

Preparation and Characterization of Polybutadiene/Allylisobutyl Polyhedral Oligomeric Silsesquioxane Nanocomposites by Anionic Polymerization

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ABSTRACT: Polybutadiene (PB)/Allylisobutyl Polyhedral Oligomeric Silsesquioxane (A-POSS) nanocomposites have been prepared by using A-POSS and butadiene (Bd) as comonomers, *n*-BuLi as initiator, cyclohexane as solvent, ethyltetrahydrofurfuryl ether as structure modifier through the anionic polymerization technique. The reaction conditions, the kind and content of the modifier and POSS, etc. affecting the copolymerization process and the microstructure of the nanocomposites were also investigated. The results showed that POSS incorporation obviously decreased the rate of polymerization and the molecular weight of the copolymers, increased polydispersity index of the copolymers. The reaction condi-

tions (the reaction time and reaction temperature) had little effect on copolymerization. However, the addition of the modifier could increase the rate of polymerization significantly. In particular, the POSS incorporation resulted in dramatically increasing the content of 1,2-units in PB. POSS and the modifier had the excellent cooperative effect modifying the microstructure of the PB. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2800–2808, 2011

Key words: anionic polymerization; polybutadiene; polyhedral oligomeric silsesquioxane; nanocomposites; microstructure

INTRODUCTION

Organic-inorganic nanocomposites have drawn great attention from polymer scientists since they combine the advantages of the inorganic materials (i.e., thermal and oxidative stability, high modulus) and the organic polymers (i.e., processibility, ductility, flexibility). For polymer-based nanocomposites, numerous approaches have been developed, including *in situ* sol-gel chemistry, organoclay intercalation and exfoliation, nanoparticle filling and use of hybrid inorganic-organic monomers (macromers), such as polyhedral oligomeric silsesquioxane (POSS). In particular, the use of POSS has been regarded as an efficient way in the design of nanohybrids at the molecular level. The cage-shaped POSS molecules have an empirical formula $(\text{RSiO}_{1.5})_n$ composed with a silicon-oxygen framework, with an inorganic Si_8O_{12} nanostructured skeleton, surrounded by several R groups that can be either unreactive organic groups on the corners to promote solubility in conventional solvents or reac-

tive groups for polymerization purposes. POSS monomers can be classified into monofunctional and multifunctional POSS chemicals.¹ Unlike silica, metal oxides, layered silicates and hydroxides, carbon nanotube, POSS is an organic-inorganic molecule with sizes from 1 to 3 nm in diameter, well-defined chemical structure and versatile reactivity. Generally speaking, the incorporation of POSS into polymeric matrix can result in dramatic improvements of polymer properties, which include increases in glass transition temperature (T_g), heat stability, oxidation resistance, high modulus, surface hardening, hydrophobicity, wear resistance, as well as reductions in flammability and viscosity.²

A variety of POSS-containing copolymers have been prepared with radical bulk free polymerization (both conventional and atom transfer radical polymerization), coordination polymerization, condensation, and ring-opening metathesis polymerization techniques. The copolymerization of POSS macromers with organic monomers has been proved to be easy.^{3–6} So far, POSS has been successfully incorporated into numerous existing resin systems, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), epoxide resin, polynorbornene, polyacrylate, nylon, etc., to prepare different kinds of polymer/POSS nanocomposites.^{3–6} However, the study on elastomer/POSS is still at an early stage of development. Haddad and coworkers⁷ designed hybrid

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organic/inorganic triblock copolymer of polystyrene-butadiene-polystyrene (SBS). The POSS molecules were used to graft onto the dangling 1,2-butadienes in the polybutadiene soft block utilizing a Pt catalyst and the POSS behavior in the SBS matrix was investigated. Results of DMA showed that the POSS had sterically hindered the motion of the polybutadiene blocks. The presence of POSS in the soft segments resulted in increasing the elastic storage modulus (E') and T_g of PB and PS blocks without affecting the elongational behavior of SBS at temperatures above T_g of polybutadiene. It indicated that the incorporation of POSS could not affect the toughness and elasticity of SBS. Coughlin and coworkers^{8,9} prepared POSS/polybutadiene (PBD) nanocomposites with the random structure and chain backbone containing cyclopentane (coming from norbornylene) by ring-opening metathesis copolymerization of cyclooctadiene and POSS bearing a polymerizable norbornene group. The results showed the formation of self-assembled layered nanostructure of POSS aggregated. The length of the lamellae and the spacing between lamellae could be changed by the relative ratio between POSS and PBD. The incorporation of POSS had less effect on T_g of PBD. When the content of POSS exceeded 40 wt %, PBD/POSS nanocomposites displayed elastomeric behavior. He concluded that the POSS nanoscale crystals effectively acting as "anchors" might be the main reason for the elastomer behavior. Recently, Seurer and Coughlin reported elastomers containing POSS with stronger physical and mechanical properties, namely ethylene-propylene-POSS elastomers.¹⁰ The mechanical studies of ethylene-propylene-Ph POSS polymers indicated that POSS acted as a physical crosslink for use in thermoplastic elastomers. Seurer and Coughlin¹¹ also incorporated POSS into fluoroelastomer. The incorporation of POSS had increased T_g and decomposition temperature (T_d) of fluoroelastomer. Rheological studies of these copolymers showed a significant increase in rubbery plateau region and modulus.

Since the anionic polymerization allows the construction of the polymer with precise control of the microstructure, it has been widely used in industry to produce large amounts of butadiene rubber (BR), styrene-butadiene rubber (SBR), and SBS thermoelastomer. Moreover, POSS exhibits unique chemical structure and wide chemical versatility. If we combine the advantages of these two kinds of materials to prepare PB/POSS nanocomposites, it could affect the structure and property of rubber and also provide valuable attempts to prepare rubber nanocomposites via anionic polymerization. However, there are very limited reports on polymer/nanocomposites prepared by living anionic polymerization. More recently, Padma and coworkers¹² prepared two kinds of POSS/PS and

PMMA block copolymers by living anionic polymerization. The formation of well-defined self-assembled hierarchical nanostructures in bulk and thin films was observed. But up to now, no work has been done to study preparation of PB/POSS nanocomposites by anionic polymerization.

In this work, PB/POSS nanocomposites has been successfully prepared by using butadiene (Bd) and monofunctional POSS with cage structure containing one allylisobutyl and seven isobutyl side groups as comonomers, *n*-BuLi as initiator, cyclohexane as solvent, ETE as structure modifier through anionic polymerization, and the structures of these nanocomposites have been characterized also.

EXPERIMENTAL

Materials and instrumentations

Allylisobutyl POSS (name as A-POSS) and monovinylisobutyl POSS (name as M-POSS) were purchased from Hybrid Plastic, San Diego, California, USA (Scheme 1). POSS was dried under vacuum at 70–80°C for 12 h. A solution of this purified POSS in cyclohexane and 5 Å molecular sieve was injected into a sealed, dried, glass flask of 100 mL. The monomer concentration was 10 wt %. Then the soak period should last for more than 1 week before using to make the moisture content less than 10 ppm.

The Bd and *n*-BuLi were obtained from SINOPEC Beijing Yanshan Petrochemical, Beijing, China. The Bd was used as received (the moisture content was <20 ppm). The concentration of *n*-BuLi was determined by Gilman-Haubei method.¹³

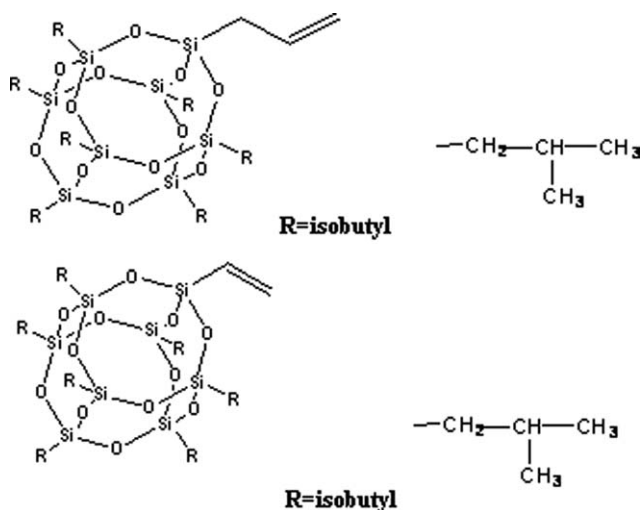
Cyclohexane and tetrahydrofuran (THF) were commercially available. The soak period of 5 Å molecular sieve in cyclohexane lasted for more than 2 weeks before using. So did in THF. Then THF was further distilled from CaH₂ under nitrogen protective atmosphere after refluxing for at least 4–6 h and preserved in the sealed, dried flask.

ETE was synthesized in our laboratory. The reaction equation was as follows (Scheme 2). Please refer to the reference of the specific method.¹⁴

Polymer characterization

¹H NMR and ¹³C NMR spectra were obtained in chloroform-*d* using a Bruker DPX-400 FT-NMR spectrometer. According to the peak area of proton peaks, the content of POSS in the nanocomposites, as well as 1,2-units or 1,4-units content of PB can be calculated. The following Figure 1 is an example.

1,2-units or 1,4-units content of PB can be calculated by the following formula: $N_v = [(A_c + A_d)] / [(A_e + A_f) + (A_c + A_d)/2]$; $N_{c+t} = [(A_e + A_f) - (A_c + A_d)/2] / [(A_e + A_f) + (A_c + A_d)/2]$ (where N_v , N_{c+t}



Scheme 1 The structures of allylisobutyl POSS and monovinylisobutyl POSS.

are 1,2-units, 1,4-units content of PB respectively; A_n , A_c , A_d , A_e , and A_f are the peak areas of Peak n , c , d , e , and f , respectively)

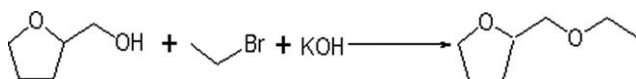
If $A_m = 0$ in the spectra, it indicates that there is no free POSS and it has copolymerized with Bd completely. But if $A_m \neq 0$, it indicates that A-POSS does not copolymerize with Bd completely. As a result, the content of POSS in the nanocomposites is $M = (A_n/14) - A_m$.

Fourier transform infrared analysis was performed using a Nicolet 20DXB spectrometer. Spectra were obtained from films.

Molecular weights and molecular weight distribution (MWD) were characterized by PI-GPC220 using a Waters differential refractometer detector at 40°C. The mobile phase was THF with a flow rate of 1.0 mL/min. Molecular weights were calibrated versus narrow molecular weight polystyrene standards.

Polymerization

The copolymerization was carried out in a 100 mL glass reaction flask. A solution of purified POSS in cyclohexane (The concentration was 10 wt %) and a solution of Bd also in cyclohexane (The concentration was 10 wt %) were mixed and then injected into this sealed, dried glass flask. According to the designed molecular weight of every A-POSS/PB sample which is 70,000 g/mol, the initiator and modifier were added, too. [THF]/[n -BuLi] and [ETE]/[n -BuLi] were mole ratio ([THF]/[n -BuLi] = 30, 50 or [ETE]/[n -BuLi] = 0.5–10). The reaction temperature was con-



Scheme 2 The reaction equation to synthesize ETE.

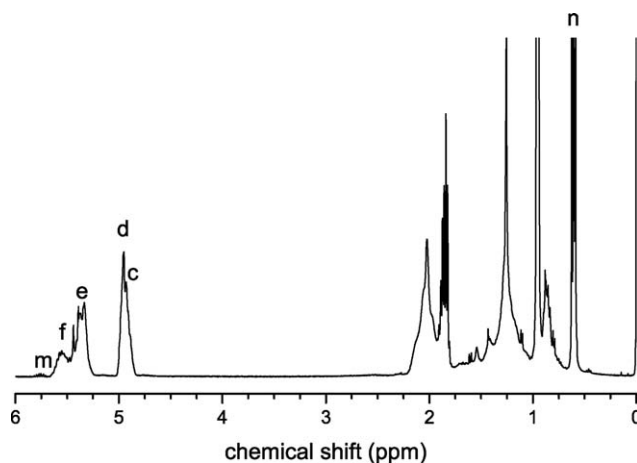


Figure 1 The ^1H NMR Spectra of A-POSS /PB nanocomposites.

trolled by using a 50°C water bath. After 2–3 h for polymerization, the reaction was terminated by the terminator which was isopropanol. The polymers were precipitated in ethanol solution, and then dried under vacuum until a constant weight.

RESULTS AND DISCUSSION

Preparation of PB/POSS nanocomposites

Polymerization

Anionic polymerization requires harsh reaction conditions and synthesis techniques. The polymerization reaction can occur only in the absence of water and oxygen. At present, the polymer-based nanocomposites are prepared by anionic polymerization, and the inorganic nanoparticles are needed to be purified through a complicated procedure before the polymerization. Take the synthesis of polymer/clay nanocomposites for example, a great deal of catalyst (n -BuLi) has been used to purify solution system before copolymerization in order to remove impurities.¹⁵ However, since POSS has well-defined chemical structure and high-class purity, it can apply to anionic polymerization directly without complicated purification.

The experimental results revealed that if the conventional volume of catalyst n -BuLi was added in the solution of POSS and Bd, the polymerization was difficult to carry out, even if raised the temperature (to 70°C) or extended the reaction time (>8 h). The copolymerization could be carried out only if a great deal of catalyst n -BuLi was added. However, the yields and molecular weights were quite low. It indicates that the activity of POSS is so low via anionic initiation that POSS is hard to copolymerize with Bd by changing reaction conditions only.

The polar structure modifier is used to disassociate n -BuLi for anionic polymerization to increase the

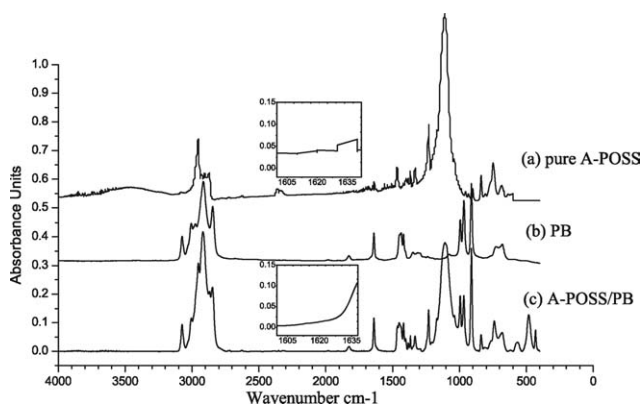


Figure 2 IR spectra of the A-POSS (a); PB (b); A-POSS/PB nanocomposites (c) (A-POSS wt % = 3.49 wt %). The insets are the zoom-in plots of 1635.63 cm^{-1} for the C=C bond before and after copolymerization.

reaction activity of *n*-BuLi and the rate of polymerization. When asymmetrical ether, ETE, was chosen as the structure modifier and was incorporated into the solution of POSS and Bd, the polymerization was observed visibly with a ratio of [ETE]/[*n*-BuLi] was only 0.5. If THF was chosen as the structure modifier, the polymerization could be observed when a ratio of [THF]/[*n*-BuLi] was beyond 30. The results show that during the process of Bd and POSS polymerization, the activity of *n*-BuLi and the rate of polymerization can be raised by the addition of effective structure modifier.

IR spectroscopy

Figure 2 shows the IR spectra of A-POSS, PB, and A-POSS/PB nanocomposites. From Figure 2(a) can be seen that the characteristic absorption peaks of A-POSS are ascribed to 1110.67 cm^{-1} for the Si—O—Si stretching vibration, 1230.89 cm^{-1} for the Si—C bond and 1635.63 cm^{-1} for the C=C bond. Figure 2(b) shows the characteristic absorption peaks for *cis*-1,4-PB at 729.99 cm^{-1} , *trans*-1,4-PB at 966.79 cm^{-1} and 1,2-PB at 911.37 cm^{-1} . In Figure 2(c), all of the characteristic peaks of A-POSS and PB are observed,

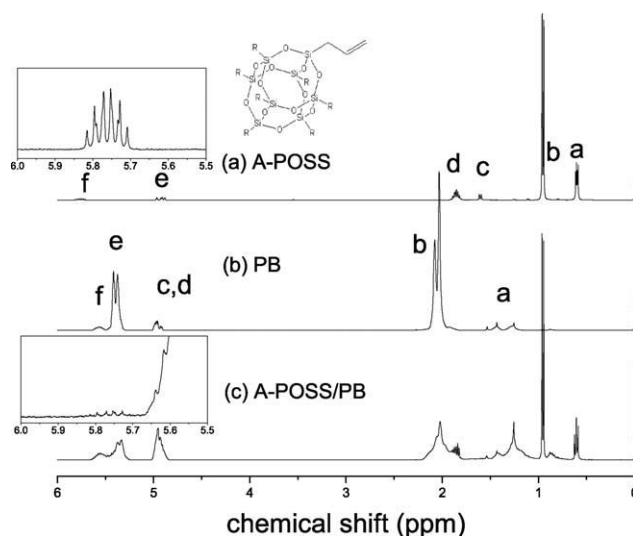


Figure 3 ^1H NMR spectra of the A-POSS (a); PB (b); A-POSS/PB nanocomposites (c) (A-POSS wt % = 3.05 wt %). The insets are the zoom-in plots of Peak f before and after copolymerization.

indicating that the polymerization of butadiene occurred at existence of POSS.

^1H NMR characterization

The ^1H NMR spectra of PB, POSS, and A-POSS/PB nanocomposites are shown in Figure 3. The assignments of peaks are listed in Table I.

Whether the copolymerization of POSS and PB has been carried out, it can be indicated by the ^1H NMR spectra. However, the characteristic peaks of =CH_2 (Peak e) which is the terminal group of A-POSS are covered by the characteristic peaks of 1,2-units (Peaks c, d) in PB. As a result, we should choose multi-peaks corresponding to the —CH= of the allylisobutyl group in POSS to analyze whether the copolymerization between POSS and PB occurs rather than the chemical shifts from 4.89 ppm to 4.96 ppm. Figure 3(c) indicates that 5.7–5.8 ppm multi-peaks of —CH= nearly disappeared, which suggests that POSS and Bd are successfully copolymerized.

TABLE I
Assignment of the Peaks in the ^1H NMR Spectra of A-POSS, PB, and A-POSS/PB Nanocomposites

Peak	(a) A-POSS					
	a	b	c	d	e	f
Chemical Shift (ppm)	0.59–0.61	0.95–0.96	1.60–1.61	1.8–1.9	4.89–4.96	5.7–5.8
Assignment	$\text{—CH}_2\text{—}$ of isobutyl group	—CH_3 of isobutyl group	$\text{—CH}_2\text{—}$ of allyl group)CH— of isobutyl group	=CH_2 of allyl group	—CH= of allyl group
Peak	(b) PB					
	1,2-units			1,4-units		
Chemical Shift (ppm)	a	b	c, d	f	b	e
Assignment	1.26, 1.43, 1.53	2.1	4.9–5.0	5.3–5.4	2.03, 2.08	5.5–5.6
	$\text{—CH}_2\text{—}$)CH—	$\text{CH}_2\text{=}$	=CH—	$\text{—CH}_2\text{—}$	—CH=

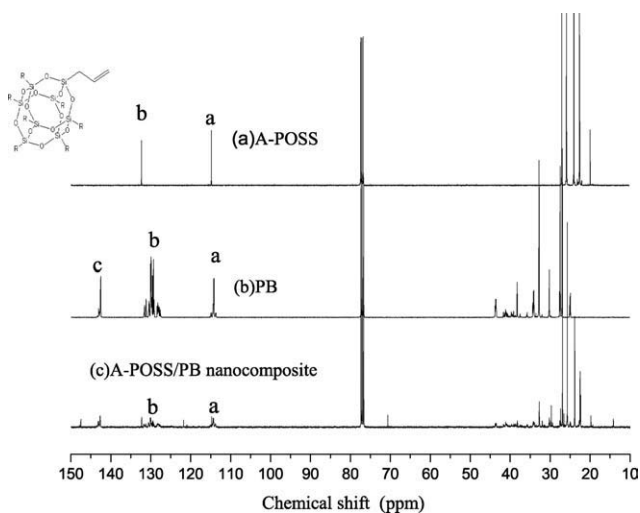


Figure 4 ^{13}C NMR spectra of the A-POSS (a); PB (b); A-POSS /PB nanocomposites (c) (A-POSS wt % = 8.89 wt %).

Furthermore, we also used ^{13}C NMR spectra to study on the polymerization between POSS and Bd. The ^{13}C NMR spectra of PB, POSS, and POSS/PB nanocomposites are shown in Figure 4. As seen from Figure 4(a), the characteristic peaks of A-POSS at 114.77 ppm and 132.28 ppm correspond to the $=\text{CH}_2$ for allyl (Peak a) and $-\text{C}=\text{C}$ (Peak b). Figure 4(b) shows that the characteristic peaks of PB at 114.23–114.41 ppm and 127.69–131.71 ppm correspond to the $=\text{CH}_2$ of 1,2-PB (Peak a) and $-\text{C}=\text{C}$ of 1,4-PB (Peak b). The significant decreases in the intensity of characteristic peaks are observed after the polymerization [Fig. 4(c)], indicating that the copolymerization of A-POSS and Bd carried out. This result is in accord with the ^1H NMR spectra.

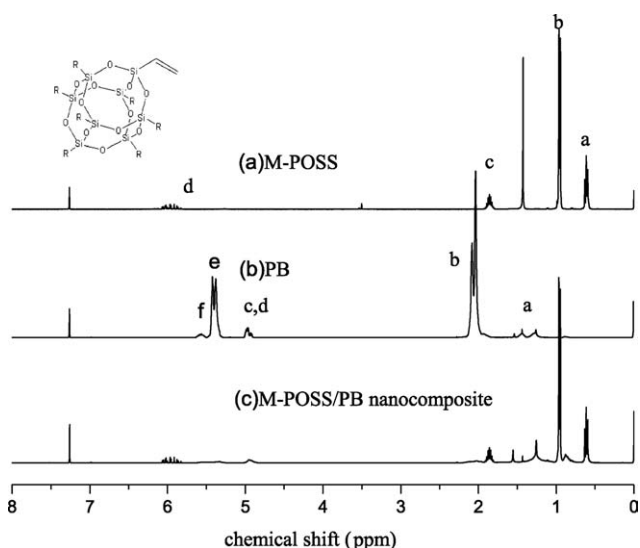


Figure 5 ^1H NMR spectra of the M-POSS (a); PB (b); M-POSS/PB nanocomposites (c) (M-POSS% = 4.27 wt %).

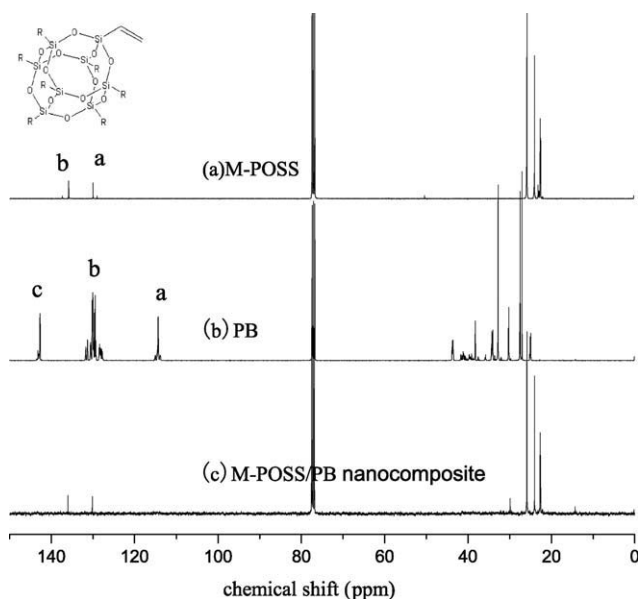


Figure 6 ^{13}C NMR spectra of the M-POSS (a); PB (b); M-POSS/PB nanocomposites (c) (M-POSS% = 4.27 wt %).

Under the same conditions, we also did some researches on the copolymerization between M-POSS and Bd. The ^1H NMR spectrum and ^{13}C NMR spectrum of M-POSS, PB and M-POSS/PB nanocomposites are shown in Figure 5 and 6.

It can be seen from Figure 5(a,c) that the chemical shifts in the range of 5.9–6.1 ppm (Peak d) corresponding to $-\text{CH}_2=\text{CH}_2$ of M-POSS still exist after the polymerization and the intensity of these peaks do not change. The characteristic peaks of PB at 4.9–5.0, 5.3–5.4, and 5.5–5.6 ppm corresponding to the 1,2-PB (Peaks c, d, f) and 1,4-PB (Peak e) almost do not appear after polymerization. It can also be seen from Figure 6(a,c) that the characteristic peaks at 129.93 ppm (Peak a) and 135.81 ppm (Peak b) correspond to $=\text{CH}_2$ and $-\text{CH}=\text{C}$ of M-POSS. The peak intensity does not change before or after polymerization. Moreover, the characteristic peaks at 114.23–114.41, 142.18–142.64, and 127.69–131.71 ppm corresponding to $=\text{CH}_2$ (Peak a) of 1,2-units, $=\text{CH}-$ (Peak c) of 1,2-units and $-\text{CH}=\text{C}$ (Peak b) of 1,4-units in PB do not appear after polymerization. It indicates that the copolymerization between M-POSS and Bd does not carry out.

By comparing the structure of A-POSS and M-POSS, it is clear that the allyl group of A-POSS has certainly more flexibility than vinyl of M-POSS. Because of the vinyl group and M-POSS large dimensional size, the steric effect of M-POSS is increased considerably. Thus it impedes the copolymerization of M-POSS with Bd. Obviously, the chain flexibility of the reactive groups of POSS monomer is a key factor affecting the polymerization. Consequently, based on the above results of different POSS, only the A-POSS is chosen to incorporate into Bd solution in the following researches.

TABLE II
The Microstructures of Copolymers at Different Contents of POSS

Sample	A-POSS (wt %)	1,2-PB (wt %)	1,4-PB (wt %)
1	0	7.38	92.62
2	0.38	10.18	89.82
3	1.03	10.44	89.56
4	1.65	11.76	88.24
5	3.57	12.63	87.37
6	5.38	15.90	84.10

Structure of A-POSS/PB nanocomposites

The microstructure of polymer is an important factor affecting the material properties. This article puts emphasis on two critical factors which affect the microstructure of A-POSS/PB. They are the A-POSS content and the structure modifier.

Effect of the A-POSS content

Effect of different A-POSS contents on the microstructure of A-POSS/PB without adding the structure modifier is listed in Table II.

The results show that 1,2-units content of PB is only 7.38 wt % without incorporating A-POSS; 1,2-units content of PB increases remarkably when a little A-POSS is incorporated (Samples 2–4) and 1,2-units content increases with the increasing content of A-POSS. Up to 5.38 wt % of A-POSS (Sample 6), 1,2-units content is 15.90 wt %, twice as much as that of the pure PB. This finding first indicates that the incorporation of POSS influences the polymerization mechanism and changes the microstructure of polymers. It implies that the A-POSS has played the role of polar modifier which could increase 1,2-units con-

tent. Herein, we speculate that the interaction of POSS and Li^+ makes the end of active chain produce delocalized π -allyl structure. Therefore, the 1,2-units content increases (Scheme 3).

Effect of the structure modifier

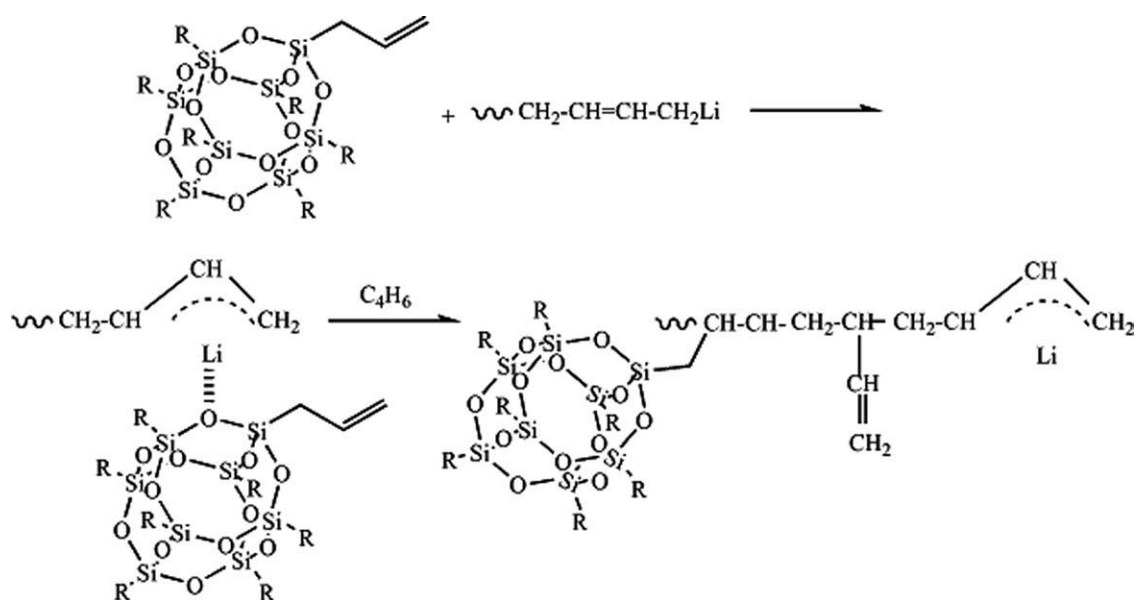
In the anionic polymerization, the addition of polar structure modifier does not only raise the rate of polymerization, but also increases the 1,2-units content of PB. Well, when POSS is incorporated, how will the 1,2-units content of PB change? How do both the modifier and POSS have influence on 1,2-units content? New changes of 1,2-units content were observed. The results are shown in Table III.

As listed in Table III, when $[\text{ETE}]/[n\text{-BuLi}]$ is 0.5 without any POSS, 1,2-units content increases significantly from 7.39 to 44.40 wt %. It indicates that ETE has strong ability to modify the structure. With the increasing content of ETE continuously, 1,2-units content increases slowly (Samples 2 and 3).

When a little POSS (Samples 4 and 7 vs Samples 2 and 3) has been added, the content of 1,2-units continues to increase remarkably, and 1,2-units content of all samples are over 50 wt %. With increasing the content of A-POSS (Samples 5–6 and 8), 1,2-units content is still rising. It reveals that A-POSS can affect the microstructure of PB evidently when ETE exists.

The effect of structure modifier content on the microstructure of PB was investigated when the A-POSS content was 2–3 wt %. The results are shown in Table IV.

The results from Table IV show that the 1,2-units content of PB increases more evidently with the



Scheme 3 Copolymerization Mechanism of Bd and A-POSS.

TABLE III
Effect of ETE on the Microstructures of PB and A-POSS/PB

Sample	[ETE]/[<i>n</i> -BuLi]	A-POSS (wt %)	1,2-PB (wt %)	1,4-PB (wt %)
0	0	3.57	12.63	87.37
1	0	0	7.39	92.62
2	0.5	0	44.40	55.60
3	1.0	0	46.60	53.40
4	0.5	2.16	51.22	48.78
5	0.5	3.06	55.92	44.08
6	0.5	5.93	60.56	39.44
7	1.0	1.98	66.69	33.31
8	1.0	3.14	70.58	29.42

increasing content of ETE. Especially, when [ETE]/[*n*-BuLi] is 1.0, 1,2-units content of PB raises to above 70 wt %. When [ETE]/[*n*-BuLi] exceeds 1.0, 1,2-units content increases slowly. From these results it is easy to think that the increasing content of 1,2-units may be mainly affected by ETE.

As seen from Table III, it is prone to draw a conclusion. The addition of 3.57 wt % POSS without ETE shows 5.24 wt % increase in 1,2-units content of PB (Sample 0) as compared with the pure PB (Sample 1). When the ETE is added and the content of ETE is controlled as the same, 1,2-units content of PB increases significantly with increasing the content of A-POSS (Samples 4–6) compared with the sample without any POSS (Sample 2). When [ETE]/[*n*-BuLi] is 1.0, there are more great differences between 1,2-units contents of PB (Samples 3, 7, and 8). All these results confirm that POSS has an effective ability to modify the microstructure of PB, especially when A-POSS and the structure modifier coexist. The ability to modify the microstructure is more effective than only one modifier existed. These two display excellent cooperative effect modifying the microstructure of PB.

As a comparison, another structure modifier THF was used for A-POSS/PB nanocomposites, the results are listed in Table V.

Comparing Table V with Table III, there are great differences between the ability of THF and ETE to

TABLE IV
The Microstructures of A-POSS/PB Nanocomposites at Different [ETE]/[*n*-BuLi] Ratio

Sample	[ETE]/[<i>n</i> -BuLi]	A-POSS (wt %)	1,2-PB (wt %)	1,4-PB (wt %)
1	0	3.57	12.63	87.37
2	0.5	3.06	55.92	44.08
3	1	3.14	70.58	29.42
4	2	3.20	76.61	23.39
5	5	1.92	79.97	20.03
6	10	2.15	81.22	18.78

TABLE V
Effect of THF on the Microstructures of PB and A-POSS/PB

Sample	[THF]/[<i>n</i> -BuLi]	A-POSS (wt %)	1,2-PB (wt %)	1,4-PB (wt %)
1	0	0	7.38	92.62
2	30	0	11.42	88.58
3	50	0	49.17	50.83
4	30	8.89	46.25	53.75
5	50	13.19	61.36	38.64

modify microstructure of PB. For ETE, when [ETE]/[*n*-BuLi] is 0.5, the 1,2-units content of PB increases by more than 6 times (Table III). For THF, when [THF]/[*n*-BuLi] is 50, 1,2-units content of PB could only increase by about 6 times (Table IV). It indicates that ETE has more effective ability to modify microstructure of PB than THF. Since ETE has one more oxygen atom than THF, it has higher polarity and stronger ability to complex with active centers of *n*-BuLi than THF. This can promote dissociation of more active centers. Due to the structure differences between THF and ETE, ETE reveals a stronger ability to modify the rate of polymerization and microstructure of polymer.

Similarly, the results from Table V also show that under the same ratio of [THF]/[*n*-BuLi], the 1,2-units content of PB increases with the addition of A-POSS (Samples 2 and 3 via Samples 4 and 5) and the degree of increase is more evident. It also further demonstrates that POSS has the ability of modifying the microstructure, and both A-POSS and the modifier display the wonderful cooperative effect modifying the microstructure of PB.

Molecular weights and MWD of A-POSS/PB nanocomposites

The molecular weights and PDI of A-POSS/PB nanocomposites are listed Table VI. The gel permeation chromatography (GPC) curves are shown in Figure 7.

The results from Table VI indicate that the molecular weights of A-POSS/PB nanocomposites decrease and the PDI becomes wider, and the

TABLE VI
Effect of A-POSS Contents on M_n and PDI of the Copolymers

Sample	[ETE]/[<i>n</i> -BuLi]	A-POSS (wt %)	$M_n \times 10^4$ (g/mol ⁻¹)	PDI
1	0.5	0	6.70	1.09
2	0.5	1.71	1.79	1.35
3	0.5	2.97	1.84	1.44
4	0.5	3.06	1.84	1.45
5	0.5	5.75	2.21	1.42

corresponding values are in the range 1.35–1.45. This observation was reported in literatures,^{15,16} which used coordination polymerization to prepare the nanocomposites. In these reports,¹⁷ dichloro[*rac*-ethylenebis-(indenyl)]zirconium /MAO (methylaluminoxane) was used as the catalyst to prepare PP/norbornylene-substituted POSS nanocomposites. With the increasing of POSS content, considerable decreases in molecular weights were observed. Coughlin considered that the observed decreases could be attributed to the coordination polymerization mechanism. On the basis of these reports, we suggest that during copolymerization of Bd and A-POSS by using the mechanism of anionic polymerization, however, because of the presence of very bulky A-POSS and possible polar interaction between the oxygen atom of the POSS cage and Li⁺, it leads to the low reactive activity of A-POSS. However, even if A-POSS has been initiated, due to the steric effect of A-POSS, the activity of anionic center is decreased remarkably and the propagation rate is much slower than that for Bd. Wider PDI indicates that there are differences between the process of chain initiation and chain propagation, that is to say, chain initiation becomes too slow and occurs on a too long period of time with a clear impact on PDI. Since A-POSS has steric hindrance when copolymerized with Bd via anionic polymerization mechanism, it results in differences among the rate of copolymerization, molecular weights, and PDI.

Effect of different contents of ETE on the molecular weights and PDI of nanocomposites are shown in Table VII. The molecular weights data from Table VII show the increasing trend with adding ETE and the trend is much more significant when the ETE content increases gradually. The results reveal that the addition of ETE could increase the initiative activity of copolymerization.

In addition, as seen in Figure 7, besides the corresponding peaks of PB, there is a small peak near the

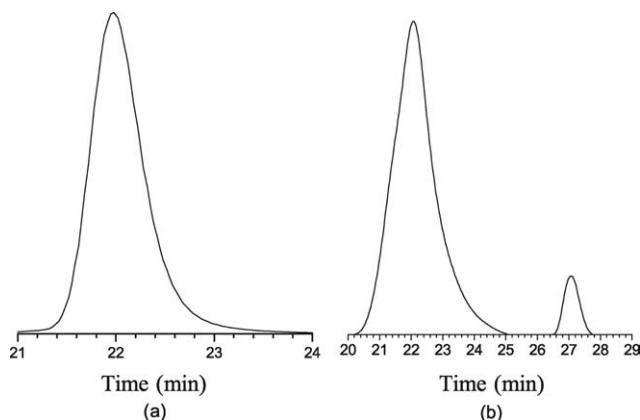


Figure 7 GPC curves of PB (a); A-POSS/PB nanocomposites (b) (A-POSS wt % = 3.14 wt %).

TABLE VII
Effect of Different ETE Amounts on M_n and PDI of the Copolymers

Sample	[ETE]/ [<i>n</i> -BuLi]	A-POSS (wt %)	$M_n \times 10^{-4}$ (g/mol ⁻¹)	PDI
1	0.5	3.06	1.84	1.45
2	1	3.14	1.2	1.53
3	2	1.89	2.69	1.35
4	5	1.92	2.99	1.46
5	10	2.14	3.56	1.46

retention time of 27 min. According to the peak time and molecular weights, we speculate that some polymer with low molecular weights may be created during the polymerization, which needs to be investigated in further research.

CONCLUSIONS

PB/A-POSS nanocomposites were successfully prepared by using *n*-BuLi as initiator, cyclohexane as solvent, ethyltetrahydrofurfuryl ether (ETE) as structure modifier through the anionic polymerization technique. Under conventional conditions, *n*-BuLi could not initiate the copolymerization between A-POSS and Bd, even if raising the temperature and reaction time. The ¹H NMR spectra and ¹³C NMR spectra indicates that only when the structure modifier (THF or ETE) was added, *n*-BuLi could initiate the copolymerization of A-POSS and Bd. However, under the same condition, *n*-BuLi could not initiate the copolymerization of M-POSS and Bd. These results reveal that the chain flexibility of the reactive groups of POSS monomer affects the polymerization significantly. The results of investigation on the structure modifiers (THF and ETE) show that ETE had more effective ability to modify microstructure and the rate of polymerization than THF. The 1,2-units content of PB increased with the addition of A-POSS and the degree of increase was more evident with the increasing content of POSS. It also further demonstrates that POSS has the ability of modifying the microstructure, and both A-POSS and the modifier display the wonderful cooperative effect modifying the 1,2-units content of PB. GPC chromatograph indicates that with the addition of POSS, the molecular weights of nanocomposites decreased evidently and the PDI became wider.

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