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Poly(ethylene glycol) Octafunctionalized Polyhedral Oligomeric Silsesquioxane: WAXD and Rheological Studies

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ABSTRACT: A homologous series of PEG (various chain length)-substituted octasilsesquioxanes prepared by the hydrosilylation of unsaturated PEGs (poly(ethylene glycol)s) with octa(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$) were studied by wide-angle X-ray diffraction WAXD and rheology. The WAXD results indicate that neat POSS is highly crystalline material, while its PEG hybrids show evidence of small, disordered POSS crystals. Rheological characterization shows largely Newtonian behavior of POSS−PEG materials, with an interesting interplay between attached PEG chain length and weight fraction of POSS, with regards to melt viscosity and activation energy of flow.

Introduction

In the past decade, the area of inorganic−organic materials has led to growing attention to one example of such material, polyoctahedral silsesquoxanes, with such interest increased by the increasing commercial availability of such materials. The relative ease of functionalizing these silica-like cage structures facilitates their covalent incorporation into the organic polymers. Polyoctahedral silsesquioxanes (POSS) are thus unique three-dimensional nanobuilding blocks that can be used to create a wide variety of hybrid materials, where precise control of nanostructures and properties is required.[1−4] POSS nanocomposites are thus often materials that contain nanoscale, silicate cagelike segments directly bound to the polymer chains,[5] although there is some work where such materials are physically blended.[6]

POSS compounds can be modified into such octafunctionalized macromonomers by a hydrosilylation reaction between the terminal Si−H groups on the POSS cube with an unsaturated C═C bond in the presence of a platinum catalyst.[7,8]

POSS compounds are used as precursors in the synthesis of hybrid nanocomposites; examples of octafunctionalized include alkyl,[9] allyl alcohol, 2-allyloxyethanol,[10] epoxy,[11−13] styryl,[14,15] norbornyl,[16] mesogen,[17] methacrylate,[18] amine,[19,20] and amino- and bromophenyls.[21,22]

Herein we report WAXD and rheological studies of poly(ethylene glycol) (PEG) derivatives of octa(dimethylsiloxy)silsesquioxane ($Q_8M_8^H$), which we have previously synthesized[23] where the attached PEGs have varying chain lengths ($n = 2-6$). Poly(ethylene glycol)s are commonly used in variety of applications because of their hydrophilic chemical structure, low toxicity, solubility in water, and lubricating properties. Because of their accessible terminal OH groups, they have potential as useful intermediates, capable of further modification. This is enhanced because the POSS−PEG monomers described here are very hydrophilic and can be readily dispersed in polar monomers due largely to the solubilizing effect of all of the corners of the POSS cage being modified. However, it also is of much interest to characterize the materials themselves in terms of physical properties within a clearly defined series; that is the subject of this paper. In previous work, thermal analyses (calorimetry and thermogravimetric experiments) showed that such a homologous series of ethylene glycol monoallyl ethers revealed a chain-length-dependent increase in the onset of weight loss, while DSC data for allyl-PEGs indicated the degree of semicrystallinity of such materials. As expected, the glass transition of the allyl glycols increases with chain length, and the tetra- and hexaallyl-PEGs showed distinct melting points. The attachment of allyl-PEGs onto POSS cages modified the thermal properties of the newly synthesized hybrids; the POSS−PEG hybrids have increased PEG T_g values compared to their allyl-PEG counterparts although the order of T_g (higher glass transition for hybrids with longer arms) is retained. The bulky POSS cage clearly retards molecular motion and interestingly continues to retard molecular motion even for higher molecular weight POSS−PEG hybrids, even though the weight concentration of POSS units in higher order materials would be lower. In this work other physical properties such as X-ray diffraction are necessary to understand the degree of molecular order (or packing) of the POSS units or glycol chain. But particularly, rheological measurements are used for the first time in such materials to understand their molecular relaxation.

Instrumentation

X-ray Diffraction. Wide-angle X-ray diffraction measurements were performed at room temperature on Philips 1140 diffractometer using 40 kV and 30 mA from 2θ 2° to 45°.

Rheological Measurement. The rheology measurements were conducted on a Rheometrics SR200 controlled stress rheometer. The measuring geometry was parallel plate (torsional flow) of 40 mm diameter and between 0.1 and 0.5 mm gap, depending on available samples size (0.13−0.63 mL). Shear stresses between 0.1 and 60 Pa were applied in a stepwise fashion for 30 s periods to overcome the effects of instrument inertia (a problem for low-viscosity samples). Temperature was controlled to ±0.2 °C via a recirculating water bath acting through the bottom plate.

Results and Discussion

Wide-Angle XRD Studies of POSS−PEGs. Figure 1 shows the structures of materials studied in this work. WAXD profiles

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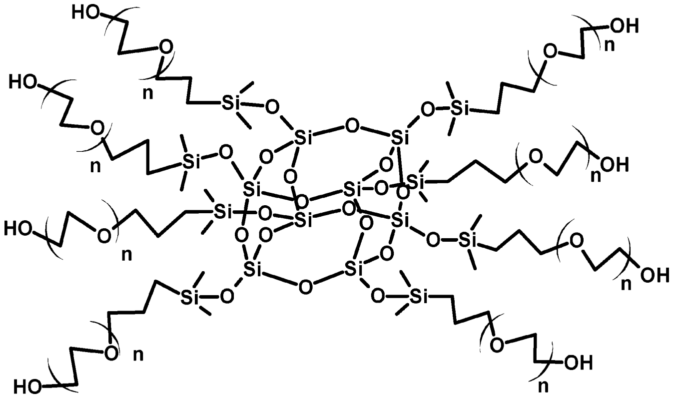

n = 2 (I)
n = 3 (II)
n = 4 (III)
n = 6 (IV)

Figure 1. Structure of various chain-length PEG-functionalized POSS macromonomers.

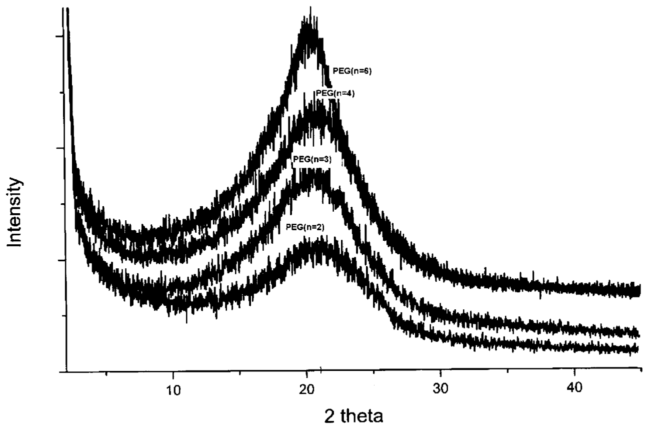

Figure 2. Wide-angle X-ray diffraction (WAXD) pattern of PEGs.

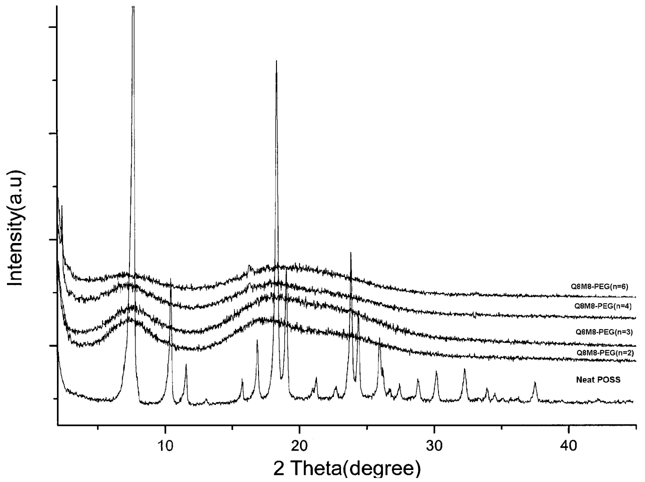

Figure 3. Wide-angle X-ray diffraction (WAXD) pattern of neat POSS (Q_8M_8) and POSS−PEGs [$Q_8M_8^{PEG(n=2-6)}$].

of all the PEG compounds. PEG($n = 2$) (Figure 2) exhibited a broad, amorphous hump centered at $2\theta = 21°$, and all the other PEG materials show a similar feature. Both tetra- and hexaethylene glycols appear a little sharper, due to the emerging order and crystallinity, as seen in the DSC experiments. Such relatively featureless XRD traces for various poly(ethylene glycol) materials has been previously reported.[24]

The WAXD patterns of neat POSS cages, the (octa(dimethylsiloxy)silsesquioxane), Q_8M_8 molecule, in comparison with the substituted PEGs with varying chain length (di, tri, tetra, and hexa) are shown in Figure 3. The neat POSS material is highly crystalline and shows strong peaks at 2θ of 8.1° (d-spacing 10.9 Å), 10.8° (8.2 Å), 18.7° (4.7 Å), and 24.2° (3.7 Å). Such dimethylsiloxy-substituted units have been characterized by Anuar et al.[25] as trigonal rhombohedral. The diffraction spectrum is also similar to those recently reported for other POSS molecules. For example, Chen et al.[26] studied the methacryl functional group with POSS (MA-POSS) and observed five distinct peaks at $2\theta = 8.2°$, 11.1°, 12.3°, 19.2°, and 24.9°, which correspond to d-spacings of 10.7, 7.9, 7.1, 4.6, and 3.6 Å. They suggested that the peak corresponding to the d-spacing of 10.7 Å is related to the size of POSS molecule. The remaining peaks are due to the rhombohedral crystal structure of the POSS molecules.

WAXD profiles of PEG-substituted POSS copolymers are clearly not as sharp as the POSS precursor, but a number of broad peaks relating to POSS crystallinity can be observed. As well as the broad amorphous peak related to the PEG chains based around 22°, there appears to be peaks related to the POSS structure at 7.8°, 18.2°, and 19.1°. These peaks are broad, indicative of small or disordered regions of POSS crystals, and become broader and more diffuse with longer chain lengths, which causes more disruption to organization of the POSS cages. The broad peak centered around $2\theta = 8°$ can also be seen to diminish with length of PEG chain, as the concentration of POSS cages concomitantly reduces.

Similar observations about broadened peak appearance of POSS units in polymers have been reported by number of workers, for example, Carroll et al.[27] in POSS−polystyrene nanocomposites. In other systems, very sharp peaks relating to the POSS crystallinity are seen, even at low POSS concentrations. Zheng et al.[28] synthesized POSS hybrids based on copolymerization with ring-opening metathesis of cyclooctadiene, and a peak was observed related to POSS crystallization at only 1 wt %, indicative of good organization. Other peaks in that work point to the fact that even in this case the crystal shape is distorted and anisotropic. In recent work by Kim and Mather[29] which involved the study of poly(ethylene glycol) chains of varying molecular weight end-capped at both ends by monofunctional POSS molecules (amphiphilic POSS telechelics), crystalline peaks due to the POSS end groups were seen, at almost the same location as neat POSS. The PEO diffraction peaks phase in that work showed a disruption to PEO ordering, although it persisted for a range of molecular weights. Clearly, microcrystalline phases of POSS remained, disrupting PEO crystallinity. The above are all examples of where the POSS units are pendently attached, and although the other corners have some moiety on them, are still able to cluster to some degree. In our work, all corners of the POSS molecules are functionalized and the ethylene glycol units likely to sheath the cage and be particularly disruptive to crystallization of the POSS

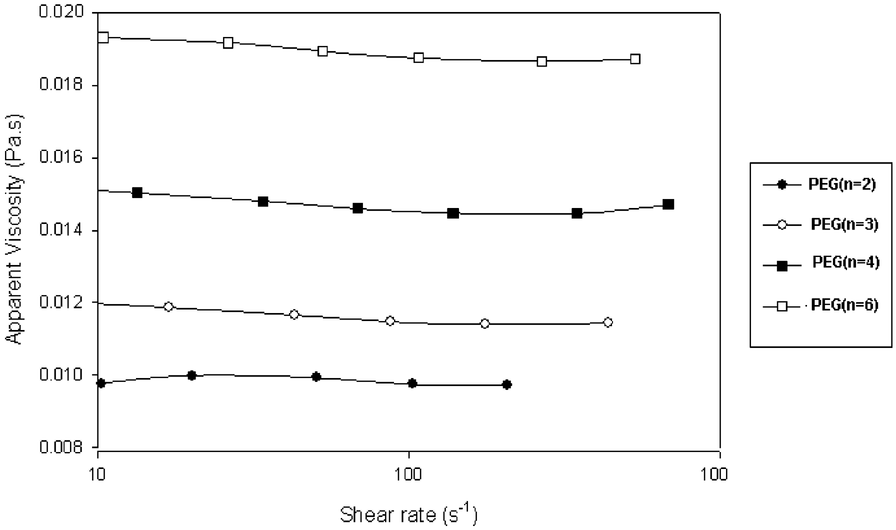

Figure 4. Apparent viscosity of PEG materials at 50 °C.

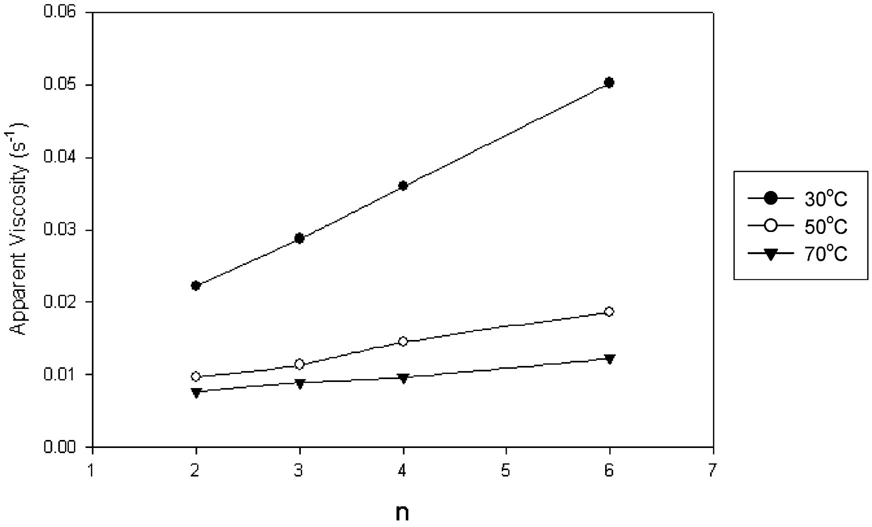

Figure 5. Apparent viscosity vs PEG chain length of various starting PEG materials at a shear rate of 100 s^{-1} for various temperatures.

units. Nonetheless, some low level of order or interaction does appear to persist.

Rheological Studies of POSS−PEG Hybrids. Given the low molecular weight of the PEGs used, it is not surprising that the materials showed Newtonian behavior at all temperatures measured. This can be seen in the 50 °C data presented in Figure 4 for the neat PEGs. PEG samples were measured at different temperatures, and the data for the various materials are plotted at 100 s^{-1} (Figure 5), where it can be seen that as well as Newtonian behavior PEG viscosity increased with molecular weight and decreased with temperature.

Interestingly, it was also found that the shear viscosities of the POSS−PEGs were also largely Newtonian (Figure 6). This was despite the presence of a significant amount of "bound additive" (POSS units) in which the di-, tri-, tetra-, and hexa-POSS−PEG component is 47, 40, 35, and 28 wt %, respectively. The sample with the lowest concentration of POSS cage attached ($Q_8M_8^{PEG(n=6)}$) did show some very slight non-Newtonian behavior and will be discussed further later because it also showed unusual activation energy behavior.

Comparison of absolute values of resistance to flow in Figures 4 and 6 makes it clear, however, that the viscosity is significantly greater for the POSS−PEG samples than for the PEG materials, as would be expected for systems with well-dispersed additives. It appears that the connectedness of the PEG molecules with all points of the POSS cage prevents significant interaction between cubic units during flow. The effect of chain length in the POSS−PEG materials is of particular interest. The viscosity of POSS−PEG material varies as a function of PEG molecular weight, as is shown in Figure 7.

It can be seen that there is a minima in viscosity as a function of the PEG chain length. This is likely due to the competing effects of longer PEG chain length meaning greater dilution (lower weight percent) of the POSS unit in the PEG hybrid, while at the same time longer PEG molecules themselves contributing to a higher viscosity (Figure 10) (note that the ratio of increase in viscosity from the [$Q_8M_8^{PEG(n=4)}$] to [$Q_8M_8^{PEG(n=6)}$] is roughly the same as for PEG(n=4) to PEG(n=6). Thus, [$Q_8M_8^{PEG(n=3)}$] is synergistically low in viscosity because it has a relatively low concentration of POSS cage and a fairly short PEG tail on each cubic point. An additional or alternative explanation of the behavior in Figure 7 may lay with recent work done in modeling[30,31] and experimentation[31] with nanocluster assemblies (experiments reported on octasilsesquixanes surrounded by hydrocarbon layers). Here it is suggested[31] that for longer lengths of chains attached to nanoparticles the degree of interdigitation is greater, as has been seen in modeling.[30] This may encourage hindrance of chain motion, which could also

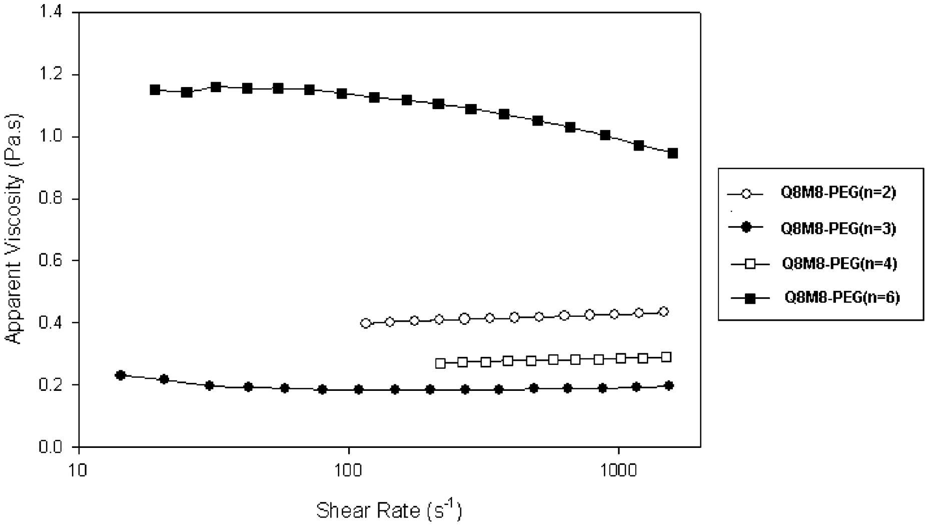

Figure 6. Apparent viscosity vs shear rate of various POSS PEG [$Q_8M_8^{PEG(n=2-6)}$] materials at 50 °C.

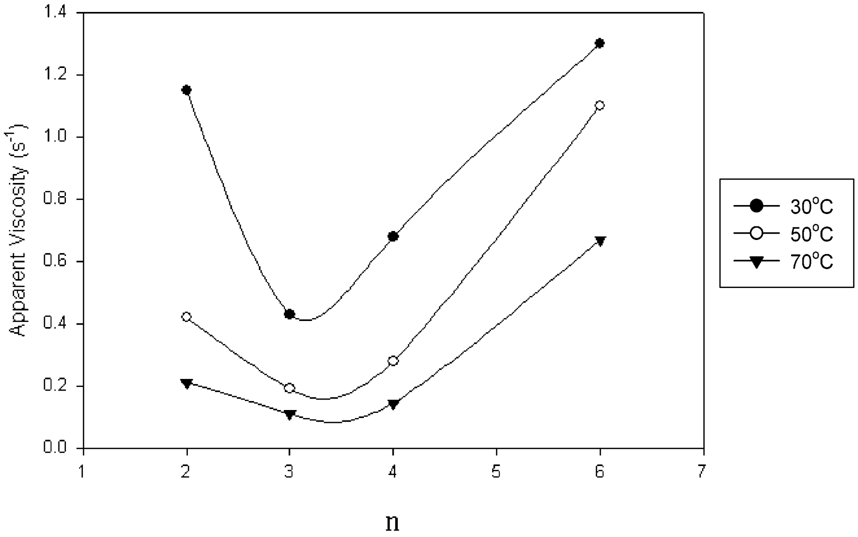

Figure 7. Apparent viscosity vs PEG chain length of various POSS−PEG materials at a shear rate of 100 s^{-1} for various temperatures.

contribute to a higher viscosity energy for longer PEG chain lengths. Interestingly, thermal analyses of these hydrocarbon-sheathed POSS units also found that different chain lengths influenced crystalline melting points (an upturn for longer lengths), and there was also some odd−even fluctuation in these properties for different carbon chain lengths. Some oscillatory rheological work was also done on the system of Kim and Mather[29] on the amphiphilic POSS telechelics mentioned above. In that case, the situation was more complex than in our work due to the persistence of the crystalline POSS nanocrystalline phase after the PEO itself has melted, leading to an order−disorder transition which occurred at the point of the POSS melting.

It has often been found that the addition of filler particles generally causes non-Newtonian behavior (not observed here). It has been reported in a PMMA system filled with 20 wt % PS nanospheres of various sizes that the Non-Newtonian effect increased with smaller filler particles (1300−100 nm). The weight percent of fillers used (20 wt %) was close to content of the POSS−PEG system with the least POSS component [$Q_8M_8^{PEG(n=6)}$] all the other POSS−PEG systems containing a higher filler content.[32] Indeed, some nanofilled systems can show non-Newtonian behavior at much lower concentrations, blends of nanosized calcium carbonate blends showed non-Newtonian behavior even at 5 wt %,[34] and blends of poly(propylene) and carbon nanotubes show Newtonian only below 2 wt %,[35] where of course the carbon nanotubes have a higher aspect ratio. In our work, however, Newtonian behavior was largely observed in all systems.

The properties of flow of nanoparticulate suspensions (known as nanofluidics) is a new and developing area, with morphology, the dispersant chemistry/surface treatment, and shear stresses important (since shear stresses are able to break down the microstructure which cause the non-Newtonian behavior).[36] This behavior is likely due to diffusion-limited cluster−cluster aggregation.[34] Theoretical modeling of nanoparticle clusters in solution found both that shear viscosity was greater for highly dispersed systems due to changes in conformation near the particles and that shear stresses were well able to disperse clustered nanoparticles.[38] It is clear from this work, however, that the good dispersion achieved in this work due to covalent connection to the PEG molecules and the level of nanoseparation it engenders discourages significant POSS interaction in the melt, and thus Newtonian behavior is observed over the shear rate range measured.

It is of interest to determine the activation energy of flow of both the PEGs and the POSS−PEG materials. Small amounts of materials meant that measurements could be made at only

Table 1. Activation Energy of Neat PEG and POSS−PEG [$Q_8M_8^{PEG(n=2-6)}$] Materials in kJ/mol at a Shear Rate of 100 s^{-1} (in Parentheses Is Correlation Factor, R^2, To Indicate "Goodness" of Fit)

monoallyl PEG	E_a (kJ/mol)	POSS−PEG	E_a (kJ/mol)
PEG($n = 2$)	23.2 (0.924)	$Q_8M_8^{PEG(n=2)}$	35.9 (0.995)
PEG($n = 3$)	25.5 (0.918)	$Q_8M_8^{PEG(n=3)}$	30.3 (0.993)
PEG($n = 4$)	28.5 (0.966)	$Q_8M_8^{PEG(n=4)}$	33.1 (0.997)
PEG($n = 6$)	30.5 (0.962)	$Q_8M_8^{PEG(n=6)}$	14.2 (0.904)

three temperatures (30, 50, and 70 °C). The results of this are shown in Table 1 for 100 s^{-1} shear rate.

It was found that for the PEG materials the activation energy of flow increased only slightly with increased PEG molecular weight, as may be expected for larger molecules. (Note that in the case of high polymeric materials the opposite can be observed—activation energy inversely related to molecular weight—explained on the basis of entanglement theory which does not apply for the low molecular weight reactants used here.[39]) In other systems, it has been found to vary in the opposite manner,[40] or not at all with molecular weight increase,[41,42] which is explained by the fact that the unit of flow, even in a macromolecule, is due to motion of a collection of chain segments, rather than whole-body motion.

The activation energy of flow of the POSS hybrid materials generally is higher than those of the neat PEG and remains fairly constant with PEG chain length (at around 30 kJ/mol), decreasing only for the hybrid with the longest chain, [$Q_8M_8^{PEG(n=6)}$]. Thus, the barrier to flow is dominated by the presence of the cages in the hybrids, until the samples are those in which the PEG chains are long enough to dominate flow and ease motion. There is little data in the literature on the addition of nanofillers on the activation energy of flow. A recent study which looked at dual-phase fillers involving silica found a slight increase in activation energy of flow of styrene−butadiene rubber at low shear rates, provided that the filler surfaces were functionalized (by silanes) and thus melt adhesion of the particles was good.[43]

Note that it was the [$Q_8M_8^{PEG(n=6)}$] hybrid of the homologous series which demonstrated a high viscosity because of the long chain length, as opposed to the other hybrids which had higher silicate content. Of interest, however, is that the activation energy of the [$Q_8M_8^{PEG(n=6)}$] material is similar (or a little less) than that of the neat PEG(n=6) itself (recall that the viscosity of [$Q_8M_8^{PEG(n=6)}$] was still substantially above that of the PEG). It appears that once the chain is of sufficient length the energy barrier to flow is dominated by the chain and indeed its mobility may be lubricated (enhanced) by the presence of some POSS units, possibly being disruptive to interchain interactions or entanglements. In addition, this material was the only POSS−PEG material to show some very slight non-Newtonian behavior, as mentioned above.

Conclusions

The WAXD studies showed that the homologous series of PEG-modified POSS materials are amorphous, although some presence of a small disordered regions of POSS crystals can be seen, in contrast to neat POSS which is a highly crystalline material. Rheological characterizations suggest largely Newtonian behavior of POSS−PEG materials, the viscosity of POSS−PEG material changing as a function of PEG molecular weight. A minimum in POSS−PEG viscosity was found as a function of PEG molecular weight, and this is explained as a competition between increasing PEG length, causing an increase in viscosity due to higher molecular weight and lower viscosity because of a reduced weight fraction of POSS unit. Activation energies of the hybrids were higher than for the neat PEG due to the bulky POSS unit and decreased as its concentration reduced with increasing molecular weight (opposite of the influence of degree of polymerization on the activation energy of neat PEG flow).

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