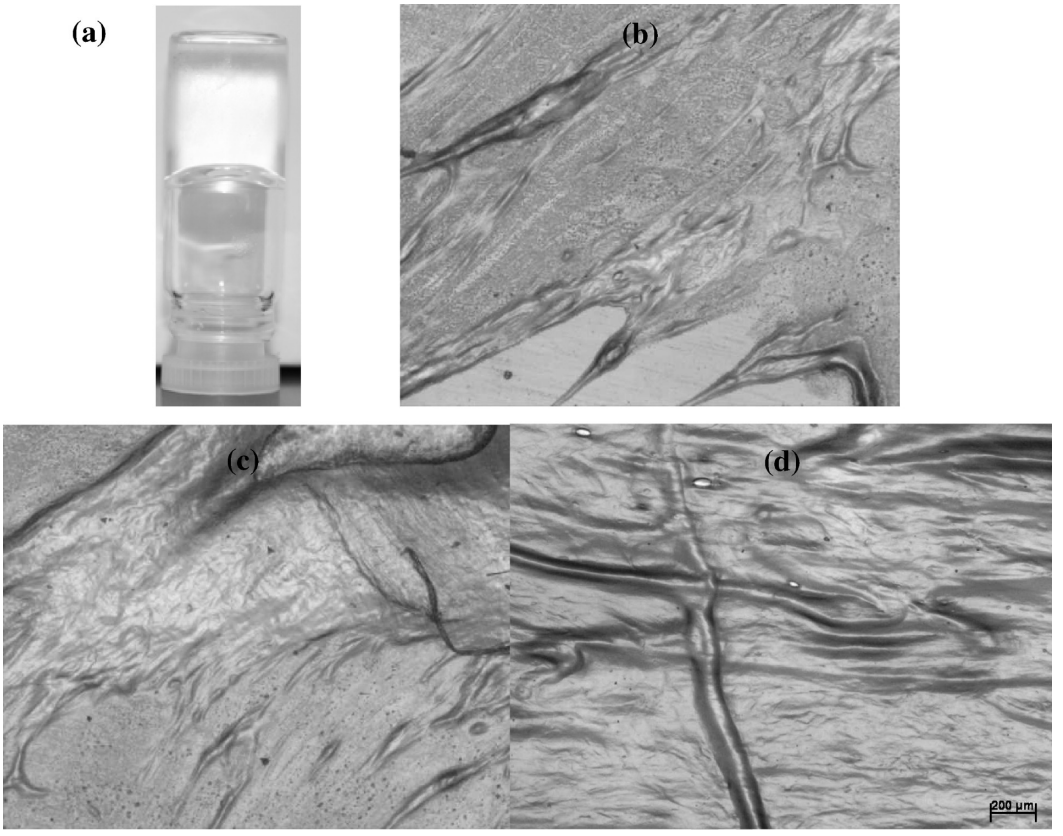

Figure 1. (a) Photograph of the gel formed by **2** in toluene. (b−d) Optical micrograph of *drum* gels in toluene: (b) **1**; (c) **2**; (d) **3**.

Table 2. T_{gel} (°C) for Various Organostannoxane Gels

	stannoxanes									
solvent	**1**[a]	**2**[b]	**3**[b]	**4**[a]	**5**[b]	**6**[a]	**7**[b]	**8**[b]	**9**[a]	**10**[b]
benzene	42−45	50−52	50	50	55		52−55	50	50−53	57−60
toluene	45	48−50	50−53	48−50	55	45	55	50	48−50	53−55

[a] At 8 wt % of stannoxane concentration. [b] At 5 wt % of stannoxane concentration.

Although tentative, we propose a gelation mechanism for the formation of the fibrous network in *drum* gels **2** and **3** (Scheme 5). Each *drum* contains six alkoxy groups in the periphery in an approximate hexagonal arrangement. Interaction of each drum with six others (hydrophobic interactions of the alkyl chains) results in a two-dimensional hexagonal disk. Similar examples of hydrophobic interactions are known in the literature.[20] At this point, there are six trigonal-shaped voids created within the hexagonal supramolecular architecture around each drum. These two-dimensional hexagonal disks further interact with each other to form a three-dimensional network. This process can occur in two ways (Scheme 5). In *model A*, the hexagonal disks stack one above the other. The driving force for this is the hydrophobic alkyl chain interactions (between *n*-Bu groups on tin). Such stacking leads to the formation of columns and eventually hexagonal columnar fibers. The surface of the fibers contains alkoxy groups, hydrophobic interactions among which can cause cross-linking. In the second model, *model B*, the above-described two-dimensional hexagonal disks are proposed to propagate to form a two-dimensional sheet. Side-wise folding of the sheet can result in the formation of a fiber where the inner and outer surface of the fiber contains noninteracting alkyl chains (*n*-Bu groups on tin). These can be utilized for hydrophobic interactions between the fibers.

Conclusion

We have successfully assembled a series of dendritic organostannoxane *drums* and *ladders* containing multiple substituents. The design of these assemblies was carried out in such a manner that the peripheral substituents present around the organostannoxane core would form supramolecular networks in solution through hydrophobic, weak intermolecular van der Waals, or $\pi-\pi$ interactions. All of these organostannoxanes function as low molecular weight organometallic gelators in aromatic solvents. A few dendritic organostannoxane *drums* are supergelators with critical gelation concentrations of < 1.5 wt % for toluene, *p*-xylene, mesitylene, and chlorobenzene. The morphology of these organometallic sol−gels was studied by optical and ESEM techniques. Also, the xerogels can be readily transformed to gels by addition of aromatic solvents. We are extending these studies to investigate sensor applications of organostanoxane gels.

Experimental Section

Reagents and General Procedure. Solvents and other general reagents used in this work were purified according to standard procedures.[21] The following chemicals were purchased and

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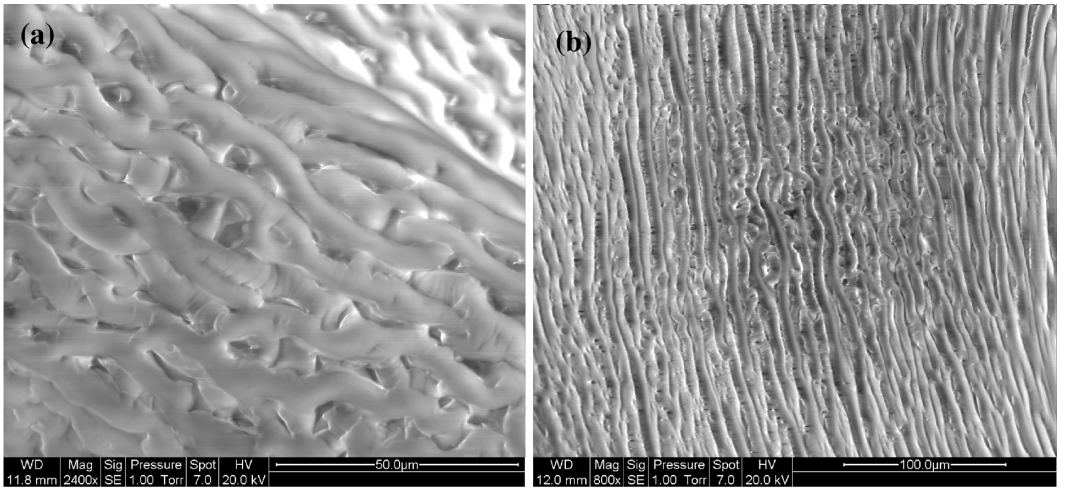


Figure 2. ESEM micrographs of *drum* gel **2**. (a) Close view of **2** showing the cross-linked fibers in toluene. (b) Close view of long fibers of the gel formed by **2** in chlorobenzene.

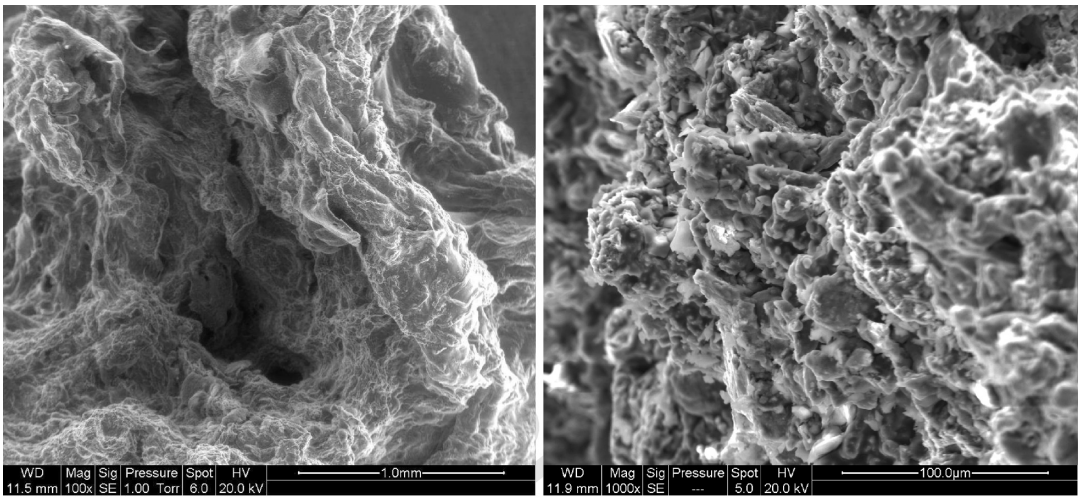


Figure 3. ESEM micrograph of the xerogel formed from sol−gel. (a) Xerogel of **2**. (b) Xerogel of **3**.

used as such without further purification: $[n\text{-BuSn(O)OH}]_n$, $[n\text{-Bu}_2\text{SnO}]_n$, $HO_2C\text{-}C_6H_4\text{-}4\text{-}OC_9H_{19}$, $HO_2C\text{-}C_6H_4\text{-}4\text{-}OC_{11}H_{23}$, $H_3CO_2C\text{-}C_6H_3\text{-}3,5\text{-}(OH)_2$ (all from Aldrich, USA), $HO_2C\text{-}C_6H_4\text{-}3,5\text{-}(OCH_3)_2$ (Fluka, Switzerland), and $HO_2C\text{-}C_6H_4\text{-}4\text{-}OCH_3$ (Spectrochem, India).

Instrumentation. Melting points were measured using a JSGW melting point apparatus and are uncorrected. Elemental analyses were carried out using a Thermoquest CE instruments model EA/110 CHNS-O elemental analyzer. ^{1}H and ^{119}Sn NMR spectra were recorded in $CDCl_3$ solution (unless specified) on a JEOL JNM Lambda spectrometer operating at 400.0 and 150.0 MHz, respectively. The chemical shifts are referenced with respect to tetramethylsilane (for ^{1}H) and tetramethyltin (for ^{119}Sn). All the ^{119}Sn NMR spectra were recorded under broadband decoupled conditions. Optical images were obtained with a LABOMAD DIGI 3 optical microscope operating from 40× to 1000×. ESEM measurements were performed on a FEI QUANTA 200 microscope equipped with a tungsten filament gun and operating at 20 keV. The micrographs were recorded at WD 10.6 mm in varied magnification. TEM images were recorded on a JEOL JEM 2000 FX-II transmission electron microscope operating at 200 keV.

Nitrogen Sorption Measuremets. The samples of xergels of **2** and **3** were degassed at 100 °C for 4 and 5 h, respectively, prior to the nitrogen adsorption measurements. Measurements were carried out using Smart Sorb 92/93 suface area analyzer, made by Smart Instruments Co. Pvt. Ltd.

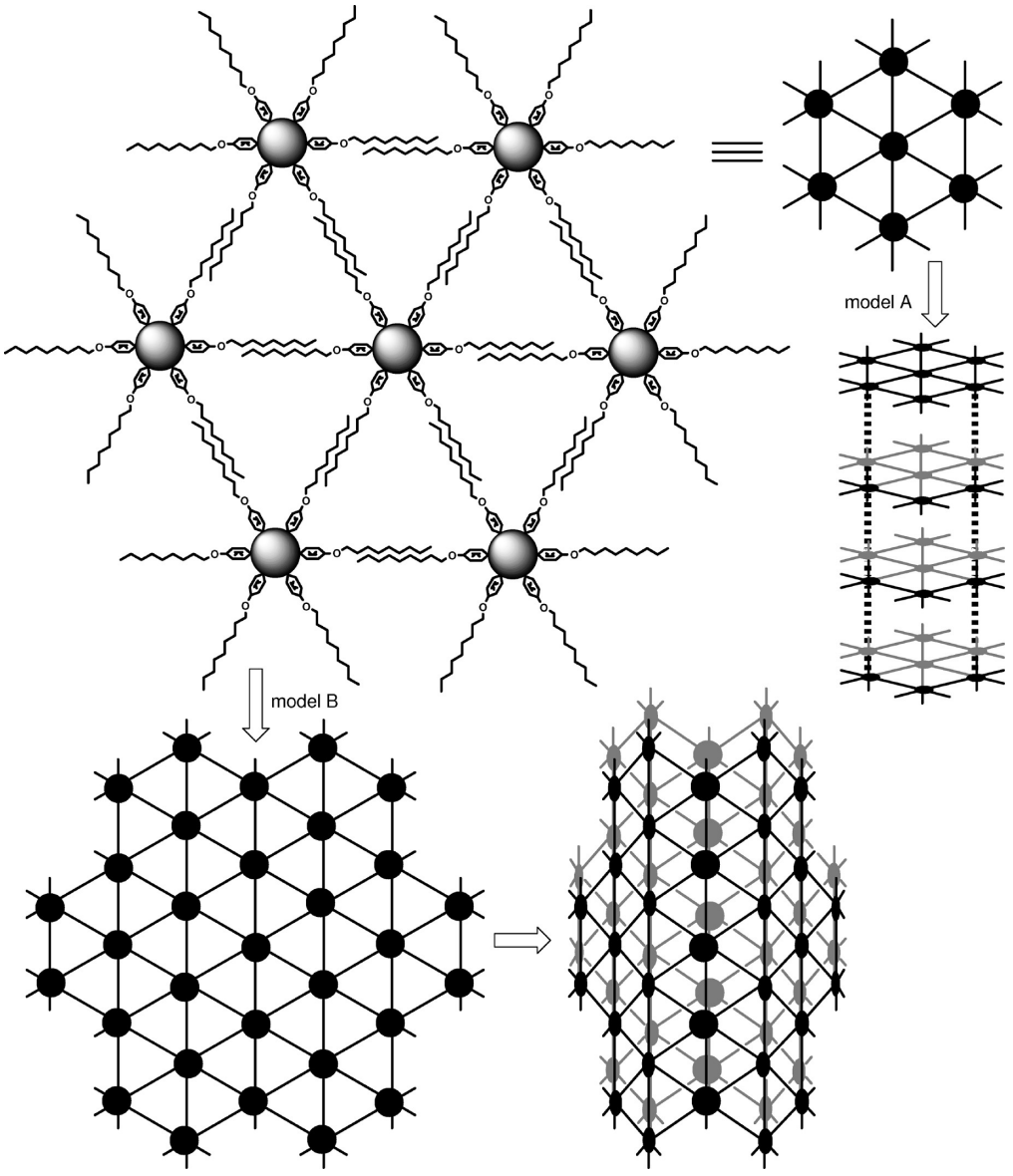
Solid state ^{119}Sn NMR of xerogels of compound **2** and **3** were measured using a Jeol Eclipse Plus 400 spectrometer (at 149.05 MHz) equipped with a 6 mm MAS probe and were referenced against $SnMe_4$. The spectra were obtained using cross-polarization (contact time 5 ms, recycle delay 10 s). Crystalline *c*-Hex_4Sn (δ −97.35) was used as a secondary reference.

Thermogravimetric analysis was carried out on a Perkin-Elmer Pyris 6 thermogravimetric analyzer.

General Synthetic Procedure. Synthesis of $HO_2C\text{-}C_6H_4\text{-}3,5\text{-}(OC_9H_{19})_2$. This compound was prepared by adopting a literature procedure.[22] A mixture of K_2CO_3 (16.59 g, 120.00 mmol) and $H_3C\text{-}O_2C\text{-}C_6H_3\text{-}3,5\text{-}(OH)_2$ (3.36 g, 20.00 mmol) in MeCN (50 mL) was refluxed for 30 min under a N_2 atmosphere. To this was added dropwise a solution of $n\text{-}C_9H_{19}Br$ (12.43 g, 60.00 mmol) in MeCN (10 mL), and the mixture was stirred for 20 h. The reaction mixture was then cooled to room temperature and filtered. Evaporation of the solvent from the reaction mixture resulted in a residue, which

(22) Schultz, A.; Diele, S.; Laschat, S.; Nimtz, M. *Adv. Funct. Mater.* **2001**, *11*, 441.

Scheme 5. Proposed Mechanism for the Gelation Process in *Drums* 2 and 3



was washed with CH_2Cl_2 (2 × 50 mL). The filtrate was washed with a 0.5 M NaOH solution (50 mL) and water (2×50 mL), dried in $MgSO_4$, filtered, and evaporated, yielding a colorless oil. The latter was treated with KOH (15.71 g, 280.00 mmol) in EtOH (75 mL) and heated under reflux for 6 h. An oily solid was obtained after evaporation of the solvent from the reaction mixture. This was cooled to 0 °C and treated with H_2O (50 mL) followed by 36.5% HCl (20 mL). A white precipitate was formed. This was filtered, washed with water, dried under vacuum, and identified as the title compound. Yield: 6.86 g (84.4%). ^{1}H NMR (δ, ppm): 0.88 (t, J = 6.01 Hz, 6H, CH_3), 1.28−1.81 (m, 28H, CH_2), 4.01−4.06 (m, 4H, −OCH_2), 7.33 (s, 2H, aromatic C*H*), 7.71 (s, 1H, aromatic C*H*).

Synthesis of Organostannoxanes 1−10. Two synthetic procedures were adopted for the preparation of **1−10** as outlined below.

Conventional Method. A stoichiometric mixture of the organotin precursor and a substituted benzoic acid was taken in toluene (70 mL) and heated under reflux for 6 h. The water formed in the reaction was removed by using a Dean−Stark apparatus. The reaction mixture was filtered and evaporated to dryness to afford the corresponding products.

Solvent-Free Method. This involved the grinding of a stoichiometric mixture of the organotin precursor and a substituted benzoic acid at room temperature using a mortar and a pestle. The progress of the reaction was monitored by noting the morphological changes of the mixture as well as monitoring its solubility (in organic solvents) with time. When the mixture was completely soluble, it was extracted with a minimum amount of dichloromethane. Evaporation of the solvent afforded the product, whose structural identity was established by its ^{119}Sn{^{1}H} NMR spectroscopy.

Specific details of each reaction and the characterization data of the products obtained are given below.

[*n*-BuSn(O)O$_2$C-C$_6$H$_4$-4-OCH$_3$]$_6$ (1). Conventional method: [*n*-BuSn(O)OH]$_n$ (0.63 g, 3.00 mmol), $HO_2C-C_6H_4$-4-OCH_3 (0.46 g, 3.00 mmol), yield 0.89 g (85.8%).

Solvent-free method: [*n*-BuSn(O)OH] (0.11 g, 0.50 mmol), HO_2C-C_6H_4-4-OCH_3 (0.08 g, 0.50 mmol), grinding time 30 min, yield 0.16 g (88.4%).

Mp: 145 °C (dec). Anal. Calcd (%) for $C_{72}H_{96}O_{24}Sn_6$: C, 42.02; H, 4.70. Found: C, 42.03; H, 4.69. ^{1}H NMR (δ, ppm): 0.86 (t, J = 7.32 Hz, 18H, *n*-butyl CH_3), 1.18−1.83 (m, 36H, *n*-butyl CH_2), 3.75 (s, 18H, −OCH_3), 6.79 (d, J = 8.39 Hz, 12H, aromatic

C*H*), 7.96 (d, J = 8.39 Hz, 12H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −484.9 (s).

[*n*-BuSn(O)O$_2$C-C$_6$H$_4$-4-OC$_9$H$_{19}$]$_6$ (2). Conventional method: [*n*-BuSn(O)OH]$_n$ (0.42 g, 2.00 mmol), HO$_2$C-C$_6$H$_4$-4-OC$_9$H$_{19}$ (0.53 g, 2.00 mmol), yield 0.87 g (95.3%).

Solvent-free method: [*n*-BuSn(O)OH] (0.11 g, 0.50 mmol), HO$_2$C−C$_6$H$_4$-4-OC$_9$H$_{19}$ (0.13 g, 0.5 mmol), grinding time 30 min, yield 0.21 g (90.9%).

Mp: 120 °C (dec). Anal. Calcd (%) for $C_{120}H_{192}O_{24}Sn_6$: C, 52.77; H, 7.09. Found: C, 52.70; H, 7.00. ^{1}H NMR (δ, ppm): 0.80 (t, J = 6.83 Hz, 18H, CH_3), 0.85 (t, J = 7.31 Hz, 18H, *n*-butyl CH_3), 1.19−1.41 (m, 96H, CH_2), 1.67−1.78 (m, 24H, CH_2), 3.89 (t, J = 6.46 Hz, 12H, −OCH_2), 6.77 (d, J = 8.79 Hz, 12H, aromatic C*H*), 7.94 (d, J = 8.55 Hz, 12H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −485.1 (s).

[*n*-BuSn(O)O$_2$C-C$_6$H$_4$-4-OC$_{11}$H$_{23}$]$_6$ (3). Conventional method: [*n*-BuSn(O)OH]$_n$ (0.42 g, 2.00 mmol), HO$_2$C-C$_6$H$_4$-4-OC$_{11}$H$_{23}$ (0.59 g, 2.0 mmol), yield 0.93 g (95.3%).

Solvent-free method: [*n*-BuSn(O)OH] (0.11 g, 0.5 mmol), HO$_2$C-C$_6$H$_4$-4-OC$_{11}$H$_{23}$ (0.15 g, 0.5 mmol), grinding time 30 min, yield 0.22 g (87.7%).

Mp: 110 °C (dec). Anal. Calcd (%) for $C_{132}H_{216}O_{24}Sn_6$: C, 54.68; H, 7.51. Found: C, 54.65; H, 7.55. ^{1}H NMR (δ, ppm): 0.80 (t, J = 6.59 Hz, 18H, CH_3), 0.85 (t, J = 7.31 Hz, 18H, *n*-butyl CH_3), 1.19−1.43 (m, 120H, CH_2), 1.66−1.80 (m, 24H, CH_2), 3.89 (t, J = 6.59 Hz, 12H, −OCH_2), 6.77 (d, J = 8.75 Hz, 12H, aromatic C*H*), 7.94 (d, J = 8.79 Hz, 12H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −485.1 (s).

[*n*-BuSn(O)O$_2$C-C$_6$H$_3$-3,5-(OCH$_3$)$_2$]$_6$ (4). Conventional method: [*n*-BuSn(O)OH]$_n$ (0.42 g, 2.00 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OCH$_3$)$_2$ (0.37 g, 2.00 mmol), yield 0.71 g (93.7%).

Solvent-free method: [*n*-BuSn(O)OH]$_n$ (0.11 g, 0.50 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OCH$_3$)$_2$ (0.09 g, 0.50 mmol), grinding time 30 min, yield 0.18 g (94.8%).

Mp: 155 °C (dec). Anal. Calcd (%) for $C_{78}H_{108}O_{30}Sn_6$: C, 41.86; H, 4.86. Found: C, 41.81; H, 4.91. ^{1}H NMR (δ, ppm): 0.79 (t, J = 7.33 Hz, 18H, *n*-butyl CH_3), 1.04−1.71 (m, 36H, *n*-butyl CH_2), 3.44 (s, 36H, −OCH_3), 6.91 (s, 6H, aromatic C*H*), 7.78 (s, 12H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −486.1 (s).

[*n*-BuSn(O)O$_2$C-C$_6$H$_3$-3,5-(OC$_9$H$_{19}$)$_2$]$_6$ (5). Conventional method: [*n*-BuSn(O)OH]$_n$ (0.21 g, 1.00 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OC$_9$H$_{19}$)$_2$ (0.41 g, 1.00 mmol), yield 0.54 g (89.6%).

Solvent-free method: [*n*-BuSn(O)OH]$_n$ (0.11 g, 0.50 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OC$_9$H$_{19}$)$_2$ (0.21 g, 0.50 mmol), grinding time 30 min, yield 0.29 g (95.2%).

Mp: 110 °C (dec). Anal. Calcd (%) for $C_{174}H_{300}O_{30}Sn_6$: C, 58.30; H, 8.44. Found: C, 58.29; H, 8.48. ^{1}H NMR (δ, ppm): 0.79 (t, J = 7.03 Hz, 36H, CH_3), 0.84 (t, J = 7.33 Hz, 18H, *n*-butyl CH_3), 1.14−1.55 (m, 168H, CH_2 CH_2), 1.71−1.79 (m, 36H, CH_2), 3.64 (t, J = 6.78 Hz, 24H, −OCH_2), 6.81 (s, 6H, aromatic C*H*), 7.65 (s, 12H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −486.0 (s).

{[*n*-Bu$_2$SnO$_2$C-C$_6$H$_4$-4-OCH$_3$]$_2$O}$_2$ (6). Conventional method: [*n*-Bu$_2$SnO]$_n$ (0.50 g, 2.00 mmol), HO$_2$C-C$_6$H$_4$-4-OCH$_3$ (0.30 g, 2.00 mmol), yield 0.75 g (97.0%).

Solvent-free method: [*n*-Bu$_2$SnO]$_n$ (0.10 g, 0.40 mmol), HO$_2$C-C$_6$H$_4$-4-OCH$_3$ (0.06 g, 0.40 mmol), grinding time 30 min, yield 0.14 g (91.6%).

Mp: 260 °C (dec). Anal. Calcd (%) for $C_{64}H_{100}O_{14}Sn_4$: C, 49.01, H 6.43. Found: C 49.05, H 6.45. ^{1}H NMR (δ, ppm): 0.84 (t, J = 7.31 Hz, 24H, *n*-butyl CH_3), 1.22−1.81 (m, 48H, *n*-butyl CH_2), 3.81 (s, 12H, −OCH_3), 6.79 (d, J = 8.40 Hz, 8H, aromatic C*H*), 7.96 (d, J = 8.40 Hz, 8H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −199.2 (s), −203.5 (s).

{[*n*-Bu$_2$SnO$_2$C-C$_6$H$_4$-4-OC$_9$H$_{19}$]$_2$O}$_2$ (7). Conventional method: [*n*-Bu$_2$SnO]$_n$ (0.50 g, 2.00 mmol), HO$_2$C-C$_6$H$_4$-4-OC$_9$H$_{19}$ (0.53 g, 2.00 mmol), yield 0.90 g (89.0%).

Solvent-free method: [*n*-Bu$_2$SnO]$_n$ (0.10 g, 0.40 mmol), HO$_2$C-C$_6$H$_4$-4-OC$_9$H$_{19}$ (0.11 g, 0.40 mmol), grinding time 30 min, yield 0.18 g (88.8%).

Mp: 230 °C (dec). Anal. Calcd (%) for $C_{96}H_{164}O_{14}Sn_4$: C, 57.16, H 8.19. Found: C 57.11, H 8.21. ^{1}H NMR (δ, ppm): 0.79 (t, J = 7.33 Hz, 12H, CH_3), 0.86 (t, J = 7.33 Hz, 24H, *n*-butyl CH_3), 1.23−1.39 (m, 80H, CH_2), 1.58−1.72 (m, 24H, CH_2), 3.84 (t, J = 6.45 Hz, 8H, −OCH_2), 6.92 (d, J = 8.44 Hz, 8H, aromatic C*H*), 7.88 (d, J = 8.44 Hz, 8H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −188.9 (s), −204.1 (s).

{[*n*-Bu$_2$SnO$_2$C-C$_6$H$_4$-4-OC$_{11}$H$_{23}$]$_2$O}$_2$ (8). Conventional method: [*n*-Bu$_2$SnO]$_n$ (0.25 g, 1.00 mmol), HO$_2$C-C$_6$H$_4$-4-OC$_{11}$H$_{23}$ (0.29 g, 1.00 mmol), yield 0.49 g (92.8%).

Solvent-free method. [*n*-Bu$_2$SnO]$_n$ (0.10 g, 0.40 mmol), HO$_2$C-C$_6$H$_4$-4-OC$_{11}$H$_{23}$ (0.12 g, 0.40 mmol), grinding time 30 min, yield 0.20 g (93.9%).

Mp: 210 °C (dec). Anal. Calcd (%) for $C_{104}H_{180}O_{14}Sn_4$: C, 58.66, H 8.52. Found: C 58.65, H 8.55. ^{1}H NMR (δ, ppm): 0.82 (t, J = 7.29 Hz, 12H, CH_3), 0.96 (t, J = 7.29 Hz, 24H, *n*-butyl CH_3), 1.12−1.40 (m, 96H, CH_2), 1.61−1.84 (m, 24H, CH_2), 3.78 (t, J = 6.50 Hz, 8H, −OCH_2), 6.88 (d, J = 8.46 Hz, 8H, aromatic C*H*), 7.78 (d, J = 8.46 Hz, 8H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −188.2 (s), −205.0 (s).

{[*n*-Bu$_2$SnO$_2$C-C$_6$H$_3$-3,5-(OCH$_3$)$_2$]$_2$O}$_2$ (9). Conventional method: [*n*-Bu$_2$SnO]$_n$ (0.50 g, 2.0 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OCH$_3$)$_2$ (0.37 g, 2.0 mmol), yield 0.78 g (93.5%).

Solvent-free method: [*n*-Bu$_2$SnO]$_n$ (0.10 g, 0.40 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OCH$_3$)$_2$ (0.07 g, 0.40 mmol), grinding time 30 min, yield 0.16 g (94.2%).

Mp: 195 °C (dec). Anal. Calcd (%) for $C_{68}H_{108}O_{18}Sn_4$: C, 48.37, H 6.45. Found: C 48.38, H 6.50. ^{1}H NMR (δ, ppm): 0.84 (t, J = 7.32 Hz, 24H, *n*-butyl CH_3), 1.22−1.61 (m, 48H, *n*-butyl CH_2), 3.74 (s, 24H, −OCH_3), 6.71 (s, 4H, aromatic C*H*), 7.61 (s, 8H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −192.72 (s), −205.7 (s).

{[*n*-Bu$_2$SnO$_2$C-C$_6$H$_3$-3,5-(OC$_9$H$_{19}$)$_2$]$_2$O}$_2$ (10). Conventional method: [*n*-Bu$_2$SnO]$_n$ (0.25 g, 1.00 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OC$_9$H$_{19}$)$_2$ (0.41 g, 1.00 mmol), yield 0.60 g (92.3%).

Solvent-free method: [*n*-Bu$_2$SnO]$_n$ (0.10 g, 0.40 mmol), HO$_2$C-C$_6$H$_3$-3,5-(OC$_9$H$_{19}$)$_2$ (0.16 g, 0.40 mmol), grinding time 30 min, yield 0.23 g (90.6%).

Mp: 220 °C (dec). Anal. Calcd (%) for $C_{132}H_{228}O_{18}Sn_4$: C, 61.50, H 8.91. Found: C 61.46, H 8.96. ^{1}H NMR (δ, ppm): 0.85 (t, J = 7.31 Hz, 24H, CH_3), 0.92 (t, J = 7.31 Hz, 24H, *n*-butyl CH_3), 1.21−1.54 (m, 120H, CH_2), 1.66−1.74 (m, 32H, CH_2), 3.90 (t, J = 6.75 Hz, 16H, −OCH_2), 6.68 (s, 4H, aromatic C*H*), 7.45 (s, 8H, aromatic C*H*). ^{119}Sn NMR (δ, ppm): −195.4 (s), −206.8 (s).

Gelation Experiments and Determination of Critical Gelation Concentrations (CGC). A weighed amount of organostannoxane along with an appropriate solvent (2 mL) were placed in a glass vial (2.5 cm length and 1 cm diameter) and heated with a hot-gun until the solid completely dissolved, affording an anisotropic solution. This was cooled to room temperature and left for 4 h. At this stage the state of the solution was monitored visually by turning the test vial upside-down. The material was classified as a *gel* if it did not exhibit gravitational flow while turning down the vial.

Sample Preparations. Optical Microscopic Experiments. A small amount of gel was taken on a plain glass slide (gel samples were fabricated using 8 wt % of the gelators **1**, **4**, **6**, and **9**; for other samples 5 wt % of gelators was used), air-dried for 15 min, and viewed under an optical microscope.

ESEM Experiments. Samples of the sol−gels were prepared by the freeze-drying method from their gel phases.[23] In a typical procedure, the gel was prepared in a rectangular thin wall glass container [1 × 3 × 3 cm^3]. After gelation, it was cooled by using liquid nitrogen and sealed. This was used for taking ESEM pictures. For the xerogel samples, the above-described gel was placed on a plain glass slide. Over a period of 2 days, the solvent

(23) For the preparation of dry samples for SEM observations, see: Jeong, S. W.; Shinkai, S. *Nanotechnology* **1997**, *8*, 179.

was removed under vacuum (~3 Torr) to produce a dried material (xerogel). This was then examined by ESEM.

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Supporting Information Available: Thermogravimetric curves for xerogels of compound **2** and **3** and additional optical and SEM images of gels and xerogels. This material is available free of charge via the Internet at http://pubs.acs.org.