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“Plug and Play” Polymers. Thermal and X-ray Characterizations of Noncovalently Grafted Polyhedral Oligomeric Silsesquioxane (POSS)−Polystyrene Nanocomposites

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Noncovalent polymer side-chain modification is a versatile tool for the creation of complex assemblies.[1] The dynamic and modular nature of supramolecular assembly provides a unique approach to polymer structure, allowing multiple systems to be assembled using the same polymer chain.[2] Using these “plug and play” tailored polymeric systems, the efficiency and specificity of interactions between polymers and guests can be tailored through choice of recognition element. Additionally, the diversity of recognition motifs available[3] greatly expands upon the binary nature of simple electrostatic systems.[4]

Nanocomposite materials[5,6] with controlled structure and improved thermal and mechanical properties are key components in a range of emerging fields. In the area of hybrid materials, organic/inorganic additives such as polyhedral oligomeric silsesquioxane (POSS)[7] modifiers in polymeric systems have been used to create nanocomposites with improved thermal and mechanical properties.[8] POSS units have also recently drawn attention for their use as nanoscale, noncovalent “building blocks” in areas outside of polymeric additives, including self-assembled nanoparticle motifs,[9] surface modification,[10] and preparation of thin films.[11]

POSS molecules contain an inorganic cubic core surrounded by seven solubilizing organic groups (i.e., cyclopentyl or cyclohexyl) on the corners with the ability to add functionality at the eighth position.[12] The sterically influential (∼1.5 nm diameter) POSS units are stable to a variety of conditions, making them useful modifiers in multiple applications including nonablatives, atomic oxygen resistance, and fire protection.[12,13] Among the many attributes of POSS units is their strong tendency to crystallize,[14] as demonstrated by Coughlin et al., who not only showed that covalently attached POSS units on polyethylene copolymers aggregate and crystallize as nanocrystals,[15] but this aggregation can be controlled through choice of crystallization conditions.[16]

The coupling of engineered hydrogen-bonding interactions[1] with the ability to control POSS−POSS crystalline packing provides a versatile assembly strategy[8a] that augments the covalent methods that have recently been developed.[16] In this study, we report the noncovalent formation and characterization of POSS−thymine copolymer nanocomposites using thermal analysis and wide-angle X-ray scattering (WAXS) techniques.

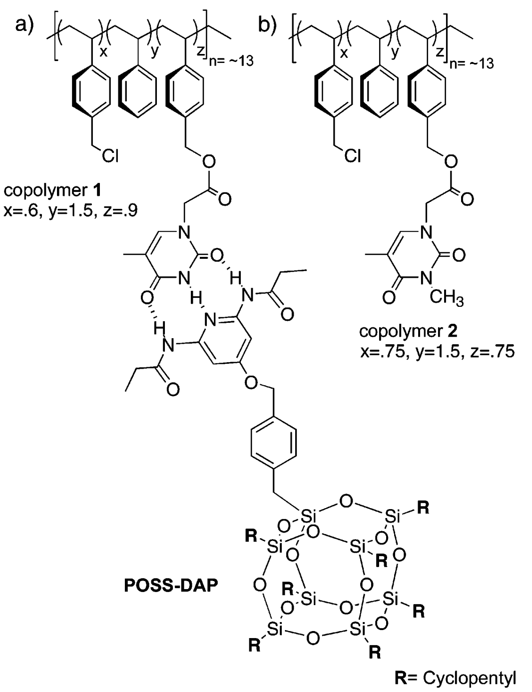

Figure 1. (a) Three-point hydrogen-bonding recognition between diamidopyridine-functionalized POSS monomer (POSS-DAP) and thymine-functionalized random copolymer **1**. (b) N-Methylated thymine copolymer **2** used as a non-hydrogen-bonding control.

Materials. Cyclopentyl-POSS-benzyl chloride monomer, containing seven cyclopentyl and one benzyl chloride group at the corner positions, was obtained from Hybrid Plastics, Inc. Diamidopyridine-functionalized POSS modifier (POSS-DAP), thymine-functionalized styrene copolymer **1**, and control N-methylated thymine copolymer **2** (Figure 1) were prepared according to previous reports.[17]

Experiment. *POSS-DAP/Thymine Copolymer Nanocomposites.* POSS-DAP units and thymine copolymer **1** were dissolved in $CHCl_3$ in ratios based upon thymine/DAP recognition unit. Nanocomposites mixed in 1:1 and 1:2 (diamidopyridine:thymine) ratios were dissolved in $CHCl_3$ and allowed to evaporate slowly under air. Films of POSS-DAP alone, thymine copolymer **1**, control N-methylated thymine copolymer **2** alone and with POSS-DAP (1:1) were prepared in analogous fashion. Upon drying, samples were powdered and placed into WAXS capillaries.

Materials Characterization. Crystal ordering in the POSS-DAP/thymine copolymer **1** and control N-methylated thymine copolymer **2** nanocomposites was characterized by X-ray powder diffractometry using a Siemens D500 diffractometer operating in normal-transmission mode with Ni-filtered Cu Kα radiation.

Thermogravimetric analysis was carried out using a TA Instruments TGA 2050 thermogravimetric analyzer with a heating rate of 20 °C/min from room temperature to 700 °C under a continuous air purge of 50 mL/min.

Results. Wide-angle X-ray scattering (WAXS) studies were performed to assess the crystal order of POSS domains in the POSS-DAP−polymer **1**/**2** systems (Figure 2). X-ray powder diffraction patterns reveal the presence of defined POSS crystalline regions in all

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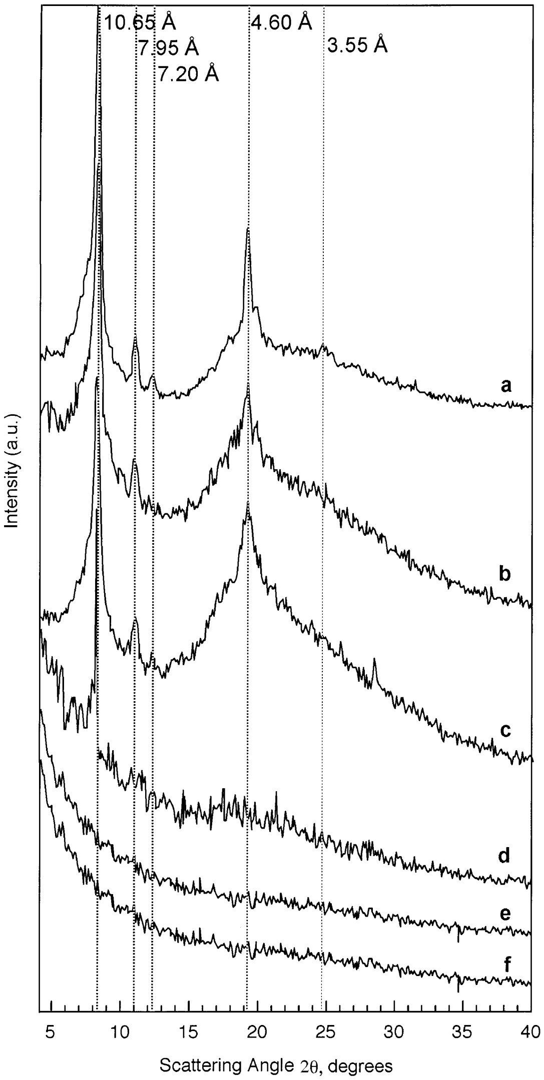

Figure 2. Line profiles of WAXS data of thymine−copolymer/POSS-DAP nanocomposites: (a) POSS-DAP, (b) POSS-DAP/thymine copolymer **1:1**, and (c) **1:2** showing substantial crystallinity. (d) Control N-methylated thymine copolymer **2** with POSS-DAP exhibiting limited crystallinity. Random copolymers with (e) thymine and (f) N-methylated thymine functionality showing no crystalline domains.

mixed ratio, hydrogen-bonding samples. Neither diffractograms of the thymine copolymer **1** alone or the control N-methylated thymine copolymer **2** show any signs of crystalline order (e and f). Also, neither shows the usual halo at the intermediate angles normally found in amorphous polymers, but both clearly show an increase in scattered intensity at low angle, indicative of unspecified structural features of relatively large size scale. Diffractograms of POSS-DAP alone (a) show very intense, characteristic POSS crystalline peaks at ~8.1° (equivalent to an interplanar spacing of 10.65 Å), 11.0° (7.95 Å), 12.2° (7.20 Å), 19.1° (4.60 Å), and 24.8° (3.55 Å). These intense reflections are also observed in nanocomposites with thymine copolymer **1**. In both 1:1 (b) and 1:2 (c) POSS-DAP/thymine copolymer ratios, the intense POSS peaks remain, although with broadening of the reflection at 19.1° (4.60 Å) in particular. This suggests that the POSS crystalline domains are disordered or that crystallite size is limited in the system with three-point hydrogen bonding with thymine copolymer **1**.

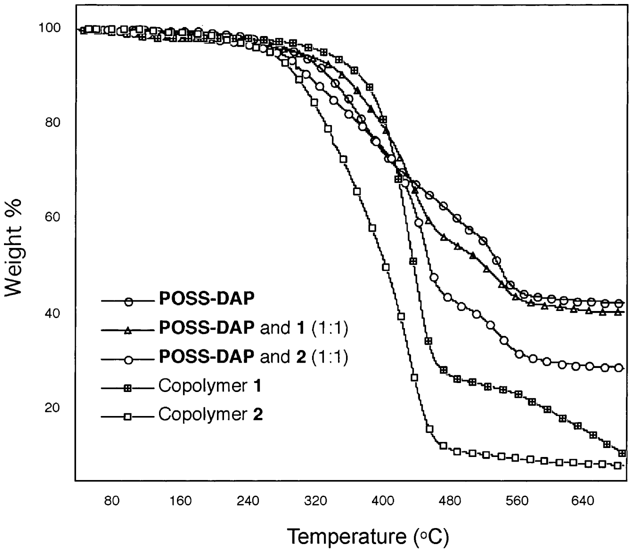

Figure 3. TGA traces of POSS-DAP/thymine copolymer nanocomposites under air.

Control samples of N-methylated thymine polymer **2** show only a hint of POSS crystalline packing (d), with only the strongest POSS reflection at ~8.1° (1.065 nm) clearly visible while the others have all but disappeared. This indicates that hydrogen bonding with copolymer **1** strongly enhances POSS crystalline growth relative to the N-methylated thymine polymer **2**.

Investigations into the thermal stabilities of these mixed POSS−polymer systems were conducted using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). DSC studies suggest that POSS-DAP hydrogen bonding with **1** is hindering movement of the polymer chain. A glass transition temperature (T_g) of 195 °C is observed for copolymer **1**. Subsequent addition of POSS-DAP effectively halts any movement of the polymer chain, implying that crystallites of POSS "pin" the polymer chain, as indicated by the disappearance of a polymer T_g in the DSC (see Supporting Information).

Solid-state TGA studies collected from single traces effectively demonstrate the role that multiple hydrogen-bonding interactions play in enhancing the thermal stability of the composite structures (Figure 3). The temperature at 10% weight loss for control copolymer **2** of 329 °C is significantly lower than copolymer **1** with a 10% weight loss observed at 372 °C, presumably due to stabilization of the matrix through thymine−thymine hydrogen bonding. In POSS-DAP nanocomposites composed of copolymer **1** and control copolymer **2** (1:1), a distinct modulation in thermal stability is observed in nanocomposites that can hydrogen bond vs control nanocomposites that cannot. Interestingly, in nanocomposites with POSS-DAP (1:1), the temperature at 10% weight loss increases very slightly to 338 °C with control copolymer **2** and slightly decreases to 351 °C with copolymer **1**. The decrease in temperature observed with the POSS-DAP−**1** composites presumably arises from the destabilization of the intramolecularly hydrogen-bound thymine−thymine interactions in order to incorporate the POSS units. In strong contrast, the temperature at 50% weight loss increases from 474 °C with control copolymer **2** to 521 °C with copolymer **1**. This increase in thermal stability can be attributed to the POSS−POSS crystalline packing interactions within copolymer **1** arising from multiple hydrogen bond interactions.

In summary, recognition unit-modified POSS units self-assemble in the presence of a random thymine copolymer **1**. In contrast, with N-methylated thymine copolymer **2** POSS crystalline growth is halted altogether. Taken together, these studies demonstrate cooperative self-assembly based on hydrogen bond recognition coupled with POSS–POSS interactions. Thermal characterization of the POSS/copolymer nanocomposites effectively demonstrates the advantages of POSS crystallinity and the overall benefits of multiple hydrogen-bonding interactions within polymer systems. Further studies of the structural and thermal properties of these polymers are underway.

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Supporting Information Available: Gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy of thymine copolymer **1** and control N-methylated thymine copolymer **2**; thermal analysis by DSC of thymine/POSS-DAP nanocomposites. This material is available free of charge via the Internet at http://pubs.acs.org.

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