Synthesis of Polyethylene Hybrid Copolymers Containing Polyhedral Oligomeric Silsesquioxane Prepared with Ring-Opening Metathesis Copolymerization

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ABSTRACT: Ring-opening metathesis copolymerizations of cyclooctene and the polyhedral oligomeric silsesquioxane (POSS) monomer 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 (POSS–norbornylene) were performed with Grubbs's catalyst, $RuCl_2$(=CHPh)(PCy$_3$)$_2$. Random copolymers were formed and fully characterized with POSS loadings as high as 55 wt %. Diimide reduction of these copolymers afforded polyethylene–POSS random copolymers. Thermogravimetric analysis of the polyethylene–POSS copolymers under air showed a 70 °C improvement, relative to a polyethylene control sample of similar molecular weight, in the onset of decomposition temperature based on 5% mass loss. The homopolymer of POSS–norbornylene was also synthesized. This polymer had a rigid backbone according to ^{1}H NMR evidence of broad olefinic signals. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 2920–2928, 2001
Keywords: polyethylene (PE); polyhedral oligomeric silsesquioxane (POSS) copolymers; ring-opening metathesis copolymerization; polyolefin nanocomposites; organic–inorganic hybrid material

INTRODUCTION

Hybrid materials with both inorganic and organic components are interesting from the standpoint of increased performance capabilities relative to either of the nonhybrid counterparts. A variety of physical property enhancements are expected to result from the incorporation of an inorganic component into an organic polymer matrix (e.g., improved thermal stability). The use of polyhedral oligomeric silsesquioxanes (POSS) as modifiers of organic polymers has received a great deal of attention recently.[1] This is due, in part, to the development of efficient synthetic protocols for the preparation of the inorganic Si_8O_{12} core. Notable among these procedures is the ability to prepare an inorganic core surrounded by seven hydrocarbyl groups to promote solubility in conventional organic solvents and a unique group capable of undergoing polymerization.[2] One special feature of POSS particles is that their size, about 15 Å in diameter, is comparable to that of polymer segments. By placing nanometer-scale inorganic particles into organic polymers, we may dramatically enhance the physical properties of the resulting copolymers because of the sizable interfacial interactions between composite particles and polymer segments. For example, chain dynamics may be altered dramatically by the incorporation of POSS nanoparticles onto the chain.

A variety of POSS-containing amorphous polymers, including poly(methyl methacrylate),[3,4] poly-

styrene,[5] epoxide,[6] polysiloxane,[7] and polynorbornene[8] copolymers, have been prepared with radical, conventional[3,5] and atom-transfer protocols,[4] condensation,[6,7] and ring-opening metathesis polymerization (ROMP)[8] techniques. However, there are few reports of semicrystalline copolymers.[9] Simple copolymers such as polyethylene (PE)–POSS have not been prepared in accordance with the development of more efficient routes for preparing POSS macromonomers. A preliminary report suggested that POSS macromonomers were not capable of undergoing coordination polymerization with Ziegler–Natta catalysis, presumably because of their large dimensional size.[2] The copolymers of PE–POSS are desired because interesting rheology behavior and thermal and mechanical properties are expected. Noteworthy is that PE–clay nanocomposites, somewhat akin to PE–POSS nanocomposites, have failed to produce complete dispersal or exfoliation of clay nanolayers because of unfavorable interactions between hydrophilic clay and hydrophobic polyolefin.[10] Therefore, the synthesis of PE–POSS copolymers is crucial for developing an understanding of this type of hybrid material because the POSS nanoparticles have the potential to be well distributed into a PE matrix through copolymerization or via modification of the POSS periphery.

Herein we report a two-step synthetic route for preparing semicrystalline PE–POSS copolymers that exhibit a large degree of control over the incorporation levels of the POSS comonomer. Our strategy involved the ROMP of cyclooctene and the POSS monomer **1**, containing one norbornylene and seven cyclopentyl side groups. The initially formed copolymers were polycyclooctenamer–POSS random copolymers. We then used diimide reduction to completely remove the unsaturated units from the polymer backbone to afford PE–POSS copolymers.

EXPERIMENTAL

Materials

The cyclopentyl–POSS–norbornylene monomer 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**) was provided by the Air Force Research Laboratory (Propulsion Directorate, AFRL/PRSM, Edwards Air Force Base, CA). Re-

agents were obtained from Aldrich and were used as received unless otherwise indicated. Grubbs's catalyst, $RuCl_2(=CHPh)(PCy_3)_2$, was purchased from Strem Chemical. Cyclooctene and tri-*n*-propyl amine were vacuum-distilled from CaH_2 prior to use. Methylene chloride and xylenes were passed through columns of basic activated alumina prior to use.

Polymer Characterization

^1H spectra were obtained at 300 and 500 MHz with Bruker DPX-300 and AMX-500 FT NMR spectrometers. ^{13}C NMR were recorded at 90 °C in toluene-d_8 or tetrachloroethane-d_2 with a Bruker AMX-500 FT NMR spectrometer operating at 125 MHz. Gel permeation chromatography (GPC) was performed with a Polymer Lab LC1120 high performance liquid chromatography (HPLC) pump equipped with a Waters differential refractometer detector. The mobile phase was tetrahydrofuran with a flow rate of 1 mL/min. Separations were performed with 10^5-, 10^4-, and 10^3-Å Polymer Lab columns. Molecular weights were calibrated versus narrow molecular weight polystyrene standards.

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2910 equipped with a liquid nitrogen cooling accessory (LNCA) unit under a continuous nitrogen purge (50 mL/min). Data were gathered on the second melt with heating and cooling scan rates of 10 °C/min unless otherwise noted. Thermogravimetric analysis (TGA) was carried out with a TA Instruments TGA 2050 thermogravimetric analyzer at 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).

Procedures for the Homopolymerization of POSS–Norbornylene (1)

$RuCl_2(=CHPh)(PCy_3)_2$ (4.87 mg, 6 μmol) was dissolved in 1 mL of CH_2Cl_2 and added to a solution of 0.33 g of **1** (0.32 mmol, 10 wt %) in 1.5 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h at room temperature. The reaction was stopped with the injection of 5 mL of CH_2Cl_2 containing a trace amount of ethyl vinyl ether. The polymer was precipitated in 50 mL of methanol, recovered by filtration, and dried overnight under vacuum
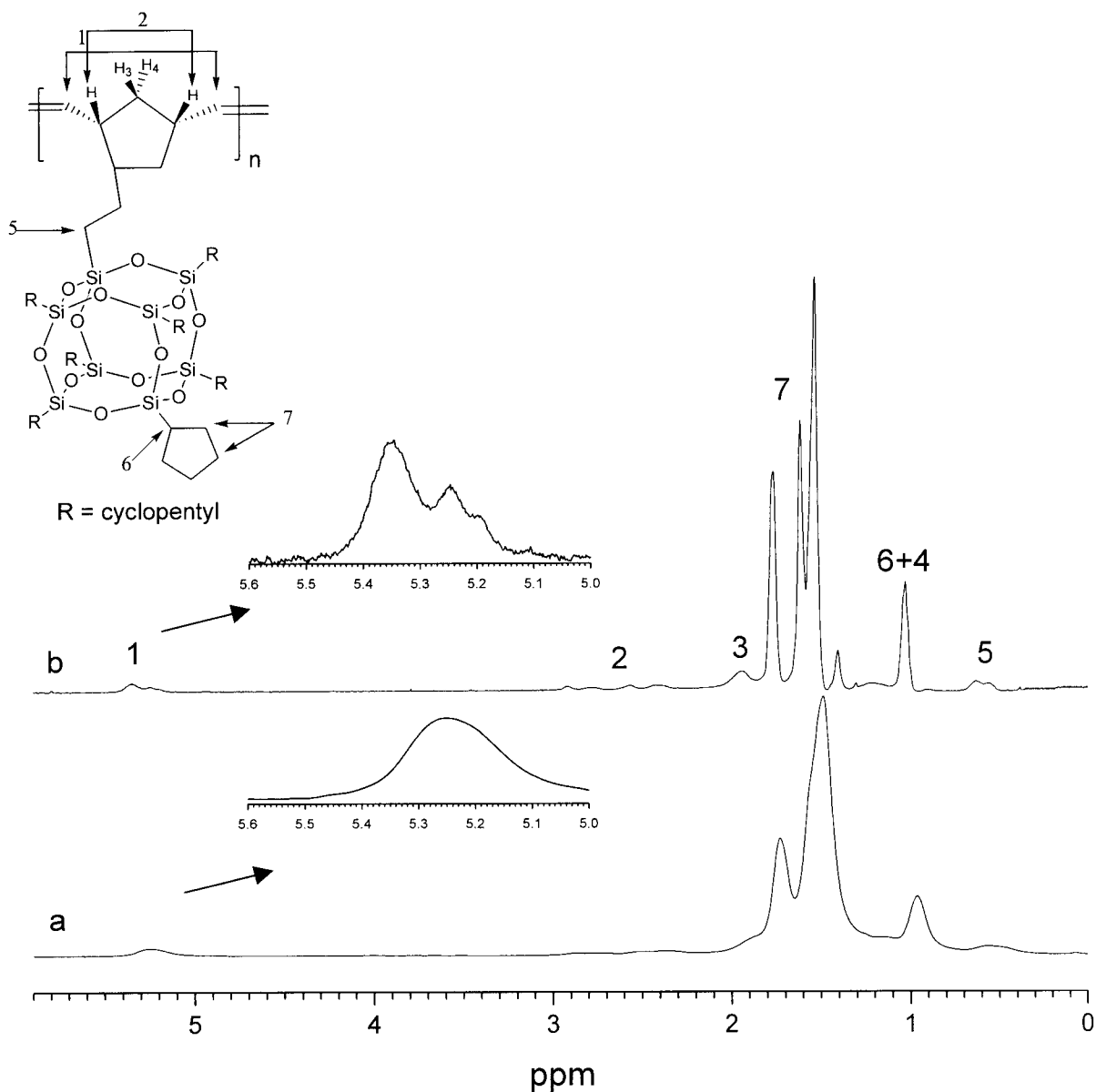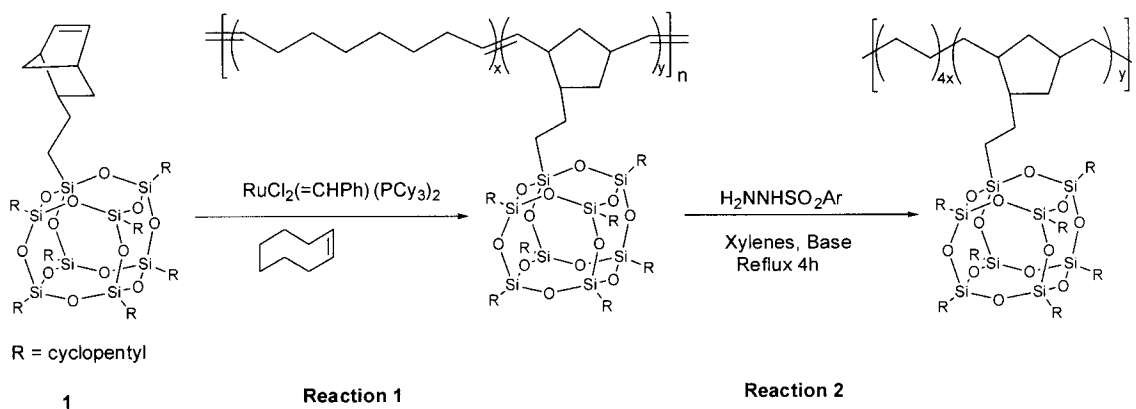
Figure 1. ^{1}H NMR spectra of the homopolymer of **1** in (a) CDCl$_3$ at room temperature and (b) C$_2$D$_2$Cl$_4$ at 100 °C.

at room temperature. The isolated yield was 0.29 g (88%).

General Procedures for the Copolymerizations of Cyclooctene and 1

RuCl$_2$(=CHPh)(PCy$_3$)$_2$ (4.87 mg, 6 μmol) was dissolved in 1 mL of CH$_2$Cl$_2$ and added to a solution of 0.33 g of cyclooctene (3 mmol, 500 equiv) and 0.0367 g of **1** (0.036 mmol, 10 wt %) in 1.5 mL of

CH$_2$Cl$_2$. The reaction mixture was stirred for 2 h at room temperature. The reaction was stopped with the injection of 5 mL of CH$_2$Cl$_2$ containing a trace amount of ethyl vinyl ether. The polymer was precipitated in 50 mL of methanol, recovered by filtration, and dried overnight under vacuum at room temperature. We repeated the polymerizations with various amounts of **1,** 0–50 wt %, to prepare a range of copolymers. The isolated yields were generally above 90%.

R = cyclopentyl

1

Reaction 1

Reaction 2

Scheme 1. Copolymerization of cyclooctene and **1** and hydrogenation.

General Procedures for the Hydrogenation of Polycyclooctenamer–POSS Copolymers

The polymer backbone was hydrogenated with *p*-toluenesulfonylhydrazide (TSH) in refluxing xylenes with a slight modification of a literature procedure.[11] To a solution of 0.30 g of polycyclooctenamer–POSS copolymers in 20 mL of xylenes was added TSH and tri-*n*-propyl amine (a ratio of 2 mol of TSH and 2 mol of amine per mole of olefin on the backbones was used). The solution was heated to reflux for 4 h under a positive pressure of nitrogen. The resulting PE–POSS copolymers were isolated by the cooling of the xylene solution to room temperature and precipitation in a large excess of methanol. The copolymers were filtered and washed with methanol before being dried in a vacuum oven overnight at 60 °C. The extent of hydrogenation was judged, in all cases, to be greater than 99% on the basis of ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

Homopolymerization of 1

Despite the large size of POSS cages, the ROMP of **1** went smoothly. On the basis of ^{1}H NMR, the reaction was complete in a few minutes. However, we used a reaction time of 2 h to obtain a similar microstructure (e.g., trans/cis ratio of backbone double bonds) for comparison with the copolymers. The weight-average molecular weight was estimated to be 41 kg/mol (DP, degree of polymerization = 41), with a polydispersity of 1.5, according to GPC versus polystyrene standards. The

polymer is soluble in most nonpolar organic solvents, such as hexanes and ether. Interestingly, ^{1}H NMR shows very broad olefinic peaks at room temperature [Fig. 1(a)]; this strongly indicates restricted backbone mobility in solution. On heating to 100 °C, the flexibility of the polymer backbone is still relatively low, with only partial resolution of the olefinic resonance in ^{1}H NMR [Fig. 1(b)]. The backbone of the homopolymer is very rigid in solution, demonstrating that the incorporation of POSS into polymer chains dramatically retards the chain movement and changes the chain dynamics in solution because of its large dimensional size.

Copolymerizations of Cyclooctene and 1

ROMP has proven to be a versatile approach for the preparation of polymers with a wide range of functionalities and macromolecular architectures.[12] We used Grubbs's catalyst,[13] $RuCl_2$(=CHPh)(PCy$_3$)$_2$, for the copolymerization of cyclooctene and **1** to make the model copolymers for this study (Scheme 1, reaction 1). We fixed the molar ratio of cyclooctene to catalyst at 500:1 to yield moderately high molecular weight polycyclooctenamer. For the various copolymerizations 10–50 wt % **1,** relative to cyclooctene, was added prior to the addition of catalyst. We were limited to a maximum of 50 wt % **1** in the reaction feed because of solubility limitations. The copolymerizations remained visibly homogeneous throughout the entire reaction. The reactions were terminated with the injection of a solution of ethyl vinyl ether in CH$_2$Cl$_2$, followed by precipitation into methanol. All isolated yields were greater than 90%. The level of incorporation of **1** in the
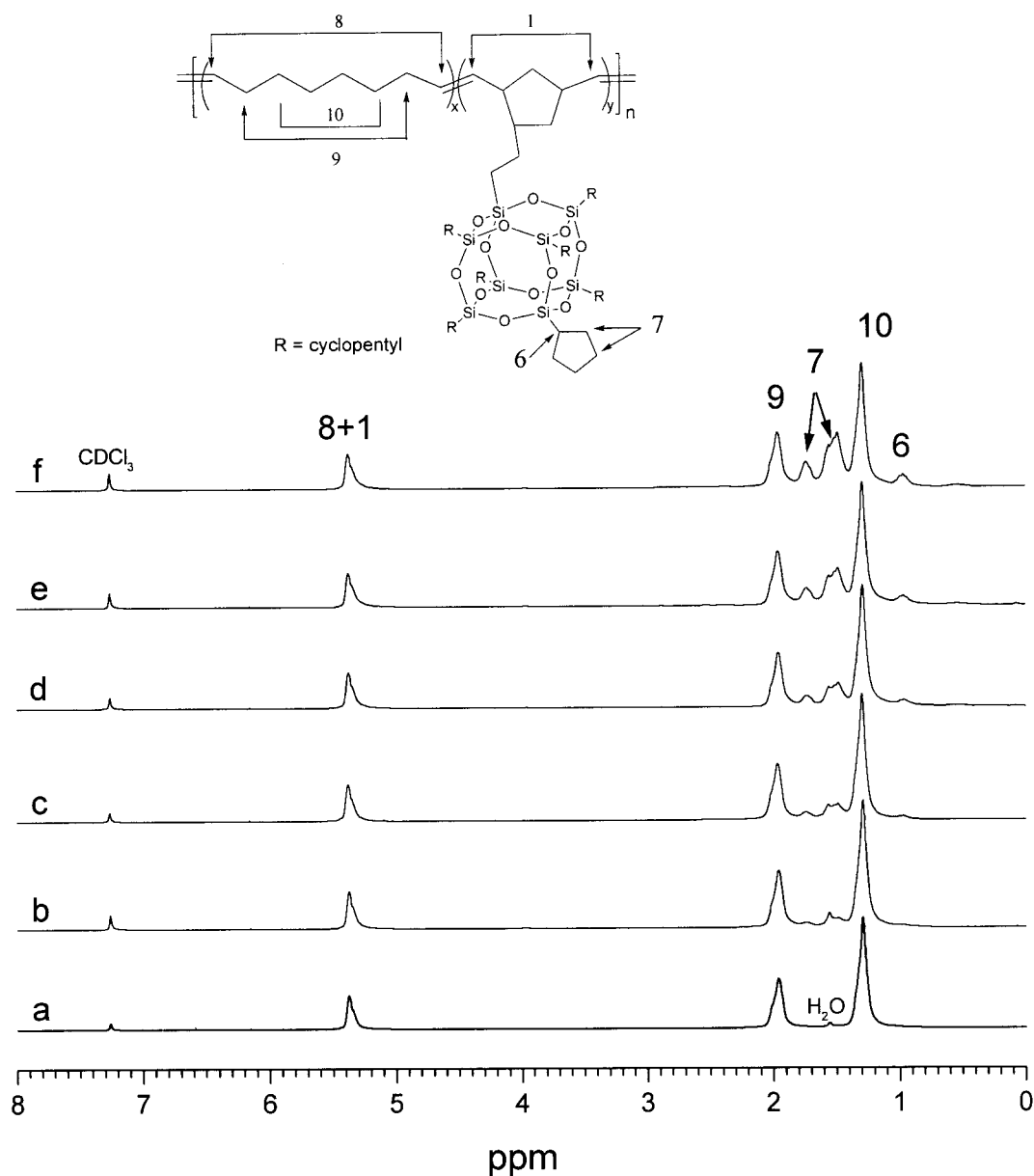
Figure 2. ^{1}H NMR spectra of polycyclooctenamer–POSS copolymers in CDCl$_3$ (entries 1–6, Table I). The POSS concentrations in the copolymers were (a) 0 mol %, 0 wt %; (b) 1.39 mol %, 12 wt %; (c) 3.06 mol %, 23 wt %; (d) 4.62 mol %, 31 wt %; (e) 7.96 mol %, 45 wt %; and (f) 11.9 mol %, 56 wt %.

copolymers was determined with ^{1}H NMR by the monitoring of the resonances for the cyclopentyl groups of POSS cages. A steady increase in the level of incorporation in the copolymers was seen as the amount of **1** in the feed increased (Fig. 2). The calculated concentrations of POSS in the copolymers are consistent with the feed ratio. The molecular weight characterization data of the polycy-

clooctenamer–POSS copolymers are listed in Table I. The molecular weight and polydispersity of the copolymers increase with increasing comonomer incorporation.

From ^{1}H NMR reaction studies, the addition of RuCl$_2$(=CHPh)(PCy$_3$)$_2$ to a mixture of **1** and cyclooctene in CDCl$_3$ shows very rapid consumption of **1.** The complete disappearance of the nor-

Table I. Summary of the Molecular Weight Data of the Polycyclooctenamer–POSS Copolymers

Entry	POSS (wt %) in Feed	POSS in Copolymer[a] wt %	Copolymer[a] mol %	M_w ($\times 10^3$ g/mol)[b]	M_n ($\times 10^3$ g/mol)[b]	Polydispersity Index	Melting Temperature (°C)[c]	Heat of Fusion (J/g)[c]
1	0	0	0	100	56	1.79	46	56
2	10	12	1.39	105	57	1.84	43	45
3	20	23	3.06	143	69	2.06	38	36
4	30	31	4.62	144	68	2.13	36	28
5	40	45	7.96	151	66	2.37	33	24
6	50	56	11.9	168	68	2.47	30	19

[a] Determined by ^{1}H NMR.
[b] Weight- and number-average molecular weights as measured by GPC relative to polystyrene standards.
[c] Data were gathered on the second melt with a heating rate of 10 °C/min on thermally quenched samples (quenching rate ~ 30 °C/min).

bornylene vinyl resonances is seen in minutes, followed by a slower disappearance of the cyclooctene vinyl resonance. Rather than isolating a blocky copolymer, we choose sufficiently long reaction times to allow for significant interchain cross metathesis to occur to ultimately afford a random copolymer. The ability to successfully perform this copolymerization relies on the tricyclohexylphosphine ligands of the catalyst to ensure that the cross metathesis of norbornylene and the less strained cyclooctene will occur.[14] Further evidence for efficient cross metathesis comes from ^{1}H NMR studies of the final copolymers. The ^{1}H NMR spectrum of the copolymer with 56 wt % POSS (entry 6, Table I) at 100 °C in $C_2D_2Cl_4$ does not show any characteristic olefinic peaks from the homopolymer of **1** (Fig. 3); therefore, no significant amounts of **1** block segments are present in the copolymer.
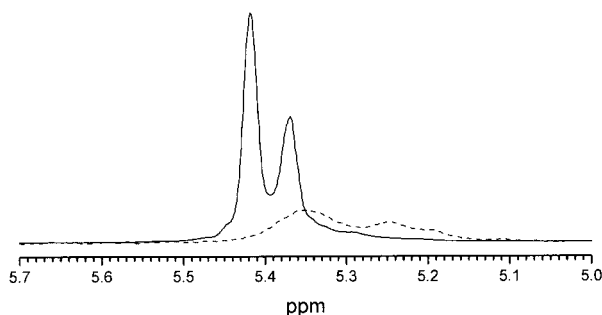

Figure 3. Olefinic-region ^{1}H NMR spectra of the poly(cyclooctenamer–POSS) copolymer (entry 6, Table I; solid line) and poly(POSS–norbornylene) (dashed line) at 100 °C in $C_2D_2Cl_4$.

A thermal analysis of the polycyclooctenamer–POSS copolymers clearly showed a decrease in the melting temperature and a concomitant heat of fusion as the concentration of POSS increased (Fig. 4). This observation is consistent with the random incorporation of POSS comonomer along the polycyclooctenamer main chain, which is disrupting crystallinity. The evidence from decreasing melting temperatures and ^{1}H NMR clearly supports the assumption that random copolymers were obtained. No glass-transition temperature (T_g) was observed for these copolymers, presumably because of their semicrystalline nature.

The backbone unsaturation in the polycyclooctenamer–POSS copolymers was removed with diimide reduction, as shown in Scheme 1, reaction 2.[11] The isolated yields of the hydrogenated copolymers were all above 90%; ^{1}H NMR showed complete saturation of the backbone. ^{1}H and ^{13}C NMR spectra of the hydrogenated product confirmed that the inorganic POSS cage structure was unaffected, whereas the double bonds were cleanly hydrogenated.

Thermal Properties of PE–POSS Copolymers

The resulting PE–POSS copolymers all displayed a decrease in the observed peak melting point as the weight percentage of **1** increased. No T_g was observed for these copolymers. The thermal properties of the saturated copolymers are shown in Table II. Our results indicated a moderate increase in the thermal stability of these PE–POSS copolymers, with the onset of decomposition temperature increasing 12–17 °C for all of the POSS-
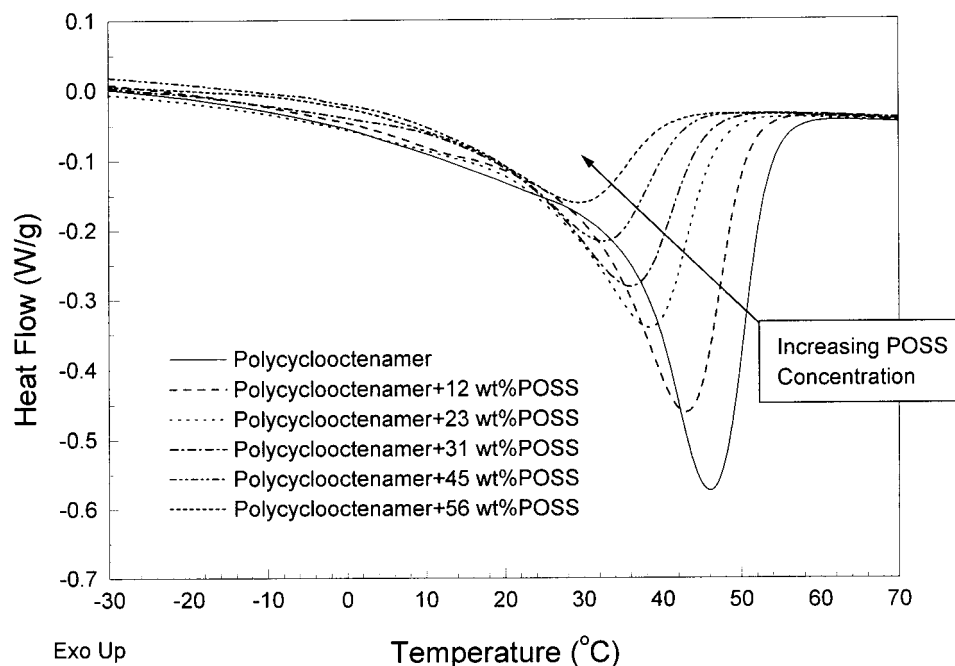
Figure 4. DSC thermograms of polycyclooctenamer–POSS copolymers.

containing samples relative to the PE control sample (entries 8–12 vs entry 7). The slight increase in the onset of decomposition temperature under nitrogen might be due to crosslinking between scissioned PE chains and the POSS silicone core.[15] More interestingly, we observed a dramatic improvement in the thermooxidative resistance of these PE–POSS copolymers when air was used as the carrier gas during TGA (Fig. 5). For example, at a 5% weight loss, the temperature of the PE–POSS copolymer with 12 wt % POSS was 368 °C, compared with 298 °C for the PE control

sample (entry 8 vs entry 7). This increase of 70 °C indicates that the PE modified by the incorporation of POSS improves the thermal degradation behavior toward oxygen and enhances overall thermal stability. One possible explanation 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 underlying polymer.[16] However, this improvement decreases as the POSS concentrations exceeds 23 wt % (entries 10–12). Further investigation is currently underway.

Table II.   Summary of the Thermal Characteristics of the Polyethylene–POSS Copolymers

Entry	POSS (wt %)	Melting Temperature (°C)[a]	Heat of Fusion (J/g)[a]	Onset of Decomposition Temperature (°C)[b]	Char Yield in N_2 (%)[b]	5% Weight Loss in Air (°C)[b]	Char Yield in Air (%)[b]
7	0	133	200	449	0	298	2
8	12	130	134	461	1	368	5
9	23	126	112	461	1	362	8
10	31	122	75	466	1	329	4
11	45	115	61	462	1	290	19
12	56	115	41	463	2	326	21

[a] Data were gathered on the second melt with heating and cooling rates of 10 °C/min.
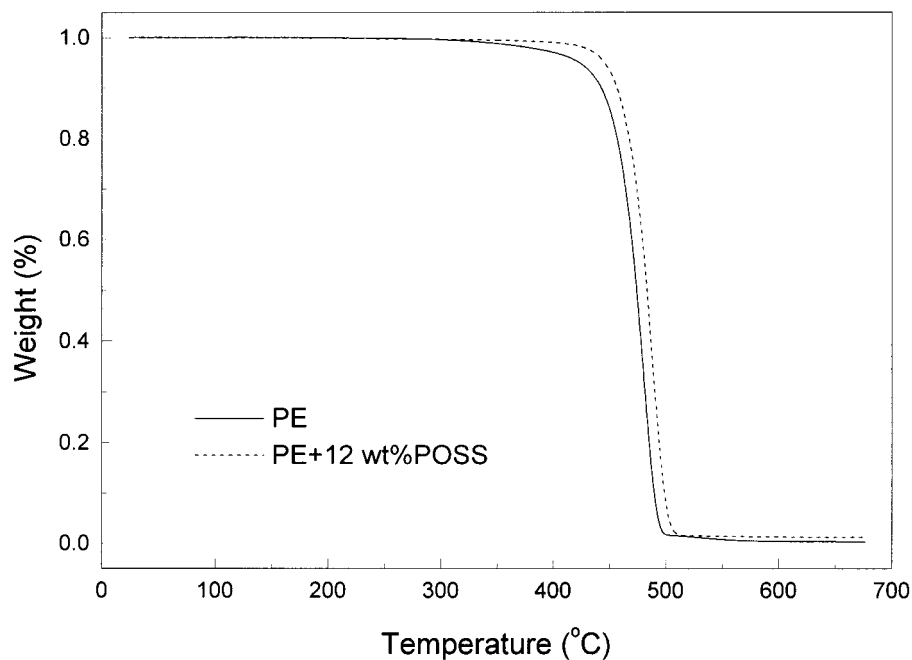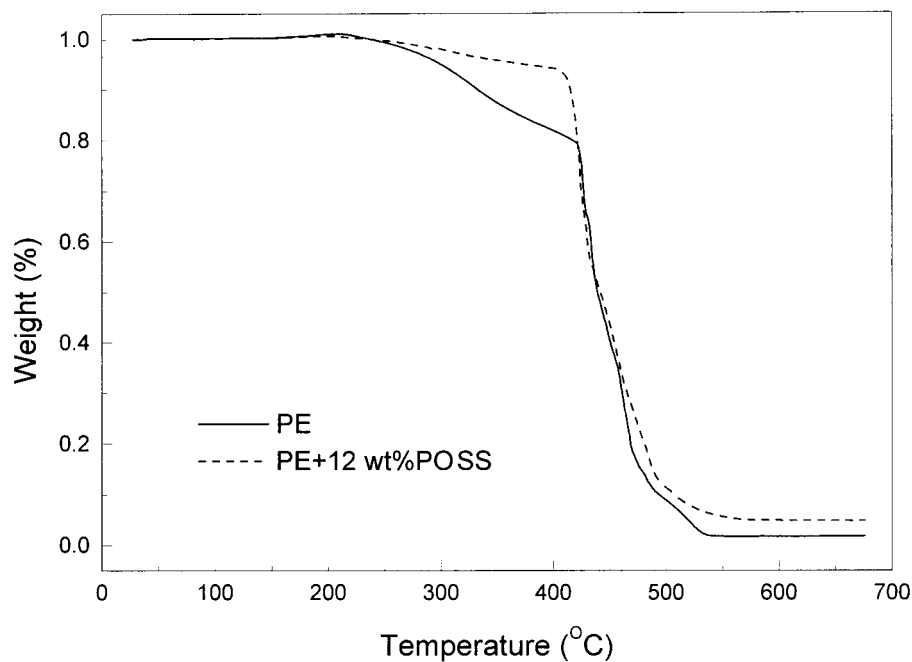[b] The temperature ramp was 20 °C/min under nitrogen or air.

Figure 5. TGA traces of PE and PE–12 wt % POSS copolymers under air (top) and nitrogen (bottom).

CONCLUSIONS

A two-step synthetic route for preparing PE–POSS copolymers has been described. The ROMP of cyclooctene and **1** afforded random copolymers. Subsequent diimide reduction of these copolymers gave hybrid PE–POSS copolymers. Preliminary results point to improved thermal stability

and oxidative resistance of these hybrid copolymers relative to PE.

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