

Novel Polyolefin Nanocomposites: Synthesis and Characterizations of Metallocene-Catalyzed Polyolefin Polyhedral Oligomeric Silsesquioxane Copolymers

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ABSTRACT: Novel organic/inorganic hybrid copolymers have been prepared using single site catalysis. Ethylene copolymers incorporating a norbornylene-substituted polyhedral oligomeric silsesquioxane (POSS) macromonomer have been prepared using a metallocene/methylaluminumoxane (MAO) cocatalyst system. Isotactic polypropylene-containing POSS nanoparticles were also synthesized for the first time using a similar approach utilizing a C_2 symmetric *ansa*-metallocene. A wide range of POSS concentrations were obtained in these polyolefin POSS copolymers under mild conditions, up to 56 wt % for PE-POSS copolymers and 73 wt % for PP-POSS copolymers. Initial findings point to improved thermooxidative stability for these nanocomposite polyolefins containing the “molecular silica” side groups relative to their homopolymer analogues. Thermogravimetric analysis of the PE-POSS copolymers under air shows a 90 °C improvement, relative to a polyethylene control sample of similar molecular weight, in the onset of decomposition temperature based upon 5% mass loss. On the basis of dynamic mechanical thermal analysis, the tensile properties of the PE-POSS copolymer were maintained at low POSS loadings. A modulus plateau at temperatures above 175 °C is observed, indicating suppression of melt flow for polyethylene POSS copolymers.

Introduction

Composite materials are common in the production of modern plastics. A second component is often added to polymeric materials to enhance properties, such as thermal stability and mechanical strength. Among composite materials, organic–inorganic hybrid materials have drawn great attention from the standpoint of advantageous performance relative to either of the nonhybrid counterparts.¹ With the developing interests in nanocomposite materials,^{2,3} typically referring to discontinuous particulate inclusion with one major dimension on the scale of 1–100 nm, it is recognized that behaviors at the nanoscale are not necessarily predictable from that observed at larger length scale. Many studies have shown dramatic improvement of physical properties compared with pure materials by placing inorganic particles into an organic polymeric matrix at the nanometer scale. This is presumably due to the predominant interfacial interaction between nanoparticles and polymer segments. It is envisaged that nanocomposite materials have the potential to bridge the gap between ceramics and polymers.

In particular, the use of polyhedral oligomeric silsesquioxane (POSS) nanoparticles as modifiers of organic polymers has received a great deal of attention recently following the development of efficient synthetic protocols for the preparation of the inorganic Si_8O_{12} core.⁴ Notable among these procedures is the ability to prepare the nanocage of a POSS macromonomer: an inorganic core surrounded by seven alkyl groups to promote solubility and a single unique group capable of undergoing polymerization.⁵ In contrast to organoclay fillers,² POSS nanoparticles have the advantages of being monodisperse and lower in density, have high-temperature

stability, and contain no trace metals. More importantly, it has tailorable interfacial properties and the potential for undergoing copolymerization reactions. These latter factors are especially noteworthy given that polyolefin–clay nanocomposites have failed to produce complete dispersal or exfoliation of clay nanolayers due to unfavorable interactions between hydrophilic clay surfaces and hydrophobic polyolefins.⁶

A variety of POSS-containing copolymers have been prepared using radical (both conventional^{7,8} and atom transfer protocols⁹), condensation,¹⁰ and ring-opening metathesis^{11,12} polymerization techniques. The ability to copolymerize POSS macromonomers with olefins using coordination polymerization is still at an early stage of development. Preliminary results showed that POSS macromonomers with seven cyclopentyl or cyclohexyl groups and one alkenyl group (approximately 1.5 nm in diameter) did not undergo Ziegler–Natta catalyzed copolymerization with 1-hexene.⁵ Even a less sterically hindered ethyl-substituted POSS macromonomer with a long alkyl spacer between the pendant unsaturation group and the POSS core showed low activity and low incorporation of POSS when copolymerized with ethylene.¹³ Furthermore, an attempt to obtain polypropylene copolymers resulted in only oligomeric atactic polypropylene copolymers ($M_n \sim 2200$). In an earlier report, polyethylene POSS copolymers have been synthesized using a two-step procedure: ring-opening metathesis polymerization followed by hydrogenation.¹² Thermal studies on these model copolymers revealed substantial improvement in thermal oxidative stability. Therefore, a practical and direct method to synthesize polyolefin POSS copolymers was desired.

In this paper, an efficient synthetic route is reported for the preparation of hydrocarbon POSS copolymers with control over the incorporation level of POSS macromonomer using metallocene catalysis. Ethylene

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was directly copolymerized with a POSS macromonomer containing seven cyclopentyl and one polymerizable norbornylene group using classical metallocene catalysis to produce polyethylene POSS hybrid copolymers. Isotactic polypropylene POSS copolymers were also synthesized for the first time using a C_2 symmetric *ansa*-metallocene. To the best of our knowledge, this POSS macromonomer is to date the largest well-defined macromonomer copolymerized into polyolefins using metallocene catalysis.

Experimental Section

Materials. Cyclopentyl-POSS-norbornylene macromonomer 1-[2-(5-norbornen-2-yl)ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}] octasiloxane (**1**), cyclopentyl-POSS-vinyl macromonomer 1-vinyl-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}] octasiloxane (**2**), and cyclopentyl-POSS-allyl macromonomer 1-allyl-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1.^{3,9}1.^{5,15}1^{7,13}] octasiloxane (**3**) were provided by the Air Force Research Laboratory, Propulsion Directorate, AFRL/PRSM, Edwards Air Force Base, CA. Other reagents were obtained from Aldrich and used as received unless otherwise indicated. Polymer grade ethylene and propylene were purchased from Matheson Gas Products and were passed through a Drierite drying unit and a OxiClear inline gas purifier before use. Toluene was passed sequentially through columns of activated alumina (LaRoche A-2) and Q-5 supported copper redox catalyst (Engelhard CU-0226S) under a prepurified nitrogen atmosphere. Methylaluminoxane (MAO) was obtained from Akzo Nobel Chemicals as a 10 wt % Al solution (3.36 M) in toluene.

Polymerization Procedures for Polyethylene POSS Copolymers. The ethylene POSS macromonomer copolymerizations were carried out in a 100 mL Schlenk flask equipped with a magnetic stirring bar, 0.51 g of **1** (0.5 mmol, 250 equiv to Zr), and 19 mL of toluene. The sealed flask was removed from the glovebox and charged with ethylene gas (1 atm). A solution of 0.84 mg (2 μ mol) of dichloro[*rac*-ethylenebis(indenyl)]zirconium in 1.0 mL of toluene and 0.36 mL of 3.36 M MAO (1.2 mmol) were mixed and then preactivated for 15 min prior to injection into the flask. Ethylene pressure was kept constant throughout the polymerization through use of a bubbler. The reaction temperature was controlled using a 20 °C water bath. The copolymer was observed to precipitate from solution during the reaction. After 1 h, the reaction was terminated by addition of methanol. The polymers were precipitated in 100 mL of a 10% HCl/methanol solution. The polymers were recovered by filtration, washed with 2 \times 10 mL hexanes to remove residual **1**, and dried overnight under vacuum at 60 °C. The polymerizations were repeated using 0.5, 1.0, 1.5, and 2.0 mmol of **1** to prepare a range of copolymers.

Polymerization Procedures for Polypropylene POSS Copolymers. The propylene POSS macromonomer copolymerizations were carried out in a 100 mL Schlenk flask equipped with a magnetic stirring bar, 0.51 g of **1** (0.5 mmol, 125 equiv to Zr), and 18 mL of toluene. The sealed flask was removed from the glovebox and charged with propylene gas (1 atm). A solution of 1.68 mg (4 μ mol) of dichloro[*rac*-ethylenebis(indenyl)]zirconium in 2.0 mL of toluene and 0.72 mL of 3.36 M MAO (2.4 mmol) were mixed and then preactivated for 15 min prior to injection into the flask. Propylene pressure was kept constant throughout the polymerization through use of a bubbler. The reaction temperature was controlled using a 20 °C water bath. The polymer did not precipitate from solution during polymerization. After 2 h, the reaction was terminated by addition of methanol. The polymers were precipitated in 100 mL of a 10% HCl/methanol solution. The polymers were recovered by filtration, washed with 2 \times 10 mL hexanes to remove residual **1**, and dried overnight under vacuum at 60 °C. The polymerizations were repeated using varying amounts of **1**, 0.5, 0.75, and 1.0 mmol to prepare a range of copolymers. When 1.0 mmol of **1** was

used, 1:1 hexane/ethanol was used to wash the polymer due to the copolymer being partial soluble in hexane.

Polymer Characterization. ¹H NMR spectra were obtained at 300 and 500 MHz using Bruker DPX-300 and AMX-500 FT NMR spectrometers. ¹³C NMR were recorded at 100 °C in tetrachloroethane-*d*₂ with a Bruker AMX-500 FT NMR spectrometer operating at 125 MHz. The quantitative spectra were obtained using a standard inverse-gated proton decoupling pulse sequence and a relaxation delay of 6 s. Gel permeation chromatography was performed using a Polymer Laboratories high-temperature GPC PL-220 equipped with a Wyatt high-temperature light scattering detector miniDAWN (HTmD) at 135 °C in trichlorobenzene. The miniDAWN detector contains a 690 nm diode laser. We used values of -0.104 for the dn/dc of polyethylene and -0.102 for polypropylene.¹⁴

Differential scanning calorimetry was performed under a continuous nitrogen purge (50 mL/min) on a TA Instruments DSC 2910 equipped with a liquid nitrogen cooling accessory (LNCA) unit. Data were gathered on the second heating cycle using a heating and cooling scan rate of 10 °C/min. Thermogravimetric analysis was carried out using a TA Instruments TGA 2050 thermogravimetric analyzer with a heating rate of 20 °C/min from room temperature to 700 °C under a continuous nitrogen or air purge (nitrogen, 100 mL/min; air, 50 mL/min).

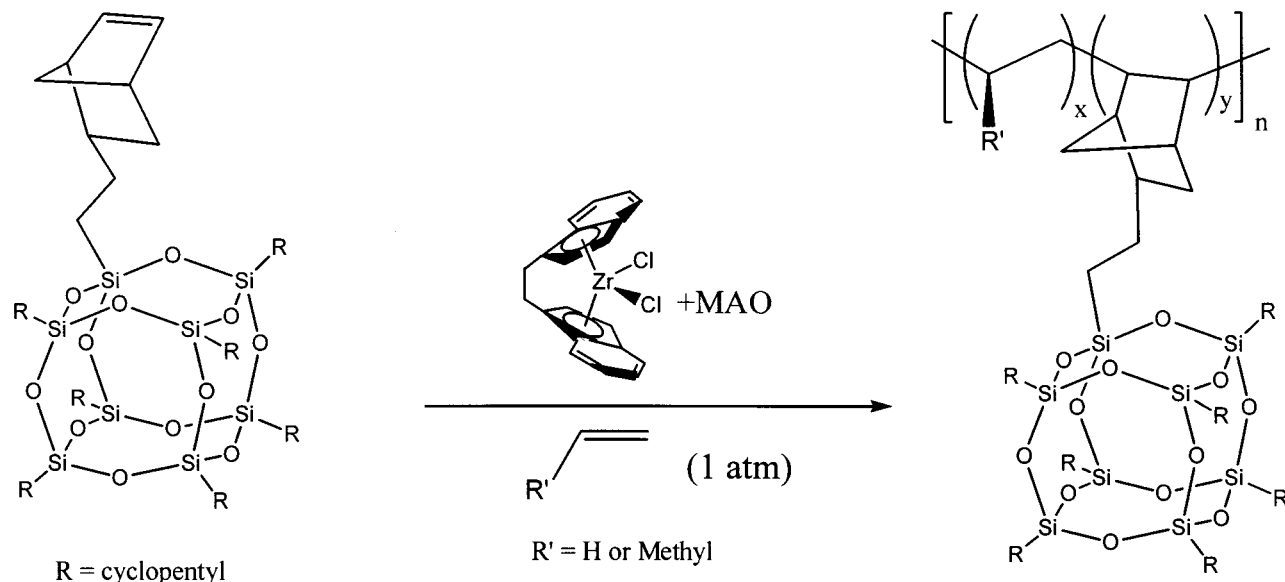
Samples for mechanical tests are made from the synthesized polymer powders, which were preheated in a Carver press at 180 °C for 10 min between two Kapton films before being pressed into thin films. The press was then cooled to room temperature by circulating tap water through the two hot plates.

Dynamic mechanical thermal analysis was collected on a Rheometric Scientific DMTA Mark IV running in tensile mode at an oscillation frequency of 1 Hz. Rectangular samples were used with approximate length of 5 mm, width of 2 mm, and thickness of 0.2 mm. The strain amplitude was set to 0.1% strain, well within the linear viscoelastic range. A gaseous nitrogen purge and a heating rate of 5 °C/min were used.

Results and Discussion

Copolymerization of Ethylene and POSS-Norbornylene 1. The low activity observed for previous copolymerizations of POSS macromonomers was presumably due to its steric bulkiness. Our experimental data from attempted copolymerization of ethylene with POSS-vinyl **2** or POSS-allyl **3** showed an order of magnitude decrease in activity with only homo-polyethylene being obtained. Likewise, attempts to use the spacing strategy of placing long methylene units, such as $-(CH_2)_8-$, between the vinyl groups and the POSS core also resulted in low or no incorporation of POSS at all.^{5,13} These results suggest that electron pairs from the oxygen of POSS core may play a role through reversibly coordinating to the zirconium catalysts despite the cyclopentyl "coating". To increase the activity, norbornene was chosen as the polymerizable linkage. There are a number of advantages to doing so. First of all, the rigid structure of norbornene prevents the simultaneous interaction of a zirconium catalyst with the double bond and lone pair of electrons on oxygen, which makes the oxygen atom inaccessible during polymerization. A similar strategy was adopted in the copolymerizations of 5-norbornen-2-yl esters with olefins using vanadium based Ziegler-Natta catalysts.¹⁵ Second, norbornene has higher reactivity than α -olefin in copolymerizations with ethylene. It has been demonstrated that norbornene can be copolymerized with ethylene using dichloro[*rac*-ethylenebis(indenyl)]zirconium/MAO to generate cyclic olefin copolymers with norbornene concentration up to 30 mol %.^{16,17} This relatively high reactivity, due to the ring strain on

Scheme 1. Copolymerization of Ethylene or Propylene with POSS-Norbornylene

Table 1. Copolymerization of Ethylene with 1^a

entry	POSS conc (mol/L)	yield (g)	activity ^c (kg/(mol h))	POSS (wt %) ^d	POSS (mol %) ^d	M_w ($\times 10^3$ g/mol) ^e	PDI ^e
1	0	0.86 ^b	3440	0	0	328	1.26
2	0.025	1.85	925	19	0.64	315	1.43
3	0.050	0.93	465	27	1.0	315	1.67
4	0.075	0.66	330	37	1.6	516	1.73
5	0.10	1.02	510	56	3.4	446	2.07

^a Experimental conditions: 2 μ mol of dichloro[*rac*-ethylenebis(indenyl)]zirconium (0.84 mg) and 1.2 mmol of MAO, total 20 mL of toluene, and 1 atm of ethylene. Reaction time: 1 h. ^b 1 μ mol of dichloro[*rac*-ethylenebis(indenyl)]zirconium (0.42 mg) and 0.6 mmol of MAO, total 20 mL of toluene, and 1 atm of ethylene. Reaction time: 15 min. ^c Activity in [kg of polymer/(mol of catalyst·h of reaction time)]. ^d As determined by ¹³C NMR. ^e As determined by GPC coupled with light scattering detectors in trichlorobenzene (TCB) at 135 °C.

norbornene, should be applicable to POSS-norbornylene macromonomers. In addition, POSS-norbornylene macromonomer **1** is much simpler to synthesize and commercially available.

According to our strategy, we have successfully prepared a series of ethylene copolymers with varying amounts of **1** (Scheme 1, R' = H) using a metallocene polymerization catalyst. The reaction conditions, yield of copolymer obtained, and the determination of the extent of POSS incorporation are shown in Table 1. The reactivity of **1** is sufficiently comparable to ethylene at 1 atm pressure to afford the possibility of adjusting the POSS concentration in the copolymer by simply changing the feed ratio. A broad range of POSS containing copolymers have been prepared (from 18 to 58 wt %). These values are much higher than that achieved using a vinyl POSS macromonomer with ethyl side groups and a long alkyl spacer that was copolymerized with ethylene using either metallocene or constrained geometry catalysts.¹³ The absolute molecular data obtained by light scattering indicated no significant change at low POSS loadings (entries 2 and 3 vs 1, Table 1). The extremely high molecular weight measured at high POSS loadings may be exaggerated since a dn/dc value of homo-polyethylene was used in our calculations. Nevertheless, the copolymerization of POSS macromonomer with ethylene has no adverse effect on molecular weight.

In an independent experiment **1** was found to be unaffected by an excess of MAO after 1 week in solution. The peripheral cyclopentyl groups are presumably shielding the siloxane core from cleavage by the alumi-

num alkyls. These results bode well for the use of POSS macromonomers in copolymerization with olefins using single site catalyst/MAO cocatalyst systems.

Copolymerization of Propylene and 1. We were also interested in extending our copolymerization method to α -olefin. Polymerization of an α -olefin is more challenging due to both stereo- and regioregular concerns. One advantage of our method is the use of the well-studied metallocene catalyst dichloro[*rac*-ethylenebis(indenyl)]zirconium, which is known to control tacticity as well as molecular weight.¹⁸ Propylene was used in our experiment to demonstrate the feasibility of this approach (Scheme 1, R' = methyl). The copolymerizations were quite successful. A wide concentration range of polypropylene POSS copolymers was obtained with up to 73 wt %, or 10 mol %, of POSS macromonomers. The polymerization conditions and results are listed in Table 2. Since the relative reactivity between propylene and POSS-norbornylene is higher than that between ethylene and POSS-norbornylene, a much lower POSS feed concentration was used to produce the copolymers with the same POSS molar concentration (entry 7 vs entry 3). The molecular weight decreased moderately with increasing POSS concentration. The molecular weight can be fine-tuned by altering experiment conditions (entry 10 vs entry 7). The copolymers have moderately high isotacticities with [mmmm] pentad sequences comparable to that of a propylene homopolymer (entries 7 and 8 vs entry 6). Optimization of molecular weight and activity should be achievable using any of a number of more efficient metallocene catalysts developed recently.¹⁹

Table 2. Copolymerization of Propylene with 1^a

entry	POSS conc (mol/L)	yield (g)	activity ^c (kg/(mol h))	POSS (wt %) ^d	POSS (mol %) ^d	M_w ($\times 10^3$ g/mol) ^e	PDI ^e	[mmmm] ^d
6	0	2.23 ^b	1100	0	0	24.9	1.54	90
7	0.025	2.29	290	20	1.0	15.7	1.44	89
8	0.0375	1.68	210	58	5.4	13.3	1.54	88
9	0.050	0.62	78	73	10.4	11.0	1.42	n.d.
10 ^f	0.025	0.24	2.5	4.6	0.2	28.8	2.03	84

^a Experimental conditions: 4 μ mol of dichloro[*rac*-ethylenebis(indenyl)]zirconium (1.67 mg) and 2.4 mmol of MAO, 1 atm of propylene, total toluene 20 mL. Reaction time: 2 h. ^b 2 μ mol of dichloro[*rac*-ethylenebis(indenyl)]zirconium and 1.2 mmol of MAO, 1 atm of propylene, total toluene 20 mL. Reaction time: 1 h. ^c Activity in [kg of polymer/(mol of catalyst·h of reaction time)]. ^d As determined by ¹³C NMR. ^e Determined by GPC coupled with light scattering detectors in TCB at 135 °C. ^f Reaction temperature -10 °C, reaction time 24 h.

Table 3. Summary of Thermal Characterization of PE-POSS Copolymers

entry	POSS (wt %)	T_m ^a (°C)	heat of fusion ^a ΔH (J/g)	onset of decomp temp ^b (°C)	char yield in N ₂ ^b (%)	5 wt % loss in air ^b (°C)	char yield in air ^b (%)
1	0	136	161	437	0.5	283	0
2	19	126	112	448	2	373	7
3	27	125	91	456	2	397	9
4	37	116	65	457	2	387	10
5	56			458	4	388	7

^a Data were gathered on the second melt using a heating and cooling rate of 10 °C/min. ^b Temperature ramp 20 °C/min in nitrogen or air.

Thermal Properties of PE-POSS Copolymers. A summary of the thermal characterization of PE-POSS copolymers is listed in Table 3. A gradual decrease in the melting temperature and heat of fusion of the polymers was observed with an increase in the POSS content of the copolymer, which clearly indicates a random copolymer structure (entries 2–5 vs entry 1). An interesting observation is that the PE-POSS sample with the highest POSS concentration (entry 5) has fewer polyethylene crystalline domains detectable under standard DSC conditions. This sample was partially soluble at room temperature in hexanes while all of the others of this series were not. It is also noted that the thermal stability was improved in these copolymers. A slight increase in the onset of decomposition temperature was observed similar to our previous report.¹² Again, a significant improvement of the thermal oxidative resistance in the PE-POSS copolymers was noted. The temperature of 5% weight loss of all the samples increased 90–104 °C compared with that of a PE control sample (Figure 1). The char yields, however, were low (less than 10%) under both nitrogen and air. Since polyethylene decomposition in air is through random chain scission to generate free radicals,²⁰ a cross-linking mechanism around the silicon core was speculated as an explanation for the improved thermal stability. The existence of POSS nanoparticles facilitates recombination of the free radicals and raises stable temperature regime close to 400 °C. Another possible explanation for the improvement of thermal oxidative stability is the formation of a silica layer on the surface of the polymer melt in the presence of oxygen, which serves as a barrier preventing further degradation of the underlying polymer.²¹ Further investigation is currently underway.

Thermal Properties of PP-POSS Copolymers. Similar to the PE-POSS copolymers, the PP-POSS copolymers had a slightly decreased melting temperature compared to homo-polypropylene prepared with the same metallocene catalyst. However, the thermal decomposition behavior was apparently different. The 5% weight loss in air did not increase until high POSS concentration even though the PP-POSS copolymers have a much slower decomposition rate compared with homo-polypropylene (Figure 2). The onset of decomposition temperature in nitrogen increased moderately

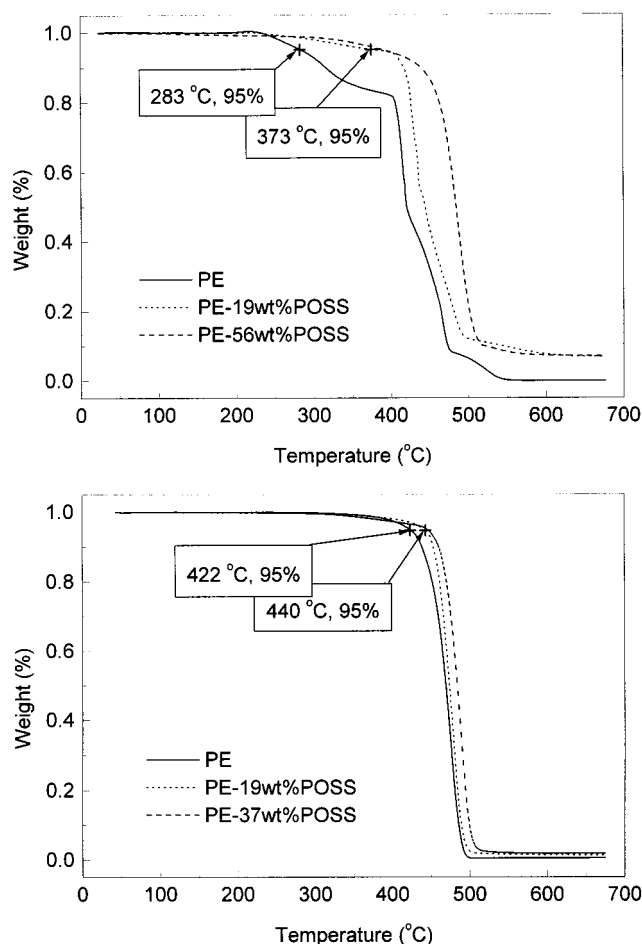


Figure 1. TGA traces of PE-POSS copolymers under air (top) and nitrogen (bottom).

(Table 4). Similar to polyethylene, polypropylene also decomposes by a mechanism of random chain scission. However, because of the existence of tertiary carbons, which are more susceptible to degradation, the existence of POSS nanoparticles merely slows down the degradation process.

Mechanical Properties of PE-POSS Copolymers. The PE-POSS copolymers can be easily pressed at 180

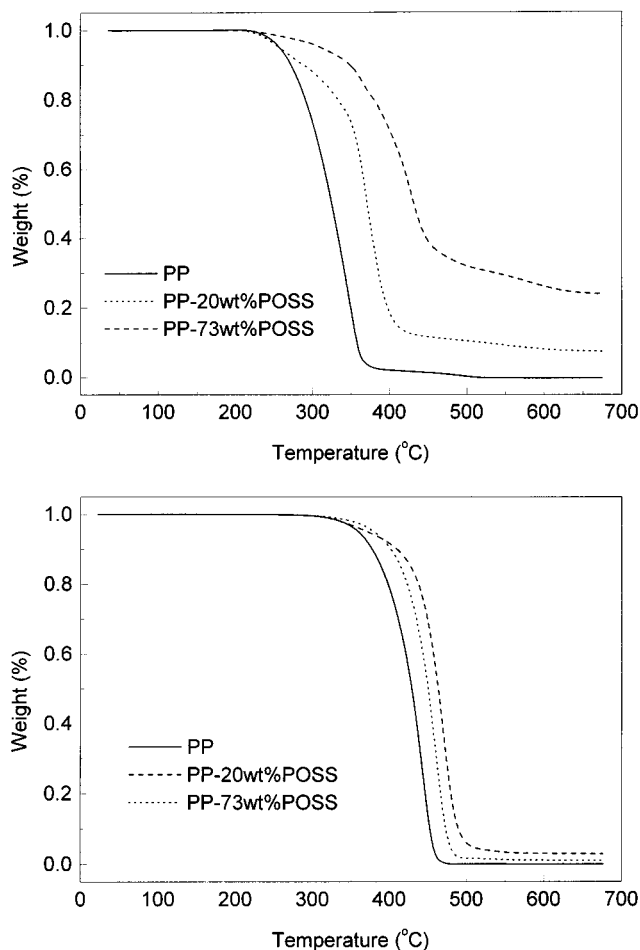


Figure 2. TGA traces of PP-POSS copolymers under air (top) and nitrogen (bottom).

°C into thin, transparent, tough films. Dynamic mechanical analysis was carried out to probe the mechanical properties of these films. Since mechanical properties (small-strain tensile deformation properties, Young's modulus, yield stress, and yield strain) of

Table 4. Summary of Thermal Characterization of PP-POSS Copolymers

entry	POSS (wt %)	T_m^a (°C)	heat of fusion ^a ΔH (J/g)	onset of decomp temp ^b (°C)	char yield in N_2^b (%)	5 wt % loss in air ^b (°C)	char yield in air ^b (%)
6	0	140	84	382	0.03	257	0
7	20	134	69	405	1	256	8
8	58	130	55	421	1	259	12
9	73	119	23	427	3	309	24

^a Data were gathered on the second melt using a heating and cooling rate of 10 °C/min. ^b Temperature ramp 20 °C/min in nitrogen or air.

polyethylene primarily depend on percent crystallinity,²² a dramatic decrease of modulus was expected due to disruption of crystallinity from the presence of bulky POSS side groups. However, the storage modulus E' of the unorientated PE-POSS sample (19 wt % POSS) was almost unchanged compared with the PE control sample in temperature range from -50 to 50 °C (Figure 3). This indicated the tensile properties were maintained even though the crystallinity of polyethylene was decreased in the copolymer with 19 wt % POSS loading (56% to 39%). We believe that this result is due to the beneficial effect of POSS nanoparticles enhancing mechanical properties countering the adverse effect of disrupting polyethylene crystallization. The storage modulus decreased with higher POSS loadings. To prevent disruption of crystallization, polyethylene-*block*-poly(POSS) copolymers might be more desirable.

The mechanical relaxation of PE-POSS copolymers was also examined. Even though the assignments of these relaxation processes are controversial,^{23,24} they can provide some information into the microstructure of PE-POSS copolymers. The γ -relaxation, a localized conformational transition, possibly due to a "crankshaft" motion in PE amorphous domain, was at the same temperature in PE-POSS copolymers (Figure 3). The α -relaxation, a mechanism involving the 180° rotational jump followed by translation of the chain along the crystallographic c -axis by one methylene group, shifted to lower temperature due to thinner crystal thickness in the PE-POSS copolymer. This result is consistent

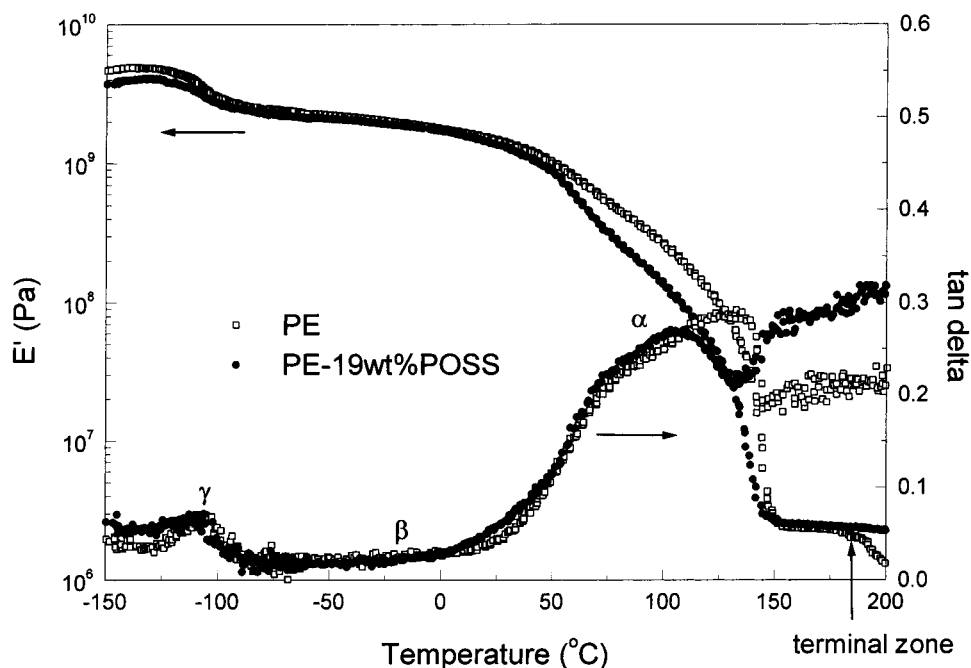


Figure 3. Dynamic mechanical spectroscopy of PE and PE-19 wt % POSS.

with the observed depression of melting temperature. Although the crystallinity of PE-POSS copolymers is lower, the β -relaxation (about $-20\text{ }^{\circ}\text{C}$), commonly believed to be the glass transition, was not observed with increasing percent of amorphous domains. Apparently, it was suppressed in the PE-POSS copolymer due to the existence of POSS nanoparticles.

The salient feature of this test was the extension of rubbery plateau for the PE-POSS sample (Figure 3). The behavior of a polyethylene melt starting to flow above its melting temperature was suppressed. This observation of a rubbery plateau at temperatures above $175\text{ }^{\circ}\text{C}$ likely indicates improved impact and toughness properties for these materials. In addition, the storage modulus of PE-POSS sample is slightly higher in the rubbery region, which suggests better enhancement from POSS nanoparticles in elastomeric materials. This observation agrees well with the mechanical results from polyurethane polymers containing POSS cages.²⁵ At this time, we believe these phenomena are attributable to the formation of nanocrystals of POSS nanoparticles on the basis of our X-ray and TEM studies.²⁶ These nanocrystals, functioning as physical cross-linking points inside polyethylene, result in the extension of the rubbery plateau. Their existence also explains the confinement of polyethylene chains for β -relaxation. Similar associative interactions of POSS nanoparticles were observed in other systems.^{11,27} However, it was reported recently that the aggregation of POSS was not required for these effects to occur on the basis of molecular dynamic simulations.²⁸ It was concluded that the chief source of reinforcement arises from the POSS nanoparticles behaving as strong anchor points in the polymeric matrix.

Conclusions

An efficient synthetic route for preparing polyolefin POSS copolymers has been described. The method involves the direct copolymerization of a POSS macromonomer having a polymerizable norbornene linkage and ethylene or propylene using metallocene catalysis. PE-POSS and PP-POSS copolymers were obtained with a wide concentration range of POSS incorporation. The hybrid copolymers showed substantial improvement in thermal oxidative decomposition with promising high-temperature applications. On the basis of dynamic mechanical thermal analysis, the tensile properties of the copolymers were maintained at low POSS loadings. These results bode well for the use of polymerizable POSS macromonomers in copolymerization with olefin using metallocene catalysis to synthesize novel polyolefin nanocomposites.

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