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Versatile grafting approaches to star-shaped POSS-containing hybrid polymers using RAFT polymerization and click chemistry†

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An alkyne-bearing polyhedral oligomeric silsesquioxane (POSS) core was used to prepare POSS-containing polymer hybrids using ‘grafting to’ or ‘grafting from’ strategies in combination with reversible chain transfer and click chemistry.

Organic–inorganic nanohybrid materials have attracted considerable scientific and technological interest, due to the combination of the properties of the organic and the inorganic components conferred upon the resulting materials.¹ These nano-structured hybrid materials have a high surface area to volume ratio. However, these characteristic properties induce agglomeration and lead to the loss of the material’s attractive properties. Surface modification with polymeric structures has shown promise in improving the dispersion stability of the nanoparticles in organic and aqueous media and in preventing the segregation of inorganic fillers in polymer matrices. Current methods for preparation of covalent polymer–silica conjugates include ‘grafting to’ methods using Huisgen cycloaddition coupling,² as well as ‘grafting from’ methods involving initiator-functionalized inorganic particles.³

Polyhedral oligomeric silsesquioxanes (POSS)–polymer hybrid materials have attracted a great deal of attention due to the enhancement of the organic matrices’ properties, *i.e.* increased thermal stability, reduced flammability and dielectric constant—upon incorporation of POSS molecules.⁴ In recent years, with the new living/controlled polymerization techniques emerging in polymer science, many novel POSS-containing hybrid polymers with well-defined topological structures (tadpole-shaped, block, and star-shaped) have been prepared.^{2c–e} However, the design of a potential method for achieving a well-defined topological structure while maintaining control over the polymer’s molecular weight and polydispersity in POSS is an extremely important challenge.

For the ‘grafting to’ or ‘grafting from’ approach to be successful, in terms of yield, specificity and reversibility; the coupling of arms, *i.e.* ‘grafts to’, or the functionalities used to

‘graft from’ a core unit must be reacted under mild conditions. Moreover, using ‘grafting from’ chemistry (or method for preparing arms for ‘grafting to’ approach), controlled radical polymerization (CRP) is able to yield well-defined polymers with controlled molecular weights, low polydispersivity, functional group tolerance that have high chain-end fidelity. Recently, reversible addition–fragmentation chain transfer (RAFT) polymerization⁵ has attracted significant attention in polymer and materials science due to its versatility and simplicity, where additionally the polymer has a high degree of chain-end fidelity.⁶ Although the RAFT technique is compatible with the polymerization of almost all conventional monomers, the covalent attachment of the RAFT agents in the cage-structure is still challenging thus restricting its utilization. Click chemistry is potentially an ideal modular methodology for the introduction of a wide variety of molecules. The copper(i)-catalyzed [2 + 3] Huisgen cycloaddition proceeds with short reaction times, a wide range of tolerated functionalities, high yields, and a tolerance towards humidity and oxygen.⁷ Therefore, when RAFT polymerization is combined with click chemistry techniques, it becomes an even more powerful tool in materials science.⁸

In this contribution, both click chemistry and RAFT polymerization were applied in the preparation of star-shaped POSS-containing polymer hybrids using ‘grafting to’ and ‘grafting from’ approaches (Scheme 1). This study provides a discussion of each method, including the effect of chain length on click reaction, how the content of multifunctional RAFT agents controls the polymer’s molecular weight (M_w) and the grafting efficiency of each method. To the best of our knowledge, nobody has reported examples featuring the combination of RAFT and click chemistry in POSS molecules.

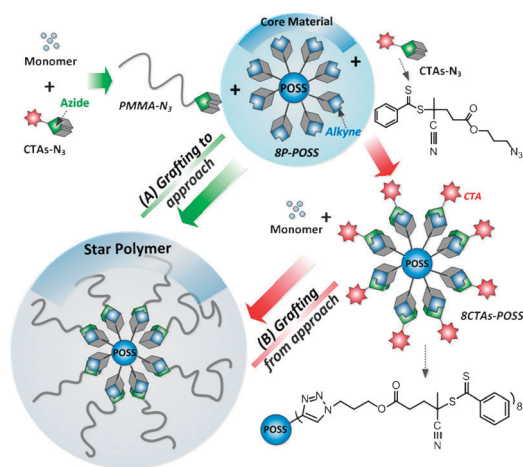
Before proceeding with the ‘grafting to’ or ‘grafting from’ approaches, we prepared the core material (alkyne-functionalized POSS; 8P-POSS), which was used to modify the azido-terminated polymethyl methacrylate (PMMA- N_3) and azido-CTAs, using click chemistry and RAFT polymerization. In the preparation of 8P-POSS (Scheme S1, ESI†), we chose the highly reactive 3-propargylcarbonylpropionic chloride (PCPCI) as the precursor, since it can effectively substitute all hydroxyl groups of 8OH-POSS. Based on the results of ¹H NMR, ¹³C NMR, gel permeation chromatography (GPC) and elemental analysis (EA) (Table S1, ESI†), high purity 8P-POSS was prepared.

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Scheme 1 Two types of grafting reactions used in the synthesis of star-shaped POSS-containing polymer hybrids.

For ‘grafting to’ approach, a series of well-defined PMMA- N_3 were prepared by the RAFT polymerization of methyl methacrylate (MMA) using a small amount of AIBN as the radical source ($[AIBN]/[charge\ transfer\ agents\ (CTAs)] < 0.2$) and azido-CTAs as the chain transfer agent. All polymerization of MMA, mediated with azido-CTAs, resulted in a linear increase in average molecular weight (M_n) with conversion (Fig. S10, ESI[†]): the correlation between theoretical and experimental values was excellent throughout the conversion ranges (Table S2, ESI[†]). The polymerizations proceeded with good control, as evidenced by the narrow and unimodal molecular weight distribution [polydispersity index (PDI) < 1.25]. Before conducting the ‘grafting to’ approach, we investigated the efficiency and fidelity of copper-catalyzed azide–alkyne coupling between azido-functionalized polymer end groups with acetylene species. We considered 3-propargyl carbonyl propionic acid (PCPA) as a model for preparing the star polymer. After the click reaction (Fig. S11, ESI[†]), the resulting polymer showed the appearance of the new methylene proton adjacent to the triazole ring at $\delta = 4.62$ ppm ($-\text{CH}_2-\text{CH}_2-\text{triazole}-$), 5.30 ppm ($-\text{triazole}-\text{CH}_2-\text{COO}-$) and 7.78 ppm ($-\text{N}-\text{CH}=\text{C}-$). The end group click reactions were efficient, the PMMA- N_3 (50) reacted with PCPA to yield carbonyl-terminated polymer with nearly 98% end groups functionalization.

Finally, the ‘grafting to’ approach *via* click chemistry between the PMMA- N_3 and 8P-POSS afforded the star shaped POSS-containing hybrid PMMA. The synthetic steps were characterized by GPC and are shown in Fig. 1. Because of the clear separation between the ungrafted PMMA peak and the PMMA–POSS hybrid, we were able to quantify the contents of ungrafted PMMA in the as-prepared PMMA-*g*/t-POSS hybrid. On the GPC traces, the peaks at shorter and longer retention times in each GPC trace corresponded to the elution of the larger PMMA-*g*/t-POSS hybrid and smaller ungrafted PMMA- N_3 , respectively. The amount of grafted PMMA was determined quantitatively by comparing the grafted PMMA peak area ratio after using Gaussian fitting and number-averaging the molecular weight of PMMA–POSS. Comparing the different chain length of the PMMA- N_3 grafting to POSS provides an indication that the polymer’s molecular

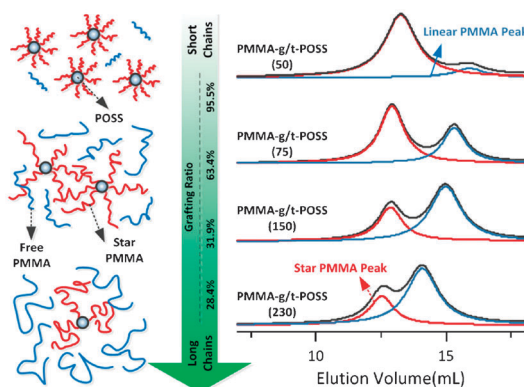


Fig. 1 GPC traces of grafted PMMA-*g*/t-POSS.

weight has an impact on the grafted ratio of the PMMA–POSS hybrids. Obviously, as the polymer’s molecular weight is increased, the graft density decreases (95.5% to 28.4%). This result can be explained by the decreased reactivity of the chain-end azide functionality that becomes less accessible as the polymer adopts a more random coil structure at this higher molecular weight.⁹

There are two types of multifunctional RAFT agents, *i.e.* those used for the Z-group and the R-group approaches, to the synthesis of the star polymer (see ESI[†]). In this study, we selected the R-group as a part of the core, due to the growing linear chains experiencing a higher probability of irreversible terminations occurring and forming dead linear polymers free of any thiocarbonylthio groups in the Z-group approach.¹⁰ To covalently attach the RAFT agents onto the POSS surface, the azide–alkyne coupling reaction was employed (Scheme S1, ESI[†]). The ¹H NMR spectra (Fig. S9, ESI[†]) show that the signals at $\delta = 4.71$ ($-\text{COO}-\text{CH}_2-\text{C}\equiv\text{CH}$) and 3.41 ppm ($\text{CH}_2-\text{CH}_2-\text{N}_3$) assigned to the methylene protons originating from 8P-POSS and azido-CTAs were shifted to 5.25 ($-\text{COO}-\text{CH}_2-\text{triazole}-$) and 4.49 ppm ($-\text{triazole}-\text{CH}_2-\text{CH}_2-$), respectively. Moreover, the peak at 7.93 ppm corresponding to the triazole ring appeared, while no residual propargyl groups ($\delta = 2.51$ ppm) were detected in 8CTAs-POSS. FTIR (Fig. S12, ESI[†]), EA and GPC results also confirmed that 8CTAs-POSS was successfully prepared (Table S1, ESI[†]).

For the RAFT polymerization to the silica based cage structure, the high surface density anchored CTAs commonly exhibited a lower polymerization resulting in a low surface density and large amounts of cross-terminated polymer, due to the ‘localized high RAFT agent concentration’ effect.^{3c,d,11} In this study, the 8CTAs-POSS used for MMA radical polymerization had a high surface density ($182\ \mu\text{mol}\ \text{g}^{-1}$) as compared with previous studies.^{3c,12} Interestingly, in comparison with the GPC traces of linear polymers prepared with azido-CTAs ($[M]_0/[CTAs] = 150$), the GPC traces of star polymer prepared with the same $[M]_0/[CTAs]$ ratio were shifted to higher molecular weights (Fig. S13, ESI[†]). Dependence of M_n and PDI on conversion for MMA polymerization (Fig. S14, ESI[†]) shows that the M_n increased in a linear fashion with monomer conversions, and no appreciable differences of the M_n were observed as compared with linear polymerization. However, the PDI of PMMA prepared with 8CTAs-POSS gradually

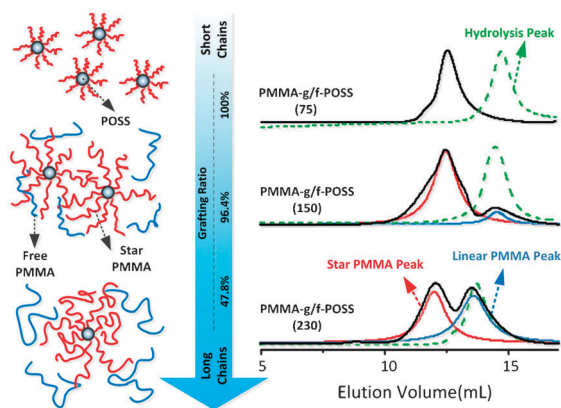


Fig. 2 GPC traces of grafted PMMA-g/f-POSS.

increased at higher MMA conversions (> 58%). This behavior can be explained by the star polymer having different hydrodynamic characteristics from the linear polymer. In fact, the HF-etched sample showed only one symmetrical peak and the PDI were as narrow as 1.15 in the final product. This result strongly suggested that the 8CTAs-POSS was an even more effective chain transfer agent than the free CTAs in solution due to the much higher fragmentation rate of the anchored intermediate radical compared with the free intermediate radicals and also a highly effective chain transfer reaction. In addition, the GPC trace of the final product shows no obvious shoulder on the high molecular weight side of the peak, which means interparticle polymeric radical coupling due to high surface densities of CTAs on POSS particle did not occur even at high conversions (> 80%). Although the exact reason for this phenomenon is not clear, we speculate that a combination of the unique confined geometry and the higher polymerization rate of the anchored intermediate macro-RAFT radical on the POSS surface may contribute to the high opportunity for star and linear chain radical termination.

The controlled character of MMA graft polymerization was investigated by using different ratios of $[M]_0/[8CTAs-POSS]$ ($[M]_0/[CTAs] = 75, 150, 230$) with identical experimental conditions to linear polymerization with azido-CTAs. The GPC traces (Fig. 2) show that the peaks of ungrafted PMMA (higher retention times) gradually increased as the $[M]_0/[CTAs]$ ratio increased, and were slightly shifted to higher molecular weights (grafting ratio: from 100% to 47.8%). This means that the predominant intermediate macro-RAFT radical on the POSS surface is more restricted in its ability to migrate to the neighboring particle's surface due to the high $[M]_0/[CTAs]$ ratio. Therefore, the intermediate macro-RAFT radical will increase the chance of migrating in solution, thereby generating a linear polymer. The GPC traces of the hydrolyzed product showed exactly the same molecular weight of the linear products and narrow polydispersities (PDI < 1.2). In addition, no shoulder was observed for the hydrolyzed product, indicating that irreversible terminations due to coupling reactions between the star and linear chain radicals

did not occur. Thus the star polymer's growth might be accompanied by a parallel polymerization of single chains. For MMA polymerization, 8CTAs-POSS is an excellent chain transfer agent, as indicated by the narrow polydispersities observed in contrast to that found with linear polymerization.

In summary, star-shaped POSS-containing PMMA was successfully prepared by the combination of RAFT and click chemistry. These powerful tools gave control over the polymer's: length, architecture and graft density in both the 'grafting to' and 'grafting from' approaches; however, graft density decreased due to the effect of steric hindrance predominating on the surface of POSS. The properties and morphologies of these hybrids are under investigation. Here, we provide a versatile strategy to prepare star-shaped POSS-containing polymer hybrids, together with valuable information showing the advantages of different grafting reactions applied to surface modification applications.

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