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THE SPECIFIC REFRACTIVE INDEX INCREMENT FOR ISOBUTYL POSS-POLYSTYRENE COPOLYMERS

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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, $(C_4H_9)_7[Si_8O_{12}](C_8H_7)$, 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/isobutyl POSS-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.

THE SPECIFIC REFRACTIVE INDEX INCREMENT FOR ISOBUTYL POSS-POLYSTYRENE COPOLYMERS

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Introduction

During recent years, there has been interest in incorporating polyhedral oligomeric silsesquioxanes (POSS) into many polymers.[1-15] 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.

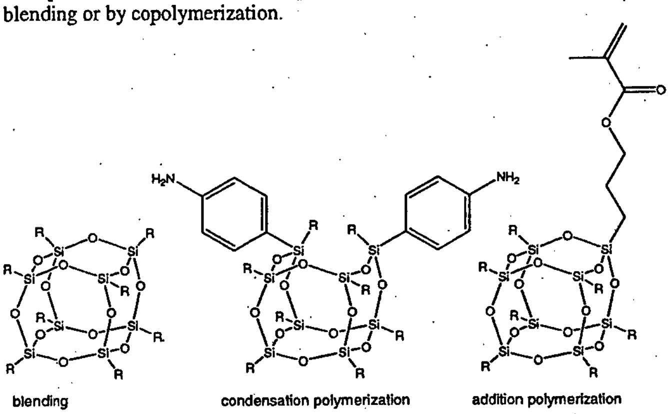

Figure 1. Typical POSS materials that are incorporated into polymers.

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 have also developed methods of determining reactivity ratios.[16] To further characterize this important family of POSS copolymers we obtain molecular weight data using a Wyatt Technologys multi angle laser light scattering system coupled with a refractive index detector. To enable obtaining better molecular weight data it would be appropriate if we knew the specific refractive index increment, dn/dc, for each copolymer we synthesized.

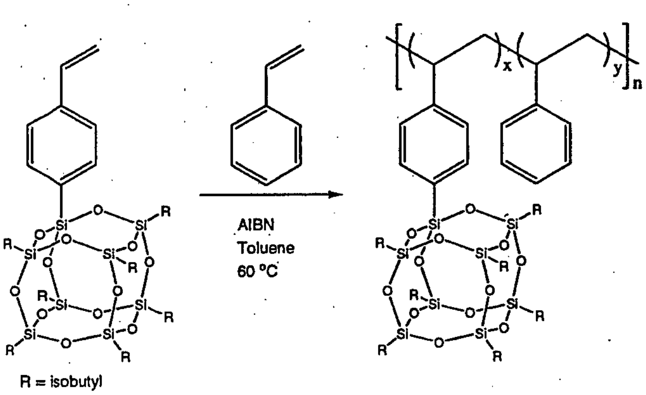

Figure 2. Synthesis of iBuPOSS-PS copolymer.

The change in refractive index with the change in concentration, dn/dc, is a constant for dilute polymer solutions. We had already observed that the dn/dc of POSS copolymer $CHCl_3$ solutions decreases with increased POSS content, but we had not yet obtained data we could analyze with any certainty. We postulated that the relationship between a bulk property such as dn/dc should be linear with respect to weight % POSS in a copolymer and not mole % POSS because the volume occupied by a POSS monomer is so large relative to that of a typical organic monomer. This paper presents data that proves the expected relationship for styrene/isobutylPOSS-styrene copolymers is, in fact, linear.

Experimental

Materials. HPLC grade Chloroform stabilized by pentene was purchased from Fisher, and filtered through a 0.22 μm filter from Millipore. Chloroform-d was manufactured by Cambridge Isotope Laboratories Inc. Tech. methanol and tech. acetone were purchased from Ashland Distribution Company. AIBN (α,α'-Azobis(isobutyronitrile) was imported by American Tokyo Kasei, Inc. Styrene (99%), inhibited with 10-15 ppm 4-tert-butylcatechol, was purchased from Aldrich. The styrene was filtered through a catechol inhibitor remover column and distilled before use. Toluene was passed through an alumina column to remove water. Both the toluene and styrene were stored in a dry box. 90,000 MW, 200,000 MW, and 400,000 MW polystyrene standards were purchased from Pressure Chemicals. The isoButylPOSS-styrene monomer, $(C_4H_9)_7(Si_8O_{12})(C_8H_7)$, was prepared according to the literature procedure.[15c]

Instrumentation. Gel Permeation Chromatography (GPC), used to determine molecular weights, consisted of the following: HP 1100 series autosampler connected to HP 1047A RI detector and DAWN DSP-F laser photometer. Calibration of the system was confirmed using 90K and 400K MW polystyrene standards. ^{1}H NMR spectra were observed using a Bruker 400 MHz spectrometer and 5 mm o.d. tubes. Chloroform-d was used as an internal reference at 7.26 ppm. An Abbe 3L Refractometer provided the index of refraction (n) for each polymer and their various concentrations. The refractometer was operated with rigid temperature control via an external water bath and circulator. It is also operated using Sodium D line (589.3nm) and RI range between 1.300 to 1.710 n_D.

Example synthesis of 6 weight % iBuPOSS-PS copolymer. Samples of iBuPOSS-PS copolymer were all prepared by free radical polymerization using AIBN as an initiator. For a 6 weight % sample, iBuPOSS monomer (0.1801 g, 0.1957 mmole) and AIBN (0.0112 g, 0.0682 mmole) were added to a 20 mL vial and taken into a dry box. After styrene (2.8195 g, 27.076 mmole), toluene (2.358 g, 2.7271 mL) and a stir bar were added, the vial was removed from the dry box and heated at 60 °C for two days with constant stirring. To purify the polymer, the gel-like or viscous solution was diluted with chloroform and, after forming a homogenous solution, precipitated by slow addition into an amount of methanol 3-4 times the volume of the polymer solution. In this instance, about 100 mL of methanol was used. The precipitated polymer was collected on a medium glass frit and dried in a vacuum oven at approximately 63 °C.

Example preparation of samples for Refractive Index (RI). For each copolymer, the RI was determined from five concentrations. For example, five 20 mL scintillation vials were prepared with increasing amounts (0.0201 g, 0.0400 g, 0.0601 g, 0.0800 g, and 0.1010 g of the 6 weight % iBuPOSS-PS) added to each. Chloroform (filtered) was added: 1.4959 g, 1.4433 g, 1.4268 g, 1.3964 g, and 1.3393 g, respectively. The density of chloroform, 1.492 g/ml, was used to convert grams of chloroform to mL, resulting in the following concentrations: 0.0200, 0.0413, 0.0628, 0.0855, and 0.1125 g of copolymer per mL of <u>chloroform</u> (*molality*). These five molality values are approximately equal to 0.02, 0.04, 0.06, 0.08 and 0.10 g of copolymer per mL of <u>solution</u> (*molarity*). RI values were taken after the solution dissolved overnight together with pure chloroform. Five data points were taken for each concentration to ensure reproducibility. A plot of RI vs concentration (*molality*) yielded a linear plot with a slope equal to the dn/dc.

Example preparation of samples for Molecular Weight data. The samples were prepared in 5 mg/mL concentrations. Filtered chloroform was used to dissolve the polymers. For instance, 0.0144 g of 6 weight % iBuPOSS-PS was dissolved in a 20 mL vial with 4.2969 g of chloroform. It was allowed to sit overnight to completely dissolve. About 1.0-1.5 mL of the solution was transferred into a 1.5 mL vial used in GPC analysis.

Results and Discussion.

Synthesis of ^{i}BuPOSS-PS copolymer. A series of 0, 6, 15, 30, 50, 75 and 100 weight % loadings of ^{i}BuPOSS-PS copolymer were synthesized and purified to obtain a good range of dn/dc copolymer values. The synthesis (see Figure 2) involved the reaction of isobutylPOSS-styrene monomer and styrene dissolved in toluene using AIBN as a free radical initiator at 60 °C. After a 2-day reaction time, the product was isolated and purified by precipitation into methanol. The copolymers had to be monomer-free before proceeding to find the dn/dc values; ^{1}H NMR was used to detect any traces of unreacted POSS monomer. Unreacted styrene is easily removed in the precipitation step, but POSS monomer is sometimes trapped in the polymer. This is easily observed with ^{1}H NMR spectroscopy by looking for vinyl resonances at about 5.3 and 5.8 ppm. If further purification was required the copolymer containing trapped POSS monomer was re-dissolved in chloroform and re-precipitated into methanol followed by washing with a 50:50 mixture of the solvents. Alternatively, stirring the copolymer in hexane for a few hours could sometimes be used to remove the monomers leaving undissolved copolymer behind.

Determination of % POSS incoroporation. For each polymer synthesized and purified, the % POSS incorporation was obtained via integration of ^{1}H NMR spectra.[16] To within a few %, the values for POSS incorporation measured by ^{1}H NMR are the same as the targeted amount of POSS (See Table 1).

Table 1: Tabulated Data for the Copolymers Synthesized.

Wt. % (used)	Mole% (NMR)	Wt. % (NMR)	dn/dc	Mn (k)	Mw (k)	PD	DP
0	---	---	0.1537	110	160	1.4	1060
6	0.62	5.2	0.1425	130	190	1.5	1200
15	2.06	15.7	0.1327	140	200	1.4	1100
30	5.46	33.8	0.1159	200	300	1.5	1300
50	10.59	51.1	0.0954	---	---	---	---
75	22.50	77.4	0.0636	---	---	---	---
100	---	---	0.0402	---	---	---	---

Wt. % (used) = weight % POSS used in the copolymer feed..
Mole % (NMR) = mole % POSS in copolymer determined by ^{1}H NMR.
Wt. % (NMR) = weight % POSS found in the copolymer product.
dn/dc = slope of the line found in a plot of RI vs concentration.
Mn = number average molecular weight in 1000's.
Mw = weight average molecultar weight in 1000's.
PD = Mw/Mn, the polydispersity index.
DP = the degree of polymerization determined from Mole % POSS and Mn.

Determination of dn/dc. For each polymer synthesized, a series of five polymer concentrations were prepared to span the range from 0 to 0.10 g/mL of solution. In all cases, a plot of RI vs concentration (molality) yielded a linear plot; the slope of this line gave us the dn/dc for each polymer. Shown in Figure 3 is a typical example; the graph is linear with a correlation coefficient of 0.996 and a slope (dn/dc) equal to 0.1425.

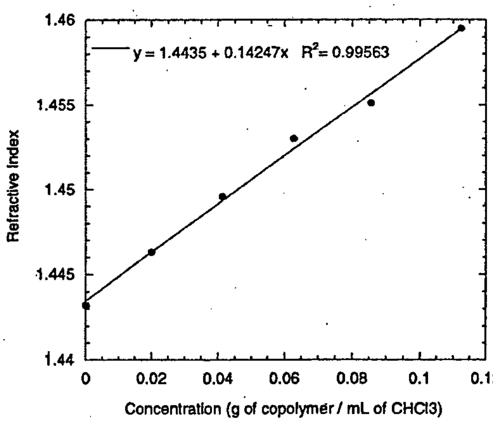

Figure 3. A representative graph for RI versus concentration (molality). Shown is the plot obtained from 6 weight % iBuPOSS-PS copolymer in $CHCl_3$.

Relationship between dn/dc and % POSS. Two plots of the seven dn/dc values determined for a range of copolymer compositions is presented in Figure 4. Clearly our postulate was correct; the relationship between dn/dc and weight % POSS is, in fact, linear. The reason that the plot using mole % POSS is a curve is because the dn/dc is a bulk property of the solution and one should expect the *volume* occupied by a polymeric component to be proportionally responsible for changes to the refractive index. A POSS monomer is commonly 10 times the molar mass of a typical organic monomer and proportionally even larger in size.

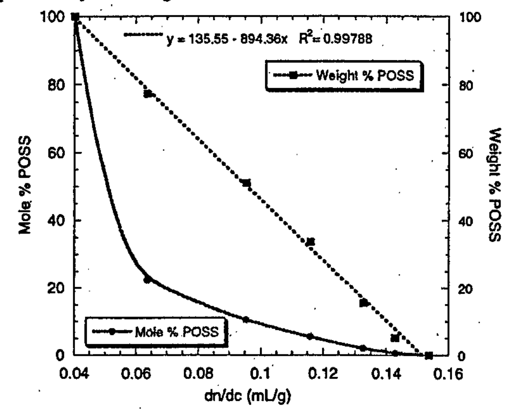

Figure 4. The plot of dn/dc vs. weight % POSS is linear (dotted line) while the plot of dn/dc vs. mole % POSS is a curve (solid curve).

Conclusions.

We have demonstrated that the dn/dc for dilute solutions of polystyrene POSS-styrene copolymers is linear with respect to weight % POSS. If one knows the weight % POSS in a styryl copolymer it is possible to use this relationship to obtain the dn/dc; a useful constant for molecular weight determinations. Alternatively, one can accurately determine the % POSS in a freshly synthesized copolymer just by measuring its dn/dc.

Acknowledgments.

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