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Structure Control in Organic−Inorganic Hybrids Using Hyperbranched High-Temperature Polymers

**J. L. Hedrick,* C. J. Hawker,* R. D. Miller,
R. Twieg, S. A. Srinivasan, and M. Trollsås**

Center for Polymeric Interfaces and Macromolecular Assemblies, IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

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Introduction

Hybrid organic−inorganic materials have received an increasing amount of attention in recent years due to ease of processing and the contribution of desirable properties from both the organic and inorganic components.[1] In choosing the precursor for the inorganic component, particular attention has been devoted to sol−gel, or spin-on-glass materials, for the preparation of the inorganic network. This reaction involves the simultaneous hydrolysis and condensation of metal alkoxides, such as tetraethoxysilane (TEOS), to produce a gel.[2−5] As the condensation reactions proceed, the formation of a continuous network causes a contraction in the gel.[6] The high interfacial area of the solid−liquid interface coupled with the reduction in chemical potential through the condensation reactions drives the shrinkage and, depending on the rate of drying, can introduce significant stress into the inorganic network.[7−9] Therefore, rapid drying can lead to extensive cracking and, for this reason, films of 1.0 μm or greater, are difficult to prepare in a manufacturing environment which severely limits the usefulness of these materials.

One method of overcoming this difficulty is to modify the spin-on-glass with an appropriately functionalized organic polymer in order to obtain nanometer scale phase separation which is highly desirable for thin film application. For TEOS-based systems, Chujo et al.[10,11] and others[12,13] have reported that nanoscale structures are only obtained when there is inorganic functionality (i.e., triethoxysilyl) on the organic polymer and a strong interaction (i.e., hydrogen bonding) between the components. Examples of such polymers include triethoxysilyl functional polyoxazolines,[11] poly(methyl methacrylate),[12] poly(vinyl acetate),[12] and others.[12,13] However, there are no examples of nanoscale organic−inorganic composite based on industrially important precondensed inorganic alkoxides, such as silsesquioxanes. This is due to the high temperatures required to cure these materials (ca. 400 °C) which demands thermally stable polymers, coupled with the much smaller role that specific interactions between the organic and inorganic phases play in controlling phase separation in these systems. To this end, we have investigated hyperbranched high-temperature polymers as the organic component in preparing nanoscale composites using silsesquioxanes.[14]

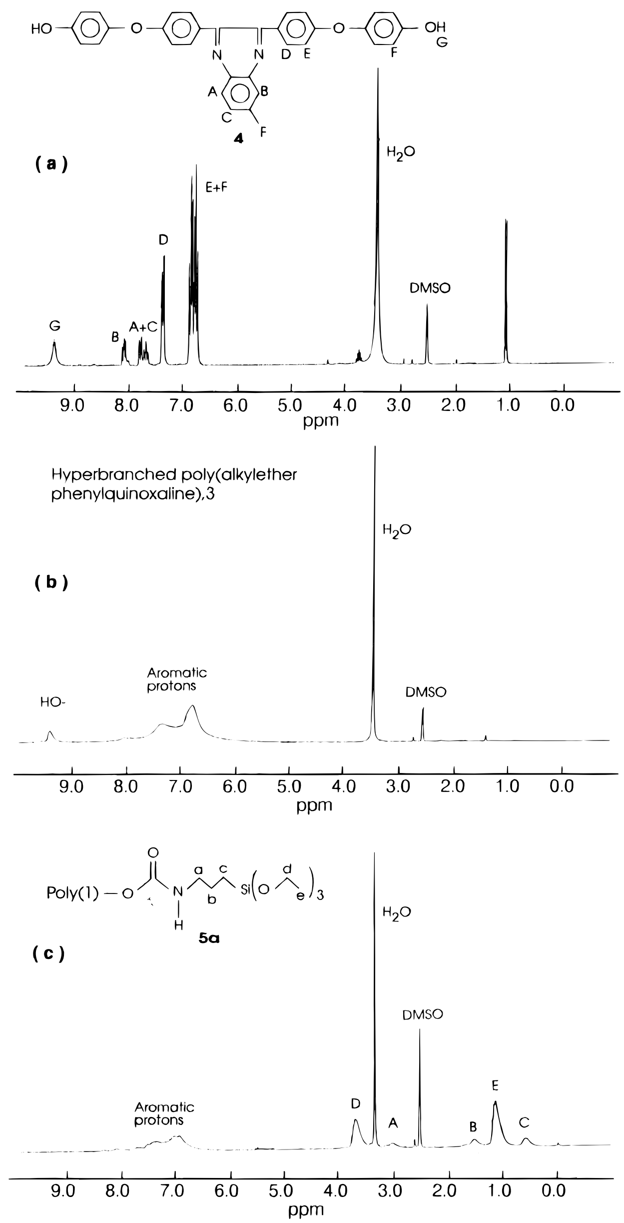
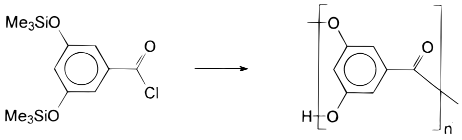


Figure 1. The ^{1}H-NMR of (a) **4**, (b) **3**, and (c) **5a**.

Scheme 1



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In this approach, the abundance of chain end functional groups in the hyperbranched system is exploited in an effort to maximize the interaction between the organic and inorganic phases. The relative ease with which the chain end functional groups of hyperbranched macromolecules can be modified also permits the interaction to be varied, therefore controlling phase separation. Due to the thermal requirements for the curing of the silsesquioxanes, hyperbranched polyesters (Scheme 1), **1**, based on 3,5-dihydroxybenzoic acid, **2**, and hyperbranched poly(aryl ether phenylquinoxaline) (Scheme 2), **3**, were chosen.[14,15] The synthesis of the AB$_2$ quinoxaline monomer, **4**, involves the initial reaction of 4,4′-difluorobenzil with 4-methoxyphenol followed by the condensation of the bisphenol-substituted benzil with 4-fluoro-*o*-phenylenediamine.[16] Polymerization of **4** was then carried out in either *N*-methyl-2-pyrrolidone (NMP) or *N*,*N*′-bis(dimethylpropylene)urea (DMPU) containing potassium carbonate and the polymer, **3**, isolated by precipitation into a 10-fold excess of methanol and refluxed in water to remove the remaining salts (Scheme 2). The resulting polymer had a T_g of 190 °C and an intrinsic viscosity of 0.48 dL/g. In both cases the parent

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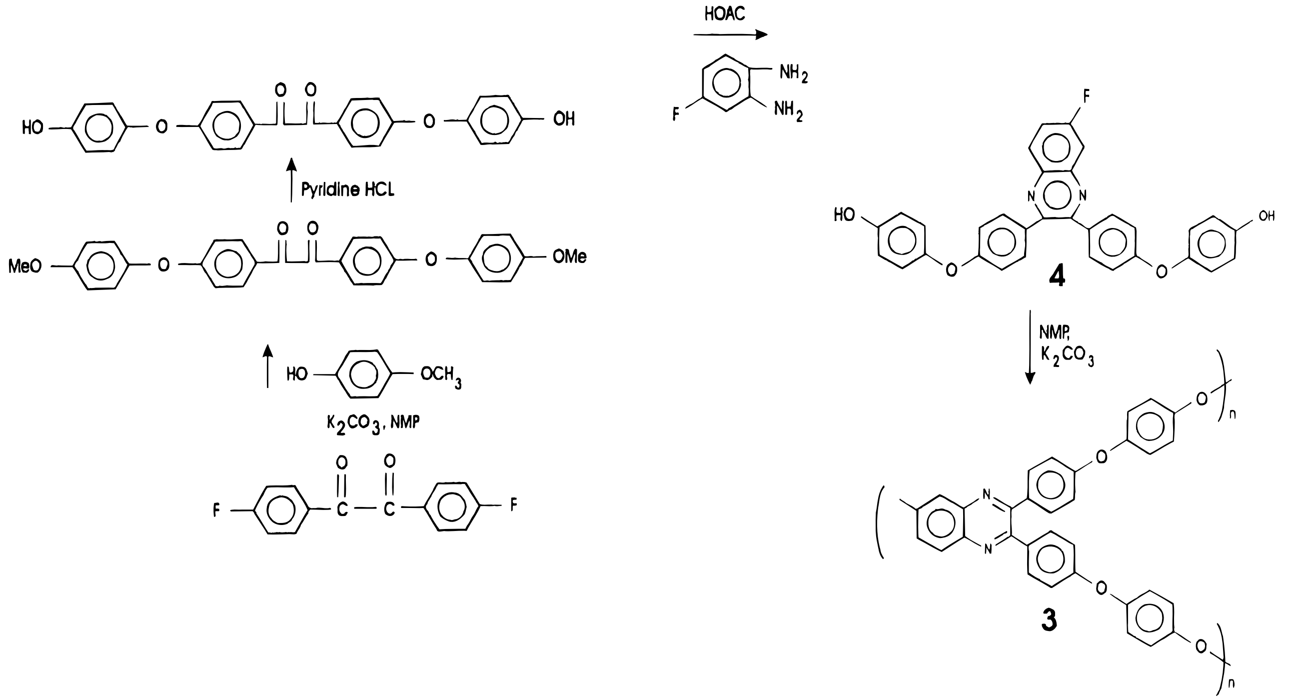
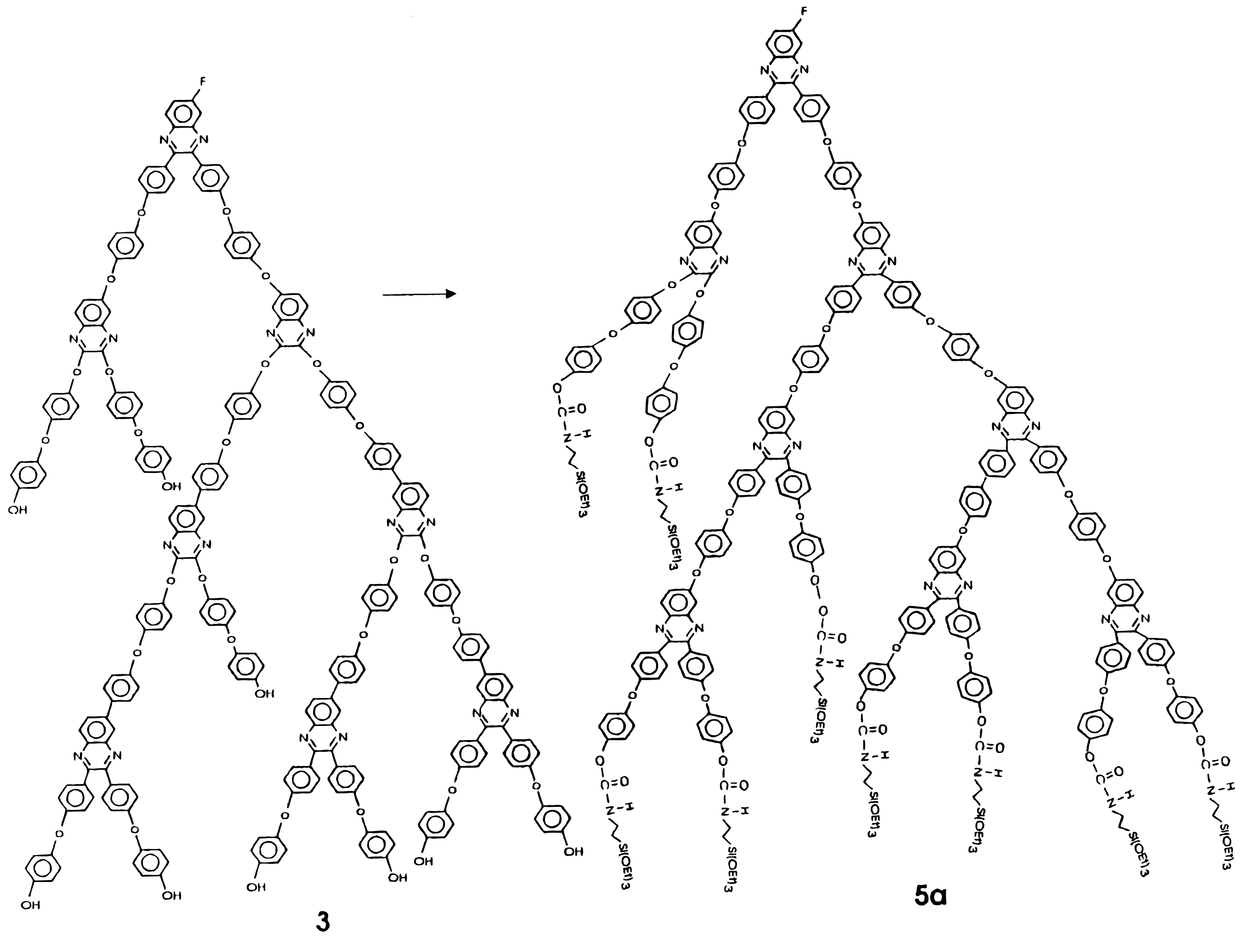
Scheme 2



Scheme 3



hyperbranched macromolecules contain numerous phenolic end groups which are capable of hydrogen bonding with the poly(silsesquioxane), albeit to different degrees.

To investigate the effect of the chain ends, the phenolic-terminated hyperbranched macromolecules were further functionalized with both 3-(isocyanatopropyl)-

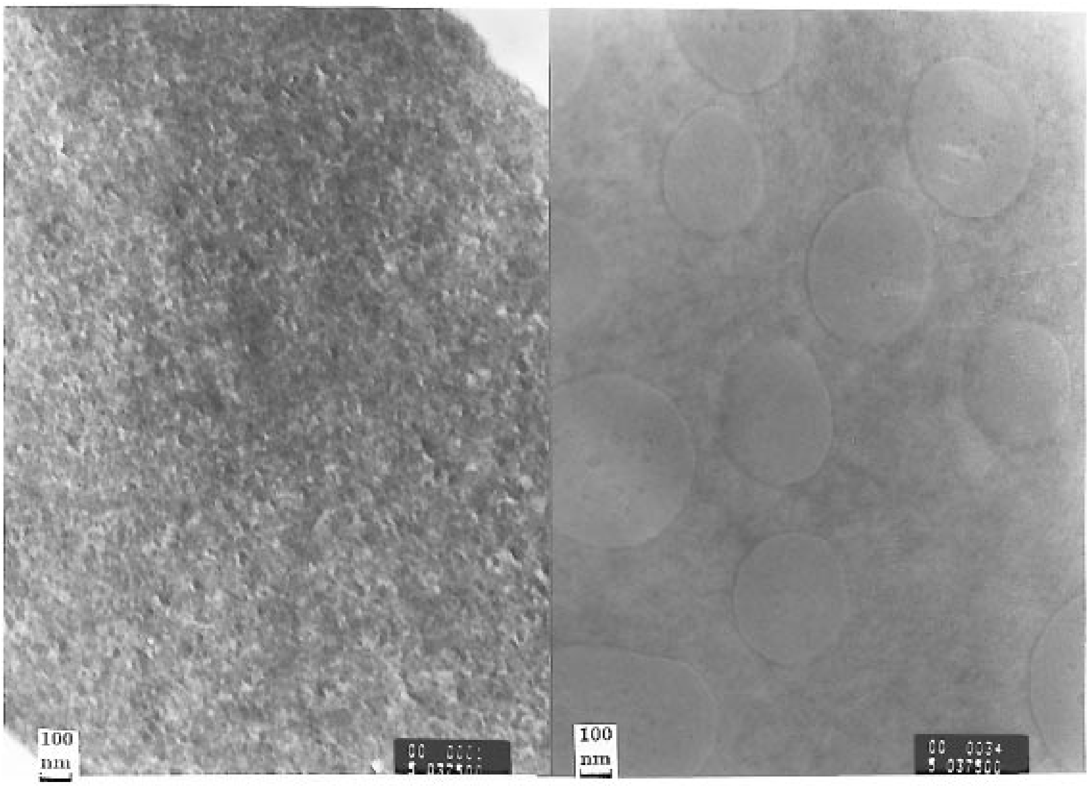
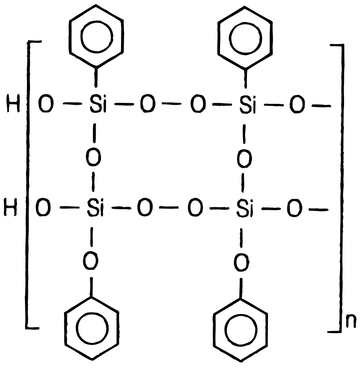


Figure 2. TEM micrograph of (right) **3** and (left) **5a**.

Scheme 4



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triethoxysilane and benzoyl chloride to give triethoxysilyl, **5a** and **6a**, and benzoyl-terminated, **5b** and **6b**, macromolecules (Scheme 3). The quantitative functionalization of the hydroxy groups of **3** could be easily followed by the change in the chemical shift of the aromatic protons ortho to the phenolic group and by the simultaneous disappearance of the phenolic proton (Figure 1). In a similar way, ^{1}H- and ^{13}C-NMR spectroscopy could be used to confirm the substitution of the hyperbranched polyester.

As described above, the inorganic matrix was derived from a precondensed poly(silsesquioxane), **7**, where the organic substituent on the silicon atom is a phenyl group (Scheme 4). Such silsesquioxanes have been variously described as a linear double chain ladder polymers, randomly linked polycyclic cages, or structurally random polymers.[17] One of the major advantages of these materials is that they show significantly less volume contraction upon condensation than TEOS-based analogs, providing inherently tougher films. Films of pure **7** were prepared by spin coating from NMP or DMPU and cured to 410 °C for 2 h. Crack and defect free films with thicknesses between 0.5 and 1.0 μm were prepared. The resulting networks were thermally stable as judged by thermogravimetric measurements, and no detectable softening point or T_g was observed by thermomechanical measurements.

Hybrid materials were prepared from (NMP) solutions of **7** and the relevant hyperbranched macromolecule containing 4% water and 2% base. The samples were initially cured to 180 °C for 2 h to initiate vitrification and prevent large scale phase separation prior to complete solvent removal. The films were then ramped to 410 °C and held for 2 h to effect complete cure. The weight percentage of the hyperbranched macromolecules in the composite was intentionally maintained low (ca. 20 wt %) in order to produce a vitrified matrix whose properties were dominated by the inorganic matrix.

Interestingly, the thermal stabilities of the composites were not compromised by the incorporation of the hyperbranched macromolecules and were comparable to that of the pure silsesquioxane materials. However, the nature of the chain ends of the hyperbranched macromolecules was shown to have a dramatic effect on the phase separation and morphology of the composite materials. For example, samples prepared using 20 wt % of the triethoxysilyl-terminated poly(quinoxaline), **5a**, were shown by TEM to undergo nanophase separation while the corresponding phenol-terminated derivative, **3**, resulted in micron-sized phase separation (Figure 2). As evidenced by the significant electron density contrast, the size scale of phase separation for **5a** is less than 50 nm and the resulting films, which were stable up to 5−10 microns in thickness, were optically transparent. In contrast, samples prepared with **3** were translucent with spherical hyperbranched “rich” regions on the order of 1−1.5 μm. Furthermore, the spatial arrangement of these regions are random which suggests a morphology resulting from a nucleation and growth mechanism. Analogous results were obtained with the hyperbranched polyester derivatives. Nanometer scale phase separation was observed for the triethoxysilyl functionalized derivative, **5b**, while micron-size phase separation was observed for phenol-terminated hyperbranched polyester, **1**. On going to the benzoyl-terminated derivative, **6**, gross phase separation on the order of hundreds of microns was observed which is fully consistent with a decreasing amount of interaction between the organic hyperbranched component and the inorganic silsesquioxane matrix as the chain end is varied from triethoxysilyl to phenolic to benzoyl.

In conclusion, it has been shown that the phase behavior of organic–inorganic composites can be controlled and manipulated by varying the nature of the chain end functionalities in thermally stable hyperbranched macromolecules. By employing reactive groups, such as triethoxysilyl, nanoscopic phase separation can be obtained leading to tough optically transparent films which has superior properties when compared to the parent sol–gel materials.

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(16) **4,4′-Bis(4-methoxyphenoxy)benzil:** To a 200 mL round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a thermometer, and a Dean-Stark trap fitted with a condenser and a nitrogen outlet were added 4,4′-difluorobenzil (50 mmol, 12.3 g), 4-methoxyphenol (110 mmol, 13.6 g), and anhydrous K_2CO_3 (70 mmol, 9.7 g). This was followed by the addition of 100 mL of *N*,*N*-dimethylacetamide and 30 mL of toluene as an azeotroping agent. The contents of the flask were maintained at 140–150 °C for 2–4 h to allow for the complete removal of water from the system. The reaction temperature was further raised to 160 °C and allowed to proceed for a further 12–14 h. The solution was subsequently cooled and filtered. Water was added dropwise to the filtrate with stirring, and the precipitate was collected by suction filtration, washed well with water, and air-dried. The pure product (22 g, 93%) was obtained by recrystallization from isopropyl alcohol (mp = 121–122 °C): ^{1}H-NMR (DMSO, 250 MHz) δ 7.84–7.9 (m, 4H), 6.97–7.13 (m, 12H), 3.76 (s, 6H); ^{13}C-NMR (DMSO, 250 MHz) δ 55.45, 115.38, 116.77, 121.92, 126.51, 132.34, 147.26, 156.67, 164.06, 193.31. **4,4′-Bis(4-hydroxyphenoxy)benzil:** In a 250 mL round-bottom flask with a stir bar were placed 4,4′-bis(4-methoxyphenoxy)benzil (7.81 g, 20 mmol) and pyridine hydrochloride (13.87 g, 120 mmol). The mixture was heated under nitrogen in a 220 °C oil bath for 45 min, after which time deprotection was complete. The mixture was cooled to 80 °C and diluted to a volume of 250 mL by dropwise addition of water. The crude product was isolated by suction filtration, washed with water, and then recrystallized from acetic acid to give the product (6.91 g, 81%) (mp = 220–221 °C): ^{1}H-NMR (DMSO, 250 MHz) δ 9.7 (s, 2H), 7.82–7.87 (d, 4H), 6.59–7.02 (m, 8H); ^{13}C-NMR (DMSO, 250 MHz) δ 116.55, 121.89, 126.34, 132.29, 145.9, 154.94, 164.32, 193.36. **2,3-Bis(4-hydroxyphenoxy)phenyl)-5-fluoroquinoxaline 2:** In a 250 mL round-bottom flask equipped with a stir bar, reflux condenser, and a nitrogen inlet was placed 4,4′-bis(4-hydroxyphenoxy)benzil (4.26 g, 10 mmol), 4-fluoro-1,2-phenylenediamine (1.36 g, 10 mmol), and acetic acid (75 mL). The resulting slurry was boiled for 2 h and then cooled and the solid isolated by suction filtration, washed with acetic acid, and air-dried. The product was recrystallized from ethyl acetate to give a light yellow colored powder (80% yield) (mp = 263–264.5 °C): ^{1}H-NMR (DMSO, 250 MHz) δ 9.41 (s, 2H), 8.11–8.18 (m, 1H), 7.73–7.88 (m, 2H), 7.41–7.45 (m, 4H), 6.77–6.93 (m, 8H); ^{13}C-NMR (DMSO, 250 MHz) δ 55.46, 115.38, 116.77, 121.92, 126.51, 132.33, 147.26, 156.68, 164.05, 193.31.

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