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Thiol-Ene Photopolymerization of Well-Defined Hybrid Graft Polymers from a Ladder-Like Polysilsesquioxane

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Abstract: A ladder-like structured poly(mercaptopropyl)silsesquioxane (LPMPSQ) was synthesized in one-bath, under mildly basic conditions at room temperature. Obtained LPMPSQ was utilized as a macroinitiator for thiol-ene graft photopolymerization of various vinyl monomers to give hard, soft, hydrophobic, and hydrophilic graft copolymers with low PDI (<1.4). Synthesized hybrid graft copolymers were characterized by ^{1}H NMR, ^{29}Si NMR, FTIR, GPC, TGA, and DSC. Thermal studies with these hybrid graft copolymers revealed that the ladder-structure substantially increased the thermal stabilities in the form of increased glass transition temperatures and higher degradation temperatures over their organic analogues.

Keywords: polysilsesquioxane, ladder-like structure, photopolymerzation, hybrids, thiol-ene.

Introduction

Polysilsesquioxanes, having molecular formula $[RSiO_{3/2}]_n$, are a class of organic-inorganic hybrid materials exhibiting excellent thermal, mechanical, optical, and chemical properties stemming from its silicon-oxide bonds.[1,2] Through modification of the -R functional group on the silicon atom, many novel properties have been examined for a wide range of applications, including semiconductor devices,[3] organic light emitting diodes,[4] molecular silicas,[5] nano-patterning in lithography,[6] and drug delivery.[7]

Polysilsesquioxanes (PSQs) can be classified by their structure, which includes random branched, cage and ladder-like structure.[1] Polysilsesquioxanes with random structure are incompletely condensed, with substantial amounts of silanol groups, which are thermally cured before they are in their final form.[8] Cage silsesquioxanes, also trademarked POSS compounds, are 3-dimensional polygons with silicon atoms located at the vertices and silicon-oxide bonds making up the edges. POSS compounds are well-defined in structure, but its effects are dampened by its low molecular weight limiting the number of functional groups available (<12).[9] Ladder-like polysilsesquioxanes (LPSQs) have a polymeric structure, as its double stranded siloxane backbone allows for high molecular weight materials with a greater number of functional groups. These ladder silsesquioxanes, while having a fully condensed siloxane backbone, exhibit enhanced thermal properties over random structures and cage silsesquioxanes.[10-15]

Functionalization of the organic-R group of PSQs with a polymerizable initiating moiety has allowed for the introduction of organic macromolecular units, leading to a variety of polymeric geometries including linear,[16] block, star-shaped,[17] random branched,[18] and graft polymers[19] through well-known controlled radical polymerization (CRP) methods such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) techniques. And while the vast majority of organic polymerizations have centered on POSS compounds, only a few ATRP studies have been conducted with ladder-like PSQs, most notably through grafting of the pendant -R group[19] or end functionalization of the ladder compound with an initiating moiety.[12]

Thiol-ene chemistry has emerged as one of the most versatile tools for polymer modification today.[20,21] Its synthetic simplicity and easy purification has allowed for a new class of materials which can be induced by a simple thiol moiety. Moreover, as thiol-ene reactions relatively insensitive to oxygen and moisture,[20] the utility and easiness of this method is often understated. Despite an overwhelming number of studies of organic polymer post-functionalization[22,23] through thiol-ene chemistry and photopolymerization, there have only been a few recent studies conducted with silsesquioxanes. These studies have either investigated the thiol-ene click reaction with trialkoxysilane monomers,[24] thermally initiated polymerization of organic polymers with a mono-substituted POSS,[16] or sol-gel derived silsesquioxanes.[25,26]

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In this study, a novel ladder-like poly(mercaptopropyl)silsesquioxane (LPMPSQ) was synthesized under one-bath, mildly basic conditions at room temperature. Synthesized LPMPSQ was fully characterized to be of a highly condensed ladder-like structure. Thiol-ene photopolymerizations with several vinyl monomers were carried out under ambient conditions to give a variety of hard, soft, hydrophobic, and hydrophilic graft polymers with low polydispersity (<1.4) and enhanced thermal properties.

Experimental

Materials. 3-Mercaptopropyltrimethoxysilane (Gelest), styrene (Aldrich, 99%), methyl methacrylate (Aldrich, 99%), n-butyl acrylate (Aldrich, 99%), dimethyl aminoethyl methacrylate (Aldrich, 99%), vinyl acetate (Aldrich, 99%), 2-vinylpyridine (Aldrich, 99%), toluene (J.T. Baker, HPLC grade), and DMF (J.T. Baker, HPLC grade) were vacuum distilled over calcium hydride before use. Potassium carbonate (Dae Jung) was dried under vacuum at 40 °C. All other solvents were of HPLC grade (J.T. Baker).

Characterization. Number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the polymers were measured by JASCO PU-2080 plus SEC system equipped with refractive index detector (RI-2031 plus), UV detector (λ=254 nm, UV-2075 plus), using THF as the mobile phase at 40 °C with a flow rate of 1 mL/min. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804, KF-805). ^{1}H NMR, ^{29}Si NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Unity INOVA (^{1}H: 300 MHz, ^{29}Si: 59.6 MHz). FTIR spectra were measured using Perkin-Elmer FTIR system (Spectrum-GX) using solvent cast films on KBr pellets. Thermal gravimetric analysis (TGA) was performed by TA Instrument TGA 2950 under N_2. Differential Scanning Calorimetry (DSC) was conducted on a TA Q20 Instrument under N_2. Photopolymerizations were conducted using a Hitachi UV-lamp with intensity 6 mW/cm^2 at a distance of 5 cm from the reaction mixture.

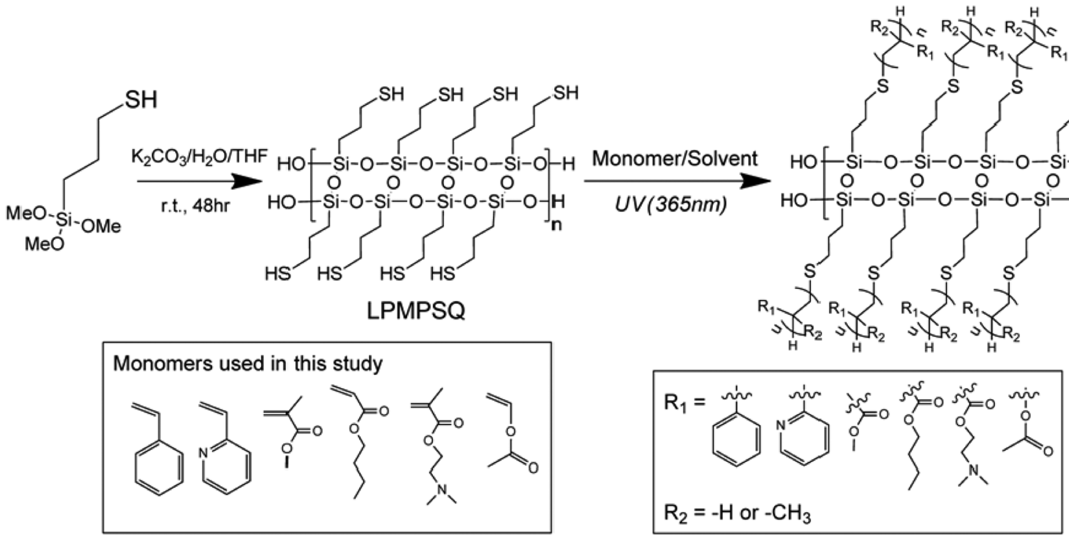
Synthesis of Ladder-Like Poly(mercaptopropyl)silsesquioxane (LPMPSQ). Synthesis of highly condensed ladder-like silsesquioxanes followed a modified literature procedure.[12] In a 50 mL round bottom-flask, potassium carbonate, K_2CO_3 (0.04 g, 0.29 mmol) dissolved in 4.8 g of deionized water with 16 g of THF was prepared. To this solution, 3-mercaptopropyltrimethoxysilane (15.71 g, 80 mmol) was added dropwise under nitrogen flow. After stirring vigorously at room temperature for 48 h, a tacky white precipitate formed. After decanting the THF/water reaction mixture, the white precipitate was dissolved in 50 mL of THF and precipitated into 500 mL of deionized water. After decanting the aqueous portions, the white tacky solid was dissolved in 200 mL of methylene chloride and extracted with water several times to remove the residual base catalyst. After drying the organic layer with anhydrous magnesium sulfate, filtering, and evaporating, a clear viscous liquid was obtained as a mixture of ladder-like and cage-like structures. Precipitation in a cold 1:9 volume ratio of MC:ethanol yielded high molecular weight ladder-like poly(mercaptopropyl)silsesquioxane (LPMSQ) as a glassy solid in high yield (80%). ^{1}H NMR ($CDCl_3$, ppm): 0.732-0.757 (t, $\mathrm{SiC}\mathit{H}_2\mathrm{CH_2CH_2SH}$, 2H), 1.68-1.71 (t, $\mathrm{SiCH_2C}\mathit{H}_2\mathrm{CH_2SH}$, 2H), 2.53-2.57 (t, $\mathrm{SiCH_2CH_2C}\mathit{H}_2\mathrm{SH}$, 2H), 1.40-1.52 (s, $\mathrm{SiCH_2CH_2CH_2S}\mathit{H}$, 1H). ^{13}C NMR ($CDCl_3$, ppm): 12.3 ($\mathrm{SiCH_2CH_2CH_2SH}$), 17.1 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2CH_2SH}$), 24.1 ($\mathrm{SiCH_2CH_2}\mathit{C}\mathrm{H_2SH}$). ^{29}Si NMR ($CDCl_3$): 64-69 ppm.

Typical Procedure for the Photopolymerization of Graft Polymers. In a common 50 mL test tube of conventional laboratory grade borosilicate glass, ladder-like poly(mercaptopropyl)silsesquioxane (LPMPSQ) (0.1 g, 0.01 mmol, 1 mmol mercapto groups), styrene (5.0 g, 50 mmol), and 10 mL of dry tol or DMF was added under argon flow. After degassing the reaction mixture several times, the reaction mixture was irradiated with a 6 mW/cm^2 UV lamp at a distance of 5 cm from the flask. For kinetic experiments, small aliquots of the reaction mixture were quenched with liquid N_2 for ^{1}H NMR measurements and conversions were calculated on normalized vinyl peaks of the monomers. Graft polymers were obtained by partial evaporation of the volatiles and then directly precipitating the reaction mixtures in cold hexane, filtering, and drying under vacuum at 40 °C. The obtained hybrid polymers were named as such: LPMPSQ-g-PS for polystyrene grafted ladder-like poly(mercaptopropyl)silsesquioxane.

Results and Discussion

It has been previously reported that the synthesis of ladder-like poly(mercaptopropyl)silsesquioxanes (LPMPSQ) was difficult due to the formation of insoluble gels under basic conditions, and thus copolymerization with phenyltrimethoxysilane was necessary.[26] This was probably due to the selection of triethylamine as base catalyst and high reaction temperature, which were inevitably factors in affecting the hydrolysis-condensation equilibrium. It has been reported that the synthesis of ladder-like structured in one pot is most likely probable with the proper balance of pH, water amount, solvent amount, and reaction time, in which fast hydrolysis and slow, steady, and full condensation is possible.[12,13] Thus, synthesis of LPMPSQ was possible by following a modified literature procedure[12] (Scheme I) using potassium carbonate as base catalyst, as these conditions facilitated the complete hydrolysis and full condensation of the trimethoxy moieties within 48 h.

^{1}H NMR spectrum of LPMPSQ (Figure 1(a)) showed that all the methoxy groups of the 3-mercaptopropyltrimethoxysilane were hydrolyzed as shown by the lack of peaks at 3.55 ppm. Full condensation between silanol groups was indicated by the lack of peaks at 5.0 ppm. Also, the thiol proton at 1.45 ppm remained intact under the aqueous, basic conditions as the relative integrative ratio between the methylene protons and the thiol proton was as expected. Obtained LPMPSQ



Scheme I. Synthetic scheme of ladder-like poly(mercaptopropyl) silsesquioxane (LPMPSQ) and photopolymerization of various vinyl monomers.

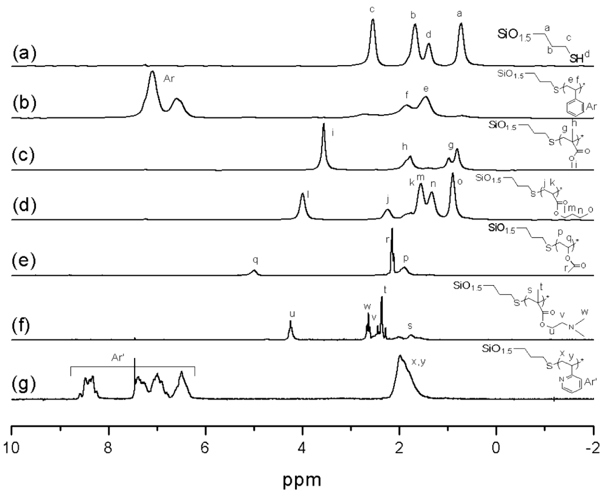


Figure 1. ^{1}H NMR Spectra of (a) LPMPSQ, (b) LPMPSQ-g-PS, (c) LPMPSQ-g-PMMA, (d) LPMPSQ-g-PnBA, (e) LPMPSQ-g-PVAc, (f) LPMPSQ-g-PDMAEMA, and (g) LPMPSQ-g-P2VP.

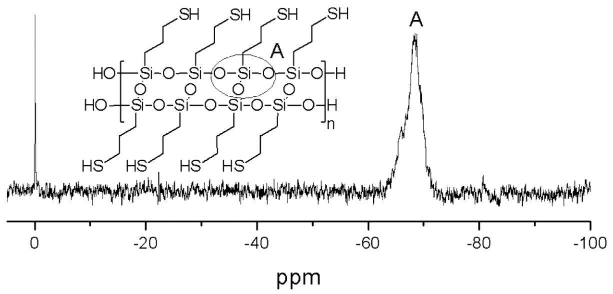


Figure 2. ^{29}Si NMR of LPMPSQ.

was then utilized as macroinitiator for the graft photopolymerization of styrene, methyl methacrylate, *n*-butyl acrylate, vinyl acetate, 2-(dimethylamino)ethyl methacrylate, and 2-vinylpyridine. These monomers were chosen because when polymerized, they represent a wide range of polymers of which includes hard, soft, hydrophobic, and hydrophilic. The graft polymers, denoted as LPMPSQ-g-PS, for polystyrene grafts, were also characterized by ^{1}H NMR (Figure 1(b)-(g)). All of the synthesized graft polymers showed the broad characteristic methylene -CH_2CRH- peaks attributed to the vinyl addition peaks after polymerization. For example, the NMR spectrum for LPMPSQ-g-PVAc (Figure 1(e)) showed the -CH_2-CHR- proton peaks at 1.9 and 5.0 ppm, as well as the acetyl protons at 2 ppm. Also, the propylene -$CH_2CH_2CH_2$- peaks stemming from the ladder structured silsesquioxane backbone were not detected because of the relatively high molecular weight of the obtained graft polymers. Furthermore, the end groups for these graft polymers, while previously reported to be terminated with hydride groups[16] as shown in Scheme I, were not conclusively determined *via* NMR, and as such the structures shown in Figure 1 were denoted as asterisks.

The siloxane structure of LPMPSQ was examined by ^{29}Si NMR (Figure 2). For a trifunctional silane, the ^{29}Si NMR peaks for fully condensed T^3 (alkyl-Si(OSi-)$_3$) and partially condensed T^3 (alkyl-Si(OSi-)$_2$OH) at -68 and -58 ppm, respectively.[26] As shown in Figure 2, the peak of LPMPSQ was entirely comprised of fully condensed T^3 structures. These results along with the ^{1}H NMR results indicated that all of the methoxy groups were hydrolyzed and fully condensed and the siloxane structure of LPMPSQ was without defect silanol groups.[26] This is in great contrast to previous reports of mercaptopropylsilsesquioxanes,[26] in which there were significant amounts of T^2 silicon atoms, meaning that several uncondensed defect silanol groups remained.

FTIR spectra of the hybrid graft polymers are shown in Figure 3. LPMPSQ (Figure 3(a)) shows the characteristic peaks for the horizontal and vertical siloxane peaks for ladder-

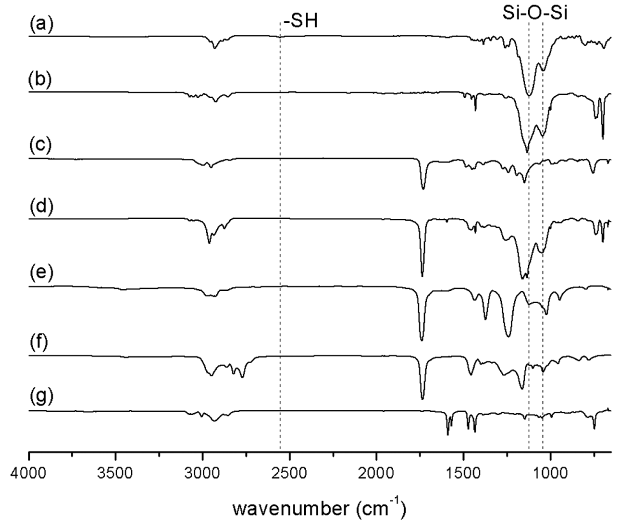


Figure 3. FTIR Spectra of (a) LPMPSQ, (b) LPMPSQ-g-PS, (c) LPMPSQ-g-PMMA, (d) LPMPSQ-g-PnBA, (e) LPMPSQ-g-PVAc, (f) LPMPSQ-g- PDMAEMA, and (g) LPMPSQ-g-P2VP.

structured polysilsesquioxanes at 1050 and 1150 cm^{-1} respectively. The sharp splitting patterns of the siloxane peaks, coupled with the lack of peaks at 3500 and 960 cm^{-1} attributed the uncondensed Si-OH moieties are representative of ladder-structured polysilsesquioxanes.[12,14] Moreover, the weak and broad peak at 2550 cm^{-1} was attributed the thiol moiety. After photopolymerizations, the thiol peaks completely disappeared (Figure 3(b)-(g)) and the corresponding peaks of the various polymeric functionalities present. For LPMPSQ-g-PS, no discernible difference was found except for the presence of aromatic phenyl moieties at 1451 and 1500 cm^{-1} attributed to the C=C stretching modes. However, for the acrylates and acetates, such as LPMPSQ-g-PMMA, LPMPSQ-g-PnBA, LPMPSQ-g-PVAc, LPMPSQ-g-PDMEMA, a sharp and unimodal peak at 1750 cm^{-1} was attributed to the C=O carbonyl group. All of the graft polymers except for LPMPSQ-g-PS did not show the siloxane Si-O-Si stretching modes. This was probably due to the fact that the other polymer units possessed a great number of aliphatic groups which overlap with those of the Si-O-Si peaks in the range of the fingerprint region of 1000-1200 cm^{-1}.

While our initial photopolymerization tests were conducted in bulk, the overwhelming fast initiation of the thiyl radical[20,21,27,28] led to low conversion rates due to the rapid increase in viscosity, led us to find the optimal solution concentration in order to control both the molecular weight, PDI, and viscosity of the reaction mixture. Table I shows the various photopolymerization conditions tested. Generally, the lower the monomer to thiol initiator ratio, gave fast polymerization rates, but low final conversion rates and low yields. However, by decreasing the total solution concentration of the initiator down to 10 mM with respect to the solvent, a reasonable polymerization rate was found in which high

Table I. Polymerization Conditions for Various Hybrid Graft Polymers

Hybrid Polymer	Monomer $[M]$: Initiator -SH $[I]$	$[I]_o^a$ (mM)	Solvent	Temperature (°C)	%Conversion^b
LPMPSQ-g-PS_r1	10:1	100	Tol	25	42
LPMPSQ-g-PS_r2	25:1	50	Tol	25	42
LPMPSQ-g-PS_r3	50:1	10	Tol	40	71
LPMPSQ-g-PMMA_r1	25:1	10	Tol	25	54
LPMPSQ-g-PMMA_r2	50:1	10	Tol	40	42
LPMPSQ-g-PMMA_r3	50:1	10	Tol	50	87
LPMPSQ-g-PnBA_r1	25:1	10	Tol	25	61
LPMPSQ-g-PnBA_r2	50:1	10	Tol	40	74
LPMPSQ-g-PnBA_r3	50:1	10	Tol	50	92
LPMPSQ-g-PVAc_r1	50:1	10	DMF	25	21
LPMPSQ-g-PVAc_r2	50:1	10	DMF	40	50
LPMPSQ-g-PVAc_r3	50:1	10	DMF	50	69
LPMPSQ-g-PDMAEMA_r1	50:1	10	DMF	25	56
LPMPSQ-g-PDMAEMA_r2	50:1	10	DMF	40	77
LPMPSQ-g-PDMAEMA_r3	50:1	10	DMF	50	89
LPMPSQ-g-P2VP_r1	50:1	10	DMF	25	31
LPMPSQ-g-P2VP_r2	50:1	10	DMF	40	61
LPMPSQ-g-P2VP_r3	50:1	10	DMF	50	77

^{a}Monomer concentration with respect to solvent. ^{b}Calculated by the normalized vinyl peaks using ^{1}H NMR.

conversions, high yields, and reasonable polydispersities obtained. By simply increasing the temperature of the reaction mixture from room temperature to 40 and 50 °C, substantially faster polymerization rates were observed, thus for monomers of low activity such as vinyl acetate and 2-vinyl pyridine, increasing the monomer:initiator ratio and increasing the temperature to 50 °C gave high conversions exceeding 70% and 80% respectively.

While these phenomena are quite common for other controlled radical polymerizations such as atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer chain transfer (RAFT), UV-initiated solution photopolymerization systems have yet to be studied in detail. The photopolymerization conditions outlined in Table I show that solution photopolymerization is indeed capable of synthesizing relatively high molecular weight polymers as such is that case for other radical polymerizations.

The molecular weights and polydispersity indices of some hybrid graft polymers obtained from the photopolymerization conditions are shown in Figure 4 in the form of GPC curves. As shown, hybrid graft polymers with high molecular weight (>70 k) were obtained with reasonably low polydispersities (PDI<1.4) (Figure 4(right)). Moreover, the molecular weight growth of LPMPSQ-g-PS as time increased is shown in Figure 4(left). This showed that the polymerization proceeded smoothly and in a semi-living manner as molecular weight increased and polydispersity indices decreased as polymerization conversion increased,[16] as indicated by the mono-modal GPC curves which improved in shape. Considering that the macroinitiator, LPMPSQ, was of substantially high polydispersity (~2.3), the obtained hybrid graft polymers can be said to be well-defined (PDI<1.4).

The thermal properties of the obtained hybrid graft polymers were analyzed by DSC and TGA. Previous studies have reported that the polymerization of organic groups on the ends of a ladder-structured polysilsesquioxane increased the organic polymer's glass transition temperature (T_g) up to 10 °C.[12] The glass transition temperatures of the obtained hybrid graft polymers as shown in Figure 5 and tabulated in Table II. While the hybrid graft polymers were of high molecular weight, the approximate molecular weight of each graft was calculated (using GPC M_n values) to be relatively small, ranging from 3 k to 4 k. Albeit this small M_n per graft unit, the T_g values of the obtained hybrid graft polymers were still 10-16 °C higher than that of the analogous organic homopolymers.[29] This was in great contrast to the previous works[12] in which each organic polymeric unit possessed molecular weights exceeding 10 k. As glass transition temperatures are dependent on molecular weight, especially in the range below 10 k,[30] the observation that the T_g values of the hybrid graft polymers increasing over 10 °C is an interesting result.

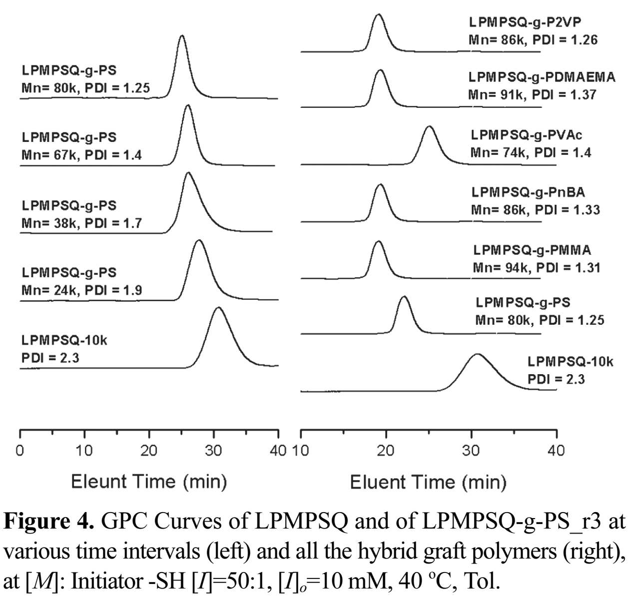


Figure 4. GPC Curves of LPMPSQ and of LPMPSQ-g-PS_r3 at various time intervals (left) and all the hybrid graft polymers (right), at [*M*]: Initiator -SH [*I*]=50:1, $[I]_o$=10 mM, 40 °C, Tol.

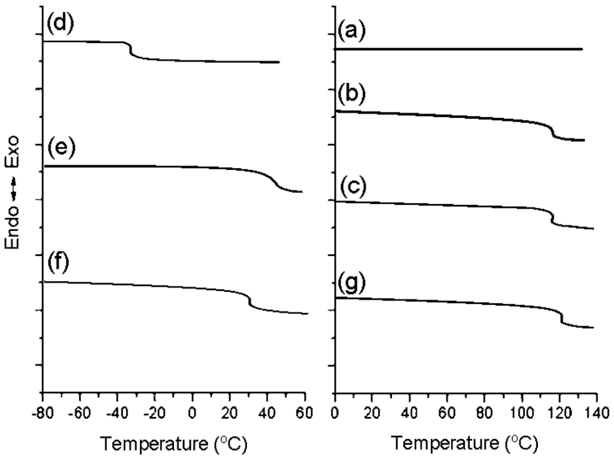


Figure 5. DSC Thermograms (second scans) of (a) LPMPSQ, (b) LPMPSQ-g-PS, (c) LPMPSQ-g-PMMA, (d) LPMPSQ-g-PnBA, (e) LPMPSQ-g-PVAc, (f) LPMPSQ-g-PDMAEMA, and (g) LPMPSQ-g-P2VP.

Also shown in Table II is the degradation temperature (T_d) of the hybrid graft polymers and the difference in T_d compared to the analogous organic polymer derivative. All of the hybrid graft polymers exhibit higher degradation temperatures and on average an increase of 18 °C over the purely organic polymer derivatives was observed. This result was highly expected, as the double-stranded siloxane backbone of LPMPSQ was able to sufficiently retard the degradation of the organic units. However, there did not seem to be a correlation between M_n per graft unit and change in T_d among the hybrid graft polymers, but instead a very pronounced relationship between the polydispersity and increase in T_d. As the PDI of the hybrid graft polymer was smaller and the polymer more well-defined, the change in T_d values increased almost twice as much. For example, the degradation temperature increase for LPMPSQ-g-P2VP with PDI 1.26 was 20 °C, but the degradation temperature increase for LPMPSQ-g-PVAc with PDI 1.40 was only 8 °C. This phenonmenon can

Table II. Molecular Weight Characterizations and Thermal Properties of LPMPSQ and Obtained Hybrid Graft Polymers

Hybrid Polymer	M_n^a	PDI (M_w/M_n)	M_n per graft unit^b	LPMPSQ Content (wt%)^c	T_g^d	ΔT_g	T_d^e	ΔT_d
LPMPSQ	10 k	2.3	-	-	none	-	400	-
LPMPSQ-g-PS_r3	80 k	1.25	3.5 k	13.8	111	+16	323	+23
LPMPSQ-g-PMMA_r3	94 k	1.31	4.1 k	11.7	116	+14	314	+18
LPMPSQ-g-PnBA_r2	86 k	1.33	3.7 k	12.8	-36	+13	303	+23
LPMPSQ-g-PVAc_r3	74 k	1.40	3.2 k	14.9	45	+18	327	+8
LPMPSQ-g-PDMAEMA_r2	91 k	1.37	4.0 k	12.1	37	+13	278	+13
LPMPSQ-g-P2VP_r3	86 k	1.26	3.7 k	12.7	114	+12	360	+20

$^a M_n$ obtained from GPC using THF as eluent (flow rate=1 mL/min). $^b M_n$ of each graft calculated based on the number of -SH initiating moieties/mol of LPMPSQ. ^{c}Calculated from the TGA using the residual weight of silica at 800 °C. ^{d}Obtained from DSC, second scan, heating rate 10 °C, under N_2(g). ^{e}Degradation temperatures obtained from onset temperature (1 wt% loss) using TGA.

be explained the higher chain termination rates of lower activity monomers, ie. such as VAc, which leads to a higher distribution of low molecular weight oligomers which decreases this effect of increasing the T_d.[20,21] These thermal studies using ladder-structured polysilsesquioxane materials are interesting compared with POSS or sol-gel derived random structures, as POSS is severely limited by its molecular weight, thus its effect is dampened, and sol-gel derived random structures do not give thermoplastic thermal properties but exhibit significant weight loss at around 150 °C due to secondary condensations of uncondensed silanol groups.[3]

In conclusion, we have demonstrated a facile method for polymerizing organic monomers onto a ladder-like structured poly(mercaptopropyl)silsesquioxane (LPMPSQ) through photoinitiated thiol-ene chemistry. Through this methodology, we have introduced well-defined hybrid graft polymers with hydrophobic, hydrophilic, hard, soft organic polymers grafted onto a hybrid polysilsesquioxane. Moreover, the thermal properties of these hybrid graft polymers exhibited increased glass transition temperatures (T_g) and degradation temperatures (T_d) over their organic polymer analogues. Moreover, these hybrid graft polymers showed exceptional free-standing film forming properties due to the rigid inorganic Si-O-Si backbone, and may be a highly useful method for improving the thermal, optical, and mechanical properties of various organic polymers for various applications in future applications.

Conclusions

A ladder-like structured poly(mercaptopropyl)silsesquioxane (LPMPSQ) was synthesized and characterized as having a fully condensed siloxane structure. Obtained LPMPSQ was then used for the graft photopolymerization of styrene, methyl methacrylate, n-butyl acrylate, vinyl acetate, 2-(dimethylamino)ethyl methacrylate, and 2-vinylpyridine to give well-defined hybrid graft polymers with low PDI (<1.4). Thermal studies of these hybrid graft polymers exhibit glass transition temperatures (T_g) about 10-16 °C higher and degradation temperatures (T_d) about 8-23 °C higher than their organic polymer analogues.

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