Study of Poly(dimethylsiloxane) and End- Tethered Polyhedral Resin Nanoparticles

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Abstract

A series of the dumbbell shape nanocomposite materials of polydimethylsiloxanes (PDMS) and polyhedral oligomeric silsesquioxanes (POSS) was synthesised through hydrosilylation reactions of allyl- and vinyl-POSS and hydride-terminated PDMS. The chemical structures of the dumbbell shaped materials, so called POSS-PDMS-POSS triblocks, were characterised by 1H NMR and FT-IR spectroscopy. The molecular weights of the triblock polymers were determined by gel permeation chromatography (GPC). Their size was analysed by small-angle neutron scattering (SANS) and pulsed-field gradient stimulated echo (PFG STE) NMR experiments. The impact of POSS on the molecular mobility of the PDMS middle chain was observed by using ^{1}H spin-spin (T_2) relaxation NMR. In contrast to the linear melts, the triblocks showed an increase in mobility with increasing molecular weight over the range studied due to the constraints imposed by the tethered nanoparticles. The triblocks were also utilized to compare the impact of tethered nanoparticles on the mobility of the linear component compared to the mobility of the polymer in conventional blended nanocomposites. It appears that up to a critical concentration the tethered chains provide more reinforcement than physically dispersed particles Add R2.

Introduction

Polymer nanocomposites have received considerable attention worldwide from research groups[1] because they offer an opportunity to modify the thermal, electrical, optical or mechanical properties of polymeric materials for use in a wide variety of practical applications.[2] Polymer nanocomposite materials based on the incorporation of polyhedral oligomeric silsesquioxane (POSS) are one of the composite materials that have drawn much interest.[3] Inclusion of POSS into polymer matrices can improve both the physical and chemical properties of the material, e.g. an increased glass transition temperature (T_g), an expanded operational temperature range, a higher degradation temperature, oxidation resistance, surface hardening and reduced oxygen permeability.[4,5] These outstanding properties provide opportunities to develop robust materials that can be used in harsh

environments.[6]

POSS is a well defined nano-sized silicon-based nanoparticle resin containing an inner inorganic framework of silicon and oxygen with the particle sizes ranging from 1 to 3 nm in diameter.[7] The empirical formula of POSS is (RSiO3/2)n, where n is commonly 4, 6, 8, 10 or 12 for a completely condensed silsesquioxane, and R can be hydrogen, inert organic groups or reactive functional groups.[1,3,7–9] An example structure of a completely 'condensed' POSS with n = 8 is shown in Figure 1. The substituent groups are used to improve solubility in solvents and to enhance miscibility with polymeric host materials.[1,8] The reactive functional groups permit the POSS cages to be a graftable and polymerisable nanoparticle.[4] The POSS materials are typically prepared by a process that involves crystallizing the target regular cage structured POSS molecules from solution.
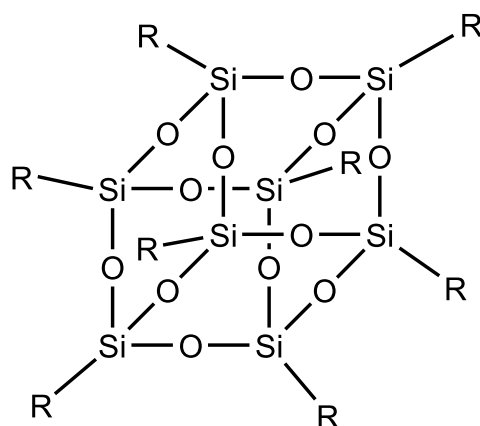

Figure 1: Molecular structure of polyhedral oligomeric silsesquioxane (POSS), (RSiO3/2)n, with n = 8., and R can be hydrogen, inert organic groups or reactive functional groups.

POSS particles can be incorporated into polymer matrices in the forms of either physically blended or chemically bonded composites.[2] There are several approaches for chemical incorporation of POSS into polymers including monofunctional POSS cages grafted onto polymer chains as a pendant group.[9] Polymerisation techniques such as ring-opening[8,10,11] radical[12,13] or condensation polymerisation[14] may be used to incorporate monofunctional POSS into host polymers. Hydrosilylation[15] is an addition polymerisation of a silicon hydride moiety across an unsaturated linkage[16] that has been widely used to prepare POSS-based polymer nanocomposites.[1,2,17,18] Al-

ternatively, nanocomposites prepared from polysilicate-based particles studied previously [19,20] also have an inner inorganic framework of silicon and oxygen and particle sizes ranging from 1-3 nm. The polysilicates are prepared and used as an amorphous mixture of structures which are grown via an acid catalyzed hydrolysis and condensation process with the size of the structures regulated through the use of trimethylsiloxy terminating groups and their quantity relative to the silicate structure building units. The trimethylsiloxy groups also provide a methylated particle surface which facilitates dispersibility and compatability with pdms polymers and matrices. In this study trimethylsiloxy silicate particles (termed R2) with a molar ratio of trimethylsiloxy groups to silicate groups near 0.95 were used to prepare comparative physical blend nanocomposites.

Miscibility between POSS, R2 and PDMS can be predicted by investigating the difference in their solubility parameters δ using the Flory interaction parameter theory, with χ :

$$\chi = (\nu/RT)(\delta_A - \delta_B)^2 \tag{1}$$

where ν is an arbitrary reference volume (conveniently selected as 100 cm^3) and δ is the solubility parameter. [21] The solubility parameter of PDMS was previously obtained: $\delta_{PDMS} = 16.5$ (J/cm^3)$^{1/2}$ [21]. For the R2 resin used in this work, the solubility parameter was estimated based on the empirical method developed by Hansen. This consisted of testing the solubility of R2 resin in a range of solvents with known solubility parameters. This results in a solubility parameter for R2 of $\delta_{MQ} = 16.4$ (J/cm^3)$^{1/2}$ which is very close to the value found for PDMS (16.5). Data for PhPOSS (R is phenyl) $\delta_{PhPOSS} = 19$ (J/cm^3)$^{1/2}$ and tBuPOSS (R is t-butyl) $\delta_{tBuPOSS} = 14$ (J/cm^3)$^{1/2}$ was obtained from Hansen. [22] Comparing solubility parameters shows that R2 and PDMS are expected to be highly miscible while both POSS nano-particles are highly immiscible with PDMS. It is therefore expected that combining R2 or POSS with PDMS will result in very different morphological behaviour.

Kopesky et al. [23] investigated nanocomposites consisting of POSS particles tethered as side groups at up to 25 wt% in high molecular weight Polymethylmethacrylate (PMMA) as well as

POSS/PMMA nanocomposite blends and compared both to the properties of PMMA alone. Viscosity measurements at temperatures above the T_G of PMMA and below the T_M of POSS showed that physical blending of POSS with PMMA showed non-einstein viscosity reduction behavior relative to PMMA alone up to a loading of 5 vol%. Above this loading the POSS particles were found to agglomerate into crystallites that resulted in a viscosity increase of the nanocomposite relative to PMMA alone consistent with behavior predicted for hard spheres.[24]

The main interest of this paper is to synthesise and characterise the dynamics of two series of POSS-PDMS-POSS triblock polymers via hydrosilylation reaction and to compare the impact of the POSS particles on the relative mobility of the PDMS block relative to a free PDMS chain and to such a chain in nanocomposites prepared by simple blending of R2 particles with PDMS. The size of the triblock polymers was characterised using small-angle neutron scattering (SANS) and pulsed-field gradient stimulated echo (PFG STE) NMR experiments. The molecular mobility of the materials themselves and their incorporation into host polymer melts was also studied by NMR spin-spin (T_2) relaxation and self-diffusion NMR.

Experimental

Materials

Hydride terminated poly(dimethylsiloxane), (Hydride-PDMS), of 0.58k g/mol and 24k g/mol molecular weight, PSS-allyl-heptaisobutyl substituted (Allyl-tBuPOSS), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyltrisiloxane complex solution in xylene (Karstedt's catalyst) were purchased from Sigma-Aldrich and used without further purification. Hydride-PDMS of nominal 13.3k g/mol was supplied by Dow Corning Corp. (USA). Hydride-PDMS 1.17k , 5.54k, 16.5k and 41.4k g/mol (nominal values) were purchased from Gelest Inc. PSS-vinyl-heptaphenyl substituted (Vinyl-PhPOSS) was purchased from Hybrid Plastics. All chemicals were used as received without further purification. Karsted's catalyst was supplied by Sigma Aldrich.

Synthesis and characterisation of POSS-PDMS-POSS triblocks:

A series of tBuPOSS-PDMS-tBuPOSS and PhPOSS-PDMS-PhPOSS triblocks were synthesised with different PDMS segment lengths varying from 0.58k to 41.4k through hydrosilylation reactions of the corresponding hydride-PDMS and allyl-POSS. Representative synthesis procedures for tBuPOSS-1.17k PDMS-tBuPOSS and PhPOSS-41.4k PDMS-PhPOSS triblocks are described. For the other samples suitable adjustments were made for the molecular weight change. Reaction times depended on the molecular weight of the hydride-PDMS. The general scheme of the hydrosilylation reactions is shown in Figure 2.
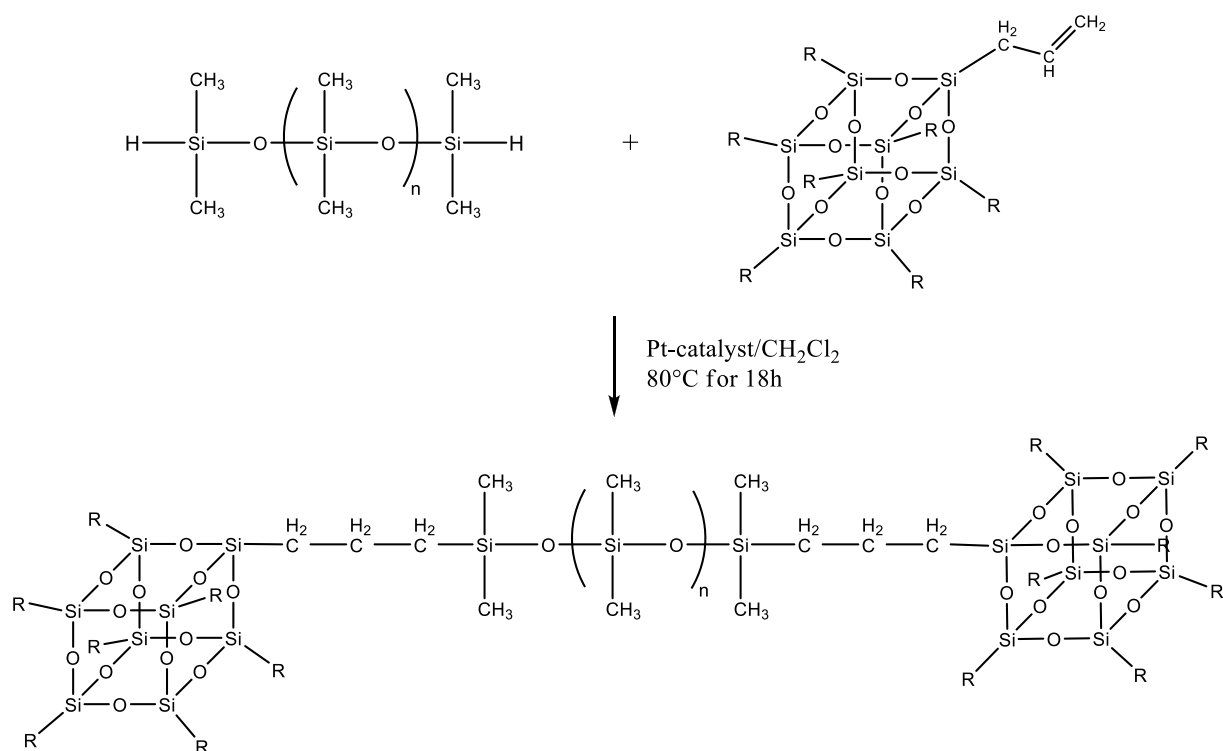

Figure 2: General scheme of hydrosilylation reaction to synthesise POSS-PDMS-POSS triblocks

Synthesis of tBuPOSS-1.17k PDMS-tBuPOSS triblocks: 1.17k hydride-PDMS (0.6825 g, 0.5833 mmol) was dissolved in < 20 mL of dichloromethane and introduced to a 100 mL three necked round-bottom flask. The flask was equipped with a magnetic stir bar and a water-cooled condenser. Allyl-tBuPOSS (1.0002 g, 1.1663 mmol) was then added to the PDMS solution. The reaction mixture was stirred for several minutes to allow the reagents to mix well. 0.0222 g Karstedt's catalyst was dissolved in 2 mL CH2Cl2 and added. The reaction mixture was refluxed at 100 $^{\circ}$C under a nitrogen atmosphere. The reaction progress was monitored by FT-IR analysis of samples taken

throughout the synthesis using the Si-H band at 2126 cm^{-1}. After the reaction was complete, the solution was stirred with silica gel and activated carbon for several hours to remove unreacted starting reagents.[25] The mixture was filtered through a glass column containing Celite and Florisil to remove Karstedt's catalyst using 1000 mL of dichloromethane as eluent. The solvent was then removed by rotary evaporation and dried in an oven for several hours at 30 $^{\circ}$C under vacuum. The product was obtained with a yield of 70%. Other tBuPOSS-PDMS-tBuPOSS triblocks were obtained with yields of 60 - 80 %.

Synthesis of PhPOSS-41.4k PDMS triblocks: A 100mL three neck round bottom flask was loaded with 41.4k hydride-PDMS (21.0616 g, 0.5084 mmol), vinyl-PhPOSS (1.0007 g, 1.0168 mmol) and 60 mL toluene. The flask was equipped with a mechanical stirrer, a temperature controller, a water-cooled condenser and a nitrogen atmosphere. The solution was heated to 100 $^{\circ}$C and stirred for several minutes. 0.0298 g of Karstedt's was dissolved in 2 mL toluene then added to the solution. The reaction mixture was refluxed and samples were removed periodically for FT-IR analysis to monitor the reaction progress. After the reaction was complete, the crude product was left to cool to room temperature. The mixture was then filtered through a column of Florisil to remove residual Karstedt's catalyst using 1000 mL toluene as eluent. Solvent was removed by rotary evaporation followed by vacuum drying at 30 $^{\circ}$C. The product with a yield of 84 % was obtained. Yields of 75 - 90 % were obtained for synthesis of other PhPOSS-PDMS-PhPOSS triblocks with different PDMS molecular weights.

Trimethylsiloxy polysilicate nanoparticles The resin nanoparticles were supplied by Dow Corning Corporation, and is designated here as R2 (representing an intermediate particle size between silicates previously investigated by the authors).[19,26] An acid-catalyzed polymerization of sodium silicate followed by a reaction with trimethylchlorosilane in a process described elsewhere[27]-using an equivalent molar ratio of trimethylsiloxy and silicate units-produced this amorphous nanoparticle with a weight-average radius of gyration of 1.5 nm and glass transition temperature of 96 $\pm$ 3 $^{\circ}$C by dynamic mechanical thermal analysis.

NMR Spectroscopy 1H NMR measurements of the starting compounds and the reaction products were performed on a Lambda300 (300 MHz) and a Varian400 (400 MHz) NMR spectrometers. Dichloromethane-d2 was used as solvent.

FT-IR Spectroscopy FT-IR spectra were measured on a PerkinElmer Spectrum One FT-IR spectrometer. A small amount of the sample was coated on a NaCl plate. Spectra were measured over the wavenumber range from 450 to 5000 cm^{-1} with an average of 4 scans.

Gel Permeation Chromatography (GPC) The GPC analysis was performed by Dow Corning Corp. All samples were prepared in HPLC grade toluene at 0.5 % w/v concentration and filtered through a 0.45 μm PTFE syringe filter. The samples were analyzed against polystyrene standards ranging in molecular weight from 580 to 1,290,000 g/mol. The chromatographic equipment consisted of a Waters 515 pump, a Waters 717 auto sampler and a Waters 2410 differential refractometer. Chromatographic separation was made with two (300 mm x 7.5 mm) Polymer Laboratories PLgel 5 μm mixed-C columns preceded by a guard column. Analysis was performed using HPLC grade toluene as the eluent with the flow rate of 1.0 mL/min. The columns and detector were both heated to 45 ^{o}C. Repeatability of the GPC measurement was ± 5 %.

Small-angle neutron scattering (SANS). Samples of hydride-PDMS melts, POSS and POSS-PDMS-POSS triblocks were prepared in D-toluene at concentrations of 10 wt% polymer. Small-angle neutron scattering (SANS) measurements were carried out on the D11 instrument at the Institut Laue-Langevin (ILL) in Grenoble, France. All samples were studied at 25 ^{o}C in 1 mm path length quartz cells and a neutron wavelength of 8 Å was used. The detector distance was 8 m. The measurements were performed with a scattering vector (Q) range of 0.01 Å^{-1} < Q < 0.4 Å^{-1} The experimental data were fitted to the Guinier - Debye model for polymers using a nonlinear least squares algorithm.

Diffusion NMR Spectroscopy All samples of the POSS-PDMS-POSS triblocks and their starting materials in D-toluene are the same set as used for SANS measurements. Pulsed-field gradient stimulated echo (PFG STE) NMR experiments were performed on a Bruker DSX-300 NMR spec-

trometer operating at 300 MHz for protons. The length of the field gradient pulse, δ, was set to 1 ms for all samples. The magnetic field gradient (g) was varied from 0.0496 to 9 T/m. The diffusion time, Δ, was set between 100 and 400 ms. The attenuation of the stimulated spin-echo signals was measured by studying the change in the integral of the sample peak area in the spectrum, A(g), as a function of the applied pulsed- field gradient. The self-diffusion coefficients, D, were calculated by using non-linear-least-square fits to the equation for unrestricted diffusion given in equation 2:[28]

$$A(g, \delta, \Delta) = \exp[-\gamma^2 g^2 \delta^2 \Delta\, D(\Delta - \delta/3)] \tag{2}$$

where γ is the magnetogyric ratio

Spin-spin relaxation NMR spectroscopy Spin-spin (T_2) relaxation measurements of all samples of the POSS-PDMS-POSS triblocks and their starting materials were measured using a Bruker MSL 300 MHz and an Xigo Area 13 MHz NMR spectrometers using the Carr-Purcell-Meiboom -Gill (CPMG) pulse sequence[29] with a 180 ^{o} pulse separation of 2 ms (for POSS-PDMS-POSS triblock polymers) and 4 ms (for hydride-PDMS samples). The signal was averaged over 64 scans with at least 2048 data points sampled at the echo maxima. This reduces errors from random noise and possible DC offsets and makes it possible to fit multiple exponentials to the data. The recycle delay for each scan was set between 10 and 15 s to ensure a full recovery of magnetization between consecutive acquisitions.

Results and discussion

The hydrosilylation reaction progress for the two POSS samples and the hydride-PDMS was monitored by FT-IR spectroscopy. The disappearance of the peaks at 2124 to 2126 cm^{-1} indicated that the Si-H group of the hydride-PDMS had reacted and the reaction was complete. This was after 50 hours for tBuPoss and 4 hrs for the PhPOSS. The reaction time was found to increase with increasing hydride-PDMS molecular weight.

^{1}H NMR: ^{1}H NMR spectra of the hydride-PDMS, allyl-tBuPOSS and the triblocks were recorded.

The completion of the hydrosilylation reaction was confirmed by the absence of peaks from the -CH=CH2 on the allyl-POSS (δ_{ppm} 4 5.75 and 4.90) and the Si-H on the hydride-PDMS (δ_{ppm} 4.69 ppm) in the final product. ^{1}H NMR was used to determine the number average molecular weight (M_N) of the polymers.[30–32] The number of protons in each polymer molecule was determined from the integration of the PDMS peak (δ_{ppm} 0.07) with the integrals calibrated to the end group protons. The calculated M_N of all the compounds was obtained from integration of their ^{1}H NMR spectra and is given in Table 1. There is good agreement between the M_N of hydride-PDMS and tBuPOSS-PDMS-tBuPOSS products indicating that the desired products were obtained. A similar approach was taken for the PhPOSS samples. Residual vinyl-PhPOSS was not expected because the molar ratio of PDMS to POSS for the synthesis was kept at 2:1 for all the samples, so the starting reagents should have been completely reacted. However, the small signal of -CH=CH2 at δ_{ppm} 5.96 - 6.28 shows that a small amount of unreacted vinyl-PhPOSS remains in the final product. The quantity of the excess POSS was approximately 2% calculated from the integral value of the peak. Assuming that the small amount of the unreacted vinyl-PhPOSS should not have a significant effect on the properties of the product, not further purification was attempted. A possible explanation for the unexpected excess vinyl-POSS found in the final product is that the reaction mixtures may contain trace amounts of water which could react with hydride-PDMS and form a side product. This side reaction would lead to a decrease in the amount of hydride-PDMS available for the reaction with vinyl-PhPOSS resulting in unreacted POSS. Less than 10 wt% of unreacted vinyl-PhPOSS was observed in all the reaction products. The number average molecular weight (M_N) for all the samples was calculated from integration of the ^{1}H NMR spectra and these data are also shown in Table 1.

GPC GPC measurements using toluene as the solvent with respect to polystyrene standards were performed by Dow Corning Corp. The GPC profile of tBuPOSS-0.58k PDMS-tBuPOSS triblock product in comparison to its starting reagents shows a shift to a higher molecular weight of the reaction product and indicates a successful reaction between the starting reagents. A small signal of allyl-tBuPOSS can be seen in the GPC profile of the final product, however, the amount of excess

POSS should be very small in comparison to the product as shown by the absence of -CH2=CH in the ^{1}H NMR analysis. The GPC curve of 41.4k hydride- PDMS shows evidence of a low molecular weight component in the sample. This component could be assigned to a species that is not involved in the hydrosilylation reaction because its molecular weight, as shown in Table 1, does not significantly change at the end of the reaction. Number average molecular weight (M_N) and polydispersity index (*PDI*) of some of the starting reagents and tBuPOSS-PDMS-tBuPOSS triblocks obtained from GPC analysis are shown in Table 1. It can be seen that the hydride-PDMS with M_N > 10K have polydispersities > 2, leading to the formation of polydisperse triblock polymers. GPC data for PhPOSS-13.3k PDMS-PhPOSS triblocks and its starting reagents were recorded; a shift in the GPC trace to a higher molecular weight for the reaction product indicates that the desired product was obtained. A peak at low molecular weight corresponded to vinyl-PhPOSS is observed in the GPC curve of the product. This evidence confirms the excess POSS remaining in the product also seen by ^{1}H NMR. However, since we are probing the mobility of the protons associated with the linear block it is believed that small amounts of residual untethered POSS will have a negligible impact and so no further efforts were made to purify the triblocks. In addition it is felt that excess POSS would have less impact on the proton mobility results than excess linear which would result in untethered chains.

In summary, the PhPOSS-PDMS-PhPOSS and tBuPOSS-PDMS-tBuPOSS triblock polymers were successfully synthesised through the Pt-catalysed hydrosilylation reaction. The final products contained small amounts of unreacted POSS starting materials.

Small angle Neutron Scattering

Small-angle neutron scattering (SANS) and pulsed-field gradient stimulated echo (PFG STE) NMR measurements were carried out on POSS-PDMS-POSS triblocks and their starting materials. The aim of these experiments was to determine the size of POSS particles, hydride-PDMS and POSS-PDMS-POS triblock polymers dispersed in D-toluene. The measurements were performed on 10% by weight solutions.

Table 1: NMR and GPC results of tBuPOSS-PDMS-tBuPOSS-triblocks, PhPOSS-PDMS-PhPOSS-triblocks and their starting materials based on polystyrene standards analysed in toluene.

Sample	M_N (NMR)	M_N	M_W	PDI
Allyl-tBuPOSS	856	836	849	1.02
Vinyl-PhPOSS	983	634	646	1.02
0.58k hydride-PDMS	726	820	1090	1.33
1.17k hydride-PDMS	1170	*	*	*
5.54k hydride-PDMS	5540	*	*	*
13.3k hydride-PDMS	17894	11600	27900	2.41
16.5k hydride-PDMS	16488	12500	25800	2.06
24.0k hydride-PDMS	25146	13800	34900	2.52
41.4k hydride-PDMS	41400	16600	77400	4.66
tBuPOSS-0.58k PDMS-tBuPOSS	2294	2320	3410	1.47
tBuPOSS-1.17k PDMS-tBuPOSS	2880	*	*	*
tBuPOSS-5.54k PDMS-tBuPOSS	7098	*	*	*
tBuPOSS-13.3k PDMS-tBuPOSS	15014	11900	31100	2.62
tBuPOSS-16.5k PDMS-tBuPOSS	18202	11600	50800	4.37
tBuPOSS-24.0k PDMS-tBuPOSS	27448	*	*	*
tBuPOSS-41.4k PDMS-tBuPOSS	33516	19300	96800	5.01
PhPOSS-0.58k PDMS-PhPOSS	2546	2000	2120	1.06
PhPOSS-13.3k PDMS-PhPOSS	15266	18200	40400	2.22
PhPOSS 16.5K PDMS-PhPOSS	20006	*	*	*
PhPOSS-24.0k PDMS-PhPOSS	25966	16900	90400	5.34
PhPOSS-41.4k PDMS-PhPOSS	42966	18400	133000	7.23

* Not Available

To determine the size of the samples, the data were fitted to the Guinier - Debye model for polymers as in equation 3.

$$I(Q) = (\phi M_w \Delta \rho_N^2 / (N_A \rho)) \exp[-(QR_g)^2/3] \frac{2(\exp[-(QRg)^2] - 1 + (QRg)^2)}{(QRg)^4} \qquad (3)$$

where ϕ is the volume fraction of polymer, $\Delta \rho$ is the difference in scattering length density of the polymer and solvent, Q is the scattering vector and Rg is the radius of gyration.

Table 2: Calculated scattering length densities (SLD) of compounds used for SANS measurements.

Compound	$\Delta \rho$ Å^{-2} /10^{-6}
D-toluene	5.68
tBuPOSS	0.63
PhPOSS	2.19
H-PDMS	0.06

Calculated scattering length densities (SLD) of the components used in the SANS experiments are given in Table 2. In the fitting, values of scattering length density (SLD), volume fraction and density were fixed. The other parameters were allowed to vary. Representative scattering data for tBuPOSS-0.58k PDMS-tBuPOSS triblocks and its starting materials are given in Figure 3. The results for the radius of gyration (Rg) for all samples obtained from the Guinier-Debye fits are shown in Figure 3. The Rg values of hydride-PDMS were also calculated using the relation:

$$R_g^2 = aM_w^b \qquad (4)$$

where M_w is weight average molecular weight of polymer in g/mol. The constants $a = 0.0666$ and $b = 1.0141$ for linear PDMS at 30 °C[33] and theoretical data based on this equation are also included in the figure.

The Guinier-Debye fit yielded an R_g of 0.57 ± 0.01 nm for allyl-tBuPOSS. This value is in agreement with the general size range expected for POSS particles (size $\sim$ 1 to 3 nm in diameter).[7] Vinyl-PhPOSS was characterised using small-angle X-ray scattering (SAXS) at a concentration of 10 wt% vinyl-PhPOSS in tetrahydrofuran. The R_g of the vinyl-PhPOSS was observed as
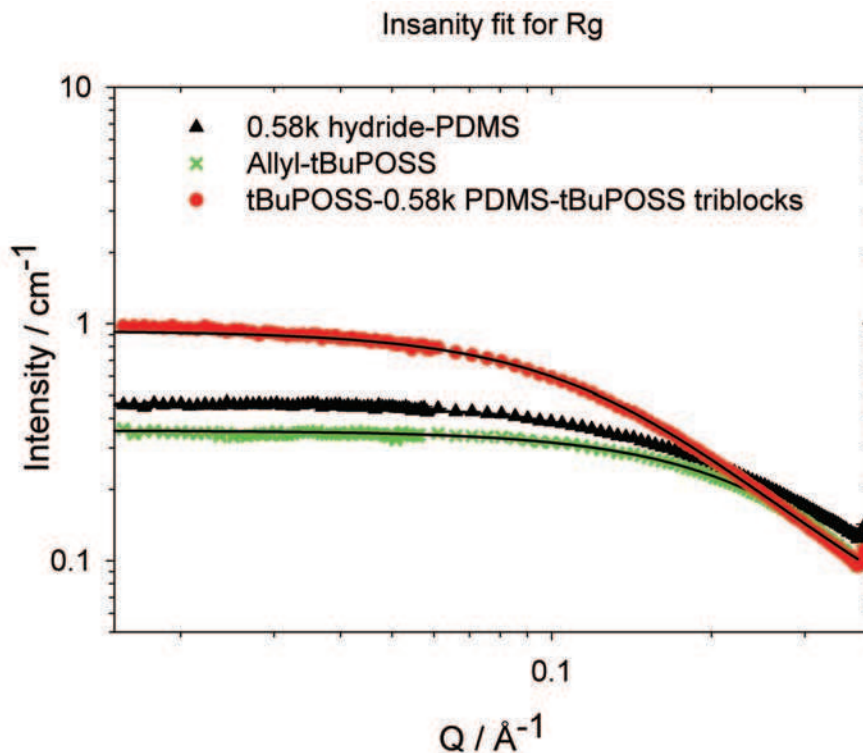
Figure 3: Small-angle neutron scattering from tBuPOSS-PDMS-tBuPOSS triblocks in 10% D-toluene solutions compared to their starting materials. Solid lines are fits to the Guinier-Debye model for polymers.

0.48 ± 0.11 nm which is slightly smaller than the size of allyl-tBuPOSS.

The R_g values obtained for 0.58k and 5.54k hydride-PDMS are in reasonable agreement with the calculated R_g using equation 4 though at higher molecular weights the values are smaller than the calculated ones. In Benton's work,[34] it was found that the R_g of linear PDMS decreased with increasing polymer concentration from 0.5 wt% to 10 wt%. The decrease in R_g could be attributed to changing from the dilute to semi-dilute solution regime which occurs at c^*.[34]

$$c^* \sim M_w/(4\pi R_g/3) \tag{5}$$

and for the highest molecular weight sample this is close to 10% (vol/vol) and hence could be a reason why the observed sizes in these experiments are smaller than the calculated ones. However, there is still an approximate linear dependence of R_g with $M_w^{0.5}$ though some anomalous data were

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found for the block copolymers. The fitted data are given in Table 3.

For the POSS-PDMS-POSS triblocks samples, the POSS particles are attached to both ends of the PDMS middle chain and hence the R_g values might be expected to be larger than the corresponding hydride-PDMS though not as large as a dumbbell model would predict. This obviously depends on the conformation, but it was found that the R_g values for the triblocks polymers were larger than the homopolymers. The difference between the two different particles is small but as the PDMS chain length increases the values approach those of the homopolymers.

Table 3: Radius of gyration from SANS. for PDMS and the tri-block copolymers

$***M_N$ of PDMS / g/mol	PDMS /nm	T-Butyl-POSS-T-Butyl /nm	Phenyl-POSS-Phenyl /nm
820	0.79	1.25	1.04
5540	2.01	2.57	2.37
11600	2.39	2.39	-
25146	2.46	2.77	2.80
41400	2.78	2.82	2.80

Diffusion NMR spectroscopy

Pulsed-field gradient stimulated echo (PFG STE) NMR experiments were performed at 25 $^{\circ}$C for samples of hydride-PDMS and the triblock polymers dispersed in D-toluene and the representative results are shown in Figure 4. The diffusion data were analysed using a non-linear-least-squares fitting routine to equation 2. The hydride-PDMS is a pure polymer, so a single diffusion coefficient was expected to fit to the data [data were fitted to a single gaussian decay though the data for the high molecular weight samples showed deviations likely to be due to polydispersity]. It is clear that the gradients of the attenuation data decrease when POSS particles were attached to the PDMS. This is a clear indication of a decrease in the self-diffusion coefficient and hence an increase in the hydrodynamic radius. Similar non-linear data were found for the other samples. The hydrodynamic radius, R_H, of a compound in a dilute solution can be calculated from the self-
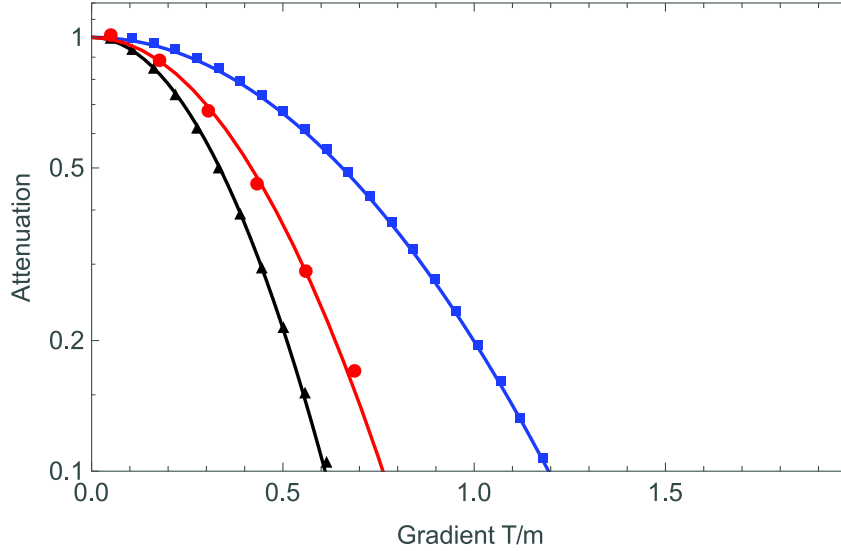
Figure 4: PFG STE NMR data at 25 °C of the 0.58k samples, ▲ starting polymer , ● tBuPOSS triblock and ■ PhPOSS triblock (Blue). All the samples were prepared at concentration of 10 wt% in D-toluene. The solid lines are fits to a single diffusion coefficient.

diffusion coefficient, Ds, using the Stokes-Einstein relation.[19]

$$D_s = \frac{k_b T}{6\pi\eta R_H} \tag{6}$$

where D_s is self-diffusion coefficient, k_B is Boltzmann constant, T is absolute temperature (K) and η is the solvent viscosity at the experiment temperature. Plots of R_H as a function of the molecular weight of the PDMS segment are shown in Figure 5 and there is a clear increase in R_H when the PDMS segment molecular weight increases. Also there is a clear difference between the two block copolymers, with the phenyl POSS samples having a larger hydrodynamic radius than the t-butyl POSS. Do note that at a solution concentration of 10wt%, the requirement for dilute solution behavior is likely exceeded. In this case polymer coil diffusion can be slowed due to hydrodynamic and thermodynamic chain interactions. In the case of the phenyl POSS triblocks, PI-PI stacking could be expected to result in extended conformations leading to the higher R_H values.

The SANS data also show a small difference in the two block copolymers. R_g and R_H for a linear polymer in dilute solution are expected to follow the simple relationship give in equa-
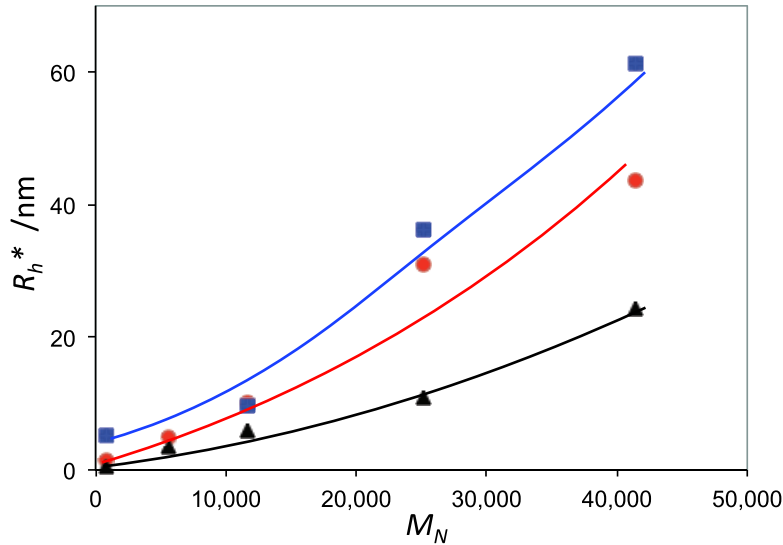
tion 7.[35,36]

$$R_g = 1.5R_H \tag{7}$$

Figure 5: Hydrodynamic radius as a function of molecular weight: (▲) homopolymer PDMS, (●) t-butyl POSS copolymer, and (■) phenyl POSS copolymer. All the samples were prepared at concentration of 10 wt% in D-toluene .

Comparison of the data in Figure 5 and Table 3 show that the R_H values are much larger than the R_g values, especially for the block copolymers, suggesting some degree of association. Theoretically, for for an isolated gaussian chain, the ratios of the radius of gyration to the hydrodynamic should be 1.5.[35,36] However, only the lowest molecular weight sample is near this value. There are several potential reasons for this including both inter-molecular hydrodynamic effects; the sample concentrations are approaching c* (the dilute concentration limit) leading to intermolecular interactions between POSS moieties. Do note that the co-solvent toluene will ensure that both blocks are molecularly dispersed which was confirmed by the optically clear appearance of the solutions and there are other intermolecular effects due to the interactions between the POSS moieties. In contrast, the next section will explore the other extreme of polymer melt behavior where intermolecular interactions will be maximized and solubility differences between the POSS or R2 and PDMS constituents will dictate the morphology and with it the block copolymer or nano-composite relaxation behavior

T2 relaxation NMR spectroscopy of polymer melts and mixtures. The T_2 relaxation of POSS-PDMS-POSS triblocks and their corresponding starting materials in the melt state were measured to study their molecular mobility. The relaxation decay curves were not single exponential decays and were fitted to a series of exponential functions using the DISCRETE program. A weight average $\overline{T}_2$ value was calculated using the following relation:

$$\overline{T}_2 = \frac{\sum w_i T_{2i}}{\sum w_i} \tag{8}$$

There are several potential reasons why non-exponential behaviour is seen in these systems and polydispersity is clearly a factor especially for the higher molecular weight samples. The observation of a single exponential relaxation would only apply to a spin system that could reorientate isotropically and in these systems that is unlikely. Several publications cite these effects for polymer systems though the techniques and samples available for this work preclude a more detailed study. However, as we have shown in previous publications[19,20] a good qualitative description can be made by using the averaged relaxation time and these are the values plotted in the subsequent figures.

Figure 6 shows plots of the spin-spin relaxation rate ($1/\overline{T}_2$) as a function of molecular weight of the PDMS segment: reduced molecular mobility of polymers is indicated by an increase in relaxation rate.

The relaxation rate of hydride-PDMS increases with increasing molecular weight as expected.[20,37] Considering a series of the triblock copolymers containing the same length of PDMS central segment, the relaxation rates of the triblocks are higher than that of hydride-PDMS in particular for the case of triblocks with short PDMS chains. This suggests that the two POSS particles attached to the central chain act as anchors and suppress the molecular motions of the chains. The tBuPOSS-PDMS-tBuPOSS triblocks are more mobile than PhPOSS-PDMS-PhPOSS triblocks and this is due to the effect of the benzene rings in PhPOSS end groups. The aromatic rings from different PhPOSS particles may form clusters because of their incompatibility with PDMS which could restrict
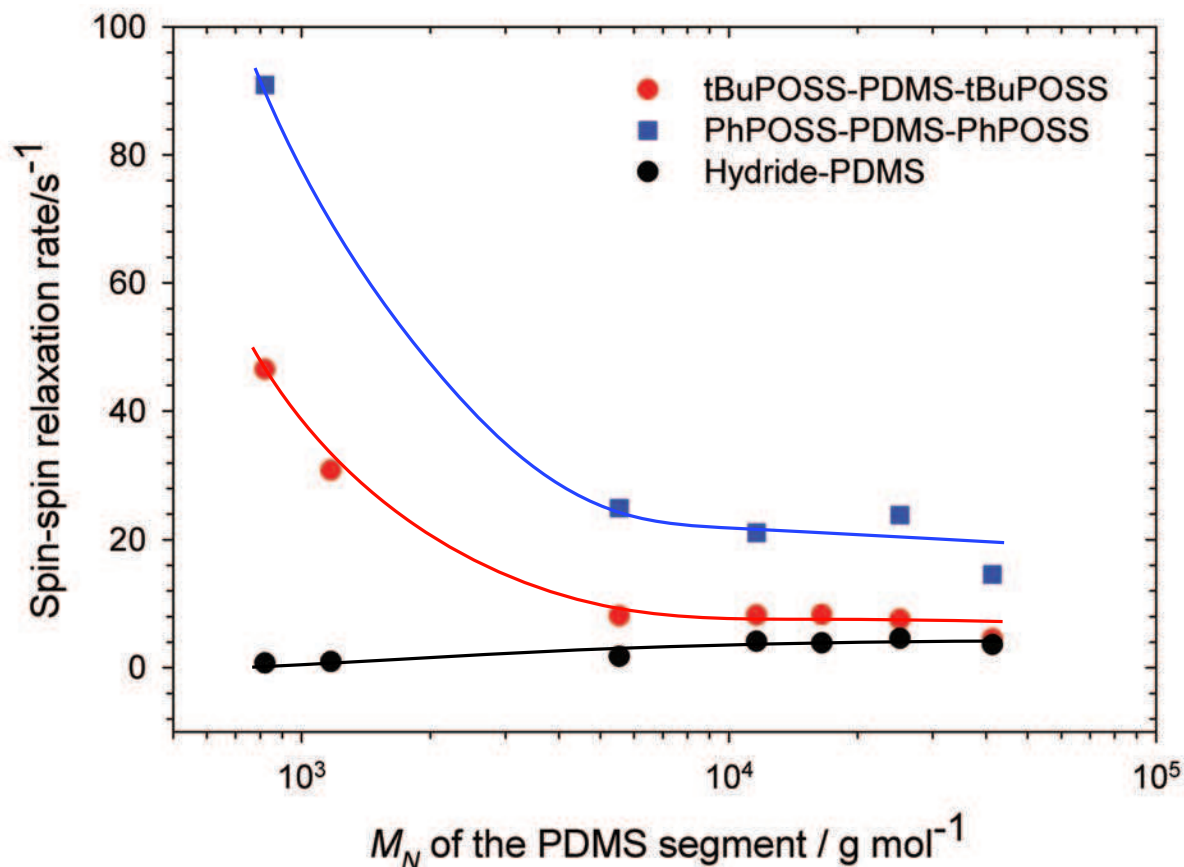
Figure 6: Relaxation rates as a function of molecular weight of PDMS segment. Lines are not fits to the data; they are guides to the eye.(▲) homopolymer PDMS, (●) t-butyl POSS copolymer, and (■) phenyl POSS copolymer.

motions of the PDMS middle blocks as the two components are incompatible. In contrast to the hydride-PDMS, the relaxation rates of tBuPOSS-PDMS-tBuPOSS and PhPOSS-PDMS-PhPOSS triblocks decrease with increasing molecular weight of the PDMS segment. This means that the triblock copolymers are more mobile as the central block becomes longer and dominates.

The relaxation rate of POSS-PDMS-POSS triblocks as a function of weight fraction of the POSS component with respect to the pure polymers is shown in Figure 7. Clearly, the relaxation rate increase with increasing the effective POSS content, indicating that the triblock copolymers are less mobile even though the polymer molecular weight is decreasing.

We also show data for a nano-sized trimethylsilyl-functionalised polysilicate (R2) resin dispersed in PDMS as was discussed in the introduction with different low molecular weight PDMS.
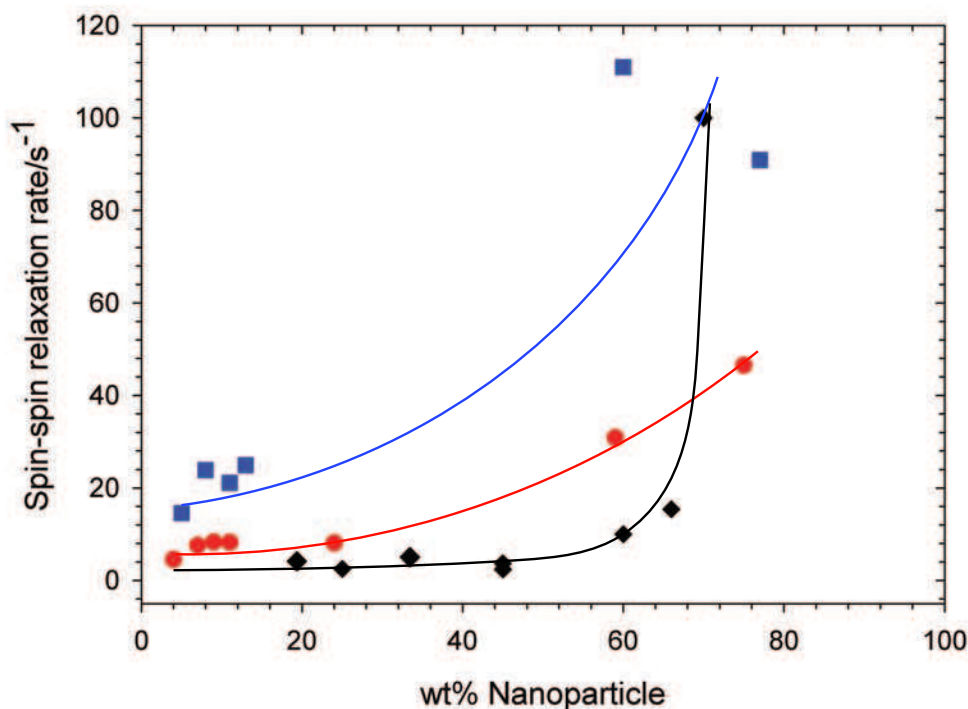
Figure 7: The specific relaxation rate as a function of weight fraction of the POSS component. Lines are not fits to the data; they are guides to the ■ Phenyl POSS triblock, ● t-butyl triblock, ♦ are the resin R2 in PDMS dispersions Check 60% point.

Two different concentrations of R2 resin (17 and 30 vol%) were blended into a range of different molecular weights of PDMS melts (Mw = 6.03k to 174k and 1.32k to 904k respectively for different R2 volume fractions). The R2 resin particles used in this work were trimethylsilyl-functionalised to avoid the complication of interfacial interactions and agglomeration of the PDMS melt and the particles. At low resin contents (high molecular weight) the block copolymers are considerably less mobile than the free resin samples but the values converge as the percentage resin content increases. The difference in compatibility may explain part of this effect as it is likely the block copolymers may aggregate forming large clusters, whereas the R2 resin may be better dispersed. The R2 system shows a very dramatic increase in relaxation rate above 60% resin. ADD percolation We should say more about the R2 PDMS systems?

Conclusions

The POSS-PDMS-POSS triblock polymers with two different pendant groups on the POSS particles, i.e. isobutyl and phenyl groups, were successfully synthesised through the hydrosilylation reaction using Karstedt's catalyst. The conformational behaviour of the linear PDMS and their corresponding triblock polymers in dilute solution was investigated by using small-angle neutron scattering (SANS). The radius of gyration (R_g) of all the polymer samples increases with increasing PDMS molecular weight. The Rg of the triblock polymers was dominated by the PDMS middle chain when the length of the middle chain increased

The mobility of the blockcopolymer

blends compared to homopolymer PDMS mixed with free resin particles copolymers with low molecular weight PDMS (give values) shows that the block copolymers systems self reinforce and are more effective than adding a compatible resin to similar PDMS melts. We should say more about the R2 PDMS systems add data for the block copolymers with homopolymers?

Supporting Information Available

This material is available free of charge via the Internet at `http://pubs.acs.org`.

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