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Hemi-Telechelic Polystyrene-POSS Copolymers as Model Systems for the Study of Well-Defined Inorganic/Organic Hybrid Materials

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The combination of different inorganic additives and organic polymers, in conjunction with the appropriate processing methods, can produce hybrid materials with new properties for electrical, optical, structural, or related applications.[1−3] Typically, properties such as the glass transition temperature, T_g, melting point, and stress−strain behavior or microphase separation can be altered by introducing an inorganic component into an organic polymer matrix.[4,5] Layered organic/inorganic nanocomposites[6] and silica gel-derived hybrids[7,8] are but two examples of organic/inorganic composites. In what is commonly called the "top-down" approach the various components are combined together with mechanical work and/or thermal energy. Blended systems suffer from a lack of further processability and control due to difficulties with dispersion of the inorganic component. On the other hand, systems such as silica gel-derived hybrids are a result of postpolymerization formation of a network that is a function of pH of the solution or the structure of the precursor. This methodology gives rise to hybrid organic/inorganic polymers which can conveniently be used for membrane or coating applications.[8] Nonetheless, the final inorganic structure is poorly defined due to the randomness of the network cross-link formation. These two approaches, component blending or postreaction cross-linking, are the most commonly taken to prepare hybrid organic−inorganic systems. Both approaches suffer from a lack of control over the microstructure giving rise to an "ill-defined" material.

An alternative approach to generating organic/inorganic hybrid structures would be to start at the molecular level using well-defined building blocks. Relatively few studies detailing the synthesis and characterization of controlled architectures using this concept have been completed.[9−15] Expanding the scope of novel hybrid materials is of interest not only from the standpoint of the overall synthetic challenge but also critical in order to validate the self-assembly properties predicted from computational investigations.[16−18] The use of anionic polymerization to produce well-defined organic−inorganic hybrid structures has not yet been fully investigated. The synthetic utility of anionic polymerization is well documented for the synthesis of organic block copolymers.[19] Replacement of one of the organic domains in a block copolymer architecture with a well-defined inorganic moiety presents the opportunity to compare, or contrast, the new hybrid copolymers obtained with their conventional organic counterparts. New chemical and physical properties are likely to be found from the resultant hybrid copolymers.

Polyhedral oligomeric silsesquioxanes (POSS) are inorganic nanosized particles and are potential candidates to control microstructure. These building blocks are of particular interest due to their molecularly precise structure as well as their solubility in common organic solvents.[20,21] Experimental protocols have been developed over the past 40 years so as to have good yield and control over the structure of the POSS macromer. The so-called T_8 POSS series has a cubic core with eight silicon atom at each corner and an oxygen bridge between each silicon atom. Seven silicon atoms bear an organic group that provides solubility, and a reactive group is generally attached to the eighth silicon atom. It is possible to incorporate this ∼1.5 nm diameter macromonomer into organic polymers. Random copolymers incorporating POSS have been prepared that are either thermosets or thermoplatics.[22−35] These represent a category of new hybrid polymers with a tremendous technological potential.[36,37] Control over the placement of the POSS within an organic polymer is possible using living/controlled polymerization methodologies. Matyjaszweski[9,10,38] has incorporated the POSS inorganic particle into both linear and star systems using ATRP. Amphiphilic telechelic polymers having a poly(ethylene oxide) backbone and POSS end groups have been independently prepared by Mather and Frey.[12,39]

The tethering of POSS to an anionically synthesized polymer will extend the range of materials as well as the morphologies that can be achieved. The living anionic synthesis of hydroxyl-terminated polystyrene has been described in the literature.[40−42] The molecular weight range of the hydroxyl-terminated polystyrene samples was chosen so that the radius of gyration of the polymer was comparable to that of the POSS particle.[43,44] Polystyrene chains with a number-average molecular weight, M_n, of 900 and 16 000 g/mol have radii of gyration of 8.5 and 34 Å, respectively, vs a radius of approximately 7.5 Å for the POSS particle. Tethering of the isocyanate-modified POSS particle (POSS-NCO) to the polystyrene chains was achieved through the formation of a urethane linkage (Figure 1). The syntheses of amphiphilic telechelic polymers having a poly(ethylene oxide) backbone and POSS end groups are straightforward as the purification of the final product can be achieved based on solubility differences of the reagents. In our case an efficient, highly yielding coupling reaction must be used due to the comparable solubility of POSS and polystyrene in common organic solvents.

To avoid extensive purification, an equimolar amount of POSS-NCO with respect to the hydroxyl-terminated polystyrene was used in the urethane formation chemistry. Urethane formation was promoted by the use of dibutyltin dilaurate at 90 °C in toluene solution.[45]

A representative synthesis of the hemi-telelchelic hybrids is the conversion of hydroxyl-terminated polystyrene PSOH 4, M_n and PDI of 4890 g/mol and 1.11, to PS-POSS 4 with a M_n and PDI of 6040 g/mol and 1.06, respectively (entry 4, Table 1). The increase in molecular weight is as expected for all samples given the molar mass of POSS-NCO (1058.56 g/mol). The retention of the narrow molecular weight distribution indicates the absence of side reactions (Figure 3). An equimolar amount of polystyrene and POSS-NCO was

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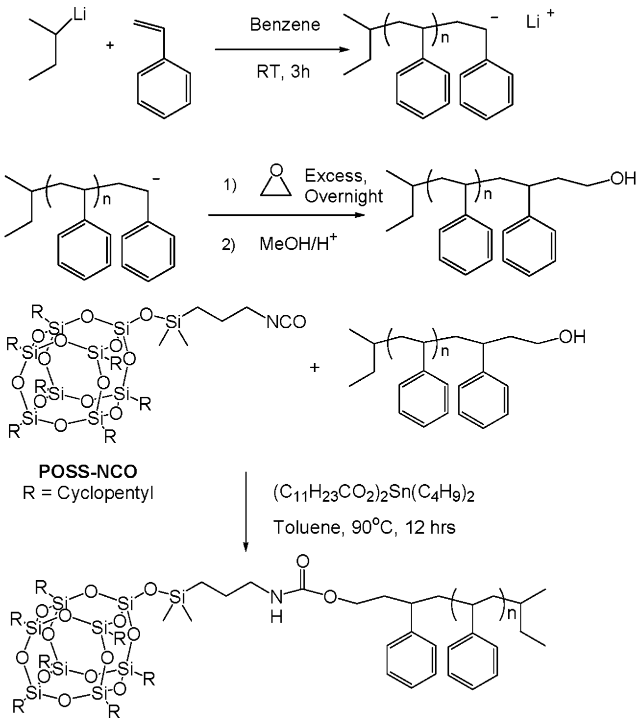

Figure 1. Synthesis of hemi-telechelic POSS−polystyrene hybrids.

used, and no residual starting material is seen within the resolution limit of the GPC, confirming that the coupling reaction goes to completion.

The exclusive formation of the expected product can be observed by comparison of the ^{1}H NMR spectra of the two starting materials and the final product (Figure 2). The methylene protons α to the hydroxyl group of the PSOH shifts downfield from δ 3.2 ppm to δ 3.67 ppm upon reaction. The corresponding methylene protons α to the isocyanate group in POSS shifts downfield from δ 3.26 ppm to δ 3.67 ppm. The newly formed urethane N−H signal appears at δ 4.38 ppm. Integration confirms that there is one molecule of POSS per polystyrene chain. Similar conclusions are drawn from the ^{13}C NMR spectra.

The FT-IR spectrum confirms the appearance of the urethane linkage as shown by the N−H absorption band at 3300 cm^{-1} and a carbonyl stretching absorption band at 1728 cm^{-1}. The isocyanate and terminal hydroxyl group absorption bands at 2272 and 3400 cm^{-1} of the two starting materials, respectively, have disappeared. Upon heating, the N−H adsorption band intensity does not change, implying that no interchain hydrogen bonding is taking place between the urethane linkages. Thus, any resultant morphology will not be dictated by hydrogen bonding in these PS-POSS copolymers.

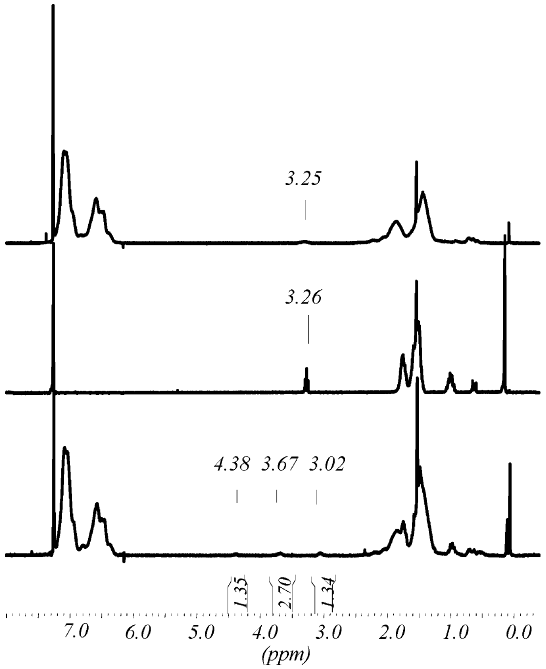

Figure 2. ^{1}H NMR spectra of hydroxylpolystyrene (top, PSOH 4), POSS-NCO (middle), and hemi-telechelic PS-POSS 4 (bottom).

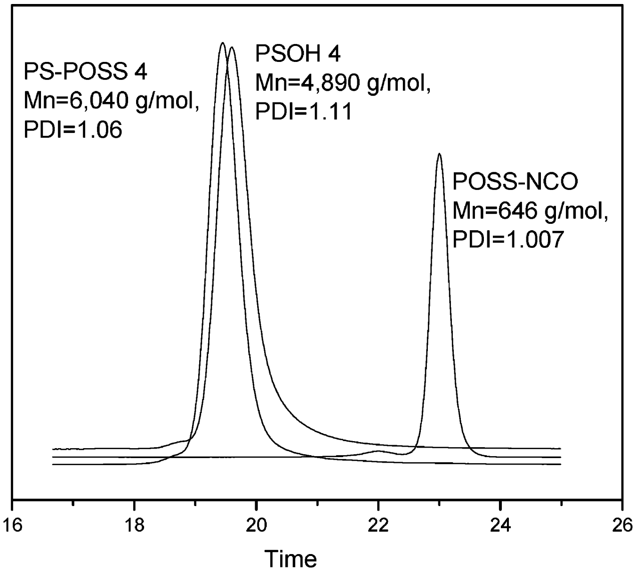

Figure 3. Overlays of the gel permeation chromatograms for the experiments in entry 4 of Table 1.

An increase in the char yield under both air and nitrogen atmospheres is observed by TGA for PS-POSS 4 hybrids compared to the PSOH 4 analogues (Figure S2, Supporting Information). The decomposition tem-

Table 1. Molecular Weights and Polydispersities of Hydroxyl-Terminated Polystyrene Precursors and the PS-POSS Hybrids

entry	sample	M_n (GPC)	PDI	T_g (°C)	sample	M_n (GPC)	PDI	T_g (°C)
1	PSOH 1	873	1.11	4.72	PS-POSS 1	1.91E+03	1.07	64
2	PSOH 2	2.03E+03[a]	1.11	79	PS-POSS 2	3.17E+03	1.11	78
3	PSOH 3	2.53E+03	1.11	77	PS-POSS 3	2.79E+03	1.12	75
4	PSOH 4	4.89E+03	1.11	90.7	PS-POSS 4	6.04E+03	1.06	92
5	PSOH 5	8.47E+03	1.05	97.9	PS-POSS 5	9.60E+04	1.06	99
6	PSOH 6	1.10E+04	1.06	104	PS-POSS 6	1.12E+04	1.07	103
7	PSOH 7	1.65E+04	1.06	105.7	PS-POSS 7	1.69E+04	1.06	104

[a] Read as 2.03 × 10^3.

perature is slightly higher for the hybrid hemitelechelic polymer than for POSS-NCO itself. A difference is exhibited between the trace of PS-POSS under an air and a nitrogen atmosphere. Under a nitrogen purge PSOH is observed to be more stable than PS-POSS due to the chemical linkage between the polystyrene and the POSS moiety. The linkage contains $-NHCO_2-$, which is an easily cleavable functional group. Under an air purge, PS-POSS 4 is more stable than PSOH 4. It is assumed that POSS decomposes in air by forming a silica-like layer, which protects the bulk material from further oxidation.[32]

The glass transition temperature for the hydroxyl-terminated polystyrene oligomers was found to be dependent on molecular weight. The T_g varies from 47.2 °C for the lowest molecular weight oligomer (PSOH 1) to 105.7 °C for the 16 500 g/mol sample (PSOH 7). No difference in T_g can be observed for the corresponding PS-POSS hybrid hemi-telechelics when compared to their PS analogues, with the exception of PSOH 1 and PS-POSS 1. The presence of POSS tethered at the end of the polystyrene chain does not alter the T_g, suggesting that the POSS moieties and polystyrene chains are secluded from each for the higher molecular weight samples. In the case of the shortest polystyrene chain the large molar mass of POSS is apparently sufficient to raise the T_g by 17 °C.

An increase in the aggregate size of POSS domains is observed by WAXS with an increase of the weight percent of POSS.[46] The main diffraction peak for the POSS monomer, observed at $2\theta = 8.6°$ corresponding to d spacing of ~10.8 Å, increases with the weight percent of POSS. The width of this peak indicates that the size of the aggregates is fairly small, only a few POSS cubes per aggregates. The aggregation diminishes, and perhaps is completely suppressed, as the polystyrene chain length increases.

In summary, a synthetic protocol for preparing well-defined POSS–polystyrene hemi-telechelic hybrids has been developed. These model systems provided an experimental opportunity to probe the ordering, or aggregation behavior, of inorganic nanoparticles within polymeric matrices. Furthermore, the versatility of the chemistry used provides an extension of traditional block copolymers currently available for study to include organic–inorganic block copolymers. Investigations in these directions are currently underway.

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Supporting Information Available: Details of the synthetic procedures for preparing POSS-PS hybrids are provided as well as characterization of these materials by ^1H and ^{13}C NMR spectroscopy, TGA, and WAXS. This material is available free of charge on the Internet at http://pubs.acs.org.

References and Notes

(1) Kickelbick, G. *Prog. Polym. Sci.* **2003**, *28*, 83–114.
(2) Gonsalves, K. E.; Merhari, L.; Wu, H. P.; Hu, Y. Q. *Adv. Mater.* **2001**, *13*, 703–714.
(3) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633–2656.
(4) Pinnavaia, T. J.; Beal, G. W. *Polymer Clay Nanocomposites*; John Wiley & Son: New York, 2001.
(5) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1755–1758.
(6) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29-&.
(7) Corriu, R. J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 1376–1398.
(8) Wen, J. Y.; Wilkes, G. L. *Chem. Mater.* **1996**, *8*, 1667–1681.
(9) Pyun, J.; Matyjaszewski, K.; Wu, J.; Kim, G. M.; Chun, S. B.; Mather, P. T. *Polymer* **2003**, *44*, 2739–2750.
(10) Pyun, J.; Matyjaseweski, K. *Macromolecules* **1999**, *33*, 217–220.
(11) Pyun, J.; Miller, P. J.; Matyjaszewski, K. *Abstr. Pap. Am. Chem. Soc.* **2000**, *219*, U390–U390.
(12) Kim, B. S.; Mather, P. T. *Macromolecules* **2002**, *35*, 8378–8384.
(13) Riggs, J. E.; Guo, Z. X.; Carroll, D. L.; Sun, Y. P. *J. Am. Chem. Soc.* **2000**, *122*, 5879–5880.
(14) Song, T.; Dai, S.; Tam, K. C.; Lee, S. Y.; Goh, S. H. *Langmuir* **2003**, *19*, 4798–4803.
(15) Song, T.; Dai, S.; Tam, K. C.; Lee, S. Y.; Goh, S. H. *Polymer* **2003**, *44*, 2529–2536.
(16) Zhang, Z. L.; Horsch, M. A.; Lamm, M. H.; Glotzer, S. C. *Nano Lett.* **2003**, *3*, 1341–1346.
(17) Thompson, R. B.; Ginzburg, V. V.; Matsen, M. W.; Balazs, A. C. *Science* **2001**, *292*, 2469–2472.
(18) Lamm, M. H.; Chen, T.; Glotzer, S. C. *Nano Lett.* **2003**, *3*, 989–994.
(19) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.
(20) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313–4317.
(21) Voronkov, M. G.; Lavrent'yev, V. I. In *Topics in Current Chemistry*; Boschke, F. L., Ed.; Springer-Verlag: Berlin, 1982; Vol. 102, pp 199–236.
(22) Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. *Macromolecules* **1993**, *26*, 2141–2142.
(23) Shockey, E. G.; Bolf, A. G.; Jones, P. F.; Schwab, J. J.; Chaffee, K. P.; Haddad, T. S.; Lichtenhan, J. D. *Appl. Organomet. Chem.* **1999**, *13*, 311–327.
(24) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromolecules* **1995**, *28*, 8435–8437.
(25) Haddad, T. S.; Viers, B. D.; Phillips, S. H. *J. Inorg. Organomet. Polym.* **2001**, *11*, 155–164.
(26) Romo-Uribe, A.; Mather, P. T.; Haddad, T. S.; Lichtenhan, J. D. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1857–1872.
(27) Lee, A.; Lichtenhan, J. D. *Macromolecules* **1998**, *31*, 4970–4974.
(28) Lee, A.; Lichtenhan, J. D. *J. Appl. Polym. Sci.* **1999**, *73*, 1993–2001.
(29) Mather, P. T.; Jeon, H. G.; Romo-Uribe, A.; Haddad, T. S.; Lichtenhan, J. D. *Macromolecules* **1999**, *32*, 1194–1203.
(30) Fu, B. X.; Hsiao, B. S.; Pagola, S.; Stephens, P.; White, H.; Rafailovich, M.; Sokolov, J.; Mather, P. T.; Jeon, H. G.; Phillips, S.; Lichtenhan, J.; Schwab, J. *Polymer* **2001**, *42*, 599–611.
(31) Zheng, L.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2001**, *34*, 8034–8039.
(32) Zheng, L.; Farris, R. J.; Coughlin, E. B. *J. Polym. Sci., Polym. Chem.* **2001**, *39*, 2920–2928.
(33) Zheng, L.; Waddon, A. J.; Farris, R. J.; Coughlin, E. B. *Macromolecules* **2002**, *35*, 2375–2379.
(34) Zheng, L.; Kasi, R. M.; Farris, R. J.; Coughlin, E. B. *J. Polym. Sci., Polym. Chem.* **2002**, *40*, 885–891.
(35) Zheng, L.; Hong, S.; Cardoen, G.; Burgaz, E.; Gido, S. P.; Farris, R. J.; Coughlin, E. B., submitted for publication.
(36) Wu, H. P.; Hu, Y. Q.; Gonsalves, K. E.; Yacaman, M. J. *J. Vac. Sci. Technol. B* **2001**, *19*, 851–855.
(37) Xiao, S.; Nguyen, M.; Gong, X.; Cao, Y.; Wu, H. B.; Moses, D.; Heeger, A. J. *Adv. Funct. Mater.* **2003**, *13*, 25–29.
(38) Miller, P. J.; Kickelbick, G.; Nakagawa, Y.; Diamanti, S.; Pacis, C.; Matyjaszewski, K. *Abstr. Pap. Am. Chem. Soc.* **1998**, *215*, U394–U395.
(39) Knischka, R.; Dietsche, F.; Hanselmann, R.; Frey, H.; Mulhaupt, R.; Lutz, P. J. *Langmuir* **1999**, *15*, 4752–4756.
(40) Morton, M. F. L. J. *Rubber Chem. Technol.* **1974**, *48*, 359.

(41) Quirk, R. P.; Ma, J. J. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 2031−2037.
(42) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 3211−3234.
(43) Ballard, D. G. H.; Wignall, G. D.; Schelten, J. *Eur. Polym. J.* **1973**, *9*, 965−969.
(44) Wignall, G. D.; Ballard, D. G. H.; Schelten, J. *Eur. Polym. J.* **1974**, *10*, 861−865.
(45) See Supporting Information for detailed synthetic protocols.
(46) See Supporting Information for WAXS profiles.

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