

Amphiphilic Norbornene-Based Diblock Copolymers Containing Polyhedral Oligomeric Silsesquioxane Prepared by Living Ring Opening Metathesis Polymerization

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Received September 10, 2007; Revised October 25, 2007

Abstract: We report the successful synthesis of poly(NBECOOH-*b*-NBEPOSS) copolymers, taking advantage of the sequential, living ring opening metathesis polymerization of NBETMS and NBEPOSS using the RuCl₂(=CHPh)(PCy₃)₂/CH₂Cl₂/20 °C system, followed by the hydrolysis of trimethylsilyl groups in poly(NBETMS-*b*-NBEPOSS) copolymers. The living behavior of ROMP of NBETMS was first investigated using two diagnostic plots, a first order kinetic plot and a \bar{M}_n vs. conversion plot. The plots confirmed that no termination and chain transfer reaction had occurred during polymerization. Poly(NBECOOH-*b*-NBEPOSS) copolymers were prepared using the sequential monomer addition of NBEPOSS to living poly(NBETMS) chain ends, followed by the hydrolysis of trimethylsilyl groups in the poly(NBETMS-*b*-NBEPOSS) copolymers. The high structural integrity of poly(NBECOOH-*b*-NBEPOSS) copolymers was confirmed by ¹H-NMR, ¹³C-NMR spectroscopy and GPC.

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

Introduction

The goal of contemporary polymer science has been to design and synthesize novel polymeric materials with tailored properties. This has been mainly enabled by the evolution of macromolecular engineering, which can be defined as the synthesis of macromolecules with control over the molecular weight, molecular weight distribution and the molecular architecture.¹⁻⁴ The prerequisite for obtaining well-defined block copolymers with the designed structure is to utilize living polymerization systems. Therefore, methods based on living polymerizations have become the most important for the macromolecular engineer.

Living polymerization is characterized by the absence of termination ($k_t = 0$) and chain transfer ($k_{tr} = 0$), thus it provides the best technique for the preparation of polymers and block copolymers with well-defined structures and, indeed, most these polymers have been prepared by using living polymerization. In general, diagnostic proof for the absence of chain transfer and termination can be obtained from both a linear first order kinetic plot ($\ln([M]_0/[M])$ vs. time) and

linear dependence of molecular weight on monomer conversion (\bar{M}_n vs. conversion plot). The linearity of the first order kinetic plot implies the constant concentration of the growing center, i.e. the absence of termination. In addition, the linearity of molecular weight vs. conversion plot proves the absence of chain transfer during whole polymerization period.

Since the first living anionic polymerization was reported in the 1950s,⁵ there has been continuing and persistent growth in the field of living polymerizations, including group transfer polymerization (GTP), carbocationic polymerization, ring opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP), etc. Specially, with the advent of the moisture/functional group tolerable ROMP catalyst, living ROMP has also become an important and convenient method to produce well-defined block copolymers.⁶⁻⁹ Strained cycloalkenes, norbornene derivatives, are known as commonly used monomers for ROMP, because their strained rings can be readily reacted with ROMP catalysts. Since then, the synthesis of a variety of homopolymers and block copolymers based on these monomers has been accomplished with living manner.

Recently, organic/inorganic hybrid nanocomposites, pos-

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sessing highly ordered morphological complexity of length scales of tens of nanometer, has also attracted considerable interest, including block copolymers with well-defined nanoparticle (e.g. polyhedral oligomeric silsesquioxane (POSS)) covalently attached to one of the polymer block. Here, POSS molecules with general formulae (RSiO_{1.5})₈ consisted of seven organic R substituents on the octa core to improve the solubility in organic solvents and compatibility with organic polymer matrix, and the eighth corner connected to a certain functional group (e.g. norbornene, vinyl, (meth)acrylate, etc) to undergo chain polymerizations. In order to achieve greater diversity in nanoscale morphologies, and to create novel potential applications in the areas such as liquid crystals,¹⁰⁻¹² nanocomposites,¹³⁻¹⁵ CVD coatings,¹⁶ and photoresists in lithographic technologies,^{17,18} based on their high temperature and oxidation resistance properties compared to non-POSS containing polymers, therefore, the synthesis of POSS-containing block copolymers with high structural integrity is of critical scientific importance. However, only a few block copolymers containing POSS nanoparticles have been reported so far.¹⁹⁻²²

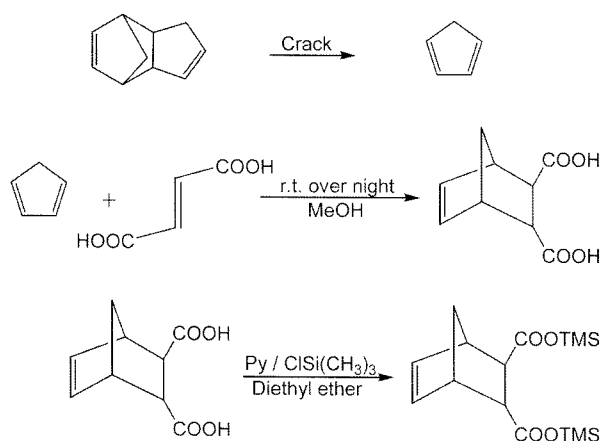
In this study, synthesis and characterization of amphiphilic organic/inorganic block copolymers containing hydrophobic POSS segments have been explored to provide key model block copolymer nanocomposites. For constructing hydrophilic segment in block copolymers, 2-endo-3-exo-5-norbornene dicarboxylic acid (NBECOOH) is considered, due to the highly polar carboxylic acid groups. Although ROMP has played a major role in the controlled construction of functional polymers because of its living nature and its remarkable functional group tolerance,^{23,24} however, an attempt to get living ROMP of NBECOOH containing carboxylic acid groups directly using the first generation Grubbs's catalyst, RuCl₂(=CHPh)(PCy₃)₂, turned out to be a failure. An alternative way to synthesize poly(NBECOOH) with living fashion by ROMP could be achieved by polymerizing 2-endo-3-exo-5-norbornene dicarboxylic acid bis trimethylsilyl ester (NBETMS) precursor first, followed by deprotecting trimethylsilyl (TMS) groups from the resulting poly(NBETMS). Kofinas *et al.* reported on synthesis, characterization and applications of poly(NBECOOH)-based amphiphilic block copolymers.²⁵⁻²⁷ As living polymerization chemists' point of view, however, the diagnostic proof for the absence of chain transfer and termination has not been clearly provided so far. So, it intrigued us to study systematically on living ROMP of NBETMS to achieve hydrophilic poly(NBECOOH) with controlled molecular weight and narrow molecular weight distribution. Furthermore, taking the advantage of living ROMP condition as well as sequential block copolymerization, amphiphilic poly(NBECOOH-*b*-NBEPOSS) copolymers, for the first time, were synthesized by ROMP using RuCl₂(=CHPh)(PCy₃)₂/CH₂Cl₂/20 °C system and characterized.

Experimental

Materials. Cyclopentyl-POSS-norbornene monomer (NBEPOSS), 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. Grubbs's catalyst, RuCl₂(=CHPh)(PCy₃)₂, was purchased from Strem Chemical Co. For the synthesis of norbornene monomers, fumaric acid and chlorotrimethyl silane were purchased from Aldrich Chemical Co. and dicyclopentadiene was obtained from ACROS Co. Dichloromethane (DC chemical, 99.5%) was refluxed over calcium hydride over 12 h and distilled just before use. Diethyl ether (DC chemical) was washed with 10% sodium sulfite aqueous solution and water, dried with magnesium sulfate overnight, and then filtered and refluxed over sodium and benzophenone until the color changed to blue, and distilled just prior to use. Pentane (Kanto chemical, Japan) was passed through silica gel, followed by refluxing over calcium hydride for 12 h, and distilled just before use. Pyridine (Showa chemical, Japan, 99.5%) was dried over 4 Å molecular sieves for more than 24 h. Ethyl vinyl ether, Celite[®], and neutral activated aluminum oxide were also purchased from Aldrich Chemical Co. All other chemicals were reagent grade and used as received unless otherwise indicated.

Synthesis of NBECOOH. In the first step, dicyclopentadiene was cracked to cyclopentadiene. In 250 mL of three-neck round-bottomed flask was placed 100 mL of dicyclopentadiene. It was refluxed under a nitrogen atmosphere. After 5 mL of distilled cyclopentadiene was discarded, the collection receiver was cooled down to -78 °C and then cyclopentadiene was distilled. Second, into 500 mL of flask containing slurry of fumaric acid (30.0 g, 0.259 mol) in 350 mL of methanol was added freshly cracked cyclopentadiene (35.9 mL, 0.431 mol) at room temperature. The reaction mixture was stirred overnight, during which all the solids went into solution to give a cloudy reaction mixture. The solvent was evaporated under reduced pressure to leave behind a white solid. This solid was washed 5 times with pentane and then dried to yield 46.9 g of NBECOOH (Yield 99.7%). ¹H-NMR (δ, D₂O, 300 MHz): 6.18-6.25 (*dd*, 1H, =CH), 5.87-6.15 (*dd*, 1H, =CH), 3.20-3.25 (*t*, 1H, *exo*-CH), 3.15 (*s*, 1H, bridge head), 3.04 (*s*, 1H, bridge head), 2.44-2.49 (*dd*, 1H, *endo*-CH), 1.41-1.47 (*d*, 1H, CH₂), 1.31-1.38 (*dd*, 1H, CH₂). ¹³C-NMR (δ, acetone-d₆, 75 MHz): 175.7, 174.4, 138.2, 135.9, 48.3, 48.2, 47.9, 47.6, 46.1.

Synthesis of NBETMS. NBECOOH (8.0 g, 44 mmol) was dissolved in 280 mL of freshly distilled diethyl ether. Dry pyridine (8.7 mL, 132 mmol) was added in one shot. Chlorotrimethyl silane (22.48 mL, 132 mmol) was added over 30 s to the reaction mixture while it was being vigorously stirred. A white precipitate of the pyridine hydrochloride salts was formed immediately. The reaction flask was stirred for further 3 h, after which the solution was filtered

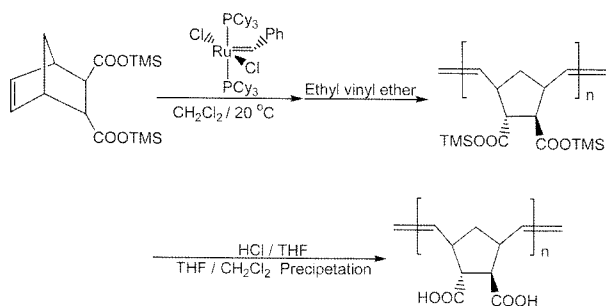


Scheme I

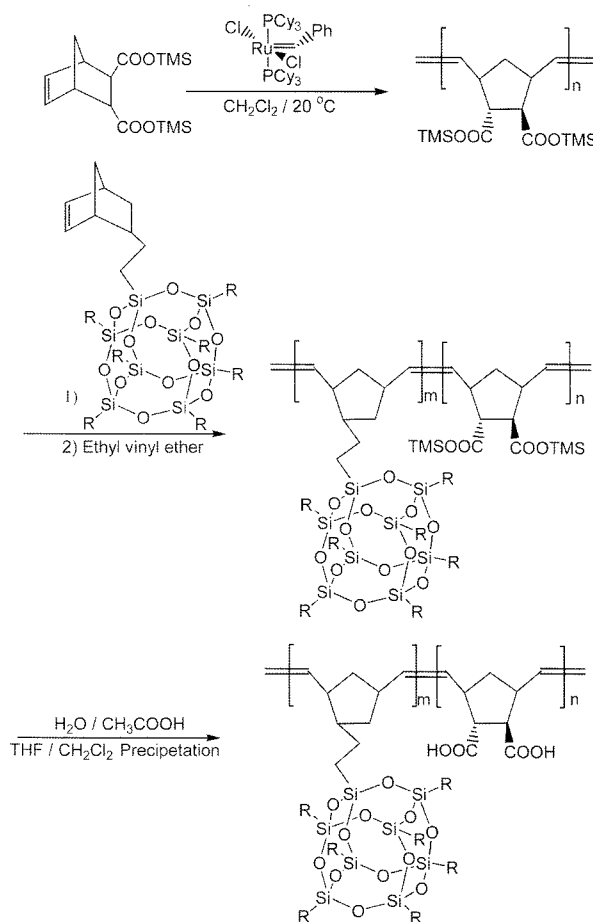
through a bed of Celite[®] to remove the precipitate. The solvent was evaporated under reduced pressure leaving behind a white solid of NBETMS (11.5 g, Yield 80.1%). Further purification was performed by redissolving the solids in dry pentane and passing the solution through a column of neutral activated alumina. The pentane was removed under reduced pressure and the white solid was recrystallized from dry diethyl ether. All synthetic procedure for NBE-COOH and NBETMS was shown in Scheme I. ¹H-NMR (δ , CDCl₃, 300 MHz): 6.27-6.30 (*dd*, 1H, =CH), 6.03-6.06 (*dd*, 1H, =CH), 3.32-3.35 (*t*, 1H, *exo*-CH), 3.22 (*s*, 1H, bridge head), 3.11 (*s*, 1H, bridge head), 2.61-2.63 (*dd*, 1H, *endo*-CH), 1.54-1.57 (*d*, 1H, CH₂), 1.42-1.45 (*dd*, 1H, CH₂), 0.23-0.28 (*d*, 18H, TMS). ¹³C-NMR (δ , CDCl₃, 75 MHz): 175.2, 174.1, 137.9, 135.1, 49.5, 49.0, 48.0, 47.6, 46.1, 0.0.

Synthesis of Poly(NBETMS) and Poly(NBECOOH).

Two-step procedure for poly(NBECOOH) was presented in Scheme II. Poly(NBECOOH) was prepared by ROMP of NBETMS inside the glove box, followed by the hydrolysis of poly(NBETMS). 2.65 mL of NBETMS (3.68×10^{-2} M) stock solution in CH₂Cl₂ was stirred at 20 °C in a small vial with a plastic screw cap. 1.1 mL of Grubbs' catalyst ([RuCl₂(=CHPh)(PCy₃)₂] = 3.68×10^{-4} M) stock solution in CH₂Cl₂ was added to each of the vials. The color of polymerization mixture was changed from pink to yellow within 10 min. 7 Parallel reactions were started at the same time, then ter-



Scheme II



Scheme III

minated separately after 1, 2, 3, 4.5, 6, 12 and 24 h by injecting 0.9 mL of ethyl vinyl ether solution to each vial, followed by stirring for another 0.5 h. The amount of ethyl vinyl ether was 75 times excess of the initiator, which could ensure efficient termination of the reactive chain ends. ¹H-NMR (δ , CDCl₃, 300 MHz): 5.18-5.54 (*m*, 2H, =CH), 3.14-2.68 (*m*, 4H, CH), 1.92 (*bs*, 1H, CH₂), 1.51 (*bs*, 1H, CH₂), 0.25 (*bs*, 18H, TMS).

The vials were then transferred out of the glove box, and hydrolyzed by adding 1 mL of hydrolysis solution, while stirring vigorously. After 2 h, the solvent was decanted, and the residue light brown solid was redissolved in 5 mL of THF, and then precipitated in 200 mL of dichloromethane in order to remove any residual initiator while vigorously stirred. The filtrate was dried for 24 h under reduced pressure at 40 °C. The moisture easy-absorbing products were immediately transferred into the glove box, and weighed after drying. ¹H-NMR (δ , THF-*d*₈, 300 MHz): 5.34-5.57 (*m*, 2H, =CH), 2.72-3.21 (*m*, 4H, CH), 2.04 (*bs*, 1H, CH₂), 1.53 (*bs*, 1H, CH₂).

Synthesis of Poly(NBECOOH-*b*-NBEPOSS) by Sequential Monomer Addition. Poly(NBECOOH-*b*-NBEPOSS) was synthesized as shown in Scheme III, with procedure as fol-

lows. After the first poly(NBETMS) block was synthesized in the same way of homopolymerization of NBETMS mentioned previously, NBEPOSS stock solution was sequentially added. The reaction mixture was stirred for further 2 h, and then quenched by injecting 50 μL of ethyl vinyl ether. 500 μL of aliquots were removed for ^1H -NMR analysis. The reaction mixture was stirred for further 0.5 h to ensure complete termination. 150 μL of acetic acid was added to the remaining mixture, several hours after which the mixture became very cloudy. The mixture was filtered and purified repeatedly by dissolution/precipitation in THF/ CH_2Cl_2 , respectively.

Instruments and Measurement. ^1H and ^{13}C -NMR spectra were recorded on an Oxford NMR 300 MHz spectrometer. Molecular weights and molecular weight distributions of synthesized homopolymers and diblock copolymers were measured at room temperature using a Waters gel permeation chromatography (GPC) equipped with a Waters 515 pump, a Waters 410 differential refractometer connected with two styragel GPC columns (10^4 and 10^5 Å). THF was used as an eluent at a flow rate of 1 mL/min. Molecular weights were calibrated with narrow molecular weight polystyrene standards. All synthetic procedures were carried out inside a nitrogen-filled glove box.

Results and Discussion

Characterization of Norbornene Monomers, NBECOOH and NBETMS. The NBECOOH and its trimethylsilylated NBETMS were identified by ^1H , ^{13}C -NMR and GC-Mass spectrometer. ^1H -NMR spectrum of NBECOOH is shown in Figure 1. In Figure 1, characteristic resonance peaks of vinyl (6,7) peaks ($-\text{CH}=\text{CH}-$) in norbornene-type ring compound at 6.18-6.25 and 5.87-6.15 ppm were clearly seen. Since carboxylic acid groups were attached at *endo*- and *exo*-positions, two methine (2,3) protons adjacent to carboxylic acid were observed at 3.20-3.25 ppm (*exo-CH*) and 2.44-2.49 ppm (*endo-CH*), respectively. For NBETMS prepared after trimethylsilylation of NBECOOH in Figure 1, all

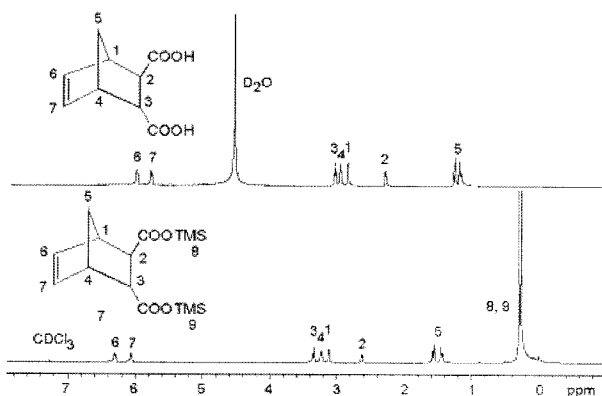


Figure 1. ^1H -NMR spectra of NBECOOH in D_2O and NBETMS in CDCl_3 .

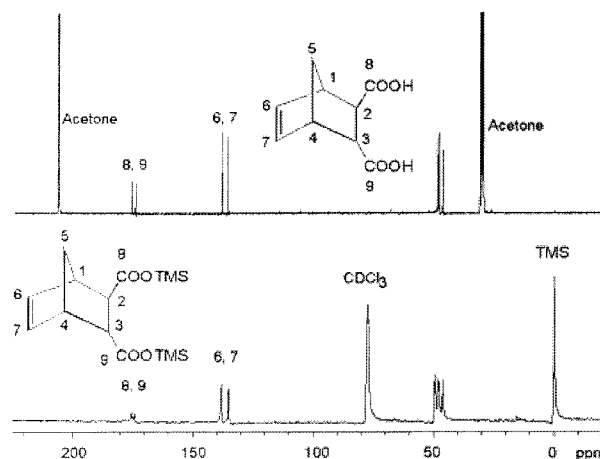


Figure 2. ^{13}C -NMR spectra of NBECOOH in acetone- d_6 and NBETMS in CDCl_3 .

other characteristic peaks remained intact, except new emerging characteristic resonance signals of trimethylsilyl groups (8,9) at 0.23-0.28 ppm. It strongly confirmed quantitative trimethylsilylation of NBECOOH. From ^{13}C -NMR spectra of NBECOOH and NBETMS in Figure 2, it was further confirmed the structure of synthesized norbornene compounds. Molecular ion peaks measured by GC-Mass spectrometer also confirmed the synthesis of monomers, showing 182 for NBECOOH and 326 for NBETMS, respectively.

It had been well known that NBETMS was so reactive that even moisture in the air could make it hydrolyzed, hence a method of removing TMS groups by neutral water was reported.²⁸ It was found in our experimental condition that NBETMS decomposed slowly even stored it at -5 °C with silica gel in a refrigerator. As presented in Figure 3, a new peak was emerged at 6.1-6.2 ppm between two vinyl peaks of the pure NBETMS, increasing with storing period. Therefore, the storage stability of NBETMS was studied as follows. At different time periods, stored NBETMS was

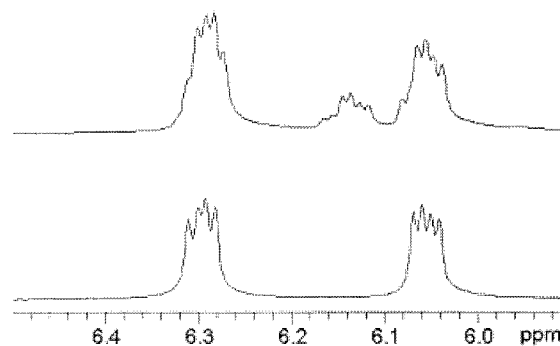


Figure 3. ^1H -NMR spectra of NBETMS for identification of decomposed compound; upper: NBETMS with mono-substituted compound; lower: pure NBETMS.

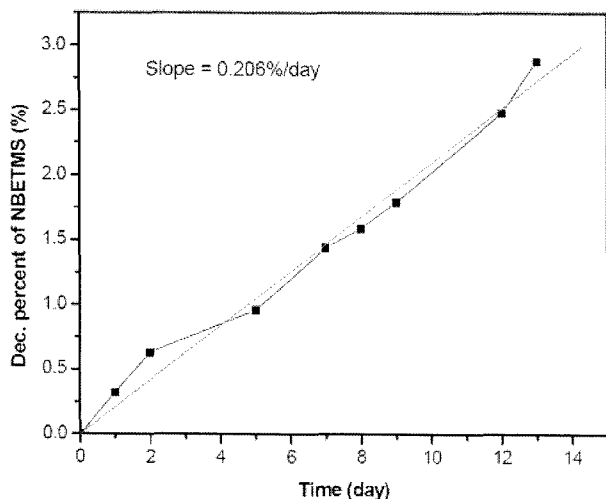


Figure 4. The rate of decomposition of NBETMS.

transferred into the glove box, and then dissolved in freshly distilled, dried pentane. Insoluble part in the pentane was filtrated through a predried glass funnel. After drying the funnel, the decomposed compound was weighed and separated. The percent of decomposition of NBETMS was calculated and plotted as a function of storage time in Figure 4. Figure 4 showed the decomposition rate of 0.206 wt%/day, which might present relatively slow decomposition. However, the decomposed compound could eventually affect on the living behavior of ROMP by destroying Grubbs's catalyst, $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$. We also experienced a lot of failure to get polymerization conditions for living ROMP of NBETMS, even though unsuccessful results were not presented in this paper. Due to the decomposition of NBETMS mentioned above, therefore, only freshly synthesized pure NBETMS was used for the subsequent kinetic study on living ROMP of NBETMS and block copolymerization with NBEPOSS.

Study on Living ROMP of NBETMS. In order to find out optimum living ROMP conditions, ROMP of NBETMS was performed using $\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2$ initiator in CH_2Cl_2 at 20 °C. The polymerization condition was as follows; $[\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2] = 3.68 \times 10^{-4} \text{ M}$, $[\text{NBETMS}] = 3.68 \times 10^{-2} \text{ M}$. After each predetermined time, the polymerizations were terminated with an excess amount of ethyl

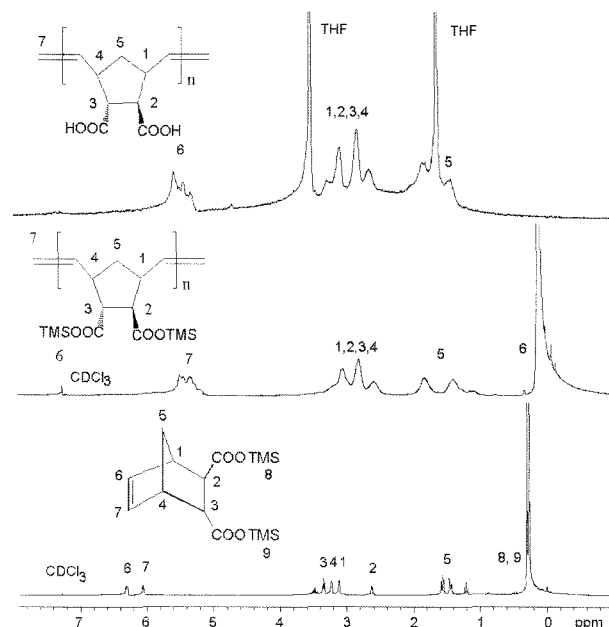


Figure 5. $^1\text{H-NMR}$ spectra of NBETMS monomer, poly(NBETMS) precursor and hydrolyzed poly(NBETMS).

vinyl ether. Results on ROMP of NBETMS at 20 °C were summarized in Table I. As can be seen in Table I, the polymerization of NBETMS proceeded smoothly after addition of the initiator stock solution, and reached at 100% of monomer conversion after 12 h. Figure 5 presents $^1\text{H-NMR}$ spectra of NBETMS monomer, poly(NBETMS) and poly(NBETMS). It was found in ROMP that double bonds in the strained ring-shaped norbornene monomer were opened with the formation of new double bonds between monomers. Hence, the vinyl protons in monomers and polymers showed different chemical situations around the vinyl protons. As a result, after ROMP of NBETMS, vinyl peaks of NBETMS monomer at the position of δ 6.0–6.4 ppm absolutely shifted to δ 5.0–5.8 ppm, which positions represented vinyl peaks of poly(NBETMS). Therefore, complete conversion of NBETMS monomer during the polymerization could also be confirmed from $^1\text{H-NMR}$ spectrum. After hydrolysis of poly(NBETMS), $^1\text{H-NMR}$ spectrum, recorded in THF-d_8 , of poly(NBETMS) showed that the trimethylsilyl groups in poly(NBETMS) were efficiently removed

Table I. Results on Ring-Opening Metathesis Polymerization of NBETMS at 20 °C^a

Reaction Time (hr)	Conversion (%)	$\ln([\text{M}]_0/[\text{M}])$	\bar{M}_n (g/mole) ^b	\bar{M}_w / \bar{M}_n ^b
1.0	27.9	0.327	9,900	1.07
2.0	49.4	0.681	17,000	1.07
3.0	66.9	1.107	22,000	1.07
4.5	82.1	1.719	26,800	1.07
6.0	89.6	2.267	29,600	1.07
12.0	100.0	---	32,500	1.07
24.0	100.0	---	32,900	1.09

^aPolymerization condition; $[\text{RuCl}_2(\text{=CHPh})(\text{PCy}_3)_2] = 3.68 \times 10^{-4} \text{ M}$, $[\text{NBETMS}] = 3.68 \times 10^{-2} \text{ M}$ in CH_2Cl_2 . ^bMeasured by GPC relative to polystyrene standards.

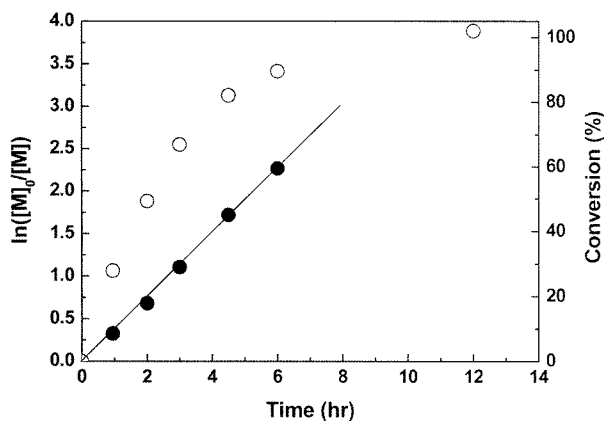


Figure 6. Conversion and $\ln([M]_0/[M])$ vs. time plots in ROMP of NBETMS. open symbols: conversion, filled symbols: $\ln([M]_0/[M])$.

with intact of other characteristic peaks in poly(NBETMS).

The first order kinetic ($\ln([M]_0/[M])$ vs. time) plot was constructed as presented in Figure 6. According to the rate of propagation (R_p), one can get the following relationship through the reaction;

$$R_p = -\frac{d[M]}{dt} = k_p[I][M] \quad (1)$$

then,

$$\ln([M]_0/[M]) = k_p[I]t \quad (2)$$

where, k_p is the rate constant of polymerization, $[M]$ is the monomer concentration in the polymerization at a certain time t , $[M]_0$ is the initial monomer concentration, and $[I]$ is the concentration of the initiator or the propagating chain ends. If the first order kinetic plot shows a linear relationship at constant temperature, it implies that the amount of propagating chain ends is constant, which can confirm no termination occurred during the polymerization. In the case of ROMP of NBETMS, a linear relationship between $\ln([M]_0/[M])$ and time was observed as shown in Figure 6, confirming absence of termination during ROMP of NBETMS using the Grubbs's catalyst.

Another diagnostic plot, \bar{M}_n vs. conversion, was constructed in Figure 7 for verifying the absence of chain transfer reaction. The relationship between \bar{M}_n and the corresponding conversion can be derived from the following equation.

$$\bar{M}_n = \frac{M_m \times [M]_0 \times \text{conversion}}{N_p} \quad (3)$$

where, \bar{M}_n is number average molecular weight of the polymer, M_m is the molecular weight of the monomer, and N_p represents the number of polymer chains. When \bar{M}_n has a linear dependence on the conversion, it means that N_p remained constant, representing no chain transfer reaction during

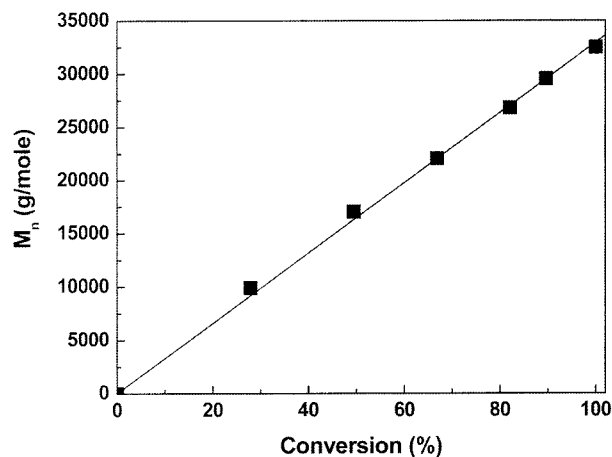


Figure 7. Number average molecular weight (\bar{M}_n) vs. conversion plot for ROMP of NBETMS.

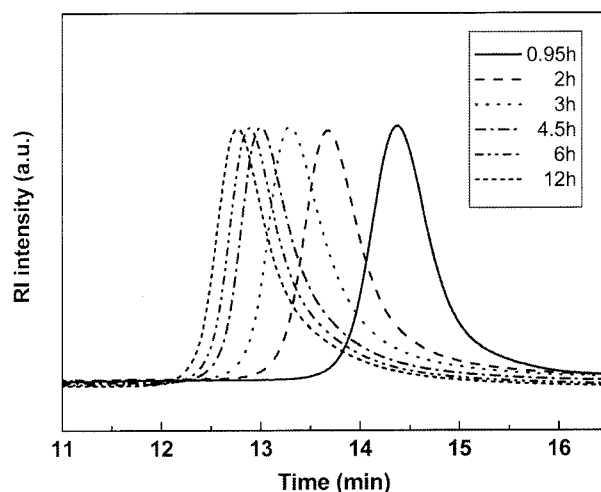


Figure 8. Shift of GPC curves of poly(NBECOOH) with increasing time.

whole polymerization period. As presented in Figure 7, linear \bar{M}_n vs. conversion plot was observed, indicating the absence of chain transfer reaction. Trimethylsilyl groups in poly(NBETMS) were so reactive to moisture that accurate molecular weight of poly(NBETMS) itself could not be measured by using GPC. Therefore, molecular weights of poly(NBECOOH) were measured and presented in Table I and Figure 7, after hydrolysis of the polymer precursors, poly(NBETMS). Figure 8 presents the shift of GPC traces to higher molecular weights with increasing conversion while maintaining narrow molecular weight distribution. These results also proved that all polymer chain ends increased without chain breaking reactions such as termination and chain transfer reaction.

To investigate whether the poly(NBETMS) chain ends remained active after complete conversion of NBETMS monomer, the second NBETMS increment was added into the polymerization mixture and kept for additional 24 h.

Table II. Characterization of Poly(NBECOOH-*b*-NBEPOSS) Copolymers Prepared via Sequential ROMP^a

Exp.	NBETMS ($\times 10^{-2}$ M)	NBEPOSS ($\times 10^{-2}$ M)	NBEPOSS (mol%)		\bar{M}_n^c	\bar{M}_w / \bar{M}_n^c
			In Feed	In Copolymer ^b		
1	3.68	---	0.0	0.0	22,200	1.16
2	3.68	0.19	5.0	3.1	26,200	1.16
3	3.68	0.41	10.0	8.1	33,200	1.23
4	3.68	0.65	15.0	15.7	45,600	1.39

^aPolymerization condition: $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2] = 3.68 \times 10^{-4}$ M, CH_2Cl_2 , 20 °C. ^bDetermined by ¹H-NMR. ^cMeasured by GPC relative to polystyrene standards.

Polymerization condition was as follow; the first $[\text{NBETMS}] = 3.68 \times 10^{-2}$ M, $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2] = 7.36 \times 10^{-4}$ M, and the second increment of $[\text{NBETMS}] = 3.68 \times 10^{-2}$ M. It was found from GPC results that the first synthesized poly(NBETMS) with $\bar{M}_n = 11,300$ g/mole and $\bar{M}_w/\bar{M}_n = 1.23$, after the second NBETMS increment, shifted toward higher molecular weight ($\bar{M}_n = 23,300$ g/mole) with unimodal and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.23$). This result proved that the propagating chain ends remained active after the polymerization of the first block. Considering all results mentioned above, it can be concluded that ROMP of NBETMS under a certain condition studied proceeds in a living fashion.

Synthesis of Poly(NBECOOH-*b*-NBEPOSS) Copolymers by Sequential Monomer Addition Followed by Hydrolysis.

Scheme III shows the synthetic scheme to poly(NBECOOH-*b*-NBEPOSS) copolymer, and the results on the block copolymerization were summarized in Table II. For the synthesis of poly(NBECOOH-*b*-NBEPOSS) copolymers, living ROMP of NBETMS was first performed to obtain poly(NBETMS) using NBETMS/ $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2/\text{CH}_2\text{Cl}_2/20$ °C system. After complete conversion of NBETMS, NBEPOSS was sequentially added into the reaction, followed by hydrolysis of the poly(NBETMS-*b*-NBEPOSS) to give rise to poly(NBECOOH-*b*-NBEPOSS) copolymers. 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 NBEPOSS. A series of poly(NBECOOH-*b*-NBEPOSS) copolymers were synthesized with 3 different NBEPOSS contents. In comparison, result of homopolymerization of NBETMS was also shown. GPC traces of poly(NBECOOH-*b*-NBEPOSS) copolymers with different NBEPOSS contents and its precursor poly(NBECOOH) homopolymer are shown in Figure 9. It appeared from Figure 9 that poly(NBECOOH-*b*-NBEPOSS) copolymers shifted to higher molecular weights, depending on the content of NBEPOSS incorporated, with maintaining narrow molecular weight distributions.

The composition of NBEPOSS in the block copolymers was determined by using ¹H-NMR, as presented in Figure 10, from the signal intensity ratio of vinyl peaks from both poly(NBETMS) block and poly(NBEPOSS) block at δ 5.18-

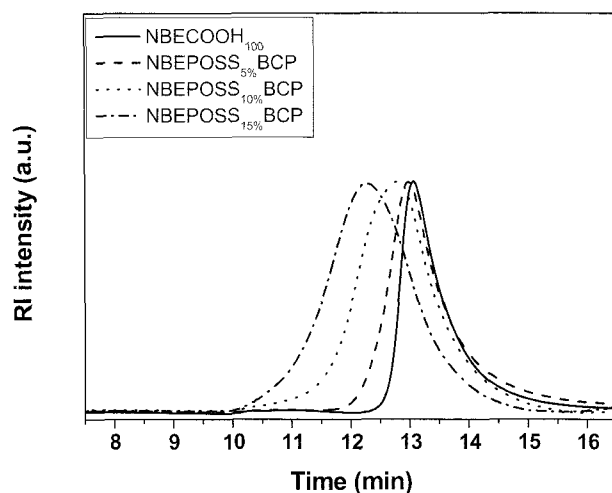


Figure 9. GPC curves of poly(NBECOOH) and poly(NBECOOH-*b*-NBEPOSS) copolymers.

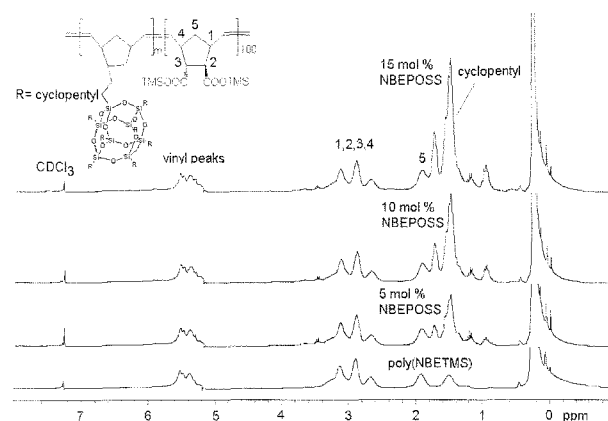


Figure 10. ¹H-NMR spectra of poly(NBETMS) homopolymer and poly(NBETMS-*b*-NBEPOSS) copolymers.

5.55 ppm, and the cyclopentyl protons from poly(NBEPOSS) block at δ 1.30-1.50 ppm. The calculated contents of NBEPOSS in block copolymers were found to be in good agreement with the feed ratio of the monomer. Figure 11 presents poly(NBECOOH) and poly(NBECOOH-*b*-NBEPOSS) copolymers prepared after hydrolysis of poly(NBETMS) and poly(NBETMS-*b*-NBEPOSS) copolymers, respectively. It appeared that the trimethylsilyl groups in

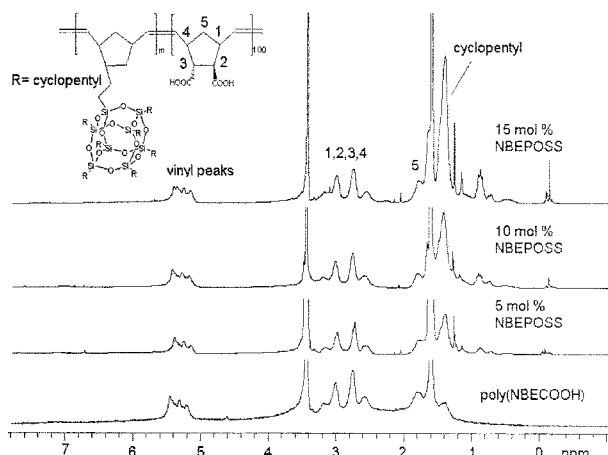


Figure 11. $^1\text{H-NMR}$ spectra of poly(NBECO OH) homopolymer and poly(NBECO OH-*b*-NBEPOSS) copolymers.

poly(NBETMS) blocks were quantitatively removed after hydrolysis. The remaining small peaks around δ 0 ppm might be attributed from proton peaks next to Si atoms on POSS cages.

Conclusions

A series of amphiphilic organic/inorganic hybrid poly(NBECO OH-*b*-NBEPOSS) copolymers was synthesized by sequential ROMP of NBETMS and NBEPOSS using $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2/\text{CH}_2\text{Cl}_2/20^\circ\text{C}$ system, followed by the hydrolysis of the resulting poly(NBETMS-*b*-NBEPOSS) copolymers. First, ROMP of NBETMS was carried out to investigate its living behavior, which was required to synthesize block copolymers by sequential monomer addition technique. It appeared that due to relatively low storage instability of NBETMS, living poly(NBETMS) without termination and chain transfer reaction was achieved with freshly synthesized NBETMS used, resulting in controlled molecular weight and narrow molecular weight distribution. The living nature of poly(NBETMS) chain ends under monomer starved condition was also confirmed by using the incremental monomer addition method. Then, poly(NBECO OH-*b*-NBEPOSS) copolymers were successfully prepared, in which sequential monomer addition of NBEPOSS to living poly(NBETMS) was utilized to achieve quantitative crossover efficiency, followed by the hydrolysis of trimethylsilyl groups in the poly(NBETMS-*b*-NBEPOSS) copolymers. Structural characterization by NMR spectroscopy and GPC confirmed the synthesis of well-defined poly(NBECO OH-*b*-NBEPOSS) copolymers with high structural integrity.

Acknowledgment. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-202-C00245).

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