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Synthesis of novel block copolymers containing polyhedral oligomeric silsesquioxane (POSS) pendent groups via ring-opening metathesis polymerization (ROMP)

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Abstract

Ring-opening metathesis copolymerization of norbornene ethyl polyhedral oligomeric silsesquioxane monomer (NBEPOSS) and 2-*endo*-3-*exo*-5-norbornene-2,3-dicaboxylic acid trimethyl ester (NBETMS) was performed using a Ru-based catalyst, $RuCl_2(=CHPh)(PCy_3)_2$. The block copolymers poly(NBETMS-*b*-NBEPOSS) were then converted to poly(NBECOOH-*b*-NBEPOSS) by hydrolysis and precipitation. The polymers were characterized by NMR and GPC and the actual NBEPOSS contents were found in good correspondence with the theoretical values. A linear dependence of M_n on conversion and a linear dependence of $\ln([M_0]/[M])$ on reaction time observed in the polymerization of NBETMS suggest that chain breaking reactions such as termination and chain transfer are minimal. Low PDI values and smooth GPC peak shifts during polymerization after addition of a second batch of the same monomer or a NBEPOSS monomer also reflect a living process.

Keywords: Living ROMP; POSS; Block copolymer

1. Introduction

POSS-containing copolymers received steadily increasing attention during the last decade as a novel category of nano-scale structured materials. These POSS-containing copolymers are attractive for their various applications in the areas such as liquid crystals [1–5], nanocomposites [6–10], CVD coatings [11], and photoresists in lithographic technologies [12–14], based on their high temperature and oxidation resistance properties compared to non-POSS containing polymers [15–17]. These properties may be attributed to unique inorganic/organic hybrid nanostructures of POSS.

POSS molecules were first synthesized in 1946 [18], with general formulae $(RSiO_{1.5})_n$, which is an intermediate between inorganic silica (SiO_2) and organic polysiloxanes $(R_2SiO)_n$. A POSS octa-cage, which is a uniform nanocomposite, always consists of nano-size molecules with a diameter of approximately 1.5 nm. As new synthetic methods were developed, special types of POSS-containing molecules were prepared, with seven organic substituents on the octa core to improve the solubility in organic solvents and the compatibility with polymer matrix, and the eighth corner connected to a certain functional group which is suitable for polymerization.

As a consequence of the emergence of the new types of POSS, a variety of POSS-containing random copolymers have been prepared, such as those with ethylene [10,19], butadiene [20], styrene [21,22], methylacrylate [23,24], and norbornene [17,25–26]. However, only a few POSS-containing block copolymers have been reported [27–29]. Well-defined block copolymers containing POSS are desirable.

It is well-known that living polymerization is an ideal tool for synthesizing well-defined block copolymers [30,31], and it may be utilized for the synthesis of POSS-containing block copolymers. Since the functional group tolerable Grubbs' and Shrocks catalysts were developed during the last decade, ring-opening metathesis polymerization has become a very

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important method for producing well-defined block copolymers [32–37]. The number of publications related to ROMP has increased year by year [38].

Herein, a synthesis of poly(NBECOOH-*b*-NBEPOSS) using poly(NBETMS-*b*-NBEPOSS) as a precursor is reported. Apparently, this is the first time that POSS has been combined with a hydrophilic group as carboxylic acid in block copolymers via ROMP. NBETMS was used as a precursor, because NBECOOH can destroy the catalyst $RuCl_2(=CHPh)(PCy_3)_2$ during polymerization. The norbornene type ester is known to be a monomer which can provide polymers with low PDI values via ROMP [39]. As an ester, NBETMS was chosen as the first monomer in sequential monomer addition. It easily undergoes polymerization and the ester function can be hydrolyzed very easily after polymerization [40,41]. However, the nature of the polymerization promoted by $RuCl_2(=CHPh)(PCy_3)_2$ has not yet been established [42,43]. Thus, it is necessary to determine whether or not this reaction displays the major characteristics of living polymerization. By confirming the linear dependence of M_n on conversion, and the linear dependence of $\ln([M_0]/[M])$ on reaction time, it could be demonstrated that chain transfer and termination during the homopolymerization are minimal. The actual NBEPOSS contents calculated from ^1H NMR results and M_n determined by GPC analysis were found in good correspondence with the theoretical values, suggesting successful synthesis of well-defined block copolymers.

2. Experimental

2.1. Materials

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(NBEPOSS), fumaric acid, chlorotrimethyl silane (97+%), $RuCl_2(=CHPh)(PCy_3)_2$, ethyl vinyl ether, Celite, and neutral activated aluminum oxide were purchased from Aldrich. 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, predried with magnesium over night then filtered and refluxed over sodium and benzphenone till color changed to blue, and distilled just before use. Pentane (Kanto chemical, Japan) was passed through silica gel, followed by refluxing over calcium hydride for 12 h, and distilled just before use. Methanol (DC chemical) was used without further purification. Dicyclopentadiene was purchased from ACROS organics. Pyridine (Showa Chemical, Japan, 99.5%) was dried over 4 Å molecular sieves for more than 24 h. 2-*endo*-3-*exo*-5-Norbornene-2, 3-dicarboxylic acid (NBECOOH) was synthesized using a previously reported procedure [42].

2.2. Instruments

^1H and ^{13}C NMR spectra were recorded using an Oxford NMR 300 MHz spectrometer. Chemical shifts were referenced to solvent peaks, $CDCl_3$, δ 7.27 ppm; THF-d_8, δ 3.58 ppm; and CD_3OD, δ 3.31 ppm. The intense peaks for TMS group on NBETMS monomer made the utilization of TMS for the establishment of δ 0.0 ppm problematic. Gel permeation chromatography (GPC) was performed using a Waters 515 pump, and two Waters styragel columns (10^4, 10^5 Å) in series connected to a Waters 410 deferential refractometer. The mobile phase was THF with a flow rate of 1 ml/min, with elution time 30 min. The M_n and PDI values were determined relative to polystyrene standard. All the reactions were performed inside a nitrogen filled glove box, with the exception of the synthesis of NBECOOH.

2.3. Synthesis of monomer

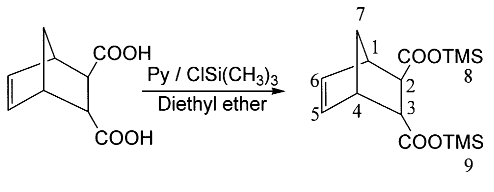
2-*endo*-3-*exo*-5-Norbornene-2,3-dicarboxylic acid bis(trimethylsilyl) ester (NBETMS) was synthesized using a modification of a previously reported procedure [42].

NBECOOH (8.0 g, 44 mmol) was dissolved in 280 ml of freshly distilled diethyl ether. To this system, dry pyridine (8.7 ml, 132 mmol) was added in a single portion. Chlorotrimethyl silane (22.48 ml, 132 mmol) was added over 30 s to the solution as it was being vigorously stirred. A white precipitate formed immediately. The reaction mixture was stirred for a further 3 h, after which the solution was filtered through a bed of Celite to remove the precipitate. The solvent was removed under reduced pressure to provide a white solid (11.5 g, 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.

^1H NMR (δ, $CDCl_3$, 300 MHz, Hs are numbered according to Scheme 1): 6.27–6.30 (dd, 1H, CH^6), 6.03–6.06 (dd, 1H, CH^5), 3.32–3.35 (t, 1H, CH^3), 3.22 (s, 1H, CH^4), 3.11 (s, 1H, CH^1), 2.61–2.63 (dd, 1H, CH^2), 1.54–1.57 (d, 1H, CH^{7a}), 1.42–1.45 (dd, 1H, CH^{7b}), 0.23–0.28 (d, 18H, TMS). ^{13}C NMR (δ, $CDCl_3$, 75 MHz, Cs are numbered according to Scheme 1): 175.2, 174.1 (C=O), 137.9, 135.1 (C^5, C^6), 49.5, 49.0, 48.0, 47.6, 46.1 (C^3, C^1, C^7, C^2, C^4), 0.0 (TMS).

2.4. Synthesis of poly(NBETMS) and poly(NBECOOH) homopolymers

All solutions were freshly prepared just before use: a catalyst solution was prepared by dissolving 90 mg (0.276 mmol) of $RuCl_2(=CHPh)(PCy_3)_2$ in 11.0 ml of CH_2Cl_2; NBETMS solution was prepared by dissolving 4.245 g (13.0 mmol) NBETMS into 25.0 ml of CH_2Cl_2; ethyl vinyl ether was



Scheme 1. Synthesis of NBETMS.

prepared by dissolving 0.1 ml ethyl vinyl ether into a 10 ml CH_2Cl_2; hydrolysis solution was prepared by mixing 1 ml of aqueous concentrated HCl acid with 10 ml of THF.

At 17 °C, 2.65 ml NBETMS solution was stirred in a small vial. Grubbs' catalyst solution 1.1 ml was added to the vial. The total reaction volume was 3.75 ml while [NBETMS] (3.68×10^{-2} mol/l) was 100 times that of [$RuCl_2$(=CHPh)-(PCy_3)$_2$] (3.68×10^{-4} mol/l). The color changed from pink to yellow over 10 min. Seven parallel reactions were started at the same time, then terminated separately after 57 min, 2 h, 3 h, 4.5 h, 6 h, 12 h, 24 h by adding 0.9 ml ethyl vinyl ether solution, followed by stirring for another 0.5 h. The amount of ethyl vinyl ether was 75 times that of the initiator, which ensured efficient termination of the reactive chain ends.

^{1}H NMR (δ, $CDCl_3$, 300 MHz, Hs are numbered according to Scheme 2): 5.18–5.54 (m, 2H, 7), 3.14–2.68 (m, 4H, H$^{1-4}$), 1.92 (bs, 1H, H^5), 1.51 (bs, 1H, H^5), 0.25 (bs, 1H, H^6).

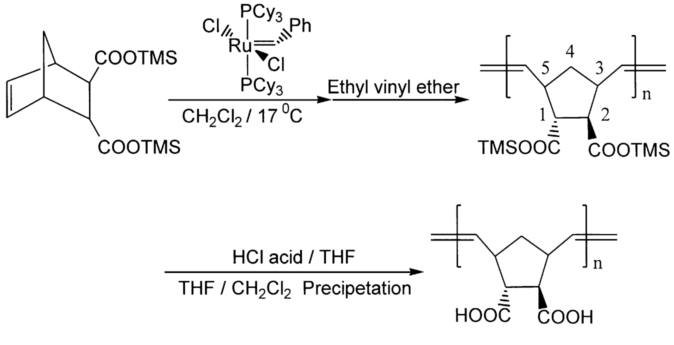
The vials were then transferred out of the glove box, and the ester pendent groups were hydrolyzed by adding 1 ml of hydrolysis solution, with vigorous stirring. After 2 h, the solvent was removed easily by pipette and the brown residual solid was then redissolved in 5 ml of THF, and then precipitated into 200 ml dichloromethane with vigorous stirring. The precipitation was collected by filtration and dried for 24 h under reduced pressure at 40 °C. The hydroscopic products were immediately transferred into a glove box, and weighted after drying.

^{1}H NMR (δ, THF-d_8, 300 MHz, Hs are numbered according to Scheme 2): 5.34–5.61 (m, 2H, 6), 2.72–3.32 (m, 4H, H$^{1-4}$), 1.92 (bs, 1H, H^5), 1.53 (bs, 1H, H^5).

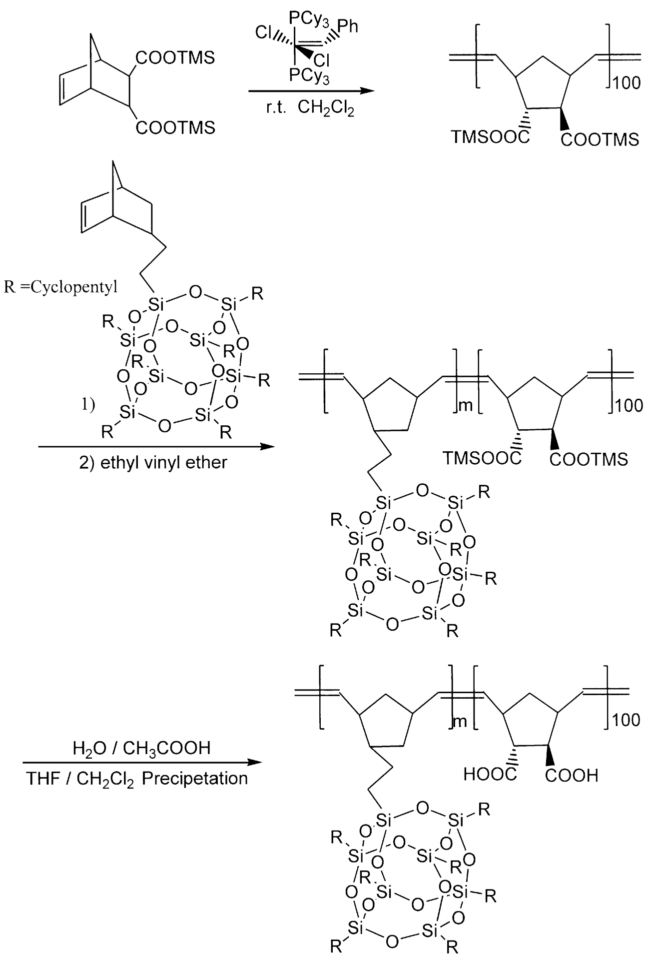
2.5. Synthesis of block copolymers

NBEPOSS solutions were freshly prepared just before use. NBEPOSS (0.070 g) was dissolved in 1 ml CH_2Cl_2 for synthesis of 5 mol% NBEPOSS-containing block copolymer, 0.141 g NBEPOSS was dissolved in 1 ml CH_2Cl_2 for synthesis of 10 mol% NBEPOSS-containing block copolymer Scheme 3.

The poly(NBETMS) block was synthesized as described in Section 2.4. After the polymerization of the first block had advanced to completion, NBEPOSS solution was added. The reaction was allowed to continue for 6 h until terminated by the addition of ethyl vinyl ether solution. A parallel homopolymerization was conducted without adding the second monomer and it was terminated after 24 h by the addition of ethyl vinyl ether solution. The ester functions of block copolymers and homopolymers were hydrolyzed and the polymers were collected from precipitation. ^{1}H NMR was used to confirm the completion of the polymerization and to calculate the actual NBEPOSS contents of the block copolymers. The M_n and PDI values were established by GPC. The NBEPOSS contents and GPC results about block copolymers and the corresponding homopolymers are shown in Table 1.



Scheme 2. Synthesis of poly(NBETMS) and poly(NBECOOH).



Scheme 3. Synthesis of poly(NBECOOH-*b*-NBEPOSS).

3. Results and discussion

3.1. Synthesis of monomer

NBETMS was successfully synthesized using a modification of a previously reported procedure, and was characterized by ^{1}NMR and ^{13}C NMR spectroscopies.

It was observed that NBETMS was so reactive to moisture that even minimal exposure to moisture in air was sufficient to effect hydrolysis of the ester function [40,41]. According to our experiment, NBETMS decomposed slowly even when stored in a tightly sealed container in refrigerator. The monosubstituted compound was readily formed. The presence of an unesterified carboxyl group could have a detrimental impact

Table 1
Data for block copolymers and the corresponding homopolymer

No[a]	NBEPOSS%[b] (Theo.)	NBEPOSS%[c] (^{1}H NMR)	M_n[d]	M_w/M_n[d]
NBECOOH$_{100}$	0	0	22,400	1.15
NBECOOH$_{100}$ NBEPOSS$_{5\ \mathrm{mol\%}}$	5	5.0	26,200	1.16
NBECOOH$_{100}$ NBEPOSS$_{10\ \mathrm{mol\%}}$	10	9.6	33,200	1.23

[a] [NBEPOSS] = 1.52×10^{-3} M (For NBECOOH$_{100}$NBEPOSS$_{5\ \mathrm{mol\%}}$), [NBEPOSS] = 3.04×10^{-3} M (For NBECOOH$_{100}$NBEPOSS$_{10\ \mathrm{mol\%}}$), total reaction volume = 4.75 ml, temperature = 17 °C. The concentration of NBETMS and RuCl$_2$(=CHPh)(PCy$_3$)$_2$ are the same with Table 2.

[b] NBEPOSS% (Theo.) were calculated according to feed ratios of NBEPOSS.

[c] NBEPOSS% was calculated from ^{1}H NMR.

[d] Number average molecular weight (M_n) and molecular weight distributions were determined by GPC in THF and reported relative to polystyrene standards.

on the initiator. The existence of the monosubstituted compound was revealed by the appearance of new vinyl peak in the ^{1}H NMR spectrum of NBETMS. ^{1}H NMR spectra of the pure NBETMS and the mixture of NBETMS and monosubstituted compound are compared in Fig. 1. In order to avoid effects of moisture, the crystal was carefully washed with freshly distilled ethyl ether and the structure was confirmed by ^{1}H NMR spectroscopy just before use.

3.2. Polymerization of NBETMS monomer promoted by Ru-based catalyst RuCl$_2$(=CHPh)(PCy$_3$)$_2$

Living polymerization is an ideal tool for synthesizing polymers with well-defined structures and narrow molecular weight distributions. It is identified by full conversion of monomer and the absence of chain breaking reactions such as termination and chain transfer during polymerization. For the first time, we fully investigated whether the monomer NBETMS could undergo a living polymerization via ROMP using RuCl$_2$(=CHPh)(PCy$_3$)$_2$.

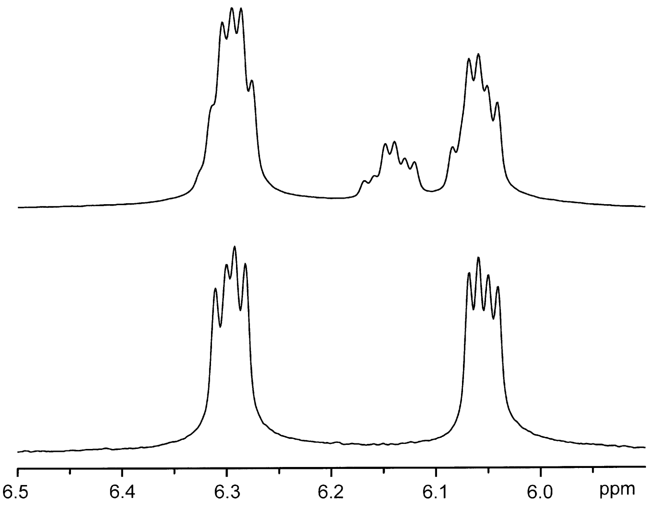


Fig. 1. ^{1}H NMR spectra for impurity identification in CDCl$_3$: (upper) NBETMS with monosubstituted compound and (lower) pure NBETMS compound.

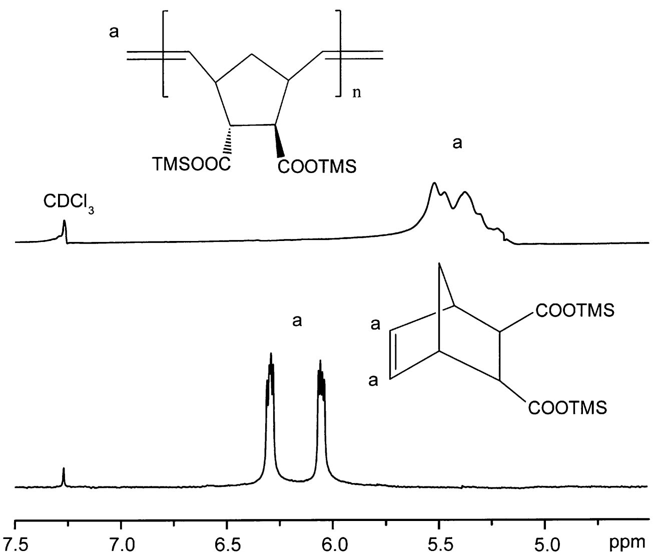


Fig. 2. ^{1}H NMR spectra for comparison between vinyl peaks of (upper) poly(NBETMS) at full conversion and (lower) NBETMS in CDCl$_3$.

Firstly, full conversion of NBETMS monomer was determined by comparing the ^{1}H NMR result of homopolymerization solution after 24 h and the ^{1}H NMR result of MBETMS monomer in CDCl$_3$. Fig. 2 shows that the vinyl peaks of monomer between δ 6.1 and 6.3 shift absolutely to δ 5.1–5.6, which were identified as vinyl peak of poly(NBETMS).

To see whether chain breaking reactions such as termination and chain transfer occurred, a series of seven parallel homopolymerizations were conducted, varying reaction time by terminating the reactive chain ends with ethyl vinyl ether at different reaction times. Because NBETMS is very sensitive to moisture, all GPC results were measured in the form of poly(NBECOOH) after hydrolysis and precipitation of the polymer precursors. Reaction time, the corresponding conversions, M_n, and PDI values are displayed in Table 2 and Fig. 3.

To test whether termination occurred during homopolymerization, we examined the relationship between ln([M_0]/[M]) and time. Because propagation is a bimolecular reaction, it

Table 2
Data for analysis of chain breaking reactions of NBETMS promoted by RuCl$_2$(=CHPh)(PCy$_3$)$_2$[a]

Time (h)	Conversion%[b]	ln([M$_0$]/[M])	M_n (g mol^{-1})[c]	PDI[c]
0.95	27.9	0.327	9900	1.07
2	49.4	0.681	17,000	1.07
3	66.9	1.107	22,000	1.07
4.5	82.1	1.719	26,800	1.07
6	89.6	2.267	29,600	1.07
12	100.0	–	32,500	1.07
24	100.0	–	32,900	1.09

[a] [NBETMS] = 3.68×10^{-2} M, [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] = 3.68×10^{-4} M, total reaction volume = 3.75 ml, temperature = 17 °C.

[b] The conversion was determined by the precipitation method described in the experimental section and the accuracy has been proved using ^{1}H NMR analysis.

[c] M_n and PDI values were determined by GPC.

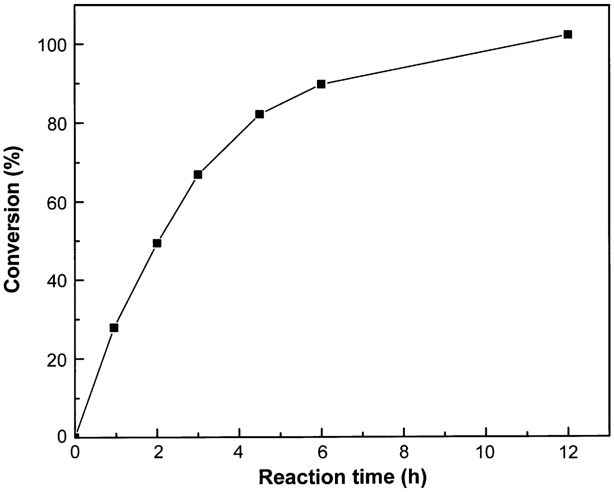


Fig. 3. Plot of conversion versus reaction time for homopolymerization of NBETMS.

takes place by the successive addition of monomer to the reactive centre, generating the same reactive intermediate with increased molecular mass. It can be expressed as:

$$R_\mathrm{p} = \frac{-\mathrm{d}[M]}{\mathrm{d}t} = k_\mathrm{p}[\mathrm{I}][\mathrm{M}] \quad \text{thus} \quad \ln([\mathrm{M}_0]/[\mathrm{M}]) = k_\mathrm{p}[I]t,$$

where k_p is the reaction constant, which is dependent on temperature, [M] is the monomer concentration in the polymerization solution, $[\mathrm{M}_0]$ is the original monomer concentration, [I] is the concentration of the initiator and propagating chain ends and t is the reaction time for the polymerization [30].

If the temperature is kept constant, then k_p is constant. And if $\ln([\mathrm{M}_0]/[\mathrm{M}])$ and time are linearly related, then the concentration of propagating chain ends [I] does not decrease. This suggests that no or minimal termination occurs during polymerization. In this case, a linear relationship between $\ln([\mathrm{M}_0]/[\mathrm{M}])$ and reaction time was observed as shown in Fig. 4.

To determine whether chain transfer occurred during homopolymerization, the relationship between the number average

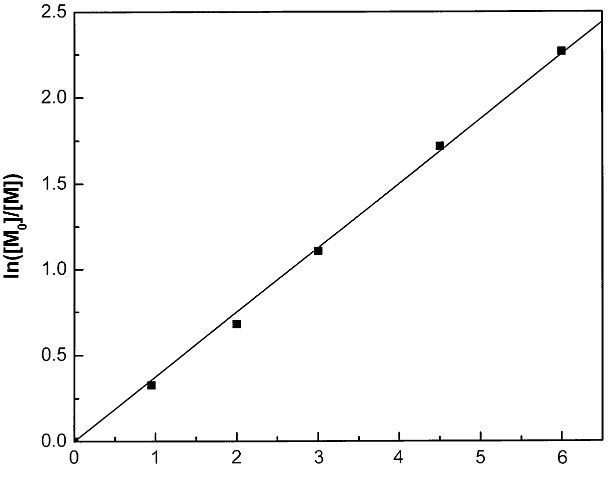


Fig. 4. Plot of $\ln([\mathrm{M}_0]/[\mathrm{M}])$ versus reaction time for homopolymerization of NBETMS.

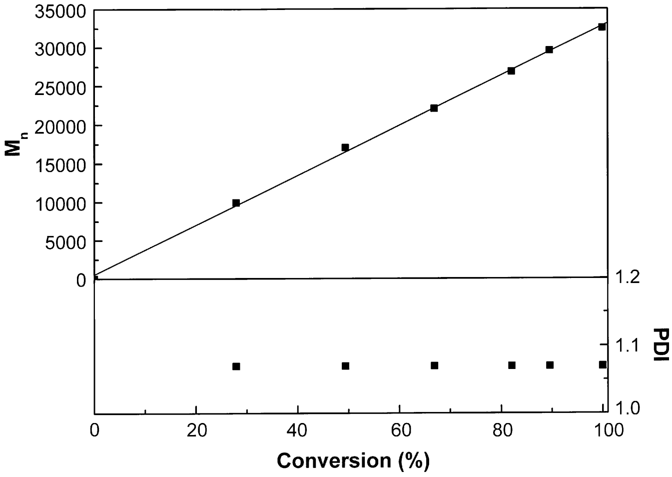


Fig. 5. Plot of M_n as measured by GPC versus conversion for homopolymerization of NBETMS and the corresponding PDI values.

molecular weight (M_n) and conversion was examined. It can be expressed as:

$$M_\mathrm{n} = \frac{M_\mathrm{m} \times [\mathrm{M}_0] \times \text{conversion}}{N_\mathrm{p}},$$

where M_n is the number average molecular weight, M_m is the molecular weight of the monomer, and N_p represents the concentration of all the polymer chains. If the increase in M_n displays a linear dependence on conversion, then [P*] doesn't increase. In this study, a linear relationship between M_n and monomer conversion was observed, suggesting chain transfer during polymerization was minimal (Fig. 5).

As displayed in Table 2 and Fig. 6, GPC analysis of hydrolyzed and precipitated polymerization mixtures demonstrates that molecular weight of the polymer formed increases regularly with reaction time while the polydispersity index for the polymer is uniformly maintained at a low value of 1.07. These results also suggest that propagating chains grew at

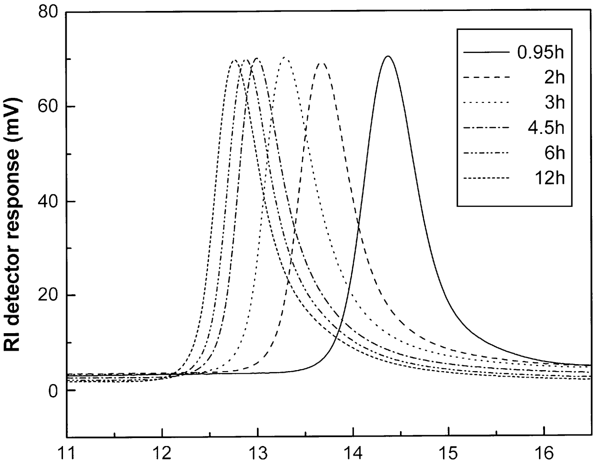


Fig. 6. GPC peaks of poly(NBECOOH) obtained at different reaction times of homopolymerization of NBETMS.

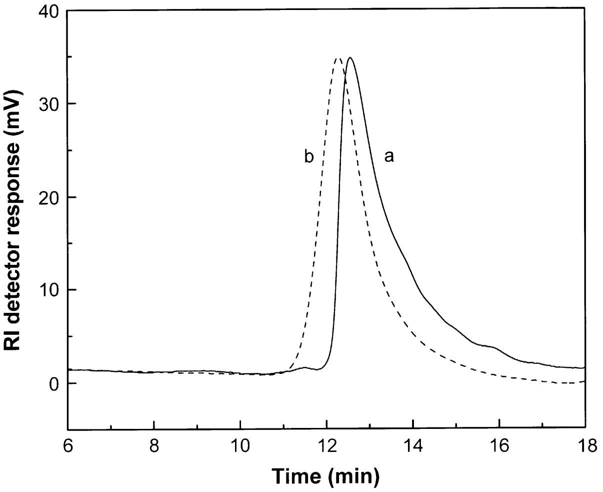


Fig. 7. GPC peaks of poly(NBECOOH) (a) before and (b) after incremental monomer addition of NBETMS.

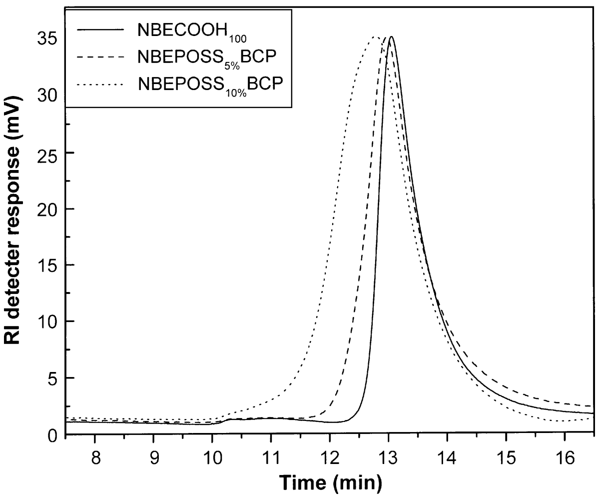


Fig. 8. GPC profile for poly(NBECOOH-*b*-NBEPOSS) block copolymers and corresponding poly(NBECOOH) homopolymer.

approximately the same rate and that minimal chain breaking reactions occurred during the polymerization.

To further confirm the living nature of this polymerization, a second batch of NBETMS was added after full monomer conversion had occurred. From the chromatograms displayed in Fig. 7, it can be seen that the molecular weight of the polymer increases after addition of a second batch of NBETMS monomer. This demonstrates that propagating chain ends remained active after the polymerization of the first block.

From all these results, it is apparent that polymerization of NBETMS promoted by $RuCl_2(=CHPh)(PCy_3)_2$ displays many of the characteristics of living polymerization.

To confirm effectiveness of purification by precipitation, the ^{1}H NMR spectra of the dried polymer precipitation and the residue from evaporation of the solvent from the filtrate were recorded in methanol-d_4 in which both NBECOOH and poly(NBECOOH) are soluble. The spectrum of the polymer contains vinyl peaks only within δ 5.18–5.54 ppm while the spectrum of the residual material from the filtrate contains vinyl peaks only between δ 6.06–6.27 ppm. This suggests that residual monomer was removed from the polymer by the precipitation procedure, and the polymer was not mixed in the filtrate.

3.3. Block copolyformation via sequential monomer addition

After the living nature of homopolymerization had been confirmed, block copolymerizations with the same block lengths of poly(NBECOOH) and different NBEPOSS feed contents as 5 mol% and 10 mol% were performed by sequential monomer addition from NBETMS to NBEPOSS. The smooth formation of the block copolymers is apparent from the GPC profiles as shown in Fig. 8. The M_n and PDI values of the block copolymers and the corresponding poly(NBECOOH) homopolymer determined by GPC were shown in Table 1.

The sequence of monomer addition typically used in this work is preferred because of the polarity of the ester group. The endo-carbonyl oxygen atom can chelate to the active Ru centre to generate a resting state during the polymerization process. This can result in a lower R_p and a correspondingly lower PDI [39]. The reduction in the activity of the catalyst and the subsequent decrease in the PDI due to the electronic effects of monomer have been previously reported [43]. The electronic effect of *endo*-dimethyl butyl silyl ester functionalized monomer on the activity of Grubbs' catalyst has been discovered previously [44]. Endo-functional groups are known to chelate with the active metal centre and change the activity of the catalyst [45].

Aliquots of the block copolymer solutions before hydrolysis were removed for ^{1}H NMR analysis in $CDCl_3$ and the spectra are shown in Fig. 9. Full consumption of the monomers can be concluded by the disappearance of vinyl peaks within δ 5.8–6.4 ppm.

^{1}H NMR spectra have also been recorded after hydrolysis and precipitation of the block copolymers as shown in Fig. 10. The majority of TMS groups have been well removed but trace amount remained in the polymers. That was because the block copolymers were very thick after hydrolysis and trace amount of hydrolyzed TMS may be carried in the polymers.

New peaks can be observed within δ 0.8–1.8 ppm for block copolymers compared with the corresponding poly(NBECOOH) and the new peaks increase with the NBEPOSS contents. The actual NBEPOSS contents can be calculated from the integral of these peaks and the vinyl peaks. The integral within δ 5.18–5.55 ppm (S_1) represented the vinyl peaks from both poly(NBECOOH) and poly(NBEPOSS) blocks. And the peak within δ 1.30–1.50 ppm (S_2) represented four of the five cyclopentyl protons on POSS cage and one of the H^7 from the poly(NBECOOH) block. From the two integral,

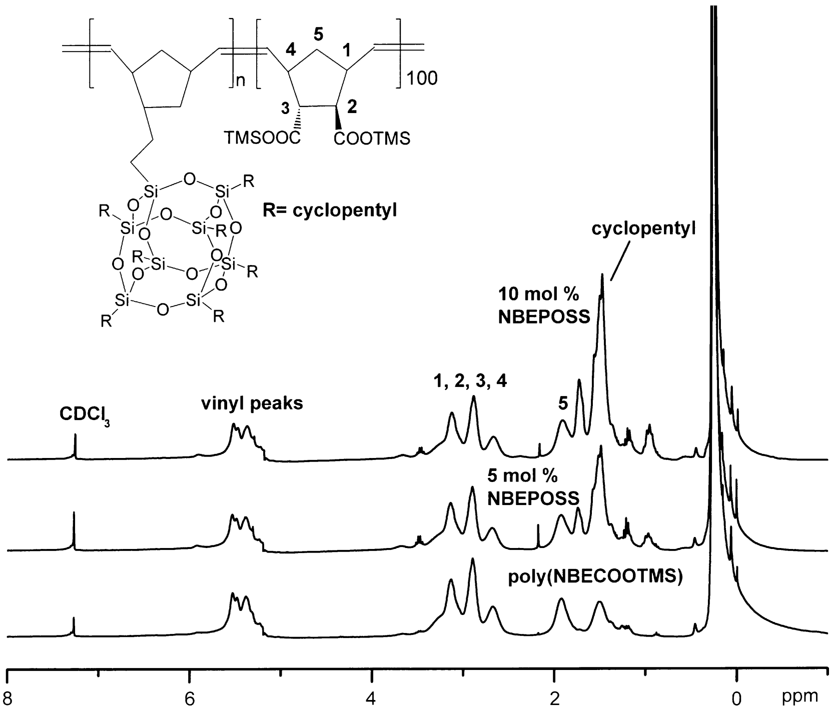


Fig. 9. ^{1}H NMR spectra for poly(NBETMS-*b*-NBEPOSS) block copolymers and corresponding poly(NBECOOH) homopolymer in $CDCl_3$.

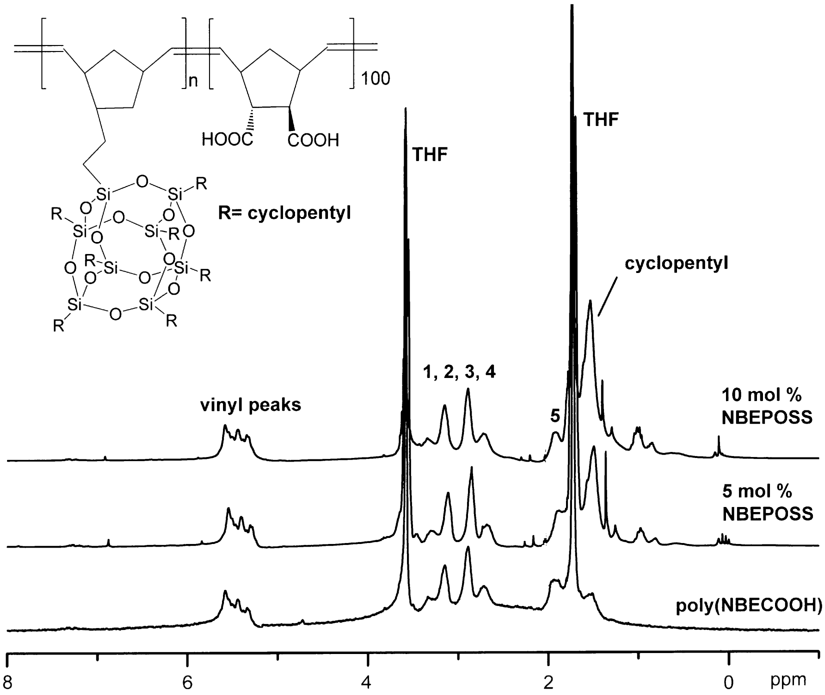


Fig. 10. ^{1}H NMR spectra for poly(NBECOOH-*b*-NBEPOSS) block copolymers and corresponding poly(NBECOOH) homopolymer in THF-d_8.

the accrual NBEPOSS contents can be calculated. For poly(NBECOOH$_m$-*b*-NBEPOSS$_n$), it can be obtained as:

$$\frac{S_1}{S_2}=\frac{2*(m+n)}{28n-m} \quad \text{thus} \quad \frac{m}{n}=\frac{28S_1-2S_2}{2S_2+S_1}=A$$

and the POSS mol% can be calculated as:

$$\begin{aligned}\text{NBEPOSS mol\%} &= 1021.75n/1021.75n+182.06\\ &= 1021.75/1021.75+182.06A\end{aligned}$$

The theoretical and actual NBEPOSS contents are compared in Table 1 and were found in good correspondence, with 5.0 mol% actual NBEPOSS content for 5 mol% NBEPOSS block copolymer and 9.6 mol% actual NBEPOSS content for 10 mol% NBEPOSS block copolymer.

4. Conclusions

Novel diblock copolymers with a polyhedral oligomeric silsesquioxane (POSS) nanocomposite as pendent group on one block and carboxylic acid group on the other block have been synthesized and characterized by NMR and GPC. The NBEPOSS contents of poly(NBECOOH-*b*-NBEPOSS) were in good correspondence with the theoretical values. This represents first time that POSS-containing block copolymers have been synthesized via ‘‘living’’ ring-opening metathesis polymerization. To protect Ru-based catalyst $RuCl_2(=CHPh)(PCy_3)_2$ from being destroyed by acid, NBETMS was used as a precursor to NBECOOH during polymerization. That is the polymerization possesses living characteristics was demonstrated by confirming the absence of chain transfer and termination, the formation of polymer with low PDI values, and resumption of polymerization upon addition of a new batch of NBETMS.

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