

Star-Shaped POSS–Methacrylate Copolymers with Phenyl–Triazole as Terminal Groups, Synthesis, and the Pyrolysis Analysis

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ABSTRACT: Star-shaped polyhedral oligomeric silsesquioxane (POSS)–methacrylate hybrid copolymers with phenyl–triazole as terminal groups had been designed and synthesized via sequential atom transfer radical polymerization (ATRP), azidation, and phenylacetylene-terminated procedures, and the hybrid copolymers here could be denoted as POSS–(PXMA–Pytl)₈, where X can be M, B, L, and S, represented four different methacrylate monomers, such as methacrylate (MMA), butyl methacrylate (BMA), lauryl methacrylate (LMA), and stearyl methacrylate (SMA), respectively. Thermal gravimetric analysis (TGA) and *in situ* Fourier transform infrared spectroscopy (FTIR) were applied for studying the thermal stability and degradation mechanism, and it was found that all of the POSS–(PXMA–Cl)₈ and POSS–(PXMA–Pytl)₈ copolymers exhibited excellent thermal stabilities, which had great potential in heat-resistant material application. Different tendencies of decomposition temperatures at 5% and 10% weight loss (T_5 and T_{10}) dependent on the side-chain length and terminal group species were investigated respectively. The longer alkyl side chains of the monomers, the lower thermal stabilities, and enhanced T_5 and T_{10} were also shown with the introduction of phenyl–triazole groups instead of chlorine groups. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40652.

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INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) are typical molecules that are considered as nano forms of silica, and in their most common form ($\text{Si}_8\text{O}_{12}\text{R}_8$) comprise a high symmetrical cube-octameric cage of eight silicon-corner atoms and twelve oxygen-edge atoms. Each of the eight silicon atoms may externally bind organic substituents that can be specially designed to be nonreactive or reactive, such as hydrogen, any of alkyl, alkylene, aryl, arylene, and organofunctional derivatives, therefore generating hundreds of possible hybrid materials.^{1–4} The incorporation of the POSS nanocluster cages into polymeric materials (e.g., polyolefin/POSS copolymers, polystyrene/POSS copolymers, poly(acrylate)/POSS copolymers, poly(ethylene oxide)/POSS nanocomposites, and polyester/POSS nanocomposites) can result in dramatic improvements in polymer properties, including temperature and oxidation resistance, surface hardening, and reductions in flammability. Therefore, researches on POSS hybrid polymers and copolymers have attracted great attention recently.

Several studies have reported that POSS has excellent heat resistance due to its polyhedral inorganic framework.⁵ When temperature rises to the critical value, the initial POSS silicon–oxygen framework is retained only during the initial stages of pyrolysis (approximately up to 500°C).⁶ POSS molecules contain organic substituents on their outer surfaces, which make them compatible with most polymers, thus introducing POSS components into polymer materials; the above advantages of POSS will be exerted to the polymer materials, hence a complementary material with molecular scale dispersion can be obtained.⁷ In addition, the POSS species have dimensions similar to those of polymer chain segments; together with the strong interaction between POSS and monomer species that existed, they may restrict motion at the molecular level, which finally results in an increasing thermal property of the hybrid nanocomposites,^{8,9} thus increasing glass transition temperature (T_g) and the decomposition temperature (T_d).^{10,11} The increases in the thermal stabilities of polymers induced by the incorporation of POSS moieties into the polymers have also been reported in other studies.^{4,12}

Here, a class of hybrid polymers with star-shaped topological structure is worth to mention. Star-like nanocomposites with POSS as the core are generally prepared using functional POSS as the micro-initiator, and exhibit enhanced comprehensive properties especially for thermal stability.^{13–16} Meanwhile, compared with the corresponding linear polymers of similar molecular weight, obtained star-shaped polymers usually exhibit higher segments mobility as a result of a decreasing interaction between polymer chains, thus lower viscosities.¹⁷ For the synthesis of these star-shaped polymers, the “core-first” method is often used, where an active multifunctional POSS core works as the initiator for polymer chain growth.^{18–24} Chen *et al.*²⁵ synthesized a series of star-like light-emitting materials by hydrosilylation of the POSS, and obtained polymers exhibited enhanced T_d temperatures.

To date, atomic transfer radical polymerization (ATRP) is used for the synthesis of well-defined star polymers with precise arm numbers and lengths. Kim *et al.*²⁶ prepared a series of organic/inorganic hybrid star-shaped polymers, using 3-(3,5,7,9,11,13,15-heptacyclohexyl-pentacyclo-octasiloxane-1-yl) propyl methacrylate (MA-POSS) and poly (ethylene glycol) methyl ether methacrylate (PEGMA) as monomers and octakis (2-bromo-2-methylpropionoxypropyldimethylsiloxy) octasilsesquioxane as an ATRP initiator, and thermal stability enhancement of polymers induced by the incorporation of POSS moieties into the hybrid polymers has also been reported. Hussain *et al.*²⁷ synthesized hybrid fluorinated star polymers by ATRP of 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA) in trifluorotoluene using octa (aminophenyl) silsesquioxane (OAPS) nano-cage as initiator, and obtained polymers exhibited more thermally stable compared with the linear poly (PTFBMA).

However, the polymers prepared through ATRP are usually terminated with halogen groups, which were easier to pyrolysis as temperature rises, and volatile products including monomers and low molecular weight polymers (such as dimer, trimer, etc.) will be obtained after depolymerization.²⁸ To decrease this adverse effects on thermal stability, various efforts have been made. Schmalz and Reinicke designed to replace the terminal halogen of the ATRP-derived polymer with azide and the subsequent click reaction by alkynyl compounds, which confirmed effectively.²⁹

In this article, POSS-(Cl)₈ with the ability to initiate polymerizations^{30–32} was firstly synthesized by hydrolysis and condensation of 3-chloropropyl trimethoxysilane as reported.³³ Using it as ATRP initiator, star-shaped chlorine-terminated POSS-methacrylate polymers (POSS-(PXMA-Cl)₈) were synthesized. These comprise POSS-poly(methyl methacrylate) (POSS-(PMMA-Cl)₈), POSS-poly(butyl methacrylate) (POSS-(PBMA-Cl)₈), POSS-poly(lauryl methacrylate) (POSS-(PLMA-Cl)₈), and POSS-poly(stearyl methacrylate) (POSS-(PSMA-Cl)₈). All intermediate products and the final star-shaped POSS-methacrylate copolymers were chemically characterized. For improving thermal stabilities of POSS-(PXMA-Cl)₈ copolymers, sodium azide and then phenylacetylene were used to exchange the terminal groups, which finally achieved the formation of a series

phenyl-triazole-terminated POSS-methacrylate polymers (POSS-(PXMA-Pytl)₈). With the help of TGA and *in situ* Fourier transform infrared spectroscopy (FTIR), the thermal stability and further degradation mechanism were investigated, and the thermal dependences on side length and terminal groups were mainly discussed.

EXPERIMENTAL

Materials

3-Chloropropyltrimethoxysilane was purchased from Nanjing forward chemical (Industrial grade, content $\geq 99\%$, density: 1.0770 ± 0.0050 g/cm³) and used as received. Methyl methacrylate (MMA) and butyl methacrylate (BMA) were obtained from Tianjin Fuyu fine chemistry and lauryl methacrylate (LMA) and stearyl methacrylate (SMA) were purchased from Aladdin reagent. They were all washed with an aqueous solution of sodium hydroxide (5 wt %) for three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate overnight MMA, BMA, LMA, and SMA were distilled under reduced pressure, and stored in refrigerator prior to use. Cuprous chloride (CuCl) obtained from Tianjin BASF Chemical Reagents was purified in acetic acid, washed with ethanol, and dried under vacuum. *N,N,N',N',N''*-Pentamethyl diethylenetriamine (PMDETA), phenylacetylene, and sodium azide (NaN₃) were purchased from Aladdin reagent and used as received. All of the other reagents used were of analytical purity and used as received.

Synthesis of POSS-(Cl)₈

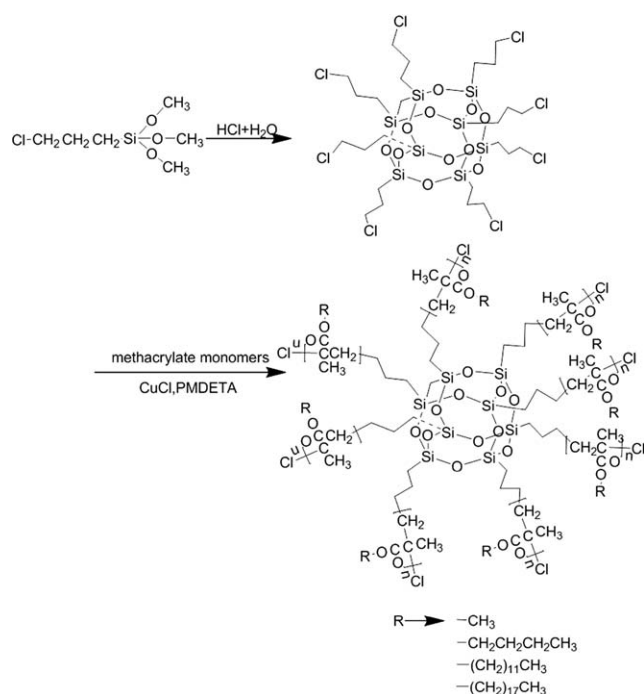
POSS-(Cl)₈ was synthesized by the following method described by Dittmar.³² Methanol (200 mL), 3-chloropropyltrimethoxysilane (10 mL), and concentrated hydrochloric acid (8 mL) were mixed in a 500 mL round-bottomed flask, and reacted in an oil bath at 40°C for 5 days under rapid stirring to completely hydrolysis and condensation. The product was washed several times with methanol, and white powder was obtained after drying in vacuo at 40°C for 24 h.

Synthesis of POSS-(PXMA-Cl)₈

In this part, four different POSS-(PXMA-Cl)₈ macroinitiators were accomplished under nitrogen atmosphere through a typical ATRP process (Scheme 1). The synthesis procedures were carried out using -CH₂CH₂CH₂Cl bonded on POSS cage as ATRP initiation groups, and CuCl/PMDETA as the catalytic system.

In a typical run, the flask in ice bath was first flushed with dry nitrogen to remove oxygen and then POSS-(Cl)₈ (0.2 g), PMDETA (0.12 mL), MMA (20 mL), toluene (20 mL), and CuCl (0.02 g) were added in this order into the flask equipped with magnetic stir bar. The system was evacuated three times, filled with dry nitrogen, and placed in an oil bath warmed at 110°C. After 48 h, the polymerization was terminated by cooling the flask in ice water. Then the mixture was diluted with tetrahydrofuran (THF), filtered over alumina column to remove the catalyst, and precipitated in tenfold methanol-water solution. The collected polymer was dried in vacuum oven at 40°C for 24 h.

For different methacrylate monomers of BMA, LMA, and SMA, the polymerization process, the purification method, and the after treatment were the same as POSS-(PMMA-Cl)₈ polymers.



Scheme 1. Synthetic route of star-shaped POSS-(PXMA-Cl)₈ copolymers.

Synthesis of POSS-(PXMA-N₃)₈

General procedures employed for the preparation of α -diazido-terminated POSS-methacrylate polymers, denoted by POSS-(PXMA-N₃)₈, were as follows (Scheme 2).³⁴ POSS-(PXMA-Cl)₈ (0.15 mmol), THF (15 mL), and NaN₃ (0.325 g) were added into a 100-mL round-bottomed flask, and the reaction mixture was allowed to stir at 30°C for 24 h. Then, the solution was concentrated and precipitated by pouring into a large amount of deionized water. The collected product was further dried at 40°C in a vacuum oven for 24 h.

Synthesis of POSS-(PXMA-Pytl)₈

Phenylacetylene was often used to react with α -diazido-terminated copolymers, that is, “click chemistry” was carried out

to afford organic-inorganic hybrid copolymers (Scheme 3).³⁴ In a typical experiment, the inclusion complexes of POSS-(PXMA-N₃)₈ (1.5 g) with phenylacetylene (0.33 mL) and toluene (20 mL) were charged to a 100-mL flask equipped with a magnetic stirrer. The system was purged with high-purity nitrogen for 40 min and then CuCl (0.01 g) and PMDETA (0.08 mL) were added into the flask. The flask was degassed by means of three freeze-pump-thaw cycles to fill with nitrogen, and then immersed in an oil bath. After being stirred at room temperature for 48 h, the solution was concentrated, precipitated in methanol, and filtered. The product was further dried at 40°C in a vacuum oven for 24 h.

Characterization

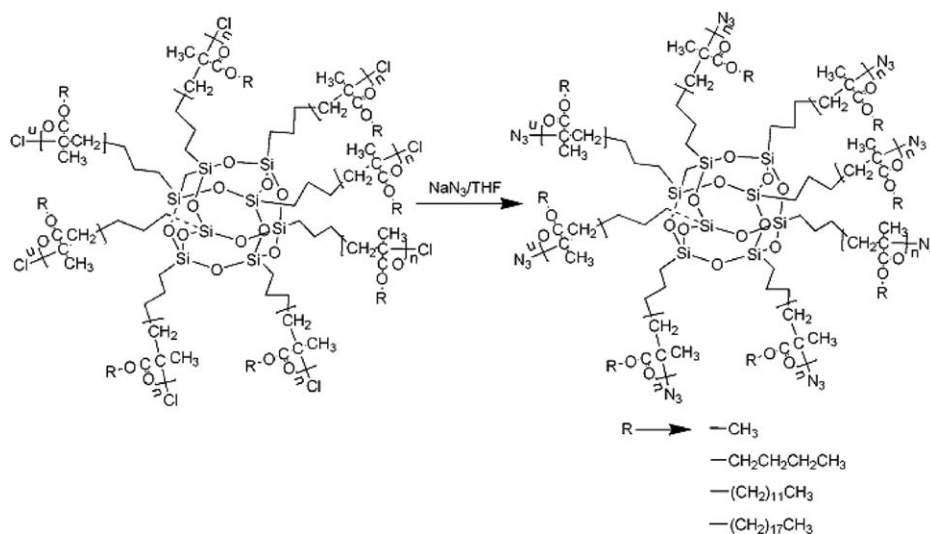
FTIR were recorded from the coating method of WQF-310 spectrometer. The spectra were collected at 32 scans with a spectral resolution of 4 cm⁻¹.

¹H, ¹³C, ²⁹Si nuclear magnetic resonance spectroscopy (NMR) measurements were carried out on a Bruker AVANCF-300 instrument with tetramethylsilane (TMS) as an internal reference. Deuterated chloroform (CDCl₃) was used as the solvent for all the samples for NMR measurement.

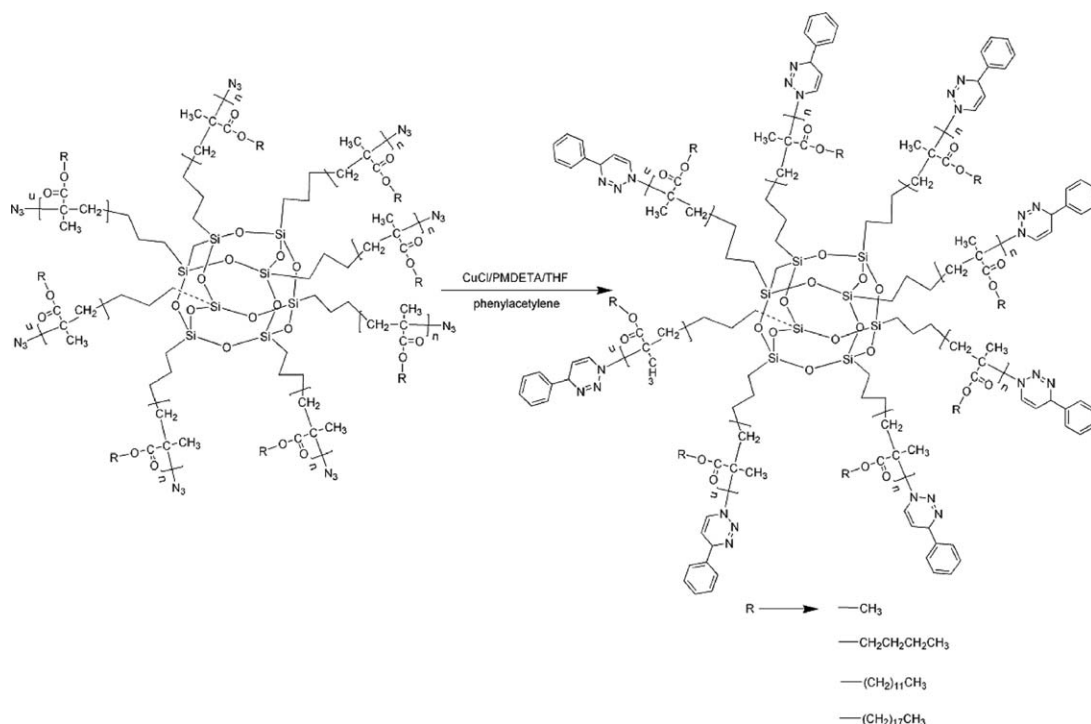
Molecular weights and polydispersity (M_w/M_n) of copolymers were determined on DIONEX BJ/U3000 gel permeation chromatograph (GPC), with Shodex OHPak SB-803 HQ (300 × 8 mm), as chromatographic column. It was carried out at 298 K with THF as solvent (0.5 mL/min) and polystyrene as calibration standard.

Thermal gravimetric analysis (TGA) was performed with a TGA Q600 SDT thermal analyzer at a heating rate of 20°C min⁻¹ under a nitrogen atmosphere, and the temperature ranged from room temperature to 600°C.

In situ FTIR was recorded on Thermo-Fisher NEXUS870 spectrometer, with a temperature reaction cell from Xia Men University. In this test, 0.7 mg sample was needed, after been mixed with 150 mg KBr powder and pressed; a transparent or even translucent pellet was obtained, with a diameter of 13 mm and thickness of 1 mm. Then, the pellet was put into the



Scheme 2. Synthetic route of star-shaped POSS-(PXMA-N₃)₈ copolymers.



Scheme 3. Synthetic route of star-shaped POSS-(PXMA-Pytl)₈ copolymers.

temperature reaction cell and prepared to be tested. Temperature range for this article was from 25°C to 465°C at a heating rate of 10°C·min⁻¹. In all cases, 8 scans at a resolution of 4 cm⁻¹ were used to record the spectra.

RESULTS AND DISCUSSION

Synthesis of POSS-Methacrylate Polymers

According to Dittmar,³² POSS-(Cl)₈ with complete cage structure and eight reactive groups was first synthesized by the hydrolysis and condensation process. Using it as the initiator, four methacrylate monomers (MMA, PBMA, PLMA, PSMA) with different side-chain lengths were added to ATRP polymerization of POSS-(PXMA-Cl)₈, as shown in Scheme 1.

In this procedure, eight terminal chlorines of POSS-(Cl)₈ acted as active points for ATRP polymerization to form star-shaped POSS-(PXMA-Cl)₈ polymers, and still existed in the terminal of each

arm of the polymers after reaction, which might easily decompose thermally and thus affect thermal stability negatively.^{28,35} Therefore, POSS-(PXMA-N₃)₈ and further POSS-(PXMA-Pytl)₈ were designed and produced through a click chemistry according to the following procedure: The terminal chlorine in hybrid macromolecule was first replaced by azide group, then end-capped by phenylacetylene via “click chemistry.” The synthetic routes were described in Schemes 2 and 3. The final POSS-(PXMA-Pytl)₈ polymers are predicted to exhibit excellent thermal stability due to the higher thermal stability of the phenyl-triazole groups.

The spatial structure of POSS-based hybrid macromolecule is the key for this kind of star-shaped polymer; therefore, whether spatial cage core of POSS is perfect should be tested at first. Here NMR spectra, as a common and effective technique for chemical structure characterization,^{2,36} was applied for the study of POSS-(Cl)₈ and the relevant results were shown in Figure 1.

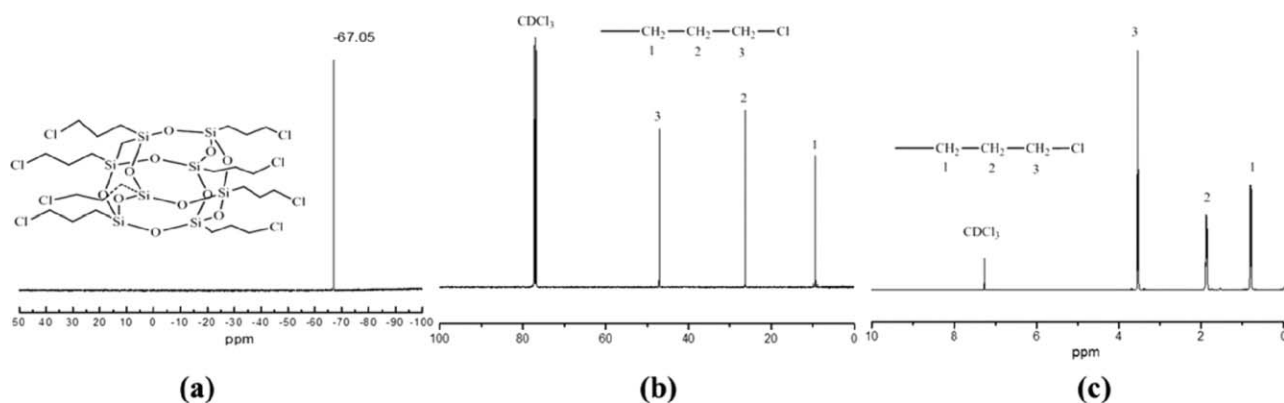


Figure 1. (a) ²⁹Si NMR, (b) ¹³C NMR, (c) ¹H NMR spectra of POSS-(Cl)₈.

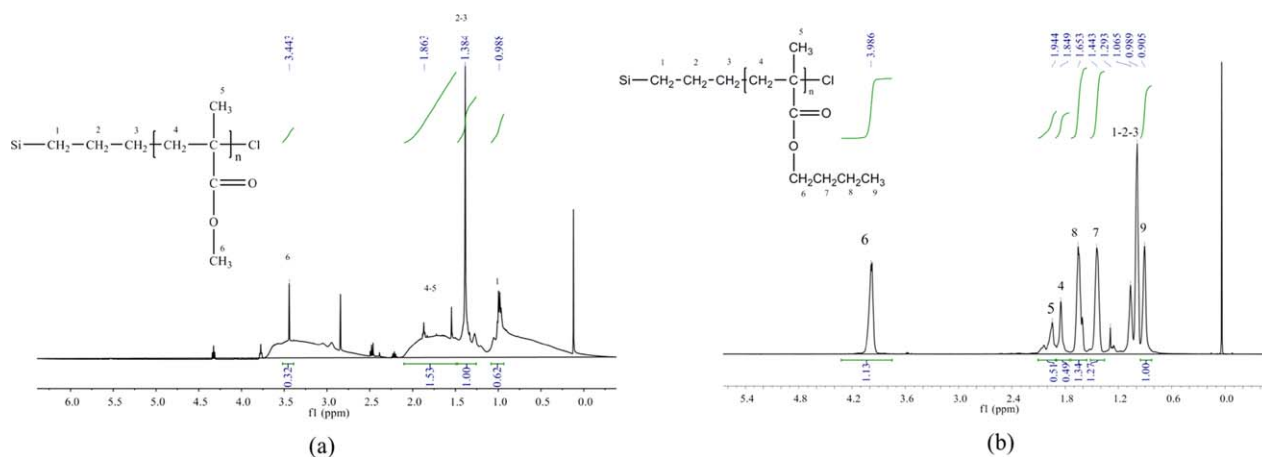


Figure 2. ^1H NMR of (a) POSS-(PMMA-Cl) $_8$ and (b) POSS-(PBMA-Cl) $_8$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

There was only one single resonance at -67.05 ppm in the ^{29}Si spectrum, which indicated that the eight silicon atoms were magnetically equivalent. The resonance that appeared in the range -50 ppm to -80 ppm was assigned to the chemical environment of T-type silanol silicon, which confirmed that each silicon atom connected with three oxygen atoms and one carbon atom; therefore, the POSS-(Cl) $_8$ with cube octameric framework was successfully synthesized. Figure 1(b,c) showed the ^{13}C NMR and ^1H NMR spectra of POSS-(Cl) $_8$, and the concrete data as follows: ^{13}C NMR (CDCl_3 , 126 MHz, δ): 9.363 ppm ($\text{Si}-\text{CH}_2$), 26.274 ppm ($\text{Cl}-\text{CH}_2-\text{CH}_2$), 47.033 ppm ($\text{Cl}-\text{CH}_2$); ^1H NMR (CDCl_3 , 500 MHz, δ): $-\text{CH}_2\text{Si}$ ($\delta=0.80$ ppm), $-\text{CH}_2\text{C}$ ($\delta=1.87$ ppm), ClCH_2 ($\delta=3.54$ ppm), due to the mutual coupling effect of different hydrogen on $-\text{CH}_2$, multiple peaks were observed. Of note was that the resonance integral ratio of 0.8 ppm, 1.87 ppm, and 3.54 ppm was about 1:1:1. Also, there was no characteristic peak at $\delta=3.48$ ppm belonging to $-\text{Si}(\text{OCH}_3)_3$, which indicated that the 3-chloropropyltrimethoxy has been completely cleaned out. All the data mentioned above clearly stated that POSS-(Cl) $_8$ with complete cube octameric was synthesized successfully.

The structures of POSS-(PXMA-Cl) $_8$ polymers were also confirmed by ^1H NMR and the spectra were shown in Figure 2.

Figure 2(a) showed the ^1H NMR spectrum of POSS-(PMMA-Cl) $_8$. ^1H NMR(CDCl_3 , 500 MHz, δ): $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-$ ($\delta_1=0.99$ ppm), $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-$ ($\delta_2=1.38$ ppm), $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-$ ($\delta_3=1.39$ ppm), $-\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$ ($\delta_4=1.86$ ppm), $-\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$ ($\delta_5=1.57$ ppm), $-\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$ ($\delta_6=3.44$ ppm). Moreover, the

integration area ratio of the peaks $\text{H}_1:\text{H}_{(2-3)}:\text{H}_{(4-5)}:\text{H}_6$ is about 0.62:1.00:1.53:0.32, which was in excellent agreement with the number ratio of protons of 2:4:5:3, verifying the molecular structure of POSS-(PMMA-Cl) $_8$. Figure 2(b) displayed the ^1H NMR spectrum of POSS-(PBMA-Cl) $_8$. ^1H NMR(CDCl_3 , 500 MHz, δ): $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-$ ($\delta_1=1.29$ ppm), $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-$ ($\delta_2=1.07$ ppm), $-\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-$ ($\delta_3=0.99$ ppm), $-\text{CH}_2\text{C}(\text{CH}_3)\text{COO}-$ ($\delta_4=1.85$ ppm), $-\text{CH}_2\text{C}(\text{CH}_3)\text{COO}-$ ($\delta_5=1.94$ ppm), $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ($\delta_6=3.99$ ppm), $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ($\delta_7=1.44$ ppm), $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ($\delta_8=1.65$ ppm), $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ($\delta_9=0.91$ ppm), and the integration area ratio of $\text{H}_{(4-5)}:\text{H}_6:\text{H}_7:\text{H}_8:\text{H}_9$ was about 1.00:1.13:1.27:1.34:1.00. Therefore, the expected polymerization that occurred under the reaction conditions were clearly confirmed by the analysis of ^1H NMR spectra, and the monomers have been grafted on the POSS core successfully.

In addition, molecular weights and polydispersity ($\text{PDI} = M_w/M_n$) of copolymers were obtained by GPC, and summarized in Table I.

Compared to linear polymers prepared through ATRP, 37,38 polymers synthesized initiated by multifunctional ATRP initiators via ATRP usually exhibited a relatively wider molecular weight polydispersity due to their large volume and high steric hindrance. $^{39-42}$ For POSS-(PXMA-Cl) $_8$ polymers synthesized as described in this article, due to the topological structure with eight chlorine-terminated arms, the molecular weight distributions were wider than those of related linear polymers synthesized by ATRP. Also, it could be found that for the four polymers, M_n decreased with the increasing length of alkyl side

Table I. Molecular Weights and Polydispersity of POSS-(PXMA-Cl) $_8$ Copolymers

Polymers	M_n (g/mol)	M_w (g/mol)	$\text{PDI} = M_w/M_n$	Yield (%)	DP
POSS-(PMMA-Cl) $_8$	123870	351330	2.84	42.2	153
POSS-(PBMA-Cl) $_8$	50930	92160	1.81	19.3	44
POSS-(PLMA-Cl) $_8$	38120	95360	2.50	7.6	18
POSS-(PSMA-Cl) $_8$	44550	97560	2.19	6.1	16

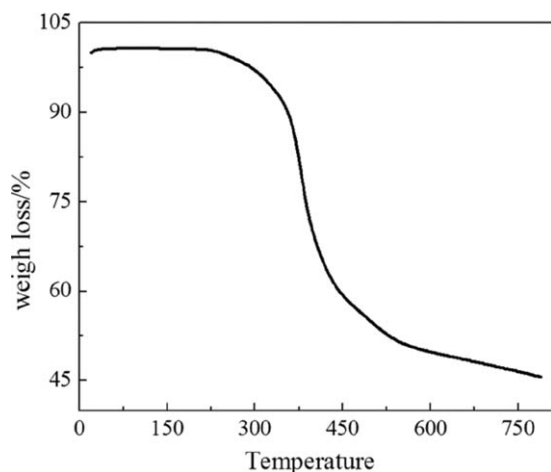


Figure 3. TGA curve of POSS-(Cl)₈.

chains of methacrylate, which may be due to the decrease of monomer's activity caused by their large volume and higher steric hindrance of longer side chains. It was worth mentioning when the length of alkyl side chains further increased, that is, from POSS-(PLMA-Cl)₈ to POSS-(PSMA-Cl)₈, the disturbance of M_n varied a little, which may be because of the similar reactivity represented by comparable D_p .

Thermal Stability of POSS-Methacrylate Copolymers

Because star-shaped POSS hybrid polymers have cubic cage consisted of eight Si-O-Si bonds, which possess higher bond energy than that of C-O and C-C bonds, the POSS moiety and its derivatives are always considered excellent thermal resistant hybrid materials. Meanwhile, the POSS species have dimensions (1–3 nm) similar to those of polymer chain segments; they may restrict motion at the molecular level, and thus have excellent thermal stabilities (>400°C). In this article, TGA was used to characterize thermal stabilities of series POSS-methacrylate polymers as well as POSS-(Cl)₈.

The TGA of POSS-(Cl)₈ is as shown in Figure 3. The TGA curve showed that the T_d at 5% weight loss (T_5) was about 322.3°C, and the weight loss up to 800°C was 55%. This implies that POSS-(Cl)₈ possessed excellent thermal stability due to the existence of the complete cage Si-O-Si core of POSS-(Cl)₈.

For comparison, linear PMMA was synthesized and thermal stability was analyzed. The differences of thermal stability between hybrid star-shaped polymer POSS-(PMMA-Cl)₈ and the linear PMMA were shown in Figure 4. It could be drawn that with the introduction of POSS cages, POSS-(PMMA-Cl)₈ exhibited a significantly increasing on thermal property.

In addition, compared with the related PMMA/POSS blends, POSS-(PMMA-Cl)₈ copolymer possessed higher thermal stability because of the stronger covalent bonding effects.⁴³

To find out the effect of the length of side chains and types of terminal species on the T_d of hybrid macromolecular, the thermal stability tendency difference with various length of side chains for series of four chlorine-terminated polymers (POSS-(PXMA-Cl)₈) and phenyl-triazole-terminated polymers (POSS-(PXMA-Pytl)₈) were analyzed and shown in Figure 5;

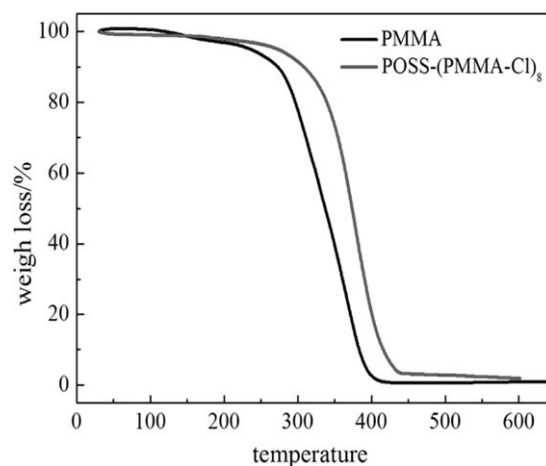


Figure 4. TGA curves of the POSS-(PMMA-Cl)₈ and PMMA homopolymer.

meanwhile the T_d at 5% and 10% weight loss of POSS-(PXMA-Cl)₈ and POSS-(PXMA-Pytl)₈ are summarized in Table II.

From the TGA data in Table II, it could be clearly found out that T_5 of all polymer samples were around 260°C, much lower than that of POSS-(Cl)₈, which were mainly attributed to the decomposition of terminal groups and side chains of copolymers.

For POSS-(PXMA-Pytl)₈ series, it was observed that T_5 decreased with increasing length of alkyl side chains along with T_{10} . The more stereospecific blockade and side-chain entanglement would exist with the longer alkyl side chains,^{44,45} which resulted in lower thermal stability by the likely occurred side-chain decomposition.

Meanwhile, the same observation occurred for POSS-(PXMA-Cl)₈ series; T_5 and T_{10} also decreased with increasing the alkyl side-chain length except those of POSS-(PLMA-Cl)₈ and POSS-(PSMA-Cl)₈. For POSS-(PLMA-Cl)₈ and POSS-(PSMA-Cl)₈, no apparent change in T_5 and T_{10} was detected, which could be attributed to the higher value of M_w of

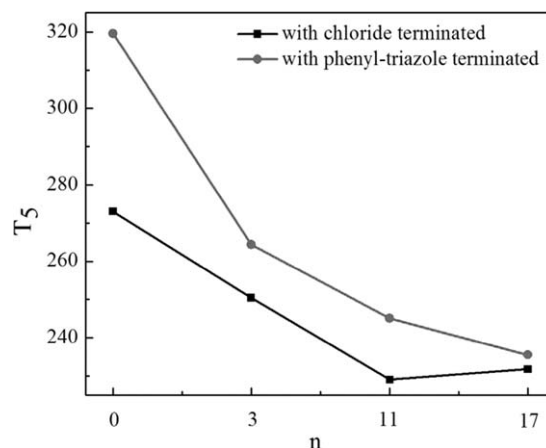


Figure 5. Thermal stability tendency with increasing n values of POSS-(PXMA-Cl)₈ and POSS-(PXMA-Pytl)₈ (where n represented the value of $(CH_2)_nCH_3$ in side chains).

Table II. TGA Parameters on the Various POSS–Methacrylate Copolymers

Composition	T_5 (°C)	T_{10} (°C)	Composition	T_5 (°C)	T_{10} (°C)
POSS–(PMMA–Cl) ₈	273.0	308.5	POSS–(PMMA–Pytl) ₈	319.6	308.6
POSS–(PBMA–Cl) ₈	250.4	263.8	POSS–(PBMA–Pytl) ₈	264.4	276.4
POSS–(PLMA–Cl) ₈	229.0	255.8	POSS–(PLMA–Pytl) ₈	245.0	258.5
POSS–(PSMA–Cl) ₈	231.8	256.9	POSS–(PSMA–Pytl) ₈	235.5	257.1

POSS–(PSMA–Cl)₈. The decomposition induced by chlorine might be restrained as the terminal chlorine embedded in entangled longer side chains.

In addition, for the same side chain length, all four phenyl–triazole-terminated polymers exhibited higher T_5 than those of chlorine-terminated polymers. This may have been due to the different decomposition mechanism occurring in this two series. For POSS–(PXMA–Cl)₈, the decomposition behavior occurred first at terminal chlorine, and the release of hydrogen chloride accelerated the decomposition of main chain in turn. The *in situ* FTIR of different temperatures would prove this prediction in the following content.

Pyrolysis Mechanism of POSS–Methacrylate Copolymers

Based on TGA analysis above, we predicted that introducing different terminal groups may cause different thermal stability behaviors. To find out the specific thermal degradation mechanism, *in situ* FTIR was used for further analysis, and in this

part POSS–(PMMA-terminated)₈ and POSS–(PLMA-terminated)₈ polymers were chosen for investigation, as shown in Figure 6.

Taking the intensity of the C=O bond between 1800 and 1700 cm^{-1} as normalization factor and benchmark to compare the other bonds in the spectra of different temperature points, a real-time monitoring for thermal decomposition process of POSS–methacrylate copolymers can be realized, and then the degradation mechanism of the copolymers can be illustrated more exhaustively. Comparing POSS–(PMMA–Cl)₈ and POSS–(PMMA–Pytl)₈ spectra in Figure 7, two characteristic absorption bonds needed to be focus upon, namely, carbon chlorine bonds and vinyl group presented at 700 cm^{-1} and 1625 cm^{-1} , respectively.

For *in situ* FTIR spectra of POSS–(PMMA–Cl)₈, as temperature increases, the decomposition mechanism includes the dropout of HCl and main chain rupture. The existence of chlorine-terminated group was deduced by monitoring of C–Cl bond at 700 cm^{-1} . With the rise in temperature, the C–Cl bond

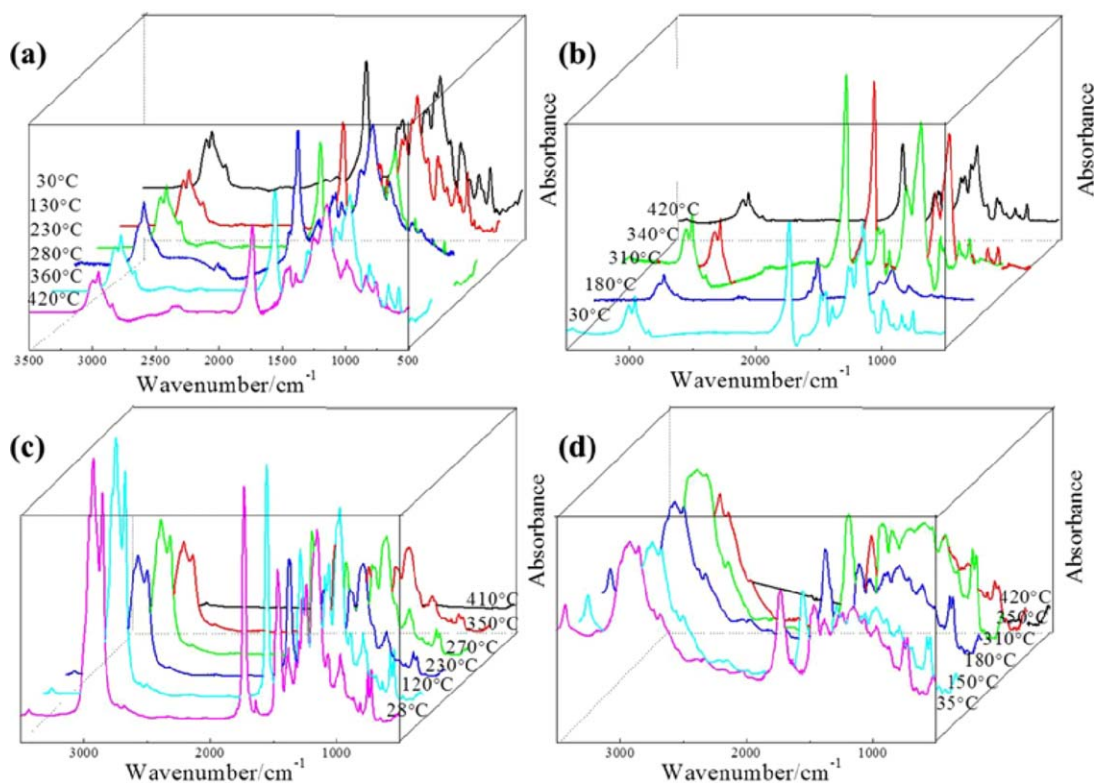


Figure 6. *In situ* FTIR spectra of (a) POSS–(PMMA–Cl)₈, (b) POSS–(PMMA–Pytl)₈, (c) POSS–(PLMA–Cl)₈ and (d) POSS–(PLMA–Pytl)₈. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

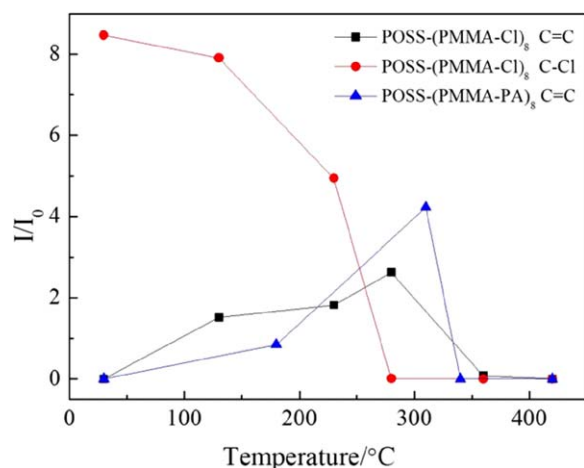


Figure 7. Intensity analysis of *in situ* FTIR for POSS-(PMMA-Cl)₈ and POSS-(PMMA-Pytl)₈. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intensity decreased, revealing that the C—Cl bond was broken, which was accompanied with the generation of HCl. In addition, vinyl group appeared at 1625 cm⁻¹ after curing at 130°C, and with increasing the temperature, the absorption peak maximized at 280°C, and then weakened to disappear at 360°C (Figure 7).

For *in situ* FTIR spectra of POSS-(PMMA-Pytl)₈, the disappearance of terminal Cl was proofed by vanishing of C—Cl bond, which indicated that the terminal chlorine had been substituted completely. Compared with POSS-(PMMA-Cl)₈, vinyl group of POSS-(PMMA-Pytl)₈ appeared at 1625 cm⁻¹ after curing at 180°C, 50°C enhanced, and achieved a maximum value at 310°C, 0°C enhanced as well.

Based on *in situ* FTIR data listed in Figure 7 and the discussion above, the thermal decomposition process of POSS-(PXMA-Cl)₈ with POSS-(PXMA-Pytl)₈ is as shown in Figures 8 and 9. For POSS-(PXMA-Cl)₈, there was a two-step decomposition procedure, C—Cl bond was first broken accompanied with C=C bond formation; meanwhile HCl was released, which facilitated the main-chain degradation. When temperature increased to 280°C, C=C-related monomers began to

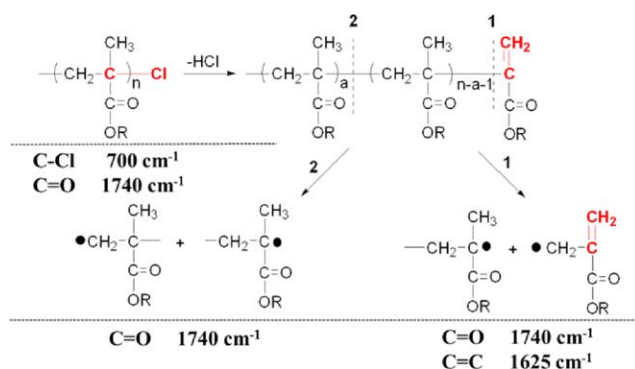


Figure 8. Mechanism of thermal decomposition process of POSS-(PXMA-Cl)₈ copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

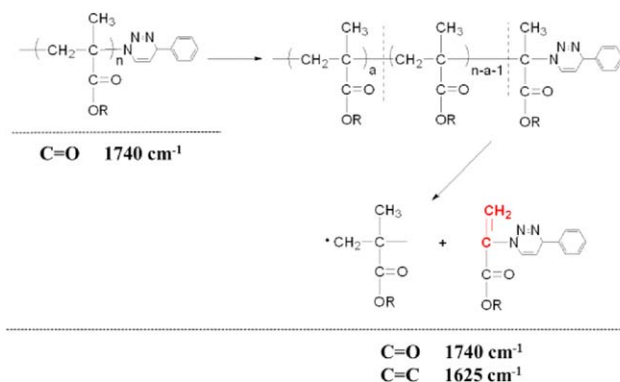


Figure 9. Mechanism of thermal decomposition process of POSS-(PXMA-Pytl)₈ copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decompose accompanied with the further radical forming, thus a decreasing of C=C intensity.

For POSS-(PXMA-Pytl)₈, the terminal chlorine was substituted completely; the temperature of appearance of vinyl group for POSS-(PXMA-Pytl)₈ was much higher than that of POSS-(PXMA-Cl)₈, attributed to no secondary reaction from HCl generated by terminated chlorine. The decomposition of POSS-(PXMA-Pytl)₈ could be considered a one-step process, and the degradation occurs only in the polymer main-chain. The enhancement of temperature for vinyl group appearing could indicate a higher stability improved by phenyl-triazole termination.

CONCLUSIONS

A series of chlorine-terminated POSS-methacrylate hybrid copolymers was synthesized through ATRP by using POSS-(Cl)₈ as initiator. The terminal chlorine was substituted by sodium azide and then terminated by phenylacetylene via click chemistry, through which imidazole group and benzene ring was introduced into hybrid polymers and thus phenyl-triazole-terminated POSS-methacrylate hybrid copolymers were obtained. Based on the TGA analysis, all of the hybrid copolymers exhibited an interesting improvement of thermal properties compared with related linear polymethacrylates, and changes of T_d (T_5 and T_{10}) among them still existed along with the different of side-chain length and terminal group species. In most cases, the longer the alkyl side chain of monomers were, the easier chain decomposition would occur, which was represented by a lower T_5 and T_{10} . *In situ* FTIR was employed to compare the differences of polymers' thermal stabilities with different terminal groups. POSS-(PXMA-Pytl)₈ were proven to have higher thermal stabilities by the terminal chlorine replacement, which was consistent with the analysis of different decomposing mechanisms. Overall, it was proved that the thermal stability of POSS-based hybrid polymers performed excellently and could be applied as heat-resistant materials.

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