

Synthesis of Norbornene Block Copolymers Containing Polyhedral Oligomeric Silsesquioxane by Sequential Ring-Opening Metathesis Polymerization

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Abstract: The synthesis of a series of poly(POSS-NBE-*b*-MTD) copolymers was successfully accomplished, taking advantage of sequential, ring-opening, metathesis block copolymerization using $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$ catalyst. By using cyclopentyl-POSS-norbornene (POSS-NBE) monomer as the first block in the block copolymer, living poly(POSS-NBE) with controlled molecular weight and narrow molecular weight distribution was produced. Then, poly(POSS-NBE-*b*-MTD) copolymers were successfully prepared, in which sequential monomer addition of methyltricyclododecene (MTD) to the living poly(POSS-NBE) chain ends was utilized to achieve quantitative cross-over efficiency. Characterization by ^1H NMR spectroscopy and GPC confirmed the high definition and structural integrity of the poly(POSS-NBE-*b*-MTD) copolymers. Thermal properties and morphologies of the POSS-containing block copolymer nanocomposites were also investigated by using thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and wide-angle X-ray scattering (WAXS).

Keywords: polyhedral oligomeric silsesquioxane, nanocomposite, ring-opening metathesis polymerization, block copolymer, sequential monomer addition.

Introduction

Recent developments of new materials based on nanoparticles in polymeric matrices have resulted in a disruptive change in the field of polymeric nanocomposites.¹⁻³ These polymeric nanocomposites can take several forms where the particles may be equiaxial (e.g. carbon black or silica particles), cylindrical (e.g. carbon nanotubes or nanofibers), or plate-like (e.g. nanoclay particles) into a polymeric matrix including such as semicrystalline polymer, glassy polymer, thermoplastic elastomer, and rubber. In each case, at least one dimension of the particle is between 1 to 100 nm of length scale. As a result of homogeneous distribution of nanoparticles, in some instances, polymeric nanocomposites have been shown to provide significantly enhanced stiffness and strength, dramatic decreases in permeability, increases in conductivity, increases in glass transition temperature and decomposition temperature, and can potentially retain transparency of the composite due to the nanometer length scale of the filler.

Polyhedral oligomeric silsesquioxane (POSS) is a monodisperse well-defined nanoparticle containing a Si_8O_{12} core with an organic periphery.⁴⁻⁸ New synthetic procedures allow for the synthesis of a molecule in which, in general, seven

of the silicon atoms have an inert organic functionality, such as an isobutyl or cyclopentyl group, and the eighth silicon atom has a reactive group, such as a (meth)acryl, styrenyl or norbornenyl group. Therefore, POSS has recently received much attention for their ability to be homopolymerized or copolymerized with common monomers to form organic-inorganic hybrid materials. These hybrid materials have the advantage of being covalently bonded to the polymer backbone.

Many linear random copolymers such as polyethylene,^{9,10} polybutadiene,¹¹ polystyrene,^{12,13} poly(meth)acrylate,^{14,15} and polynorbornene^{16,17} with POSS as a comonomer have been reported. These polymers often exhibit increased oxidative stability, mechanical reinforcement, and morphological modification. However, only a few block copolymers containing POSS nanoparticles have been reported so far.¹⁸⁻²⁰ Recently, a different highly ordered nanocomposite, possessing combined morphological complexity of length scales of tens of nanometers, which has also attracted considerable interest are block copolymers containing a well-defined nanoparticle (e.g. POSS) covalently attached to one of polymer blocks. In order to achieve greater diversity in nanoscale morphologies and to create novel potential applications, therefore, the synthesis of model POSS-containing block copolymers with high structural integrity is of critical scientific importance. The prerequisite for obtaining well-

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defined block copolymers with the designed structure is to utilize living polymerization systems.

In this article, we report synthesis and characterization of block copolymers containing POSS nanoparticles. ROMP, known as a living polymerization for cycloalkenes, was employed to prepare those block copolymers via a sequential monomer addition of cyclopentyl-POSS-norbornylene (POSS-NBE) and norbornene derivatives such as norbornene (NBE) and methyltetracyclododecene (MTD).

Experimental

Materials. Cyclopentyl-POSS-norbornylene monomer (POSS-NBE), 1-[2-(5-norbornene-2-yl)ethyl]-3,5,7,9,11,13,15-heptacyclopentylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane, was purchased from Aldrich Chemical Co. and used as received. Methyltetracyclododecene (MTD) was provided from Professor R. E. Cohen in the Department of Chemical Engineering, MIT. The donated MTD had a very slightly yellowish tint which may be removed through vacuum distillation. After vacuum distillation, several freeze-pump-thaw cycles of MTD were carried out for ROMP. Norbornene (NBE, 99%) was purchased from Aldrich Chemical Co. and vacuum distilled prior to use. Grubbs's catalyst, $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$, was purchased from Strem Chemical Co. All other chemicals were reagent grade and used as received unless otherwise indicated.

Homopolymerization of NBE or MTD. $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$ (8.7×10^{-3} M) dissolved in CH_2Cl_2 (or toluene) was added to a solution of 0.22 M of NBE in CH_2Cl_2 (or toluene). The reaction mixture was stirred for 10~30 min at room temperature. The reaction was terminated with the injection of a trace amount of ethyl vinyl ether. The polymer was precipitated in methanol, recovered by filtration, and dried overnight under vacuum at 60 °C. The polymerizations of NBE were repeated with different concentrations of NBE. At high concentration of NBE (>0.22 M), highly exothermic reaction was observed with increased viscosity.

Living nature of the poly(NBE) chain ends was investigated. After polymerization of NBE, 2nd NBE solution was freshly added to the polymerization mixture, which was allowed to further polymerize for additional 30 min at room temperature.

Homopolymerization of POSS-NBE. $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$ (1.2×10^{-3} M) dissolved in toluene was added to a solution of 0.06 M of POSS-NBE in toluene. The reaction mixture was stirred for 30 min at room temperature. The reaction was quenched with the injection of toluene containing a trace amount of ethyl vinyl ether. The polymer was precipitated in methanol, recovered by filtration, and dried overnight under vacuum at 60 °C. Living nature of the poly(POSS-NBE) chain ends was also investigated as the same way as mentioned previously.

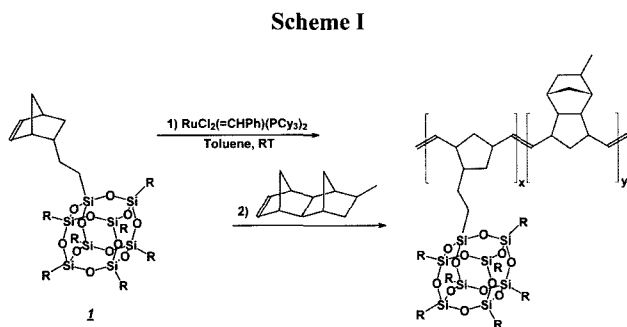
Sequential Block Copolymerization of POSS-NBE and

MTD. $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$ (8.6×10^{-3} M) dissolved in toluene was added to a solution of a certain amount of POSS-NBE in toluene. The reaction mixture was stirred for 30 min at room temperature. After complete polymerization of POSS-NBE, calculated amount of second monomer MTD dissolved in toluene was transferred to the polymerization solution of POSS-NBE, followed by further stirring for 30 min. The amount of POSS-NBE and MTD monomers was dependant on the composition of the block copolymers. The polymerization was stopped with the injection of toluene containing a trace amount of ethyl vinyl ether. The polymer was precipitated in methanol, recovered by filtration, and dried overnight under vacuum at 60 °C.

Instruments and Measurement. Molecular weights and molecular weight distributions of homopolymers and diblock copolymers were measured at room temperature using a Waters gel permeation chromatography (GPC) equipped with a Model HPLC 510 pump, a Model 712 sample processor, a Model 486 tunable absorbance detector, a Model 250 dual detector (Viscotek Co.), and five ultrastayragel GPC columns connected in the following series: 500, 10^3 , 10^4 , 10^5 , and 100 Å. THF was used as an eluent at a flow rate of 1 mL/min. Molecular weights were calibrated versus narrow molecular weight polystyrene standards. ¹H NMR spectra were measured by using a Bruker 250 MHz instrument in CDCl_3 . Thermogravimetric analysis (TGA, TA Instruments TGA 2050) was carried out at a heating rate of 20 °C/min from room temperature to 700 °C under a continuous air atmosphere. Transmission electron microscopy (TEM) was carried out to identify morphology of the block copolymers. TEM micrographs were obtained without any chemical treatment from ultramicrotomed thin sections of films of block copolymers cast from *p*-xylene. Wide-angle X-ray scattering (WAXS) was performed. A Rigaku rotating anode X-ray generator operating at 40 kV and 250 mA was employed with a Cu target and graphite monochromator. The powder specimens were mounted on pinhole collimator, and the diffraction patterns were recorded.

Results and Discussion

Homopolymerization of Norbornene Monomers by ROMP. The synthesis of linear block copolymers containing two chemically different blocks by living polymerizations can be accomplished by sequential monomer addition (SMA) in a simple and convenient way. However, the clean synthesis of block copolymers by SMA is based on the appropriate experimental polymerization conditions.²¹ Among them, the most important part of the polymerization conditions is the judicious selection of the order of monomer addition. Therefore, to study the effect of the order of monomer addition on sequential block copolymerization, the polymerization behavior of NBE, MTD and POSS-NBE using a Grubbs' initiator was investigated, respectively. First, ROMP of



NBE was performed using $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ initiator in CH_2Cl_2 or toluene at room temperature. The polymerization condition was as follows; $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2] = 8.7 \times 10^{-3} \text{ M}$, $[\text{NBE}] = 0.22 \text{ M}$. The polymerization was extremely fast, resulting in high viscosity, in some cases the formation of gel, just after addition of $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ initiator stock solution into NBE solution. The resulting polymers exhibited uncontrolled molecular weights in the range of $\bar{M}_n = 100,000 \sim 150,000$ with broad molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.76 \sim 2.63$) at close to complete monomer conversion. This implied that the ROMP of NBE using $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ as an initiator exhibited nonliving behavior. In addition, the life time of the resulting living poly(NBE) chain ends at monomer starved condition was investigated by the incremental monomer addition (IMA) technique. After ROMP of the first NBE monomer, a second NBE increment was added to the polymerization mixture. GPC traces indicated instantaneous termination of living poly(NBE) chain ends at monomer starved condition.

Second, ROMP of MTD, a strained cyclic olefin, was carried out in toluene or CH_2Cl_2 solvent at room temperature and the polymerization condition was as follows; $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2] = 1.2 \times 10^{-3} \text{ M}$, $[\text{MTD}] = 0.24 \text{ M}$. Poly(MTD) was chosen as one of the blocks because it is transparent, easily processable, and has a relatively high thermal stability. The polymerization proceeded smoothly after addition of the initiator stock solution, resulting in relatively controlled molecular weights ($\bar{M}_n = 47,300 \sim 52,900$) and molecular

Table I. Results on Ring-Opening Metathesis Polymerization of POSS-NBE

Exp	Grubbs's Initiator ($\times 10^{-3} \text{ M}$)	POSS-NBE (M)	Reaction Time (min)	\bar{M}_n^a	\bar{M}_w/\bar{M}_n
1	1.2	0.06	30	26,300	1.21
2	1.2	0.06	60	24,800	1.29
3	1.2	0.04	20	17,900	1.19
Living nature after Exp. 3				37,600	1.16

^aMeasured by GPC relative to polystyrene standards

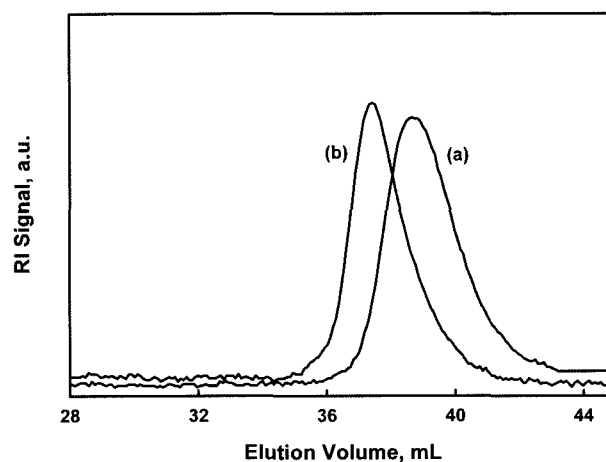


Figure 1. GPC traces of poly(POSS-NBE) by incremental monomer addition (IMA) technique; (a) original poly(POSS-NBE), $\bar{M}_n = 17,900$; $\bar{M}_w/\bar{M}_n = 1.188$ and (b) after IMA, $\bar{M}_n = 37,600$; $\bar{M}_w/\bar{M}_n = 1.159$.

weight distributions ($\bar{M}_w/\bar{M}_n = 1.56 \sim 1.61$). For sequential block copolymerization, the life time of the living poly(MTD) chain ends was examined by the IMA technique. After complete conversion of the first MTD monomer, a second MTD increment was added to the polymerization mixture at different time, and polymerized for an additional 30 min. GPC traces showed no further polymerization of the second monomer added, indicating almost complete and rapid decomposition of living poly(MTD) chain ends at monomer starved condition.

Last, ROMP of POSS-NBE was also carried out under the same polymerization condition mentioned above. As summarized in Table I, ROMP of POSS-NBE proceeded in a desired way to produce poly(POSS-NBE) in nearly quantitative yield with 20 min and produced controlled molecular weights and narrow molecular weight distributions. To investigate the life time of living poly(POSS-NBE) chain ends, after complete conversion of POSS-NBE monomer, a second POSS-NBE increment was added into the polymerization mixture and kept for an additional 20 min. GPC traces of the products obtained before and after IMA are compared in Figure 1. As presented in Figure 1, the GPC trace of poly(POSS-NBE) shifted toward higher molecular weight, and demonstrated unimodal and narrow molecular weight distribution after the complete consumption of the second monomer increment. Thus, considering our ultimate goal as the synthesis of block copolymers via sequential monomer addition, the order of monomer addition from POSS-NBE to MTD is preferred.

Sequential Block Copolymerization of POSS-NBE and MTD by ROMP. Scheme I shows the synthetic route to poly(POSS-NBE-*b*-MTD) linear diblock copolymers by the sequential monomer addition of POSS-NBE and MTD. In the first step, living poly(POSS-NBE) was prepared in toluene

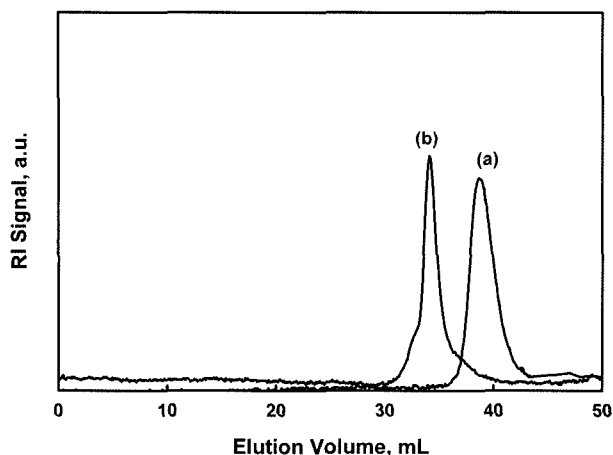


Figure 2. GPC traces of (a) living poly(POSS-NBE) precursor and (b) poly(POSS-NBE-*b*-MTD) copolymer.

ene solvent at room temperature. After ~100% conversion of POSS-NBE, the second monomer MTD dissolved in toluene was injected into the polymerization mixture. To minimize interchain cross-metathesis of the final block copolymers, the polymerization was terminated by the addition of ethyl vinyl ether just after the complete conversion of the second monomer MTD. GPC traces of a poly(POSS-NBE-*b*-MTD) copolymer and its precursor poly(POSS-NBE) homopolymer are shown in Figure 2, and a summary of characterization is given in Table II. In comparison, results of homopolymerization of POSS-NBE and MTD, respectively, are also presented. It appeared from Figure 2 that poly(POSS-NBE-*b*-MTD) copolymer shifted to higher molecular weight with maintaining narrow molecular weight distribution. However, the GPC trace of poly(POSS-NBE-*b*-MTD) copolymer exhibited negligible but detectable tailing both at higher and lower elution volume. This is presumably due to the uncontrolled initiation of MTD monomer from the living poly(POSS-NBE) chain ends.

The extent of incorporation of POSS-NBE in the poly(POSS-NBE-*b*-MTD) copolymers was determined by

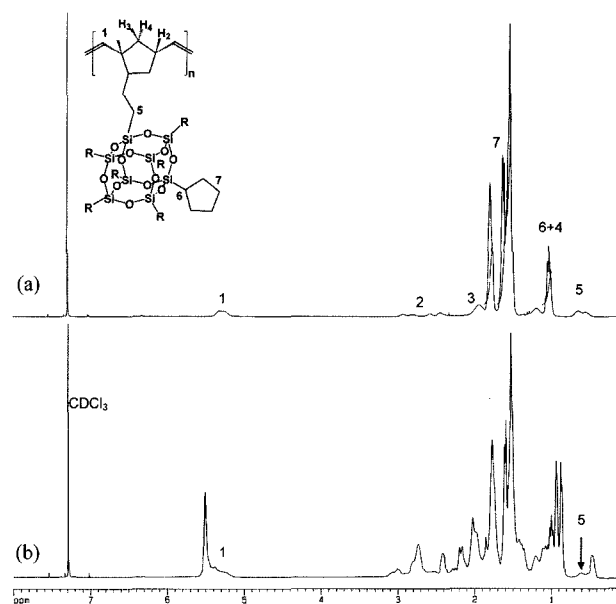


Figure 3. $^1\text{H-NMR}$ spectra of (a) poly(POSS-NBE) homopolymer and (b) poly(POSS-NBE-*b*-MTD) block copolymer (50 wt% of POSS-NBE).

using $^1\text{H NMR}$, as presented in Figure 3, from the signal intensity ratio of methylene group (5) next to Si atom on POSS cage and methine peaks (1) in the copolymer backbone. The calculated contents of POSS-NBE in block copolymers were found to be consistent with the feed ratio of the monomer.

Thermal Stability and Morphology. Results on the thermal stability of block copolymers indicated a dramatic enhancement in the thermooxidative resistance especially under an air atmosphere during TGA, as shown in Figure 4. The decomposition temperatures (T_{decomp}) at a 5% weight loss were listed in Table II. It was observed that T_{decomp} s of poly(POSS-NBE-*b*-MTD) were increased with increasing the content of POSS-NBE in block copolymers, and higher than those of homopolymers such as poly(NBE) and

Table II. Characterization of Poly(POSS-NBE-*b*-MTD) Copolymers Prepared via Sequential Ring-Opening Metathesis Polymerization

Exp.	Grubbs's Initiator ($\times 10^{-4}$ M)	POSS-NBE ($\times 10^{-2}$ M)	MTD (M)	POSS-NBE in Feed (wt%)	POSS-NBE in Copolymer ^a		\bar{M}_n^b	\bar{M}_w/\bar{M}_n	T_{decomp} (°C) ^c
					wt%	mol %			
1	1.2	-	0.24	0.0	0.0	0.0	52,900	1.56	295.5
2	8.6	0.95	0.50	10.0			78,800	1.34	-
3	8.6	2.86	0.39	30.0	34.6	8.3	47,900	1.38	283.3
4	8.6	4.76	0.28	50.0	49.6	14.4	62,500	1.32	303.7
5	1.2	4.00	-	100.0	100.0	100.0	17,900	1.16	324.6

^aDetermined by $^1\text{H NMR}$. ^bMeasured by GPC relative to polystyrene standards. ^cTemperature at a 5% weight loss measured by TGA in air; for comparison, T_{decomp} of poly(NBE) = 165.4 °C.

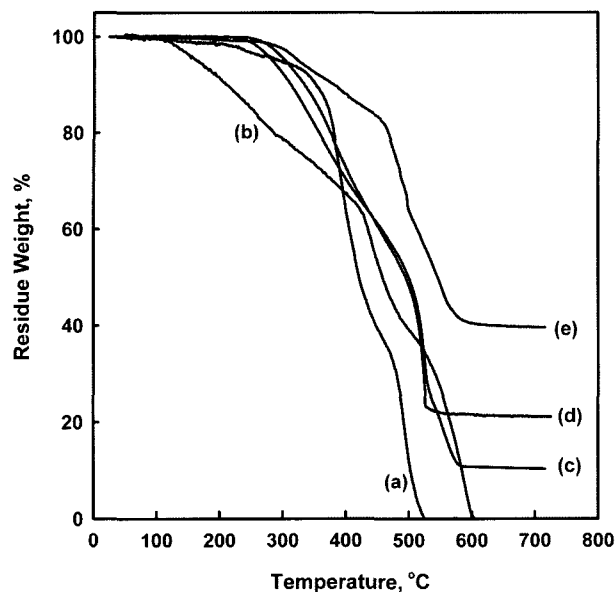


Figure 4. TGA thermograms of (a) poly(MTD) homopolymer, (b) poly(NBE) homopolymer, (c) poly(POSS-NBE-*b*-MTD) (30 wt% of POSS-NBE), (d) poly(POSS-NBE-*b*-MTD) (50 wt% of POSS-NBE), and (e) poly(POSS-NBE) homopolymer.

poly(MTD) used as reference samples. For example, T_{decomp} was increased from 283.3 °C for 30 wt% POSS-NBE content of the block copolymer to 324.6 °C for poly(POSS-NBE) homopolymer. Although T_{decomp} of poly(MTD) was measured at 295.5 °C, however, the onset decomposition temperature of poly(MTD) was measured at around 120 °C, similar to that of poly(NBE). This increased thermo-oxidative stability of block copolymers by the incorporation of POSS-NBE might be originated from the formation of silica layers on the surface of the block copolymers during the initial thermal degradation steps in the presence of oxygen, preventing further degradation of block copolymers.

Figure 5 shows WAXS profiles of poly(POSS-NBE-*b*-MTD) copolymers with two different contents of POSS-NBE, POSS-NBE monomer, poly(POSS-NBE) and poly(MTD) homopolymers. The POSS-NBE monomer as seen in Figure 5(a) showed strong reflections at $2\theta=8.1$, 12.0, and 18.9°, all corresponding to WAXS results of the POSS-NBE reported previously.^{17,22,23} This revealed that the POSS-NBE monomer formed rhombohedral crystal structures due to the association force between POSS cages. In the case of poly(POSS-NBE) homopolymer (Figure 5(b)), the amorphous fraction became so distinctive that some of the peaks were quite weak. Similar phenomena was observed with increasing the content of poly(MTD) blocks in the poly(POSS-NBE-*b*-MTD) copolymers as can be seen from Figure 5(c) and (d). However, the major three peaks of the POSS-NBE monomer could be clearly identified at the same positions in poly(POSS-NBE) homopolymer and poly(POSS-NBE-*b*-MTD)

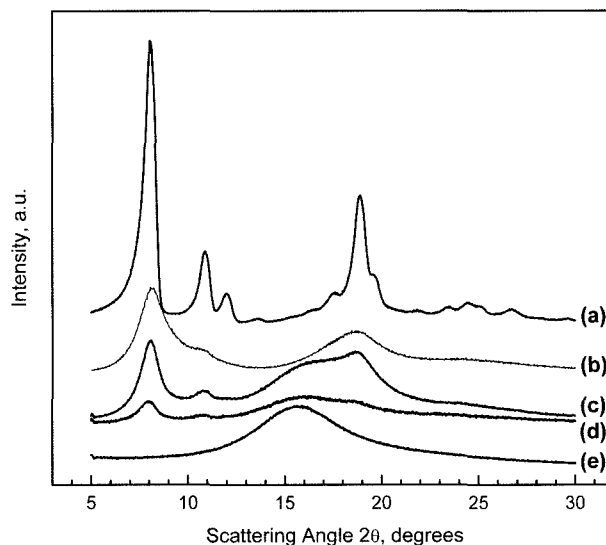
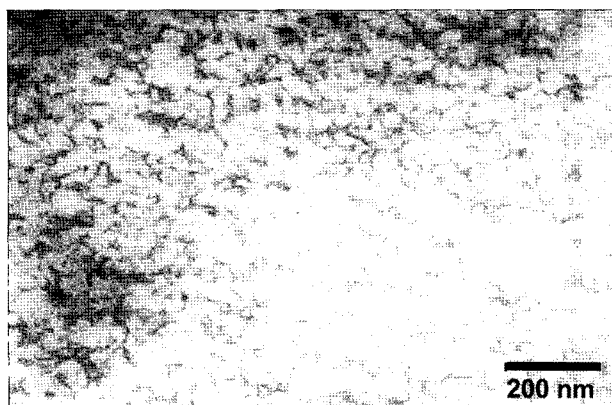


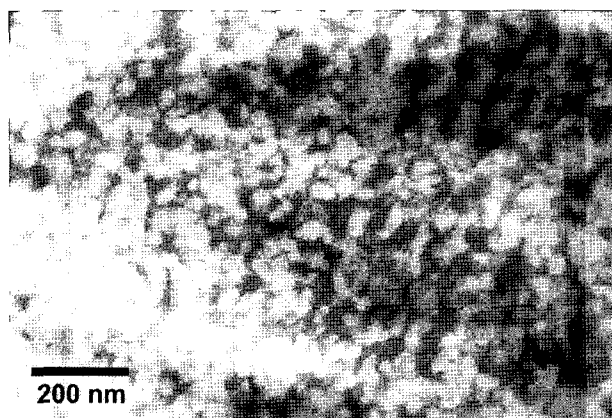
Figure 5. Powder patterns of wide-angle X-ray scattering (WAXS) for (a) POSS-NBE monomer, (b) poly(POSS-NBE) homopolymer, (c) poly((POSS-NBE)-*b*-MTD) copolymer (50 wt% POSS-NBE), (d) poly((POSS-NBE)-*b*-MTD) copolymer (30 wt% POSS-NBE), and (e) poly(MTD) homopolymer.

copolymers. This result was consistent with those reported previously in a variety of random copolymers containing POSS cages as pendent groups.^{17,23} From the fact that similar X-ray diffraction patterns were obtained in the monomer and block copolymers containing POSS-NBE, therefore, it can be concluded that the microstructure of POSS cages in block copolymers might be aggregated in a similar way as the POSS-NBE monomer.

As presented in Figure 6, TEM micrographs of poly(POSS-NBE-*b*-MTD) copolymers with 30 and 50 wt% POSS-NBE contents were taken from ultrathin sections of films prepared by slow solution casting from *p*-xylene. Due to the electron density differences between norbornene groups and POSS moieties, POSS-rich and norbornene-rich phases could be distinguished as dark domains and bright regions, respectively, without any chemical treatment. Figure 6 revealed that POSS-rich domains within poly(POSS-NBE-*b*-MTD) copolymers formed disordered and featureless structures, showing relatively irregular shape and size distributions. It was reported by Haddad *et al.*,²⁰ however, that poly(POSS-NBE-*b*-NBE) block copolymers with 30 wt% POSS-NBE content showed relatively ordered cylindrical POSS domains with poor periodicity. Compared to the results reported above, the morphology of poly(POSS-NBE-*b*-MTD) copolymers with same POSS-NBE content was on a much shorter length scale. Morphological investigation of poly(POSS-NBE-*b*-MTD) copolymers using by TEM indicated that no ordered microphase separation was induced during sample preparation.



(a)



(b)

Figure 6. TEM photographs of (a) poly((POSS-NBE)-*b*-MTD) copolymer (30 wt% POSS-NBE) and (b) poly((POSS-NBE)-*b*-MTD) copolymer (50 wt% POSS-NBE).

Conclusions

We have successfully synthesized a series of poly(POSS-NBE-*b*-MTD) copolymers by sequential ring-opening metathesis polymerization using $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ catalyst. First, the ring-opening metathesis polymerization of norbornene monomers such as norbornene, MTD, and POSS-NBE was carried out to investigate their living behavior, which is required to synthesize block copolymers by SMA technique. It appeared that with only POSS-NBE in the first step of the synthesis, well-defined poly(POSS-NBE) with controlled molecular weight and narrow molecular weight distribution was achieved. The living nature of poly(POSS-NBE) chain ends under monomer starved condition was also confirmed by using the IMA. Then, poly(POSS-NBE-*b*-MTD) copolymers were successfully prepared, in which sequential monomer addition of MTD to living poly(POSS-NBE) was utilized to achieve quantitative crossover efficiency. Structural characterization by ^1H NMR spectroscopy and GPC confirmed well-defined poly(POSS-NBE-*b*-MTD) copolymers with high structural integrity. These POSS-

containing block copolymer nanocomposites display significant improvements in their thermal stability relative to the polynorbornenes formed in the absence of POSS cages. These inorganic/organic hybrid block copolymers may serve as key model macromolecules to provide a structure/property relationship of block copolymer nanocomposites.

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