

Novel Organic/Inorganic Hybrid Star Polymer Surface-Crosslinked with Polyhedral Oligomeric Silsesquioxane

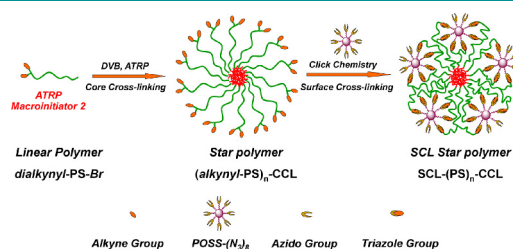
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Abstract: Novel organic/inorganic hybrid star polymer was prepared dually cross-linked within inner-core *via* divinylbenzene (DVB) and outer-surface *via* octafunctional polyhedral oligomeric silsesquioxane (POSS). Core cross-linked star polymers bearing *dialkynyl*-terminated polystyrene arms, (*dialkynyl*-PS)_n-CCL, were synthesized at first by the atom transfer radical polymerization (ATRP) of DVB using α,α -*dialkynyl*-terminated PS macroinitiator, followed by the subsequent fractionation. Under high dilution conditions, (*dialkynyl*-PS)_n-CCL was subjected to surface cross-linking with octa(3-azidopropyl) polyhedral oligomeric silsesquioxane, POSS-(N₃)₈, *via* click reaction, affording POSS-functionalized hybrid polymer doubly cross-linked within core and surface regions, SCL-(PS)_n-CCL. FT-IR, ¹H NMR, GPC, and elemental analysis results revealed that on average, the obtained hybrid polymer possesses a cross-linked PDVB inner core, ~14 linear PS arms (the *M_w* per arm of 5.1 kDa), and ~4-5 POSS moieties at outer surface. Differential scanning calorimetry (DSC) thermograms and thermogravimetric analysis (TGA) revealed that after surface cross-linking the thermal stability of SCL-(PS)_n-CCL is considerably improved. This work provides a proof-of-concept example for the preparation of dually cross-linked hybrid star polymer, which represents a novel category of organic/inorganic composite materials with unique chain architectures.



Keywords: star polymer, surface crosslinking, polymer/POSS, organic/inorganic, hybrid microstructure.

1. Introduction

Due to their unique branched architecture and interesting physical properties, multiarm star polymers have been investigated extensively and employed in a wide range as industrial and commercial materials.¹⁻¹⁸ Among them, the star polymers with crosslinked cores generally can be prepared using an “arm-first” method, typically involving the polymerization of a difunctional crosslinkable monomer in the presence of a preformed linear macroinitiator *via* anionic or ring-opening metathesis polymerization, which finally provides core-crosslinked star polymers (CCS) with specific length of arms.¹⁹⁻²¹ The boom of controlled radical polymerization (CRP) made the preparation of CCS more convenient.²²⁻³³ Taking advantage of the tolerance of CRP towards many functional groups, CCS modified with functionalities at special location of the microstructure can be obtained.^{34,35}

It is well known that the functionalities on a material can be

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utilized to further modify the precursor for various applications. And one of the most common uses is for crosslinking to regulate the microstructure and properties of the polymeric materials.³⁶⁻³⁹ Galia and Sirés groups prepared a functionalized nanogel from linear poly(vinylpyrrolidone) through intermolecular or intramolecular crosslinking by electro-Fenton process.³⁶ Sakai *et al.*,³⁸ performed a horseradish peroxidase (HRP)-catalyzed reaction for the formation of the crosslinked hydrogel sheaths on the surface of the individual cells. Turro and coworkers had achieved photoinduced surface crosslinking under UV irradiation using (NH₄)₂S₂O₈ as a photoactivated crosslinking agent, which generates superabsorbent particles with superior properties.³⁹

In most cases, bifunctional or multifunctional crosslinkers, as well as reliable reactions between the crosslinker and the precursor are necessary for a successful crosslinking operation. Polyhedral oligomeric silsesquioxane (POSS), typically possessing the structure of cube-octameric framework represented by the formula (R₈SiO₁₂) with an inorganic core (~0.5 nm) surrounded by eight organic corner groups, has drawn considerable attention during the past decades. Due to their precise structures as well as their solubility in common organic solvents, many polymer/POSS hybrid composites were successfully prepared based on the reaction of the functional groups on the corner of the inorganic nanocage.⁴⁰⁻⁴⁵ Generally, the incorporation of eight-func-

tional POSS into a polymeric system leads to the formation of polymer/POSS microcomposites with significant improvements in thermal and mechanical properties.

As we known, chain architectures play an important role in determining macromolecular properties and functions in bulk or solution states.^{46,47} So the synthesis of polymers with varying chain topologies has always been the focus of polymer chemistry field. As for the architecture of the reported polymer/POSS composites, the polymers were mainly functionalized with end-capped, pendant, or beads-like POSS. Besides that, polymer networks with POSS junctions or unbounded POSS were also covered. The most concerning and classical structures should be stars or dendrons involving multifunctional POSS as the core and polymer chains as the outer arms. Specially, Chen *et al.*⁴⁸ reported surface-initiated ATRP of POSS-containing monomer on Si wafers. However, such surface modification using POSS mainly focused on silica, gold nanoparticles, or clay intercalated.⁴⁹⁻⁵⁴ The surface modifications of star polymers with POSS derivatives were rarely reported, especially those surface-crosslinked with POSS.

On the other hand, regarding to the crosslinking reactions, there were numerous examples depending on different kinds of functionalities. The ideal reaction should be highly effective under mild reaction conditions. Click chemistry, especially the copper-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes, has been proved to be a wonderful alternative for crosslinking.¹⁶ Recently Liu group synthesized the *alkynyl*-terminated terpolymers *via* ATRP with propargyl 2-bromoisobutyrate as the initiator, which then were covalently conjugated onto a tetraphenylethylene core, thus forming a well-defined four-arm star-shaped amphiphilic copolymers with well-documented aggregation-induced emission feature.¹³

Herein, we report the synthesis of core-crosslinked star PS modified with dialkynyl groups per PS arm and further surface-crosslinked by octa(3-azidopropyl)-POSS *via* click chemistry under high dilution condition. FT-IR, ¹H NMR, GPC and elemental analysis were used to characterize the star polymer and the subsequent hybrid microstructure. The thermal property, including glass transition temperature and thermal stability of the surface-crosslinked product and the core-crosslinked precursor,

were compared using DSC and TGA, respectively. Surface-crosslinking coupled with hybrid modification by multifunctional POSS molecules on the surface would probably bring new properties to the microstructure deserving further research.

2. Results and discussion

2.1. Synthesis of alkynyl surface-functionalized PS star polymer

The core-crosslinked star PS was prepared *via* ATRP of DVB in the presence of macroinitiator **2** with dialkynyl end groups (Scheme 1), which was synthesized *via* ATRP of styrene (*St*) using small molecular dialkynyl initiator **1** (Scheme S1).

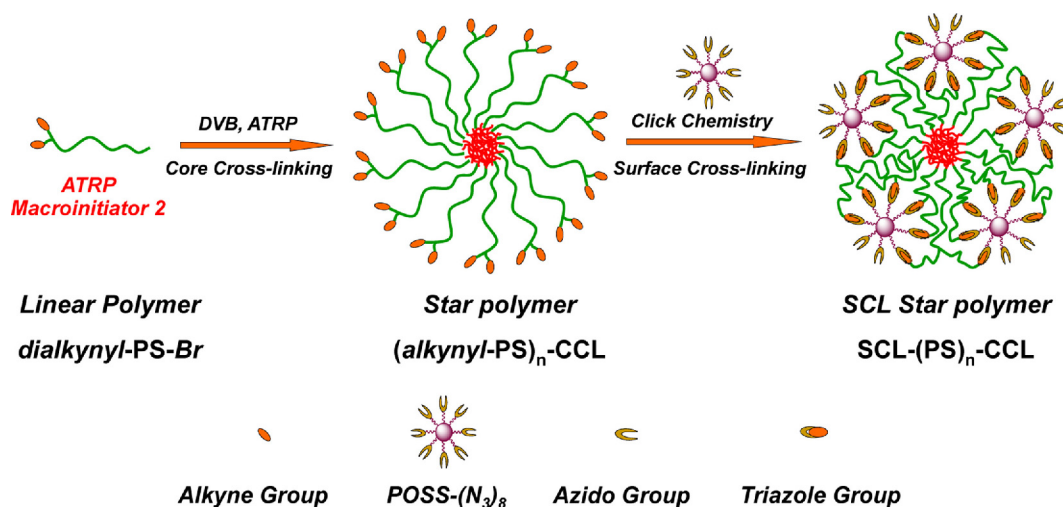
2.1.1. Synthesis of Dialkynyl Initiator **1**.

Generally, initiator with special functionalities is required to prepare CCS with functional groups on the surface during the arm-forming step, as is the case with the ATRP initiators used in this work. Considering the further crosslinking reaction with multiazido agent, the number of alkynyl groups per PS arm prefers to be equal or larger than two. As a result, ATRP initiator **1** containing two alkynyl groups was prepared *via* the esterification reaction of 3,5-bis(propargyloxy) benzyl alcohol with 2-bromoisobutyryl bromide in the presence of triethylamine (Scheme S1). The ¹H NMR spectra of the obtained ATRP initiator **1** recorded in CDCl₃ was shown in Figure S1, in which the characteristic signals corresponding to its structure can be clearly distinguished.

2.1.2. Synthesis of dialkynyl-PS-Br (ATRP Macroinitiator **2**)

ATRP has been proved to be successful by its validity for monomers with various functionalities, including alkynyl and azide groups that capable of click chemistry.⁵⁵ Thus, initiator **1** was utilized to initiate the ATRP of styrene under proper conditions, forming PS with dialkynyl groups on the chain end, i.e. *dialkynyl*-PS-Br, as ATRP macroinitiator (Scheme 1).

The ¹H NMR spectra of *dialkynyl*-PS-Br recorded in CDCl₃ was shown in Figure 1, clearly revealing all the characteristic signals of



Scheme 1. Schematic illustration for the preparation of alkynyl surface-functionalized PS star polymer with PDVB core, $(alkynyl-PS)_n-CCL$, and its intramolecular surface "click" cross-linking with $POSS-(N_3)_8$ to give organic/inorganic hybrid star polymer, $SCL-(PS)_n-CCL$.

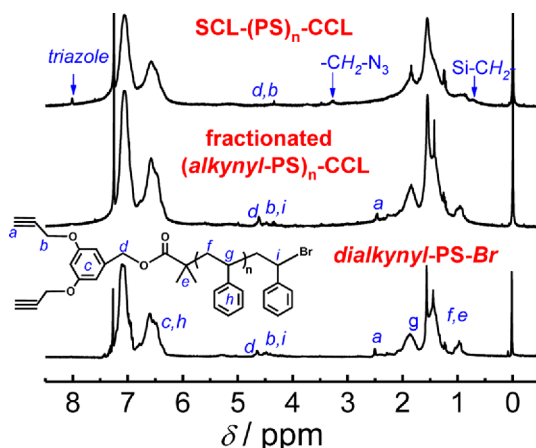


Figure 1. ^1H NMR spectra recorded for *dialkynyl-PS-Br*, fractionated *(alkynyl-PS)_n-CCL*, and *SCL-(PS)_n-CCL*, in CDCl_3 .

the styrene repeating units and the end groups. On the basis of integral ratio of peak $d+b+i$ ($d=4.3\sim 4.7$ ppm) and $f+g+e$ ($d=0.85\sim 2.2$ ppm), the actual degree of polymerization (DP) of *dialkynyl-PS-Br* was calculated to be ~ 40 . THF GPC trace of *dialkynyl-PS-Br* (Figure S3) exhibited a general monomodal and relatively symmetric peak, reporting a number-average molecular weight M_n of 4.3 kDa and a polydispersity, M_w/M_n of 1.18. The higher molecular weight (M_w) impurities, probably due to the chain-chain coupling termination, were relatively little and can be ignored. Furthermore, taking into account that the standards used for GPC calibration were low polydispersity polystyrene, the GPC result should also reflect the actual DP of *dialkynyl-PS-Br*, which agrees well with that obtained from NMR.

2.1.3. Synthesis of Core-Crosslinked *(alkynyl-PS)_n-CCL* Star Polymer

Under the reaction conditions similar to that optimized by Hawker *et al.*,⁵⁶ core-crosslinked star PS, *(alkynyl-PS)_n-CCL*, was prepared *via* ATRP of DVB using *dialkynyl-PS-Br* as the macroinitiator. The ^1H NMR spectra of *(alkynyl-PS)_n-CCL* in CDCl_3 was shown in Figure 1, resembling that of *dialkynyl-PS-Br* because of the structural similarity between PS and polymerized DVB. The signal at $\delta=2.5$ ppm (peak *a*) clearly confirmed the existence of the alkynyl groups on the surface.

From the GPC traces of *dialkynyl-PS-Br* (**2**) and *(alkynyl-PS)_n-CCL* (Figure S3), it can be seen that after core-crosslinking reaction, mostly the molecular weight of the polymers shifted to much higher M_w region, while an intermediate peak corresponding to low molecular weight components also can be discerned, which was probably attributed to several chains attached to a small core. The similar result was also reported by Hawker *et al.*⁵⁶ Fortunately, the low molecular impurities can be easily removed by fractional precipitation, and the fractionated *(alkynyl-PS)_n-CCL* exhibited a monomodal and relatively symmetric peak, revealing the successful synthesis of a core-crosslinked multiarm star polymer with an M_n as high as 40.7 kDa and a relatively narrow polydispersity of 1.35. However, the actual M_w of CCS cannot be determined by the GPC using differential refractive index detector, since the CCS possessed a much different topology compared

Table 1. Elemental Analysis Results of *(alkynyl-PS)_n-CCL* and *SCL-(PS)_n-CCL*

Samples	Content (%)		
	C	H	N
<i>(alkynyl-PS)_n-CCL</i>	89.421	7.756	/
<i>SCL-(PS)_n-CCL</i>	85.494	7.614	1.894

with that of the linear PS standard.

In order to calculate the number of PS arms of *(alkynyl-PS)_n-CCL*, the actual M_w of CCS and that of individual PS arm cross-linked with DVB (the content of PDVB per arm also concerned) were characterized. The former was determined to be 72.4 kDa with the help of GPC with multiangle laser light scattering detector, and the actual M_w per PS arm after crosslinking was calculated based on the elemental analysis results (Table 1), from which the total content of C and H element was calculated to be $89.421\%+7.756\%=97.177\%$. Considering the chemical structure of *(alkynyl-PS)_n-CCL*, the rest content of 2.823% should be ascribed to Br and O elements in the cross-linked cores. Since every *dialkynyl-PS-Br* macroinitiator contained one bromine and four oxygen atoms, the M_w per arm (containing the PS arm and equally divided PDVB core) could be calculated as:

$$M_{w,\text{arm}}=(4\times 16.0+79.9)/0.02823\approx 5.1\text{ kDa}$$

Thus, the number of PS arms can be determined to be about 14 from $M_{w,\text{CCS}}/M_{w,\text{arm}}$, the number of alkynyl groups on the surface of *(alkynyl-PS)_n-CCL* was about 28.

2.2. Synthesis of surface- and core-crosslinked PS star polymer

The objective organic/inorganic hybrid polymer was prepared *via* surface crosslinking of the PS star polymer with an inorganic multifunctional crosslinker, POSS-(N_3)₈ (Scheme 1).

2.2.1. Synthesis of surface crosslinker POSS-(N_3)₈

It is well known that crosslinking is one of the effective strategies to improve the thermal, mechanical and chemical properties of polymeric materials, as well as the hybridization with inorganic materials. As for the crosslinking, numerous chemical crosslinkers with multifunctional groups have been reported, however most of them are organic reagents since the inorganic ones often have poor solubility in organic reaction media. Therefore, if using an inorganic multifunctional crosslinker that has good solubility in organic solvent, high-performance polymer-based organic/inorganic hybrid materials can be prepared. To this end, POSS molecule, well soluble in many organic solvents, was chosen to synthesis POSS-(N_3)₈ as the surface crosslinker, which has eight azido groups on the corners and could crosslink to the surface of *(alkynyl-PS)_n-CCL* *via* azido-alkynyl click chemistry.

The POSS-(Cl)₈ precursor was firstly synthesized following the literature procedure.^{57,58} The POSS-(N_3)₈ surface crosslinker was then synthesized through the reaction of POSS-(Cl)₈ with NaN_3 .⁵⁹ In view of the rearrangement of POSS cage under azidation condition, some more rigorous purification, such as multiple column chromatography, was made to separate possible

other size-cage silsesquioxanes.⁶⁰ The ²⁹Si NMR chemical shift appeared at -67.1 ppm indicated single type of silicon atom in an octacyclic inorganic silicon and oxygen framework (Figure S2(b)). The signals in the ¹H NMR (Figure S1) and ¹³C NMR (Figure S2(a)) spectrum of POSS-(N₃)₈ shifted inconsistently to a little higher field compared with that of the precursor, indicating the structural difference between them. In the FTIR spectrum of POSS-(N₃)₈ (Figure 2(a)), the absorption bands at ~2100 and ~1100 cm⁻¹, characteristic of azido group and Si-O-Si cube structure respectively, could be clearly discerned further confirming the successfully formation of the objective inorganic azido-containing crosslinker.

2.2.2. Surface-crosslinking of (alkynyl-PS)_n-CCL

Azido-alkynyl click chemistry has been proven highly effective and extensively used in polymer chemistry, while in our research work, considering the existence of 8 azido groups of the surface crosslinker POSS-(N₃)₈ and the 28 alkynyl groups of (alkynyl-PS)_n-CCL, it was quite challenging to fulfil the surface crosslinking of (alkynyl-PS)_n-CCL with POSS-(N₃)₈ without further intermolecular reaction among star polymers. Similar problem was also encountered in some other cases, such as preparing cyclic polymers *via* intramolecular coupling of an α,ω -hetero-difunctional linear polymer precursor, during which the intermolecular reaction should be avoided.⁶¹ The most used strategy to such problem was to conduct the reaction at a high dilution concentration, making the intermolecular reaction difficult to proceed. However, as for the surface crosslinking reaction of (alkynyl-PS)_n-CCL by POSS-(N₃)₈, if the reaction solution was highly dilute for both, it would be very difficult for them to contact with each other and the crosslinking reaction would not proceed completely. To address the issue, we carried out the reaction in a deliberately regulated way, namely adding (alkynyl-PS)_n-CCL slowly to the solution of POSS-(N₃)₈ *via* a syringe pump. Under this circumstances, the concentration of (alkynyl-PS)_n-CCL was always kept at high dilute state, while the concentration of POSS-(N₃)₈ was relatively high. Thus, once (alkynyl-PS)_n-CCL molecules were introduced into the reaction system, they would be promptly surface crosslinked by large excess of POSS-(N₃)₈. Furthermore, it was also reasonable to speculate that although the concentration of POSS-(N₃)₈ was relatively high and the molar ratio of azido group to alkynyl group was much larger than 1.0, once one of the azido group of the POSS molecule reacted with one of the alkynyl group of (alkynyl-PS)_n-CCL, the POSS molecule would be connected to the surface of

the CCS and shorten the spatial distance between the two different molecules. Therefore, the unreacted alkynyl groups at the surface of CCS would prefer to react with the azido group of the connected POSS molecule instead of those of other unattached POSS molecules. As a result, (alkynyl-PS)_n-CCLs surface crosslinked by POSS-(N₃)₈, i.e. SCL-(PS)_n-CCLs, could be obtained, and the unexpected crosslinking between more than one CCS, as well as the formation of CCS modified with an independent POSS molecule at the chain end per PS arm could be avoided. The above speculation was proved by the structure characterizations on the obtained (alkynyl-PS)_n-CCL.

However, in order to prove the above speculation and fully understand the structure of the surface-crosslinked CCS, SCL-(PS)_n-CCL, several points below must be made clear: Did all the alkynyl groups on the surface engage in crosslinking reaction? Did the crosslinking reaction really take place without intermolecular way among several (alkynyl-PS)_n-CCL star polymers? How many azido groups were consumed on average per POSS during the surface crosslinking? How many POSS molecules were there averagely on the surface of per crosslinked CCS?

The ¹H NMR spectrum of SCL-(PS)_n-CCL was compared in Figure 1 with that of (alkynyl-PS)_n-CCL. After surface crosslinking, the signal at $\delta=2.5$ ppm ascribed to the proton of the alkynyl group disappeared; while two new signals emerged at $\delta=8.05$ ppm and $\delta=3.28$ ppm, ascribed to the protons of triazole groups and methylene connected with the residual azido group, respectively. Such results clearly indicated that the alkynyl groups at the surface of (alkynyl-PS)_n-CCL have been all consumed during surface crosslinking, while there were still some unreacted azido groups left on the surface. The above conclusion obtained from NMR can be further confirmed by FT-IR characterization results (Figure 2(a)), in which the absorption band at 3310 cm⁻¹ characteristic of alkynyl groups could not be found in the spectrum of SCL-(PS)_n-CCL, while the absorption band of azide groups at 2100 cm⁻¹ appeared. So it could be concluded from both NMR and FTIR results that SCL-(PS)_n-CCL have been successfully prepared through the surface crosslinking of (alkynyl-PS)_n-CCL *via* the azido-alkynyl click reaction with POSS-(N₃)₈. On the other hand, the unreacted azido groups remained after surface crosslinking rendered SCL-(PS)_n-CCL potential application for further surface modification.

The THF GPC traces of SCL-(PS)_n-CCL and the precursors, (alkynyl-PS)_n-CCL and POSS-(N₃)₈, were shown in Figure 2(b). Both the M_w and the polydispersity of the surface crosslinked prod-

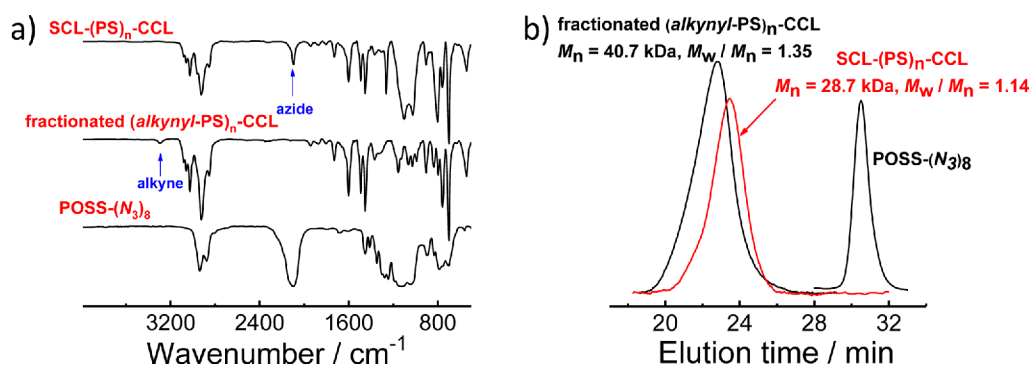


Figure 2. (a) FT-IR spectra and (b) THF GPC traces recorded for POSS-(N₃)₈, fractionated (alkynyl-PS)_n-CCL, and SCL-(PS)_n-CCL.

uct were lower than those of the star polymer precursor due to the much more compact structure of SCL-(PS)_n-CCL. Similar results also have been obtained for the crosslinked nanoparticles in previous literatures. Zimmerman *et al.*⁶² found that after intramolecular crosslinking the surface of a dendrimer, the size of the nanoparticle significantly decreased. For the shell-crosslinked micelles, the hydrodynamic radius was also smaller than the precursors. Moreover, no other peaks of high molecular species were detected, indicating that the inter-crosslinking between more than one (alkynyl-PS)_n-CCL was excluded as expected.

Subsequently, element analysis was utilized to calculate the number of the azido groups and POSS molecules on the surface of SCL-(PS)_n-CCL (Table 1). Since the content of N element was 1.894%, the content of the inner PS-PDVB should be 100%-(1.894%×1089/336)=93.861%, where 1089 and 336 were the *M_w* of POSS and whole N element per POSS molecule. Then the whole *M_w* of SCL-(PS)_n-CCL could be calculated as 72,400/0.93861 ≈ 77,100 g/mol, and the number of POSS was (77,100-72,400)/1089 ≈ 4.3 (72,400 was the *M_w* of (alkynyl-PS)_n-CCL, as measured by GPC using multiangle laser light scattering detector), while the number of azido groups left was 4.3×8-14×2 ≈ 6.4.

Based on all the characterization results above, the structure of the final product, SCL-(PS)_n-CCL, could be described as follows: this novel kind of organic/inorganic hybrid star-shaped polymer possessed a crosslinked PDVB core with about 14 PS arms (the *M_w* per arm of 5.1 kDa) crosslinked on average by about 4-5 POSS molecules on the surface. All the alkynyl groups of the CCS precursor were consumed while there were still about 6-7 azido groups left on the surface. And the schematic illustration of the core- and surface-crosslinked hybrid star polymer was shown in Scheme 1. It should be noted that the surface crosslinking was not in a complete manner due to separate POSS molecules outside PS cores, which should be in favour to maintaining the star-shaped topologies.

2.3. Thermal properties of the novel crosslinked hybrid star polymer

The synthesis and properties of POSS-containing hybrid polymers have been extensively studied.⁴² Generally, for those synthesized from monofunctional POSS, the POSS moieties can be located at the polymer chain end, on the surface of a nanostructure such as dendrimer, or pendent along the chain backbone.

While macro-crosslinked structures were often obtained from multifunctional POSS molecules. It was found that the thermal properties of the hybrid polymers were profoundly affected in terms of topological structure, the POSS content, and the existence of various substitutional moieties.⁶³⁻⁶⁷ As for SCL-(PS)_n-CCL, the multifunctional POSS molecules were crosslinked on the surface of the core-crosslinked star PS, thus may rendering the hybrid polymer novel thermal properties different from those previously reported.

2.3.1. *T_g* Test of fractionated (alkynyl-PS)_n-CCL and SCL-(PS)_n-CCL

The DSC thermograms of fractionated (alkynyl-PS)_n-CCL and SCL-(PS)_n-CCL were depicted in Figure 3(a). The precursor of star PS possessed a *T_g* of 129.5 °C, which was relatively higher than that of general linear PS (about 90~100 °C). This should be attributed to the core-crosslinked structure, which made the chain motion more difficult. While for SCL-(PS)_n-CCL, no detectable *T_g* could be found in its DSC curve. This was not surprising since after surface-crosslinking, the PS arms in SCL-(PS)_n-CCL were fixed at both ends and unable to move freely.

2.3.2. Thermal Stability of fractionated (alkynyl-PS)_n-CCL and SCL-(PS)_n-CCL

As one of the important indices of the material properties, thermal stability determines the highest temperature of the polymer in practical application. It was found the thermal stability of polymeric materials could be strengthened by incorporating inorganic nanoparticles and forming homogeneous microcomposites. Among them, POSS-containing composites have also shown elevated thermal stability.

The thermogravimetric analysis profiles and differential thermal analysis curves recorded for fractionated (alkynyl-PS)_n-CCL and SCL-(PS)_n-CCL were shown in Figure 3(b). TGA curves exhibited a first very sharp degradation stage, followed by a second one at low degradation rate. Taking the temperature at which 5% weight loss can be detected as the starting decomposing temperature, it can be seen that surface crosslinking inevitably delayed the thermal decomposition of the PS-based star polymer. SCL-(PS)_n-CCL began to decompose at higher temperature (343 °C) than (alkynyl-PS)_n-CCL (315 °C). Moreover, while the fractionated (alkynyl-PS)_n-CCL degraded completely above 680 °C, SCL-(PS)_n-CCL still evidenced a decreasing mass residue, with ~9.4% up

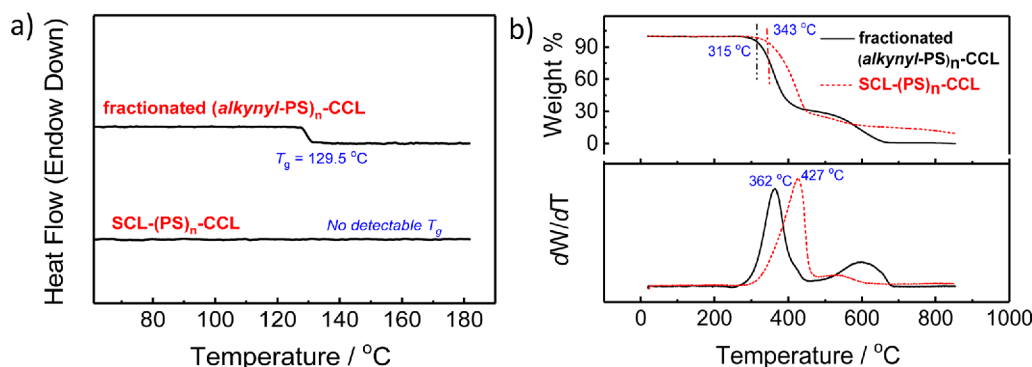


Figure 3. (a) Differential scanning calorimetry thermograms and (b) thermogravimetric analysis profiles (upper) and differential thermal analysis curves (lower) recorded for fractionated (alkynyl-PS)_n-CCL and SCL-(PS)_n-CCL.

to 850 °C, which was approximately close to the POSS content determined by elemental analysis. It further confirmed the microstructure of the *surface-crosslinking* star polymer stated above. As for the peak temperature of the differential curves, *i.e.*, the temperature at which the materials decomposed most rapidly, SCL-(PS)_n-CCL possessed a much higher value (427 °C) than fractionated (*alkynyl*-PS)_n-CCL (362 °C), also suggesting better thermal stability of the hybrid star polymer. In a word, the hybridization with POSS by means of surface crosslinking can effectively elevate the thermal stability of the star polymer.

3. Conclusions

A novel organic/inorganic hybrid microstructure with POSS moieties fixed on the surface of core-crosslinked star PS was prepared *via* the combination of ATRP and click chemistry. Structure characterization shows that this novel hybrid microstructure possesses about 14 PS arms (the M_w per arm of 5.1 kDa) cross-linked both in the core by DVB and on the surface with about 4-5 POSS molecules on average. All the alkynyl groups of the CCS precursor were consumed while there are still about 6-7 azido groups left on the surfaces of the formed microstructure. Thermal property experiments show that the T_g of dual surface- and core-crosslinked microstructure was undetectable while the thermal stability was highly elevated compared with its precursor. It can be expected that some more properties would be brought with the novel microstructure. Although many important questions remain, the current research is a small step and further research is now undertaken in needs of other interesting properties.

Supporting information: Information is available regarding the experimental procedure for the preparation of POSS-containing hybrid polymers and characterization. The materials are available *via* the Internet at <http://www.springer.com/13233>.

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