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Hybrid Organic−Inorganic Thermoplastics: Styryl-Based Polyhedral Oligomeric Silsesquioxane Polymers

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The design of new materials with enhanced properties continues to be a driver for the investigation of hybrid materials. As hybrid materials are copolymers based on inorganic and organic comonomers, they display enhanced properties by bridging the property space between two dissimilar types of materials.[1] A typical hybrid material will contain a cross-linked inorganic phase bound (often covalently) with an organic phase. Depending on the relative amounts of the two components, the properties of the resulting hybrid are intermediate between those of an inorganic and an organic polymer. Such methodology can be used to create either plastic inorganics or toughened plastics and is superior to traditional blending methods.[1b] However, because such materials are cross-linked networks, they are difficult to study and control at the molecular level and are also difficult to process.

We have taken a unique approach to the synthesis of hybrid materials by designing polymerizable inorganic oligomers[2] with an exactly defined degree of polymerization of eight, $(RSiO_{1.5})_8$. These polyhedral oligomeric silsesquioxane (POSS) macromers have an inorganic silica-like core and are surrounded by eight organic groups, of which seven are inert and one is reactive (Figure 1). Polymerization at the single reactive "P" site results in a linear polymer containing monodisperse, nanosize inorganic clusters[3,4] pendent to an organic polymer backbone.[2]

This approach allows us to study the effect of a well-defined inorganic segment intimately connected to a variety of organic polymer backbones (e.g. acrylates, styrenes, polynorbornenes, carbonates, esters, amides, LCP's, etc.) and to develop processable thermoplastic hybrid materials. By focusing on linear polymeric systems, we had hoped to obtain melt-processable hybrids amenable to study in solid, solution, and molten states. This paper presents our initial attempts at synthesizing hybrid polymers and copolymers using a POSS macromer containing a styrylethyl moiety.

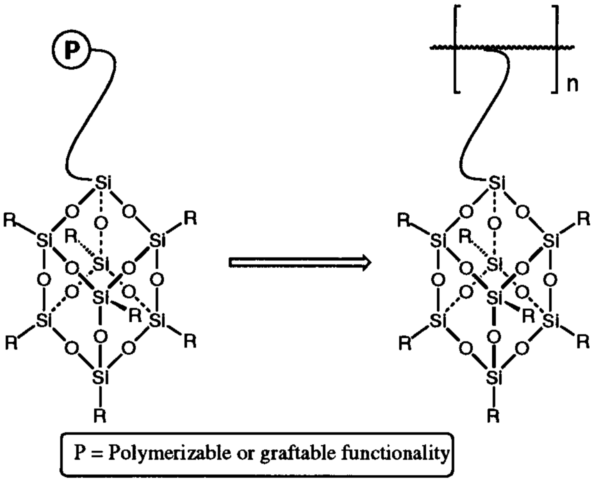

Figure 1. POSS macromer converted to a hybrid polymer with a pendent architecture.

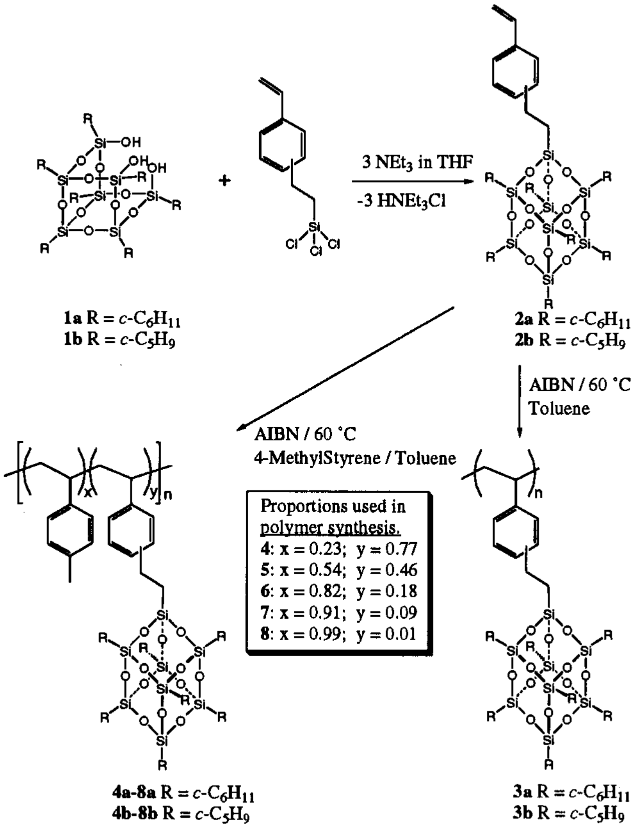

Figure 2. POSS styryl macromer synthesis and polymerization.

The synthesis of a POSS macromer containing only one polymerizable group has been achieved by derivatizing the known trisilanols $R_7Si_7O_9(OH)_3$ **1a** (R = cyclohexyl) and **1b** (R = cyclopentyl).[5] These trisilanols are quantitatively "corner capped" with (styrylethyl)trichlorosilane (a 3:1 mixture of para and meta isomers), with isolated yields greater than 90% (Figure 2).[6] The resulting macromers **2a** and **2b** have a spherical (Si_8O_{12}) inorganic core, surrounded by seven inert alkyl groups for solubility and one reactive ethylstyrene group for polymerization. An interesting observation is that the cyclohexyl derivative **2a** is about twice as soluble as its cyclopentyl counterpart **2b**, and these solubility differences are magnified for the homopolymers of **2a** and **2b**; in fact, the cyclopentyl homopolymer is insoluble in THF. This is reminiscent of the solubility of the trisilanols **1a** and **1b**, for which the cyclohexyl derivative is an order of magnitude more soluble than the cyclopentyl derivative in THF. Solubility differences among various $R_8Si_8O_{12}$ molecules have been noted before and are believed to be related to the lattice energy of the crystal. A subtle change in R group can result in significant solubility differences.[2d,3b]

The POSS macromers **2a** and **2b** have been used to synthesize a series of pendent POSS styryl polymers and copolymers by carrying out AIBN-initiated free-radical polymerizations.[7] Both the homopolymers (**3a** and **3b**) and copolymers with varying proportions of

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Table 1. Compositions, Molecular Weights, and Thermal Transitions of POSS Styryl Polymers

polymer	initial ratio[a]	mol % POSS[b]	mol % POSS[c]	$M_n \times 10^{-3}$ [d]	$M_w \times 10^{-3}$ [d]	T_g (°C)[e]	T_g (°C)[f]	T_{dec} (°C)[g]
3a	100:0	100	100	150	430	396	*h*	445
3b	100:0	100	100	200	930	343	*h*	423
4a	77:23	80	70 ± 6	150	260	202	*h*	434
4b	77:23	79	70 ± 6	87	170	272	*h*	429
5a	46:54	46	42 ± 2	210	370	179	*h*	426
5b	46:54	44	42 ± 2	110	200	241	*h*	423
6a	18:82	16	19 ± 1	66	110	148	115	410
6b	18:82	16	19 ± 1	100	150	126, 199	97, 168	407
7a	9:91	7.8	9.8 ± 0.5	41	71	132	110	402
7b	9:91	7.8	9.8 ± 0.5	45	72	127	95	399
8a	1:99	1.1	1.4 ± 0.2	23	41	112	83	378
8b	1:99	1.4	1.2 ± 0.1	30	42	113	78	383
9	0:100	0	0	21	34	116	93	388

[a] mol % POSS to mol % 4-methylstyrene used in the copolymer synthesis. [b] mol % POSS in the polymer determined from ^{1}H NMR spectra. [c] mol % POSS in the polymer determined from percent carbon content in elemental analysis.[7] Errors are calculated assuming the variation in percent carbon to be ±0.4%. [d] Molecular weights determined using 5 mg/mL THF solutions (except for **3b** in $CHCl_3$) on a Wyatt Technology Corp. DAWN spectrometer. [e] T_g determined from the softening point of a pressed pellet on second heating using thermomechanical analysis. Note that **6b** is unique in that it showed two T_g's. [f] T_g determined from powdered polymer on second heating using differential scanning calorimetry. [g] T_{dec} reported as the temperature at which 10% weight loss has occurred, from a powdered sample heated under nitrogen at 10 °C/min using thermogravimetric analysis. [h] At greater than 20% POSS loadings, a T_g is not observable by DSC.

4-methylstyrene (**4a**,**b**−**8a**,**b**) have been synthesized as shown in Figure 2. For comparison purposes, the homopolymer of 4-methylstyrene (**9**) was also synthesized using the same reaction conditions. All of the polymers are soluble in THF except for the homopolymer **3b** (cyclopentyl derivative), which can be dissolved in $CHCl_3$.

Compositions, molecular weights, and thermal properties of these polymers are summarized in Table 1. Interestingly, the mole percent POSS and methylstyrene (as determined by ^{1}H NMR spectroscopy and by percent carbon from combustion elemental analysis) are effectively identical to the percent loading of the monomers prior to polymerization. As all of the polymerizations were carried out to about 50% conversion, this result seems to indicate that the reactivity ratios of the POSS macromers are similar to that of methylstyrene. Further studies are underway to accurately determine reactivity ratios.

Molecular weights were determined using gel permeation chromatography and a combination of refractive index and multiangle laser-light scattering measurements on a Wyatt Technology Corp. DAWN spectrometer. From the number-average molecular weights, the degrees of polymerization are calculated to range from about 100 to 400. This conclusively demonstrates that despite the enormous size of the POSS cluster relative to the polymerizable styrene group, even homopolymers with a significant degree of polymerization can be achieved. We are currently investigating the molecular dimensions and conformations of these polymers with light scattering.

The thermal data summarized in Table 1 demonstrate the effect of the large[3] thermally robust[2e] inorganic POSS unit on polymer properties. The presence of a POSS moiety modifies the thermal properties drastically and allows for tailoring the polymer softening temperature (over a 200 °C range) by changing the percent POSS in a copolymer formulation. By comparison, polystyrene modified with pendent C_{60} fullerenes (diameter of 7.07 Å[8]) shows a T_g of 166 °C for an approximately 11 mol % C_{60} incorporation.[9] This is comparable to the T_g's seen in our 9 mol % POSS copolymers (R = Cy, 132 °C; R = Cp, 127 °C). Additionally, the polymer decomposition point is higher for those polymers with larger POSS content.

It is worth noting that at greater than 10 mol % POSS loadings, the effect of a cyclopentyl-substituted POSS group is significantly greater than that of the cyclohexyl variant. For example, polymer **5b**, with a 46% incorporation of a cyclopentyl-POSS group has a much larger T_g than that for **5a**, with a 46% cyclohexyl-POSS formulation. This difference indicates that there may be POSS−POSS interchain/intrachain interactions which restrict the possible polymer motions, with the cyclopentyl-POSS copolymers having the larger effect. This suggests the possibility of synthesizing elastomeric hybrid materials wherein POSS/POSS interactions could produce a hard block phase-separated from a soft block. We are currently exploring this possibility by developing living polymerization methods of our POSS monomers to enable the synthesis of phase-separated block copolymers.[10]

In summary, a series of linear thermoplastic hybrid materials containing an organic polystyrene backbone and large inorganic silsesquioxane groups pendent to the polymer backbone have been synthesized and characterized. Our preliminary results indicate that the pendent inorganic groups drastically modify the thermal properties of the polystyrene and that interchain and/or intrachain POSS−POSS interactions result in variations in solubility and thermal properties.

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(6) Synthesis of macromer **2a.** To a 125 mL dry THF solution of $(C_6H_{11})_7Si_7O_9(OH)_3$ (**1a**; 9.00 g, 9.24 mmol) and triethylamine (3.10 g, 30.5 mmol), was slowly added a slight excess of (ethylstyryl)trichlorosilane (2.70 g, 10.2 mmol). The reaction flask was stirred under nitrogen for 2 h, followed by filtration to remove the $HNEt_3Cl$ byproduct. The product was isolated by concentrating the clear THF filtrate to 25 mL and then precipitating **2a** into rapidly stirred acetonitrile (25 mL). The product was collected by filtration and dried in vacuo to yield 10.2 g of **2a** (97% yield). ^1H NMR ($CDCl_3$, 300.13 MHz) δ 7.37−7.15 (m, aromatic CH, 4H), 6.73 (m, vinyl CH, 1H), 5.75 (m, vinyl CH, 1H), 5.23 (m, vinyl CH, 1H), 2.77 (m, CH_2, 2H), 1.76 (m, Cy-CH_2, 35H), 1.25 (m, Cy-CH_2, 35H), 1.00 (m, $SiCH_2$, 2H), 0.80 (m, Cy-CH, 7H). ^{29}Si NMR ($CDCl_3$, 59.6 MHz, 5 μs pulse, 1 s acquisition, 6 s delay between pulses, $Cr(acac)_3$ used as a relaxation agent) δ −67.1, −67.2 ($SiCH_2CH_2Sty$, 1:3 ratio of meta and para isomers), −68.5, −68.6 (SiCy). Elemental Anal. (Calcd): C, 54.97 (55.27); H, 7.88 (7.85). Synthesis of macromer **2b.** A similar procedure to that used for the synthesis of **2a** was followed using $(C_5H_9)_7Si_7O_9(OH)_3$ (**1b**; 8.20 g, 9.37 mmol). However, all solvent volumes were doubled and a 4 h reaction time was employed. Isolated yield was 9.18 g (95% yield). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34−7.00 (m, aromatic CH, 4H), 6.68 (m, vinyl CH, 1H), 5.72 (m, vinyl CH, 1H), 5.20 (m, vinyl CH, 1H), 2.71 (m, CH_2, 2H), 1.76 (m, Cp-CH_2, 14H), 1.55 (m, Cp-CH_2, 42H), 1.04 (m, $SiCH_2$, 2H), 0.99 (m, Cp-CH, 7H). ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ −67.3, −67.4 ($SiCH_2CH_2Sty$, 1:3 ratio of meta and para isomers), −66.5 (SiCp). Elemental Anal. (Calcd): C, 52.08 (52.39); H, 7.41 (7.23).

(7) Polymer syntheses: The homopolymers **3a** and **3b** , the copolymers **4a**−**8b**, and poly(4-methylstyrene) (**9**) were all synthesized under nitrogen using a total of 3.00 mmol of monomers in 4−8 mL of dry oxygen-free toluene with 0.012 mmol of AIBN initiator and a reaction time of 64 h at 60 °C. The polymers were isolated (in air) by transferring the toluene solution into methanol (100 mL) and collecting the precipitate. Separation from unreacted **2** was achieved using precipitation methods and shown to be complete using ^1H NMR spectroscopy. Typical yields of polymer were between 30 and 50%. ^{29}Si NMR ($CDCl_3$, 59.6 MHz) for all polymers with R = cyclohexyl, δ −67.0 (1 Si) and −68.6 (7 Si), and with R = cyclopentyl, δ −67.1 (1 Si) and −66.4 (7 Si). Elemental Anal. (Calcd only given for homopolymers), copolymer compositions based on these % C analyses are given in Table 1: **3a**, C, 55.25 (55.27); H, 8.02 (7.85); **3b**, C, 51.68 (52.39); H, 7.40 (7.23); **4a**, C, 56.83; H, 8.15; **4b**, C, 54.20; H, 7.46; **5a**, C, 59.86; H, 7.59; **5b**, C, 57.81; H, 7.11; **6a**, C, 66.57; H, 8.10; **6b**, C, 65.33; H, 7.56; **7a**, C, 73.01; H, 7.94; **7b**, C, 73.44; H, 7.29; **8a**, C, 87.28; H, 8.23; **8b**, C, 87.77; H, 8.44; **9**, C, 91.14 (91.47); H, 8.69 (8.53).

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