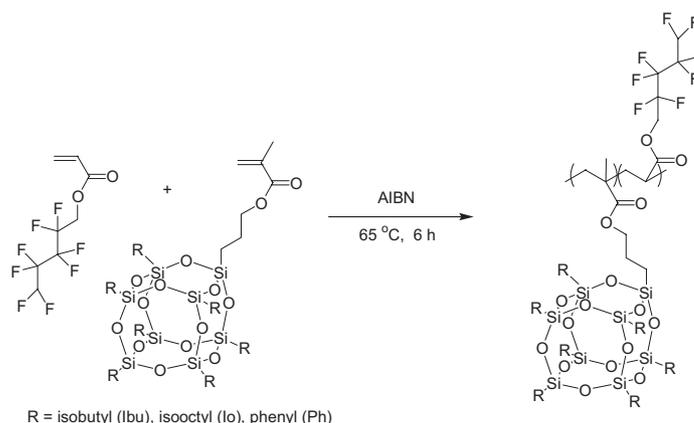


# Fluoroelastomer Copolymers Incorporating Polyhedral Oligomeric Silsesquioxane

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The aggregation of polyhedral oligomeric silsesquioxane (POSS) in copolymers was studied by incorporation of POSS into fluorinated copolymers, namely poly(octafluoropentyl acrylate) elastomers. The aggregation of POSS in copolymers affords unique materials. Studies of these novel polymers show POSS aggregates in these copolymers with both the phenyl and isobutyl peripheries, as the chain-repulsive fluorinated chains help drive this aggregation. The isooctylPOSS copolymers, however, do not have POSS aggregation. Thermal studies of these copolymers also show an increase in the decomposition temperature by incorporation of POSS, which is directly dependent on the POSS periphery.



## Introduction

Despite high monomer costs and poor base resistance, fluoropolymers find great interest due to their excellent material properties, such as good thermal, chemical, aging, and weather resistance, solvent inertness, low surface energy, low flammability, and low moisture absorption.<sup>[1,2]</sup> Fluoropolymers are found in applications such as UV and graffiti-resistant coatings, gaskets or o-rings in the automotive, petrochemical, and aeronautics industries, microelectronics, and the most well-known application, cookware.<sup>[1,2]</sup> Fluoroelastomers provide the unique properties of fluoropolymers to elastomers, which are not seen with other elastomeric materials. Some of the most common types of fluoropolymers include poly[(vinylidene

fluoride)-co-(hexafluoropropylene)], which was introduced by DuPont as Viton<sup>®</sup> in 1957 and by 3M as Fluorel<sup>®</sup> in 1958, and poly(tetrafluoroethylene-co-propylene), which was introduced by the Asahi Glass Company as Aflas<sup>®</sup>. These elastomers display strong solvent resistance, strong mechanical properties, and allow use temperatures over 200 °C. Other fluoroelastomers include fluorosilicon, fluoroethers, perfluoroethers, fluoroacrylates, and fluoroalkoxyphosphazenes.<sup>[1,2]</sup> Fluoroelastomers can be cured using diamines, diphenols, or peroxides, depending on the cure site of the parent polymer. Thermoplastic fluoroelastomers have also been the subject of much research.<sup>[3]</sup> These reports describe the utilization of iodine transfer polymerization to synthesize triblock copolymers with a hard segment–soft segment–hard segment arrangement. In one example, triblock polymers were synthesized using tetrafluoroethylene–vinylidene fluoride–hexafluoropropylene soft segments and ethylene–tetrafluoroethylene–hexafluoropropylene or vinylidene fluoride hard segments.<sup>[4]</sup> By altering the composition of the hard

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segments, the polymeric properties can be controlled to give materials with higher thermal stability, better chemical resistance, lower glass transition temperatures, and better mechanical properties.

Polyhedral oligomeric silsesquioxanes (POSS) are organic–inorganic molecules with diameter in the range of 1–3 nm. POSS consists of a cubic cage with a silicon-to-oxygen ratio of 1:1.5, and organic peripheral groups of each of the silicon atoms.<sup>[5–11]</sup> The peripheral groups are necessary for solubility in common organic solvents and for compatibility in POSS–polymer blends. POSS has been chemically incorporated into semicrystalline polymers (polyethylene,<sup>[12–15]</sup> isotactic-poly(propylene),<sup>[12]</sup> syndiotactic-polystyrene<sup>[16]</sup>), thermosets (epoxy networks,<sup>[17–24]</sup> dicyclopentadiene copolymers<sup>[25]</sup>), and amorphous polymers (styrene,<sup>[26]</sup> methylmethacrylate,<sup>[27,28]</sup> *n*-butylacrylate,<sup>[29]</sup> norbornene,<sup>[30]</sup> styrene–butadiene–styrene triblocks,<sup>[31–33]</sup> amongst others). Recently, POSS has been incorporated into perfluorocyclobutyl aryl ether polymers.<sup>[34]</sup> Generally, POSS incorporation into polymers increases the oxidative resistance, use temperature, glass transition temperature, and storage modulus of the polymers. Also, POSS has been found to aggregate in copolymers, which could be utilized in many applications. One such application is thermoplastic elastomers. Thermoplastic elastomers are materials that gain their elastic strength from physical interactions between polymer domains.<sup>[2,35]</sup> In the example of styrene–butadiene–styrene triblock thermoplastic elastomers, the formation and interaction of styrene domains act to impede polymer flow, as they act as a physical entanglement or crosslink.<sup>[2]</sup>

Recently, POSS was incorporated into polybutadiene elastomers by the ring-opening metathesis polymerization of POSSnorbornene and cyclooctadiene, producing a random copolymer of 1,4-butadiene and POSS.<sup>[36]</sup> POSS containing elastomers with stronger physical and mechanical properties, namely ethylene–propylene–POSS elastomers have recently been described.<sup>[37]</sup> Studies of the copolymers show POSS molecules disperse in the ethylene–propylene polymer matrix if the POSS periphery was ethyl (Et) or isobutyl (Ibu), but aggregate if the periphery was phenyl (Ph). This shows that the POSS periphery has an important effect on the aggregation of POSS and thus the physical properties of POSS copolymers. Mechanical studies of ethylene–propylene–PhPOSS polymers indicate POSS is acting as a physical crosslink, which can be utilized in thermoplastic elastomers.

In this current study, the aggregation of POSS was studied in a fluoroelastomer, where the highly nonfavorable fluoropolymer POSS interaction promotes POSS aggregation. Mechanical studies were also performed to show that PhPOSS addition to fluoropolymers creates an increase in the rubbery plateau region and the modulus in the rubbery plateau region.

## Experimental Part

### Materials

The POSS macromonomer 3-[(3,5,7,9,11,13,15-heptaisobutyl-pentacyclo[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]octasiloxane)]propyl methacrylate (IbuPOSS MA) was purchased from Aldrich, and POSS monomers 3-[(3,5,7,9,11,13,15-heptaisooctyl-pentacyclo[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]octasiloxane)]propyl methacrylate (IoPOSS MA) and 3-[(3,5,7,9,11,13,15-heptaphenyl-pentacyclo[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]octasiloxane)]propyl methacrylate (PhPOSS MA) were purchased from Hybrid Plastics, and used as received. Octafluoropentylacrylate (OFPA) was purchased from Oakwood Products and used as received. Reaction initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) was purchased from Aldrich and recrystallized from methanol and dried prior to use. Benzene was purchased from Aldrich and vacuum distilled over CaH<sub>2</sub> prior to use.

### Polymerization of POSS Methacrylates and Octafluoropentylacrylate

A 100 mL round-bottom flask with a stir bar and septum under nitrogen atmosphere was charged with 1.2 mL (6.24 mmol) of octafluoropentylacrylate, 7 mg (0.043 mmol) of AIBN, 10 mL of benzene, and a predetermined quantity of POSS methacrylate. The flask was heated in an oil bath at 65 °C for 6 h. The reaction was precipitated in hexane or methanol, depending on the POSS loading and POSS periphery. Residual POSS monomer was removed from PhPOSS copolymers by consecutive precipitations in hexane. Residual POSS monomer was removed from IbuPOSS copolymers by consecutive precipitations into an 85:15 v/v methanol/H<sub>2</sub>O mixture. At low POSS loadings, the precipitation of POSS copolymers in hexanes completely removed residual POSS monomer.

### Polymer Characterization

<sup>1</sup>H NMR spectra were obtained in chloroform-*d* or methylene chloride-*d*<sub>2</sub> on a Bruker DPX-300 FT-NMR spectrometer operating at 300 MHz. <sup>13</sup>C NMR spectra were obtained at 90 °C in tetrachloroethane-*d*<sub>2</sub> on a Bruker 400 FT-NMR spectrometer operating at 100 MHz. Gel permeation chromatography (GPC) studies were performed using a Polymer Laboratories PL-GPC 50 Integrated GPC System, using THF as the mobile phase. Molecular weights were calibrated against narrow molecular weight polystyrene standards.

### Differential Scanning Calorimetry (DSC)

DSC was performed under a nitrogen atmosphere on a DuPont Instruments DSC 2910. Samples were cooled to –110 °C and heated at a rate of 10 °C · min<sup>–1</sup>. Data were obtained on second heating, also at a rate of 10 °C · min<sup>–1</sup>.

### Thermal Gravimetric Analysis (TGA)

TGA was performed using a Mettler–Toledo TGA/SDTA851<sup>o</sup>. Samples were heated at a rate of 10 °C · min<sup>–1</sup> up to 800 °C under an air atmosphere.

## Wide Angle X-Ray Diffraction (WAXD)

WAXD patterns were obtained on a PANalytical's X'Pert PRO instrument in reflectance mode. Samples for this study were dissolved in a toluene solution (20 vol.-%) and cast onto a glass slide. Samples were dried in a vacuum oven at 40 °C for 24 h.

## Rheology

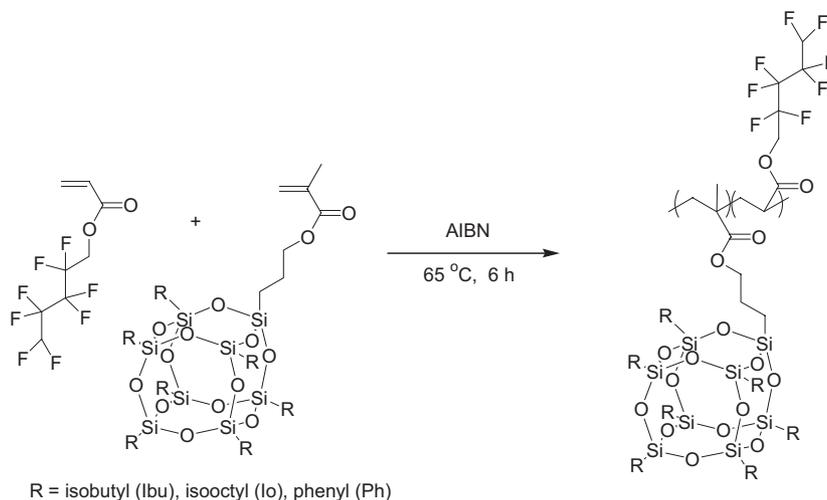
Rheological studies were performed on a TA Instrument AR 2000 rheometer using a parallel plate geometry. Samples were prepared by dissolution in toluene and casting films in aluminum pans. The films were allowed to form over 2 d. The films were then dried in a vacuum oven at 45 °C for at least 24 h.

## Results and Discussion

### Polymerization

As an initial foray into fluoroelastomers containing POSS, free radical copolymerization of octafluoropentylacrylate and POSS methacrylates was performed, as shown in Scheme 1.

Octafluoropentyl acrylate copolymers were chosen because of their robust polymerization techniques, their



■ Scheme 1. Preparation of octafluoropentylacrylate–POSS copolymers.

well-defined polymer nature, their elastomeric nature, and their presumed ability to form random copolymers with POSS methacrylates. Studying the reactive ratios of two similar monomers, trifluoroethylacrylate and methyl methacrylate, it was anticipated that random copolymers would be formed, as the  $r_1$  value of trifluoroethylacrylate was 0.1 and the  $r_2$  value was 2.1. The replacement of methyl methacrylate with the more bulky POSS methacrylates should decrease the  $r_2$  value, further assuring the formation of random copolymers. The copolymerization results are shown in Table 1.

■ Table 1. Octafluoropentyl acrylate–POSS copolymerization results.

Rxn ID	POSS loading	$\bar{M}_n$ (PDI) <sup>a)</sup>	POSS in polymer <sup>b)</sup>	Isolated yields
	wt.-%	$\text{g} \cdot \text{mol}^{-1}$	mol-% (wt.-%)	%
POFPA	–	16 000(1.54)	–	81
Ibu7	6.7	28 000(2.26)	2.0(7)	66
Ibu10	12.6	64 000(1.57)	3.0(10)	79
Ibu32	20.6	32 000(2.39)	13(32)	65
Ibu36	30.3	53 700(1.45)	15(36)	>20
Ph8	6.7	32 000(1.79)	2.2(8)	64
Ph14	12.6	44 000(1.61)	4.0(14)	62
Ph23	20.6	45 000(1.88)	7.3(23)	64
Ph32	30.3	34 000(1.66)	11.2(32)	60
Io6	7.9	70 000(2.30)	1.4(6)	69
Io13	14.7	54 000(1.93)	3.2(13)	59

<sup>a)</sup>As determined by GPC, using narrow molecular weight polystyrene standards in THF; <sup>b)</sup>As determined by <sup>1</sup>H NMR, with CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> as solvent.

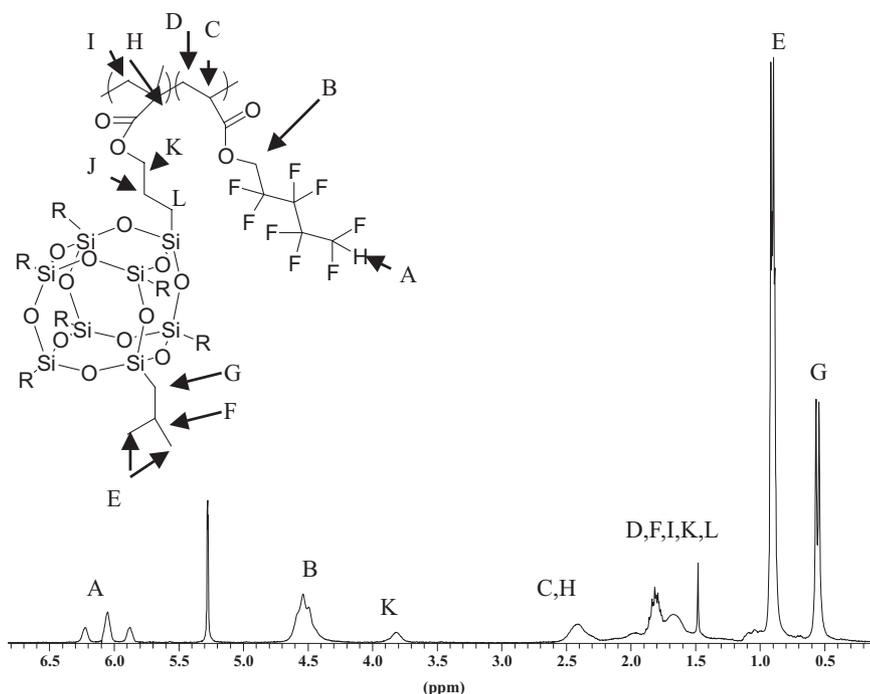


Figure 1.  $^1\text{H}$  NMR of poly(octafluoropentyl acrylate-ibuPOSS) (Ibu36) copolymer.

Polymerizations were stopped at relatively moderate conversions to reduce the likelihood of chain-branching and crosslinking reactions. The molecular weights of the copolymers ranged from 28 000 to 70 000  $\text{g} \cdot \text{mol}^{-1}$ . The molecular weights were measured by GPC, and are presumably higher than the actual values, as fluoropolymers have strongly repulsive polymer chains, thus creating a random coil with a larger radius of gyration than most organic polymers. POSS homopolymers, on the other hand, have shown lower molecular weights by GPC than determined by end-group analysis using  $^1\text{H}$  NMR spectroscopy. POSS incorporations were determined by  $^1\text{H}$  NMR, as shown in Figure 1. POSS incorporations were determined by using the methyl and methylene protons of the isobutyl periphery to the methylene protons  $\alpha$  to the carbonyl group on the octafluoropentyl side chain. Internal integrations of other protons in the copolymers were fully consistent with the calculated POSS incorporation levels.

Based on the expected reactivity ratios, and the POSS feed to incorporation comparisons, it is assumed that random copolymers are formed. In  $^1\text{H}$  NMR, the monomer sequence distribution of copolymers can be determined from resonance shifts due to the formation of different diads and triads. However, in the case of POSS-octafluoropentyl acrylate copolymers, resonances from the backbone repeat units overlap, making it difficult to observe resonance shifts. In  $^{13}\text{C}$  NMR, it is difficult to observe POSS backbone resonances, as only a small mol-% of POSS is incorporated into the copolymers, and there are very few backbone

carbons per POSS molecule. POSS incorporations ranged from 6 to 36 wt.-%, and could be relatively well controlled based on reaction conditions. Copolymers with IuPOSS were only synthesized with low POSS incorporations (<3.2 mol-%) due to the subsequent difficulty of removing residual IuPOSS monomer from copolymers that had high POSS loadings.

### WAXD

WAXD has been used to study the aggregation of POSS in copolymers.<sup>[14,35,36]</sup> The POSS monomers form three-dimensional hexagonal arrays, but when chemically incorporated into as pendant groups in copolymers, the steric restriction imposed on POSS by attachment to a polymer chain restricts aggregation to two-dimensional sheets. In WAXD, POSS monomers show their sharpest

diffraction peaks at a  $2\theta$  value around  $8^\circ$ , depending on the POSS periphery. When POSS is chemically incorporated into a polymer, the diffraction peaks broaden due to a smaller crystal size. The appearance of this diffraction peak and the relative width of the peak can be used to study the aggregation of POSS in a polymer matrix.

WAXD patterns of the POFPA-POSS copolymers are shown in Figure 2–4. Each figure shows the POFPA homopolymer diffraction pattern as the bottom trace with increasing POSS loading going upwards in the graph,

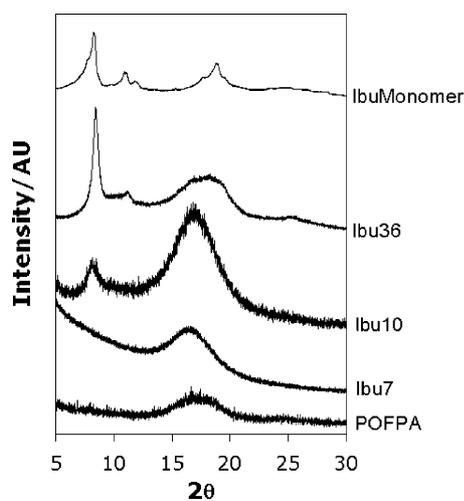
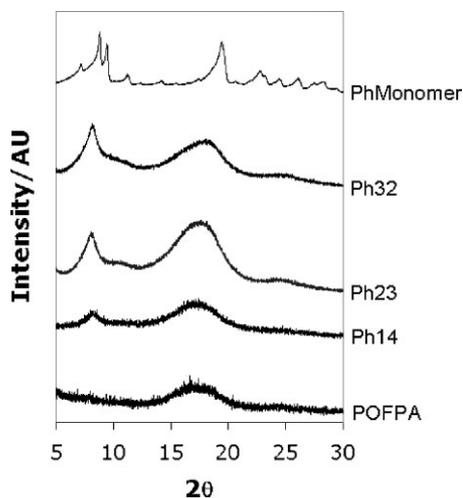
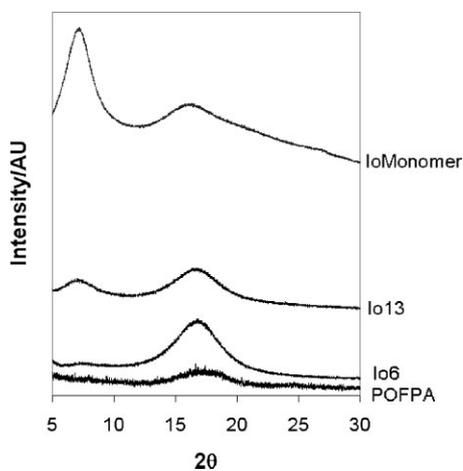


Figure 2. WAXD patterns of POFPA-IbuPOSS copolymers.



■ Figure 3. WAXD patterns of POFPA–PhPOSS copolymers.

with a corresponding POSS monomer as the top trace. The POFPA homopolymer shows an amorphous halo centered around a  $2\theta$  value of  $18^\circ$ . In Figure 2, as the IbuPOSS content is increased to 10 wt.-%, a POSS diffraction peak at a  $2\theta$  value of  $8^\circ$  appears, indicating POSS aggregation. As the POSS content is increased to 36 wt.-%, the diffraction peak increases in intensity and sharpens, indicating larger POSS aggregates. In ethylene–propylene–IbuPOSS elastomers, POSS has been shown to disperse within the ethylene–propylene matrix.<sup>[37]</sup> In Figure 3, the PhPOSS copolymers, POSS diffraction peaks are relatively sharp at all POSS incorporations above 14 wt.-%, indicating extensive POSS aggregation in the copolymers. Copolymers containing IoPOSS, Figure 4, show broad POSS diffraction peaks, indicating small POSS aggregates, or more likely simply POSS dispersion. The IoPOSS monomer is itself noncrystal-



■ Figure 4. WAXD patterns of POFPA–IoPOSS copolymers.

■ Table 2. POSS domain sizes estimated using Scherer's equation.

Sample	Domain size	~POSS per domain <sup>a)</sup>
	nm	
Ibu36	15	10
Ibu10	8.0	5–6
Ph32	7.2	4–5
Ph23	6.0	4
Io13	3.5	2–3

<sup>a)</sup>Number of POSS per domain was estimated by dividing the estimated domain size by 1.5, the approximate diameter of POSS.

line in nature, indicating that the long isooctyl chains suppress the ability of POSS to aggregate.

The approximate lateral size of the POSS aggregates can be determined using Scherer's equation,  $L = 0.9\lambda/\beta\cos\theta$  where  $L$  is the domain length,  $\lambda$  is the wavelength of the X-ray,  $\beta$  is the peak width at half maximum, and  $\theta$  is the angle. This calculation has previously been performed to estimate POSS domain sizes.<sup>[14,37]</sup> It is assumed that POSS has a 15 Å diameter, and results of the estimation of POSS aggregate sizes are shown in Table 2. These calculations simply estimate the largest domain size, and the corresponding number of POSS molecules it would take to fill a domain of this size. POSS could also be aggregating in another direction, as POSS aggregation in copolymers is confined to two dimensions, with the third dimension having either one or two POSS cubes. Therefore, the number of POSS molecules per domains is probably larger than this estimated value. This study shows POSS aggregates to form the longest domain sizes with the isobutyl periphery, as Ibu36 has a domain length of 15 nm. The PhPOSS copolymers have lengths of 6–7.2 nm per domain, which is similar to the ethylene–propylene–PhPOSS samples.<sup>[36]</sup> The Io13 sample has 2–3 POSS molecules per domain. Because the monomer is not crystalline, the relative intensity could be due to noncrystalline aggregation.

### Thermal Characterization

The thermal characterization data are shown in Table 3. The glass transition temperature of poly(octafluoropentyl acrylate) is  $-27^\circ\text{C}$ , and the polymer has a melting peak at  $96^\circ\text{C}$ . However, no diffraction peaks were seen in WAXD of this homopolymer. None of the copolymers show a melting peak, indicating that POFPA crystallization is restricted to the homopolymer. Based on the previous literature, it is expected that POSS will increase the glass transition temperature of the parent homopolymer,

Table 3. Thermal characterization of POSS–octafluoropentyl acrylate copolymers.

Rxn ID	POSS Amount	$T_g^a)$	2% Decomp. temp. <sup>b)</sup>	Char yield <sup>b)</sup>	Theoretical char yield <sup>c)</sup>
	wt.-%	°C	°C	%	%
POFPA	–	–27 ( $T_m = 96$ )	291	12.1%	–
Ibu7	7	–29	294	4.5	3.5
Ibu10	10	–28	294	10.3	5.1
Ibu32	32	–	295	18.8	16.2
Ibu36	36	–27	295	20.3	18.3
Ph8	8	–29	316	3.8	3.1
Ph14	14	–26	319	7.0	5.4
Ph23	23	–15	316	11.8	10.3
Ph32	32	–14	318	16.2	14.3
Io6	6	–26	320	2.7	2.5
Io13	13	–24	320	4.5	4.6

<sup>a)</sup>As determined by GPC, with a heating rate of  $10^\circ\text{C} \cdot \text{min}^{-1}$ ; <sup>b)</sup>As determined by TGA, with a heating rate of  $10^\circ\text{C} \cdot \text{min}^{-1}$ ; <sup>c)</sup>Theoretical calculation assumes a complete conversion of POSS to  $\text{SiO}_2$ .

as adding a bulky side group slows the segmental movement of the copolymer chain.<sup>[9]</sup> In PhPOSS copolymers, the  $T_g$  increases with increase in POSS loading, with the largest jump occurring between the Ph14 and Ph23 samples. This trend also fits with the two IoPOSS copolymers, but not with the IbuPOSS copolymers, as the  $T_g$  values remain about the same with all POSS loadings. A possible explanation is that the POSS aggregates are acting like domains in block copolymers. Thermal studies on phase separated block copolymers have shown  $T_g$  values for both blocks which are the same  $T_g$  values as the respective homopolymers. These samples do not show a  $T_g$  for the POSS block. There have been very few literature reports of  $T_g$  values for POSS blocks.

Thermal gravimetric analysis data show the strong thermal characteristics of both the fluorinated homopolymer and POSS containing copolymers (Table 3). The homopolymer, POFPA, has a 2% decomposition temperature of  $291^\circ\text{C}$ , which increases by the addition of POSS to the polymers. The periphery plays an important role in the decomposition temperature, but the POSS incorporation does not seem to play a significant role. This could be related to the amount of POSS aggregated at the surface. If the amount of POSS is similar at different loadings, the thermal decomposition data should be similar. The IbuPOSS copolymers show the lowest increase in decomposition temperature, at  $295^\circ\text{C}$  followed by the PhPOSS copolymers and IoPOSS copolymers, which are both in the range of  $319^\circ\text{C}$ . This is another important material property that depends directly upon the POSS periphery.

Another important property is the char yield. Ideally, POSS will decompose under air to form silica,  $\text{SiO}_2$ . The

theoretical char yields calculated in Table 3 are based on a complete conversion of POSS to silica. The POFPA homopolymer itself shows a significant char yield, which partially explains the fact that the measured char yields exceed the theoretical yields. PhPOSS copolymers also show higher char than expected, as the phenyl ring can also form char. Because of the high char yields that formed from the POFPA homopolymer plus POSS conversion to silica, it is expected that the experimentally determined char yields will be higher than the theoretical values. Several char yields are close to the theoretical values. A possible explanation for this is a possible POFPA scission that results in the formation of a fluoride anion, which can attack silicon, thus suppressing the formation of  $\text{SiO}_2$ , and reducing the char formed from the fluoropolymer.

### Rheology

The mechanical properties of these fluoroelastomer copolymers were studied to determine if POSS incorporation leads to stronger elastomeric properties of the polymers. Studying the five areas of viscoelastic behavior, it has been shown that crosslinked elastomers have an increase in the length of the rubber plateau region, as well as an increase in the modulus of the material.<sup>[34]</sup> Strain sweeps at various temperatures were performed to determine the crossover temperature of the POSS fluoroelastomers from the rubbery plateau region to the rubbery flow region. These plots are shown in Figure 5, which measure the storage and loss modulus as a function of temperature. Strain sweeps were performed on three different samples, the POFPA homopolymer, and Ibu10

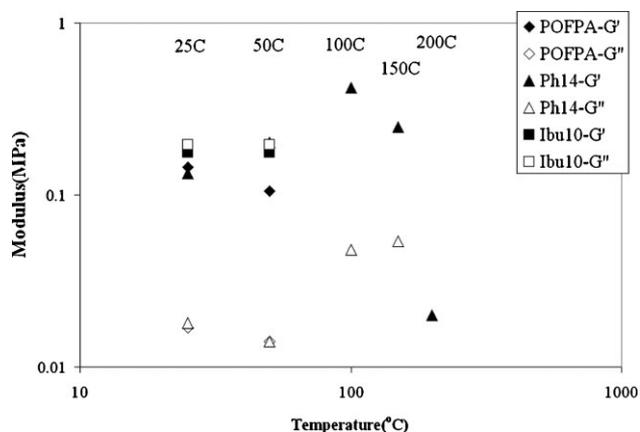


Figure 5. Modulus as a function of temperature in POFPA and POFPA copolymers.

and Ph14 copolymers. Each sample was in the linear viscoelastic regime, allowing for a single data point at each temperature. At 25 °C, Ibu10 has the highest storage modulus, but the loss modulus is higher than the storage modulus, indicating the sample already has crossed over to the rubbery flow region. The Ph14 and POFPA samples show similar behavior, with their storage modulus being much higher than the loss modulus. It is important to note that the POFPA homopolymer shows a significant melting endotherm at 96 °C by DSC. This semi-crystalline nature of the homopolymer inherently makes this material a thermoplastic elastomer, and explains the relatively strong mechanical properties of the material at both 25 and 50 °C. The Ph14 copolymer sample shows the strongest mechanical properties at 50 °C. The storage and loss modulus of both the POFPA homopolymer and Ibu10 samples decrease at this temperature, although the POFPA homopolymer remains in the rubber plateau region. When the temperature is raised to 100 °C, both the POFPA and Ibu10 samples were observed to flow off the parallel plates in the rheometer. The Ph10 sample had sufficient mechanical strength to test properties at temperatures up to 200 °C. When the temperature of the Ph10 sample was raised from 25 to 50 to 100 °C, the storage modulus increased. This is expected from rubber viscoelasticity theories.<sup>[34]</sup> At 150 °C, however, the storage modulus decreases and appears to be in the rubbery flow region. This demonstrates the ability of PhPOSS to act as a physical crosslink, as the rubbery plateau region is increased versus the homopolymer, despite the semi-crystalline nature of the homopolymer.

Frequency sweeps were also performed on the three polymer samples (Figure 6–8). Frequency sweeps give information about the response of polymeric material at different frequencies, which are related to time. High frequencies are related to short times, and low frequencies are related to long times.<sup>[34]</sup> In the POFPA homopolymer,

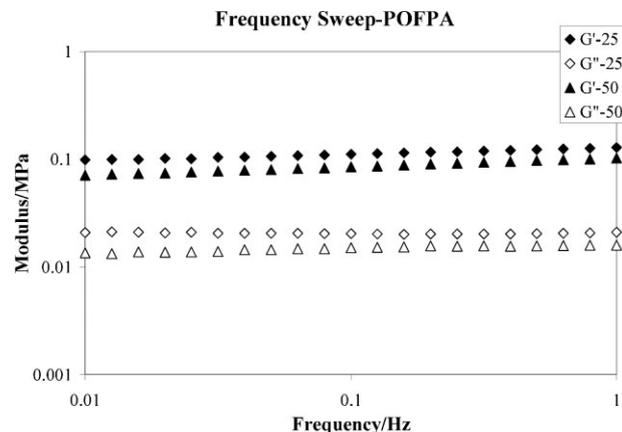


Figure 6. Frequency sweep of POFPA homopolymer sample.

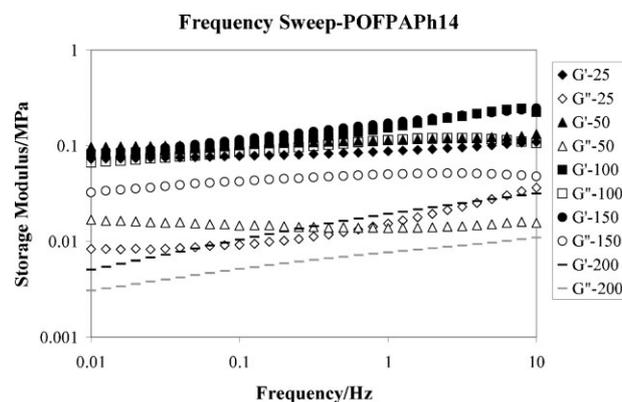


Figure 7. Frequency sweep of POFPA-Ph14 sample.

the storage modulus remains approximately the same across the frequency range, indicating a solid material that retains its properties at longer times (low frequencies). When the sample is heated to 50 °C, it has the same material response, with only a small decrease in the modulus. The Ibu10 sample shows fluid-like behavior at

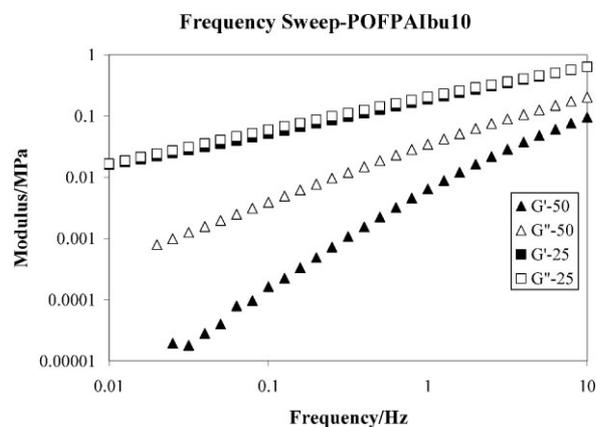


Figure 8. Frequency sweep of POFPA-Ibu10 sample.

both 25 and 50 °C. Although POSS has been shown to aggregate in POFPA–IbuPOSS copolymers, the IbuPOSS loading must be too small to drastically enhance material properties. The homopolymer has stronger material properties due to its semi-crystalline nature, making it difficult to compare the enhancement in mechanical properties by the incorporation of low loadings of IbuPOSS. The Ph14 sample has much stronger material properties. The modulus slightly decreases as the frequency is changed from 10 to 0.01 Hz, indicating a solid-like material. The material properties show a drastic change at 200 °C, as there is a larger change in modulus while decreasing the frequency. Therefore, even at small PhPOSS loadings, POSS increases the rubbery plateau region and has a higher modulus than the POFPA homopolymer.

The molecular weight between crosslinks ( $M_c$ ) was estimated from the rheological data using the equation  $M_c = \rho RT/G$ .<sup>[34]</sup> The average molecular weight between crosslinks in the range of 50–150 °C was calculated to be 24 000 g · mol<sup>-1</sup>, or 87 monomer units between crosslinks. Therefore, on average, Ph14 has two or three crosslink junctions per polymer chain. The POSS aggregates disperse at a temperature between 150 and 200 °C.

## Conclusion

The synthesis of poly(octafluoropentyl acrylate)–POSS copolymers allowed for the study of POSS aggregation in different elastomers. The synthesis of the copolymers by free radical chemistry afforded copolymers with sufficient molecular weights, relatively low polydispersities, and varying POSS peripheries such as isobutyl, phenyl, and isooctyl. Thermal studies of these random copolymers show moderate increases in glass transition temperature with PhPOSS and IoPOSS copolymers, but no increase with IbuPOSS copolymers. Thermal gravimetric analysis data show an increase in decomposition temperature by incorporating POSS, and an increase in decomposition temperatures based on the POSS periphery, with isooctyl showing the highest decomposition temperature, followed by phenyl and isobutyl. The aggregation of POSS in these fluorinated copolymers were also shown to be periphery-dependent. Unlike in ethylene–propylene–IbuPOSS copolymers, IbuPOSS was found to aggregate in these copolymers, as the chain-repulsive fluorinated chains help to drive POSS aggregation. POSS was also found to aggregate with the PhPOSS copolymers, but not with the IoPOSS copolymers, as the long isooctyl chains sterically prohibit POSS from aggregating. Rheological studies of these copolymers show a significant increase in rubbery plateau region and modulus of the POFPA–Ph14 samples as compared to the POFPA semi-crystalline homopolymer.

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