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www.rsc.org/polymersSean M. Ramirez,^{*a} Yvonne J. Diaz,^a Christopher M. Sahagun,^b Michael W. Duff,^c Olawale B. Lawal,^c Scott T. Iacono^c and Joseph M. Mabry^{*d}

Reversible addition–fragmentation chain transfer (RAFT) polymerization techniques were used to copolymerize an F-POSS macromer with methyl methacrylate (MMA) to produce novel copolymers that possess excellent wetting-resistant behaviour and are the first examples of covalently bound F-POSS nanocomposites for improved surface robustness. These F-POSS/MMA copolymers have also been used to coat cotton fabrics, resulting in both superhydrophobic and oleophobic behaviour.

Low surface energy materials have proven useful in many applications, including non-wetting fabrics,¹ smart surfaces,² membranes,³ and ice-phobic surfaces,⁴ as well as anti-fouling surfaces and coatings.⁵ Fluoroalkyl polyhedral oligomeric silsesquioxanes (F-POSS) have emerged as promising materials for these types of applications due to their low surface energy ($\gamma_{sv} = 9.3 \text{ mN m}^{-1}$).⁶ The addition of F-POSS to polymers often results in materials that possess superhydrophobic and superoleophobic properties.⁶ The production of superhydrophilic/superoleophobic surfaces is also dependent on selection of the polymer matrix.^{6a} Due to the lack of covalent bonding, spun cast films of F-POSS composites often possess poor surface robustness and are susceptible to surface abrasion. F-POSS also exhibit limited solubility in non-fluorinated solvents, thereby limiting the types of polymers into which they can be dispersed. Short chain (trifluoropropyl) F-POSS compounds have been

covalently attached to polymer chain ends through functionalization of the incompletely condensed cage but these F-POSS do not influence significant low surface energy property enhancement.⁷ Recently, a method for the synthesis of an incompletely condensed long chain fluoroalkyl silsesquioxane, an F-POSS disilanol, was reported.⁸ Reaction of this compound with a variety of dichlorosilanes resulted in a series of functional F-POSS compounds with increased solubility in organic solvents and retention of low surface energy properties.^{8a} These functional F-POSS compounds enable the covalent bonding of F-POSS to the host substrate, polymer backbone, or surface. This covalent attachment may lead to a more mechanically stable and abrasion resistance material. Among these compounds, a methacrylate based F-POSS macromer, F-POSS-MA, was produced. This macromer was initially found to produce MMA copolymers with limited control of molecular weight and PDI *via* traditional AIBN-initiated free radical polymerization.^{8b} Reversible addition–fragmentation chain transfer (RAFT) polymerization is an attractive method to gain some control of these properties.⁹ A number of review articles are available describing the mechanism of RAFT polymerization and its potential as a means of producing complex polymer architectures.¹⁰ RAFT has been used to produce a plethora of copolymers under a wide variety of reaction conditions.¹¹ This versatility makes RAFT an attractive choice for the introduction of the sterically hindered F-POSS-MA macromers into PMMA copolymers.

Herein, we report the synthesis of F-POSS PMMA copolymers *via* RAFT polymerization. This work demonstrates the utility of RAFT as a controlled polymerization technique to produce polymer architectures containing low surface energy F-POSS functionality.

The F-POSS-MA macromer was synthesized following the experimental procedure described previously.^{7a} The reaction of incompletely condensed silsesquioxane (1) with 3-methacryloxypropylmethylchlorosilane in the presence of triethylamine produced the F-POSS-MA compound (2) (Scheme 1). Methyl methacrylate modified F-POSS (2) was then copolymerized with MMA *via* RAFT polymerization in the presence of

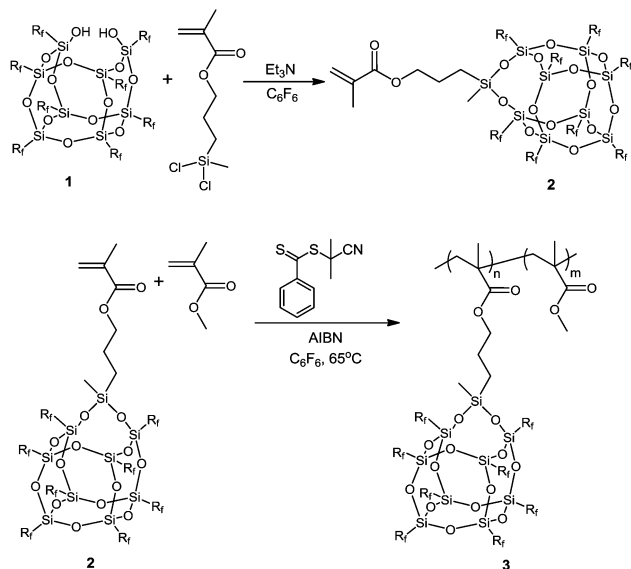
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Scheme 1 Synthesis of macromer and copolymerization of F-POSS-MA and MMA. $R_f = -\text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$.

chain transfer agent (CTA) 2-cyanopropan-2-yl benzodithioate at varying weight percentages of (2) (0–25%) relative to MMA. All polymerizations were run for 16 hours in hexafluorobenzene at 65 °C and yielded polymers with molecular weights ranging from 23–58 kg mol⁻¹ (Table 1). Polymers were characterized by multinuclear NMR (¹H, ¹⁹F). Fig. 1 presents a ¹⁹F NMR spectrum of (2), along with ¹⁹F and ¹H NMR spectra of a 5 wt% F-POSS copolymer composition. These are typical of all spectra collected. The resonance signals at 0.5–2 ppm and 3.6 ppm of the ¹H NMR spectrum are attributed to PMMA. Groups associated with F-POSS are obstructed from view by the PMMA resonance peaks (Fig. 1). The peaks observed in the ¹⁹F NMR spectrum are attributed to the fluorinated chains of F-POSS. An increase in peak broadness of F-POSS copolymer as compared to (2) was observed, providing further evidence of copolymerization. Differential scanning calorimetry (DSC) of the various compositions revealed glass transition temperatures (T_g) ranging from 126 °C to 129 °C, which indicates the F-POSS chains have little impact on PMMA chain mobility.

Polymerization of MMA homopolymers was initially performed in hexafluorobenzene to determine the impact of fluorinated solvent on the RAFT polymerization. Little to no effect was observed (see ESI[†]). However, there was a noticeable

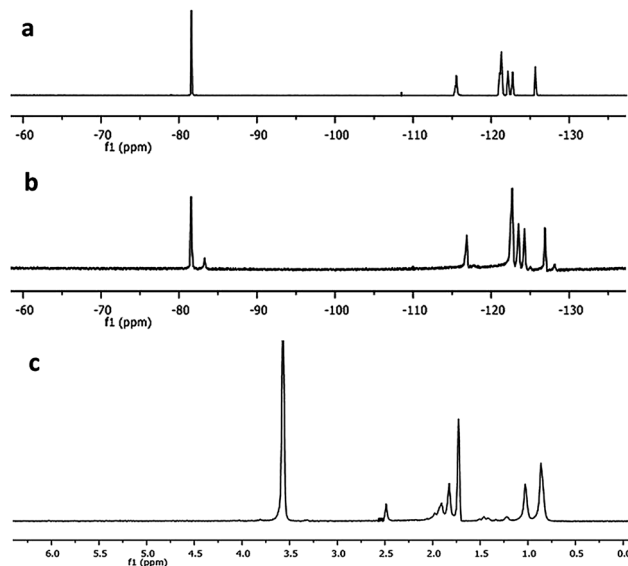


Fig. 1 (a) ¹⁹F NMR of (2) in (CD₃CD₂)₂O. (b) ¹⁹F NMR spectrum of 5 wt% F-POSS copolymer in CDCl₃. (c) ¹H NMR spectrum of 5 wt% F-POSS copolymer in CDCl₃.

decrease in polymerization conversion with the addition of macromer (2) to the copolymerization. This was attributed to the bulky nature of F-POSS leading to steric hindrance of the methacrylate group. Unfortunately, attempts at the homopolymerization of (2) did not yield any polymer, making it difficult to study the kinetic influence of (2) on copolymerization. To determine the influence of F-POSS on the copolymerization, a conversion vs. M_n study was performed with 10 wt% F-POSS copolymer compositions (Fig. 2). This plot demonstrates that molecular weight increases with time and the polydispersity index (PDI) decreases to ~1.0, indicating the polymerizations were well controlled. F-POSS copolymers with lower F-POSS compositions (<10 wt%) were found to be soluble in common PMMA solvents, while higher compositions produced stable, slightly turbid solutions. Molecular weights were determined by size exclusion chromatography, multi-angle laser light scattering (SEC-MALLS) using the fluorinated solvent Asahiklin AK-225 (a mixture of dichloropentafluoropropanes) as the mobile phase. The use of fluorinated solvent was critical due to the large amount of fluorinated chains on F-POSS. The proper selection of mobile phase is necessary for an accurate determination of molecular weight. Kawahara *et al.* found AK-225 to be a suitable SEC solvent for PMMA.¹² Because AK-225 is an

Table 1 Copolymer information and dynamic contact angle measurements

F-POSS wt% (mol%)	M_w (g mol ⁻¹)	PDI	Conv.%	T_g (°C)	Water		Hexadecane	
					(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
0	58 100	1.08	73	127	77.8 ± 1.3°	57.8 ± 2.5°	Wetted	Wetted
1 (0.02)	58 700	1.05	72	129	109.2 ± 2.4°	61.5 ± 1.9°	67.8 ± 1.4°	Wetted
5 (0.12)	23 000	1.01	30	124	117.8 ± 1.6°	95.7 ± 2.9°	76.7 ± 1.1°	68.8 ± 1.9°
10 (0.25)	26 900	1.01	29	124	118.2 ± 1.4°	101.1 ± 2.5°	77.2 ± 0.4°	69.5 ± 2.1°
25 (0.79)	37 700	1.03	41	125	120.8 ± 1.8°	97.0 ± 2.4°	82.9 ± 0.4°	74.6 ± 2.0°
F-POSS-MA	n/a	n/a	n/a	n/a	117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°

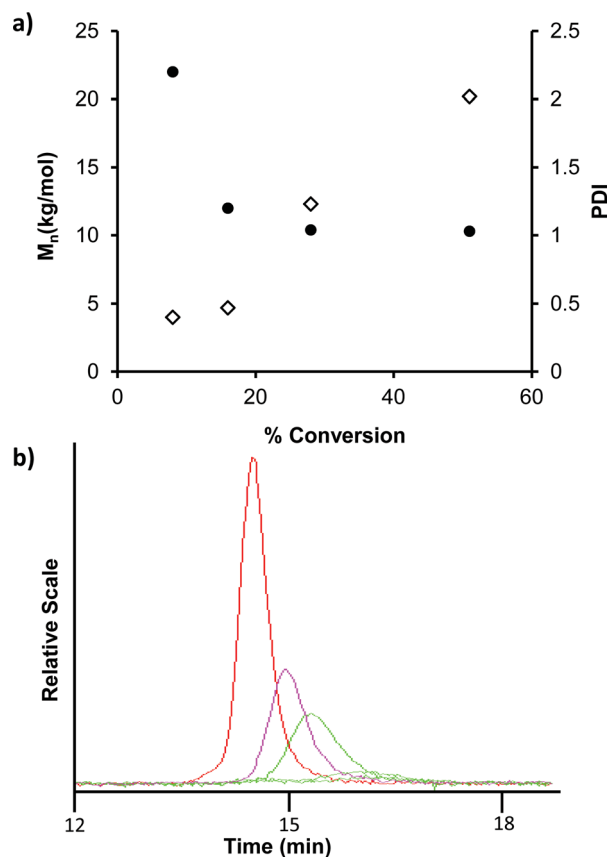


Fig. 2 (a) Polymerization of 10 wt% F-POSS copolymer: M_n vs. monomer conversion. Monomer conversion determined gravimetrically [M_n (kg mol^{-1}) (●), PDI (◇)]. (b) SEC chromatograms of copolymers. M_w increasing from right to left. SEC was run in fluorinated solvent (AK-225), $dn/dc \sim 0.121$ (mL g^{-1}).

excellent solvent for both PMMA and F-POSS, it provided an ideal mobile phase for all copolymer compositions characterized with SEC-MALLS in this work.

Low surface energy is the most-desirable property for incorporation of F-POSS into copolymers. The impact of F-POSS on the surface energy of the copolymers was determined by spin casting smooth films onto silicon wafers and measuring the advancing (θ_{adv}) and receding (θ_{rec}) contact angles or both water and hexadecane (Table 1). As expected, the contact angles for both water and hexadecane increased relative to neat PMMA. Hexadecane was found to wet neat PMMA and 1 wt% F-POSS composition films. However, these surfaces became more oleophobic with low contact angle hysteresis once F-POSS compositions reached 5 wt%. This low contact angle hysteresis (difference between advancing and receding contact angles) is vital for the production of non-wetting surfaces. The contact angle hysteresis was lower for the highest copolymer composition (25 wt% F-POSS) at 8° , compared to pure monomer (2) at 15° . The difference in contact angle was attributed to the increased fluorine content provided by F-POSS along the polymer backbone and on the surface. Hydrophobicity for the coated surfaces increased with F-POSS composition. From these measurements only a 5 wt% of F-POSS was sufficient to obtain low surface energy properties. Both advancing and receding

contact angles of F-POSS copolymer composition increased, similar to blended polymers from previously published work.^{6e-e}

In previous work, polymer blends with PMMA, F-POSS compounds were observed to bloom to the surface, rendering the surface hydrophobic/oleophobic.^{1c,6a} Atomic force microscopy (AFM) images of these surfaces exhibited crystalline features of F-POSS, which were said to be a contributing factor to the non-wetting properties of these surfaces. Fig. 3 shows AFM images of 1 to 25 wt% F-POSS copolymers after thermal annealing. Surface roughness (rms of 0.43, 0.85, 1.26 and

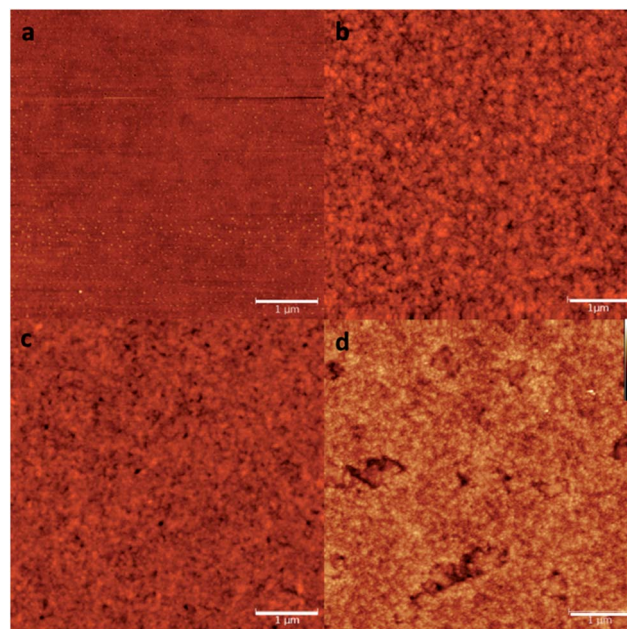


Fig. 3 AFM image of spun cast films of (a) 1 wt% (b) 5 wt% (c) 10 wt% and (d) 25 wt% F-POSS copolymer on a silicon wafer from a 10 mg mL^{-1} concentrated solution in AK-225 at 900 rpm. Each image is shown with a z-scale of 0–10 nm.

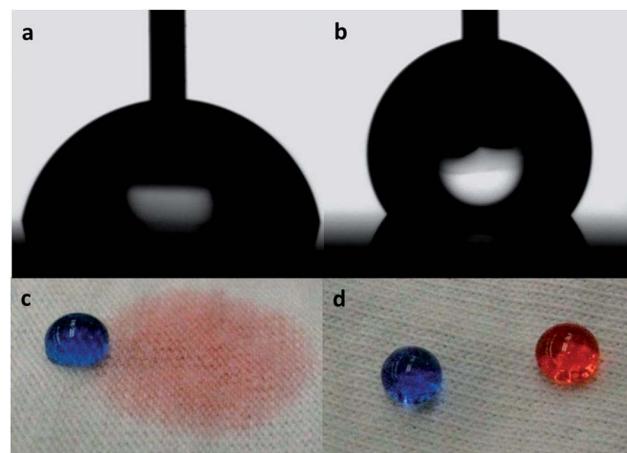


Fig. 4 Static contact angle of a water droplet on silicon wafer surfaces consisting of (a) 0 wt% F-POSS copolymer or (b) 25 wt% F-POSS copolymer. Water (blue) and hexadecane (red) droplets on a cotton fabric coated with (c) 0 wt% F-POSS copolymer (hexadecane wets fabric) and (d) 25 wt% F-POSS copolymer from 1% solution in AK-225. Fabrics were thermally annealed.

2.07 nm, respectively) was found to slightly increase with F-POSS content (1, 5, 10, and 25 wt%), respectively. Similar blooming behavior can be seen in this series after thermal annealing. The lowest F-POSS composition displays small, disperse features at the surface and these features increase in size and number with increasing F-POSS concentration.

Fig. 4 shows water droplets on a silicon wafer treated with PMMA and 25 wt% F-POSS PMMA copolymer, respectively. These same solutions were used to coat cotton fabrics to demonstrate the surface enhancing properties of the F-POSS copolymers. The 25 wt% F-POSS coated fabric was both superhydrophobic and oleophobic. Surface texture of the fabric samples helped ensure superhydrophobic and oleophobic behavior.^{1a,b}

Conclusions

Initial RAFT polymerization of F-POSS PMMA copolymers was achieved in a fluorinated solvent and F-POSS-MA was determined to be an active monomer in RAFT polymerization. Absolute molecular weights were determined with SEC-MALLS using fluorinated solvent as the mobile phase. Increased F-POSS composition in PMMA copolymers was found to increase non-wetting properties, while coating surfaces and fabrics with F-POSS copolymers was found to produce non-wetting materials. These copolymers represent the first examples of long chain F-POSS being covalently bound to polymers chains. Using RAFT polymerization with F-POSS-MA will potentially enable the production of block copolymers with superhydrophobic/oleophobic regions. These copolymer compositions will have application in low surface energy materials.

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