

REACTIVITY RATIOS OF ISOBUTYL POSS-STYRENE AND STYRENE MONOMERS

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Introduction

Polyhedral Oligomeric Silsesquioxanes (POSS) are nanoparticles that are used to enhance the thermal and mechanical properties of polymeric systems. There has been extensive research in understanding how POSS affects these properties.¹⁻¹⁵ POSS macromers can be blended with polymers or copolymerized with a wide variety of organic monomers. Three typical examples are shown in Figure 1. A model is emerging for how addition polymerized POSS copolymers can undergo a type of self assembly to form a nanocomposite.⁵

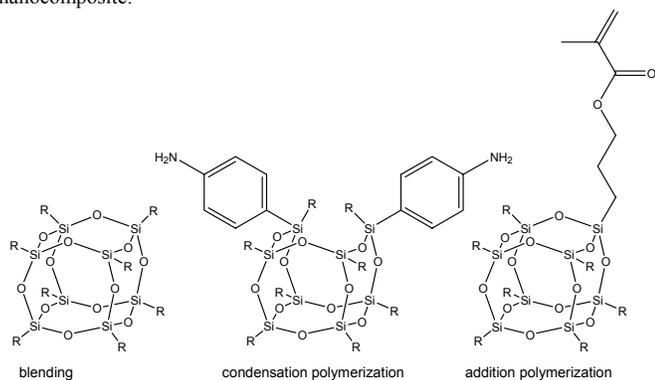


Figure 1. Typical POSS materials that are incorporated into polymers.

To help define the microstructure of the addition copolymers, the POSS macromer and organic monomer reactivity ratios need to be known. When two monomers are copolymerized, their reactivity ratios (r_1 and r_2) dictate the copolymer microstructure. When r_1 and r_2 are both >1 , the product will be a block copolymer. If r_1 and r_2 are very close to 0, the copolymer will be alternating. If r_1 and r_2 are each close to 1, the copolymer will be random.¹⁶

The styrene/POSS-styrene copolymers (See Figure 2) represent a family of glassy materials which we have extensively examined.¹⁵ To obtain detailed properties of these materials, we have determined methods of producing highly entangled materials with good mechanical properties. To help understand their microstructure we are now developing methods of determining POSS-macromer reactivity ratios.

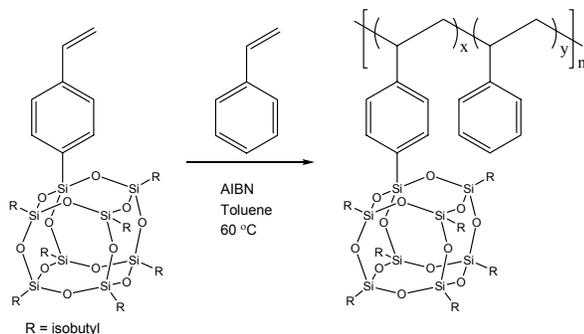


Figure 2. Synthesis of iBuPOSS-PS copolymer.

Experimental

Materials. IsobutylPOSS-styrene monomer, $(C_4H_9)_7(Si_8O_{12})(C_8H_7)$, was synthesized according to the literature method.^{15c} Styrene was obtained from

Aldrich, and was filtered through a column to remove inhibitor. 2,2'-azobisisobutronitrile was obtained from Aldrich and was used without further purification. Toluene was passed through an alumina column to remove water, and then freeze-pumped-thawed to remove oxygen. Diethyl ether and methanol were obtained from Aldrich and were used without further purification.

Instrumentation. ¹H NMR spectra were obtained on a Bruker 400-MHz spectrometer using 5 mm o.d. tubes. Sample concentrations were about 10% (w/v) in CDCl₃ and were referenced internally to residual CHCl₃ at 7.26 ppm. Spectra were run with 10 second delays to ensure accurate integrals.

Copolymerizations The copolymerization of POSS-styrene and styrene was initiated by AIBN at 60° C (Figure 2). A stock AIBN toluene solution was prepared by adding AIBN (0.042 mg, 0.256 mmol) in a 100 mL volumetric flask. For the 47 mole % reaction, the POSS-styrene (1.386 g, 1.507 mmol) was weighed into a 15 mL test tube which contained a stir bar. The test tube was then brought into a dry box under nitrogen atmosphere. Styrene (0.176 g, 1.690 mmol) was then added into the test tube. The AIBN/toluene solution (1.500 mL) was added to the reaction using a syringe. The monomer concentration was 2.13 M, and the AIBN concentration was 0.002 M. The test tube was then capped, sealed with Parafilm, and brought out of the dry box. The reaction was placed in an oil bath set at 60° C. After three hours the reaction was removed from the heat to stop the copolymerization before reaching 5% completion. Other reactions followed this same procedure. Methanol was added to the reaction to precipitate out the copolymer. To remove any POSS-styrene monomer from the copolymers, a typical workup procedure is to re-dissolve the precipitate in minimal chloroform and then slowly add methanol until the solution becomes cloudy. Centrifuging the cloudy suspension affords a clear decantate in which the unreacted POSS-styrene is soluble. The copolymers were dried overnight under vacuum at about 45 °C.

Results and Discussion

Copolymer Synthesis and Characterization. To obtain valid reactivity ratio data, it is crucial to perform a series of copolymerizations spanning the full range of mole % POSS-styrene and styrene compositions. It is also necessary to use the same concentrations of monomers and initiator in all cases, and to stop the copolymerizations before 5 % conversion to prevent compositional drift from adversely skewing the results. This was achieved following the procedure detailed in the experimental section. The % POSS in the feed and % POSS measured in the copolymers is tabulated below.

Table 1. The mole % of POSS in the nine reactions ranged from 9 to 88 %.

Experiment #	POSS in Feed		POSS in Copolymer	
	weight %	mole %	weight %	mole %
1	48.91	9.78	53.60	11.57
2	70.42	21.24	69.33	20.38
3	78.98	29.85	77.19	27.71
4	88.73	47.14	85.39	39.83
5	90.01	50.50	86.98	43.07
6	92.53	58.38	89.97	50.39
7	94.58	66.40	91.40	54.62
8	95.42	70.24	92.85	59.53
9	98.42	87.57	96.43	75.38

The mole % POSS data in Table 1 is plotted in Figure 3. Clearly the % POSS incorporation into the copolymers drops as higher POSS feed levels are used. The relationship is fairly linear, as a least squares fit to the data yields a straight line with a correlation coefficient of 0.997.

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14. ABSTRACT During recent years, there has been interest in incorporating polyhedral oligomeric silsesquioxanes (POSS) into many polymers. Due to its unique features, chemical composition and size, POSS can provide significant property enhancements to many plastics. POSS macromers, for instance, possess a hybrid inorganic-organic composition that can be tailored for incorporation into either thermoplastic or thermoset materials either by blending or by copolymerization. IsobutylPOSS-styrene macromer, (C₄H₉)₇[Si₈O₁₂](C₈H₇), will undergo free radical polymerization with styrene to form random copolymers. To obtain molecular weight data for POSS copolymers it would be useful to know the specific refractive index increment (dn/dc) for any particular copolymer system. We have now carefully measured the dn/dc values for a series of styrene/isobutylPOSS-styrene random copolymers; a plot of dn/dc is linear with respect to weight % POSS monomer incorporated into the copolymer. The plot can be used to either determine the dn/dc of an unknown POSS-content copolymer, or the % POSS incorporation depending on which variable is not known. Furthermore, for different POSS macromers, it should be possible to just measure the dn/dc for the POSS-homopolymer to generate the dn/dc values for all POSS weight %'s in a particular copolymer system.			
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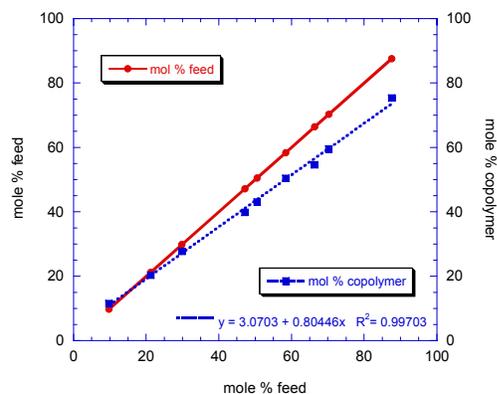


Figure 3. Comparison of the mole % POSS in the feed and the mole % POSS found in the copolymer. The dotted line is what was observed. The solid line is the theoretical composition if both monomers reacted equally.

Characterization The copolymer compositions were determined by analysis of ^1H NMR spectra. To determine the two unknowns, *mole fraction POSS-styrene* (x) and *mole fraction styrene* (y), we need two equations. Equation 1 is simply stating the reasonable assumption that the copolymer composition is based on just these two monomers.

$$x + y = 1 \quad (\text{Eq. 1})$$

The second equation is based on the fact that POSS-styrene and styrene both have different numbers of protons in the aliphatic and aromatic region. We define a term IR (Integral Ratio) as equal to the ratio of the integral value of the aromatic region divided by the integral value of the aliphatic region.

$$IR = \frac{\text{Aromatic Integral}}{\text{Aliphatic Integral}} = \frac{4x + 5y}{66x + 3y} \quad (\text{Eq. 2})$$

In every copolymer, the POSS-styrene (x component) provides 4 aromatic and 66 aliphatic protons, relative to the styrene (y component) which has 5 aromatic and 3 aliphatic protons. By combining the equations 1 and 2 and solving for mole fraction POSS-styrene (x) one obtains equation 3.

$$x = \frac{(5 - 3 * IR)}{(63 * IR + 1)} \quad (\text{Eq. 3})$$

For each ^1H NMR spectrum the aromatic integrals and aliphatic integrals were measured and equation 3 was used to determine the % POSS-styrene incorporation. Figure 2 shows a typical ^1H NMR spectrum. The increase in the aromatic integral by the CHCl_3 present in the NMR solvent could be compensated for.

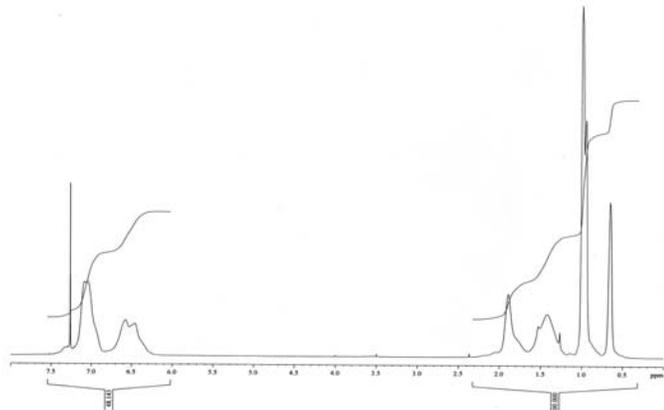


Figure 3 ^1H NMR spectrum of copolymerized POSS-Styrene/Styrene.

Reactivity Ratio Determination. The method used for determining reactivity ratios was the Tidwell & Mortimer Non-Linear Least Squares equation.¹⁷ The mole % POSS data in Table 1 yielded results that $r_{\text{styrene}} = 0.84$ and $r_{\text{POSS-styrene}} = 0.38$.

Conclusions

Copolymers of styrene and POSS-styrene were synthesized and the reactivity ratio for the two monomers was calculated. POSS-styrene was shown to be reactive when copolymerized with styrene with reactivity ratios of $r_{\text{styrene}} = 0.84$ and $r_{\text{POSS-styrene}} = 0.38$. What this means, is that one expects a free radical polymerization to yield random copolymers. A growing polymer chain with a regular styrene on its terminus only favors reaction with styrene over a POSS-styrene by a factor of 1.2 (1/0.84). A growing polymer chain with a POSS-styrene on its terminus prefers reaction with styrene over POSS-styrene by a factor of 2.6 (1/0.38). For a polymerization taken to completion, compositional drift will certainly result in polymers produced late in the reaction having a higher POSS component than polymers initially formed. However, because POSS is typically used in low mole %'s (10 mole % is around 50 weight %) it is highly unlikely that free radical polymerization will ever generate blocky copolymers. The consequences of this observation are that the POSS aggregation phenomena observed for many different copolymers is a self assembly process and not simply caused by block copolymerization.

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