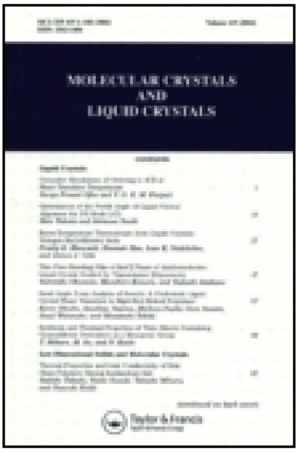

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Synthesis of Ladder-Like Polysilsesquioxane with Well-Defined Graft Polymers

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Well-defined hybrid polymers consisting of organic polymers grafted from inorganic backbone were synthesized by atom transfer radical polymerization (ATRP). Ladder-like structured polysilsesquioxane functioned as both ATRP initiator and hard inorganic backbone, while the organic polymers grafted were hard styrene and soft n-butyl acrylate. Ladder-like structured poly(chloromethylphenylsilsesquioxane) (LCMPSQ) was synthesized using sequential two-step reactions with (ρ-chloromethyl)phenyltrimethxysilane as a monomer in one bath in the presence of K_2CO_3 as a base catalyst ($M_w = 6{,}000$). Obtained LCMPSQ was then used as a multi-functional macroinitiator for graft polymerization of styrene (St) or/and n-*butyl acrylate (*n*BA) monomers via ATRP using a CuCl catalyzed system, which gave three types of hybrid graft polymers: poly(styrene-*g*-silsesquioxane) (PS-*g*-PSQ), poly(*n*BA-*g*-silsesquioxane) (PnBA-*g*-PSQ) and poly(styrene-*ran-n*BA-*g*-silsesquioxane) (P*S/n*BA-*g*-PSQ). The hybrid graft polymers were prepared with various organic/inorganic weight fractions by changing the molecular weights of the organic graft polymers, which showed narrow molecular weight distributions ($PDI < 1.4$) on less than 50% of the polymerization conversion.*

Keywords Atom transfer radical polymerization (ATRP); graft polymerization; organic-inorganic hybrid copolymers; polysilsesquioxane

Introduction

Polysilsesquioxane $(RSiO_{1.5})_n$, a new family of silicone compounds of which structures consisted of cage, ladder and their mixtures, have gained an attention as a hybrid material, because a variety of organic components are easily introduced to the inorganic siloxane frames by design of the –R group in the alkyltrialkoxysilane monomer $[RSi(OR')_3]$ [1]. Thus, these materials show a unique set of physical and chemical properties such as high thermal and mechanical stabilities with various functionalities, which are not realized from ceramic or organic polymer alone [2].

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Functionalization of polysilsesquioxane is usually achieved by modifying the –R group in the alkoxysilane monomer followed by sol-gel polymerization or in the polymer by post reaction. The –R group is usually a small functional molecule, however a macromolecule is more interesting, because many more functional groups could easily be introduced to the inorganic siloxane backbone by graft polymerization of functional monomers. In addition, obtained organic graft polymers could compensate for the brittleness and hardness of the inorganic polymer.

Controlled radical polymerization (CRP) is one of the most popular methods for such functionalization, because of tolerance to polar functional groups as well as easy polymerization system design. As an inorganic siloxane material, polyhedral oligomeric silsesquioxane (POSS) has been widely used for functionalization via graft polymerization [3–5], because of its easy synthesis with well-defined structure. In contrast, very few studies with ladder or ladder like structured polysilsesquioxane (LPSQ) have been reported, because of synthetic difficulties. Some research groups have recently been reported graft hybrid polymers from random structured polysilsesquioxanes including LPSQ using Cu based living radical polymerization (ATRP) [6,7]. However, these graft polymerizations carried out with uncontrolled structured polysilsesquioxane macroinitiator and mostly examined by homopolymerization. In this study, we synthesized well-defined ladder-like polysilsesquioxane (LPSQ) with a benzyl chloride group at each silicon atom as the –R group, by a recently developed direct hydrolysis and condensation reaction method. Obtained LPSQ was used as a macroinitiator for ATRP graft polymerization of styrene, *n*-butyl acrylate (*n*BA), and their comonomers.

Experimental

Materials

(ρ-chloromethyl)phenyltrimethoxysilane (Gelest, 95%) was vacuum distilled before use. n-butyl acrylate (nBA) (Aldrich, 99%) and styrene (Aldrich, 99%) were of commercial source, were dried overnight over calcium chloride, and purified by distillation from calcium hydride before use. Cu(I)Cl (Aldrich, 99.999%), and 4,4-di (5-nonyl)-2,2-bipyridine (dNbpy) (Aldrich, 99.999%) were used as received.

Synthesis of Poly Poly[(ρ-chloromethyl)phenylsilsesquioxane] (LCMPSQ) as Macroinitiator. In a 100 ml round-bottomed flask, deionized water (0.133 mol, 2.4 g) and K_2CO_3 (0.145 mmol, 0.02 g) were charged and stirred for 10 min. Dry THF (0.056 mol, 4 g) was added and stirred for additional 30 min. Afterwards, vacuum distilled (ρ-chloromethyl)phenyltrimethxysilane (0.04 mol, 9.87 g) was added dropwise via syringe under nitrogen, and the reaction kept for stirring at room temperature for 72 h. For purification, crude, white, viscous products were dissolved in methylene chloride (M.C) (30 ml) and extracted with deionized water (30 mL) for 2 h. M.C solution was dried overnight with $MgSO_4$. After filtering $MgSO_4$ and evaporating M.C., final white powder (6.8 g, 96% yield) was obtained after vacuum drying at 40°C.

Synthesis of Poly(styrene-g-silsesquioxnae) (PS-g-PSQ), Poly(nBA-g-silsesquioxnae) (PnBA-g-PSQ) and Poly(styrene-co-nBA-g-silsesquioxnae) (PS/nBA-g-PSQ). A typical graft polymerization procedure with styrene/LCMPSQ/CuCl/dNbpy (100/1/1/2) is as follows: styrene (0.139 mol, 14.48 g), CuCl

(1.39 mmol, 0.14 g), degassed toluene (0.13 mol, 14.5 mL), and dNbpy (2.78 mmol, 1.14 g) were added sequentially to 100 mL flamed flask equipped with a three-way stopcock under an argon atmosphere. The mixture was stirred for 10 min at 25°C and contained that 1.39 mmol of benzylchloro moieties, LCMPSQ as macroinitiator (0.13 mmol, 0.29 g) that was added. After further stirring for 5 min, five aliquots (5 mL, each) of the solution were distributed into baked glass tubes under an argon atmosphere, which were then sealed and placed in an oil bath at 90°C. In predetermined intervals, the polymerization was terminated by cooling to −78°C. The conversion was determined by ^{1}H NMR. The reaction mixture was then diluted with THF and filtered through a neutral alumina column to remove the catalyst. The solution was condensed and then poured into cold methanol. Precipitated white polymer was then filtered and dried overnight under vacuum at 40°C. The molecular weights and the chemical structures were characterized by SEC and ^{1}H NMR. Analogous PnBA-*g*-PSQ hybrid polymers were prepared under same conditions with nBA (0.139 mol, 17.82 g).

As the random grafted polymers, the three type of PS/nBA-*g*-PSQ series were prepared using the same method with PS-*g*-PSQ and PnBA-*g*-PSQ from three different mole-ratio [styrene 75: nBA 25, styrene 50: nBA 50, styrene 25: nBA 75].

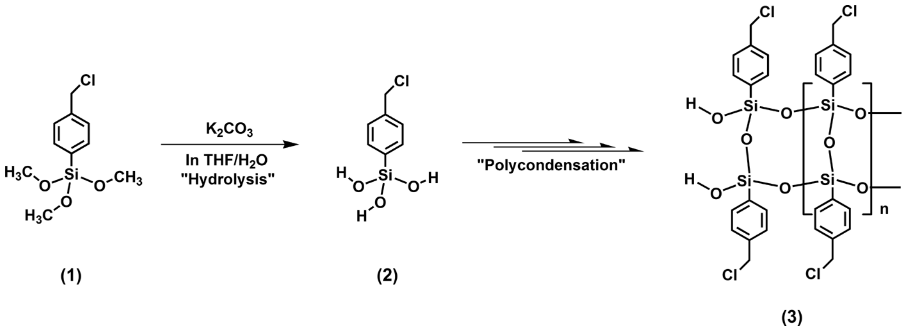
Polymer Characterization

The average molecular weight (M_w) and molecular weight distributions (M_w/M_n) of the polymers were measured using a JASCO PU-2080 plus SEC system equipped with RI-2031 plus refractive index detector and a UV-2075 plus UV detector (254 nm detection wavelength) using THF as the mobile phase at 40°C and a flow rate of 1 mL/min. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804, and KF-805). ^{1}H and ^{29}Si NMR spectra were recorded in $CDCl_3$ at 25°C on a Varian Unity INOVA (^{1}H: 300 MHz, ^{29}Si: 99.5 MHz). Fourier transform infrared (FT-IR) spectra were measured with a Perkin-Elmer FT-IR system Spectrum-GX using solvent cast films on KBr pellets. The X-ray film diffraction was examined at the beam-line 3C2 of Pohang light source (PLS) in the Pohang Accelerator Laboratory (PAL) using Cu-Kα radiation.

Results and Discussion

Synthesis of Ladder-like Poly(chloromethylphenylsilsesquioxane) (LCMPSQ) Macroinitiator. Ladder-like poly(chloromethylphenylsilsesquioxane) (LCMPSQ) as macroinitiator was synthesized using sequential two-step reactions in the presence of a base catalyst (Scheme 1) [8]. Thus, (ρ-chloromethyl)phenyltrimethxysilane monomer (CMPTMS) (**1**) was first hydrolyzed with K_2CO_3 in the mixture of THF and water at room temperature to prepare the hydrolyzed CMPTMS (**2**), where two phases of the reaction solution originated from the monomer and the solvents was changed to one phase, followed by running more reaction time to give the LCMPSQ (**3**). SEC analysis of the obtained LCMPSQ showed the weight averaged molecular weight (M_w) of 6,000 g/mol and the molecular weight distribution of 2.4.

Figure 1, A-B show ^{1}H NMR spectra of the monomer (CMPTMS) and the obtained polymer (LCMPSQ), respectively. The methoxy peaks (a) and two



Scheme 1. Ladder-like Poly(chloromethylphenylsilsesquioxane) (LCMPSQ) as macro initiator.

absorption peaks (b, c) originated from the phenyl and the chloromethyl protons (d) in Figure 1A were completely disappeared and broadened in Figure 1B, respectively. These results indicated that the methoxy silane monomer was completely hydrolyzed and then polymerized by condensation reaction to give LCMPSQ as described in Scheme 1.

This silsesquioxane polymer was then characterized by ^{29}Si NMR spectroscopy to examine the siloxane backbone structure (Fig. 2). ^{29}Si NMR spectra showed a large absorption peak (a) at -80 ppm and a small absorption peak (b) at -68 ppm, which were originated from the T_3 structure of the phenyl-siloxane bond [Ph-Si(OSi-)$_3$] and the hydroxyl end group of the T_2 structure, [Ph-Si(OSi-)$_2$-OH], respectively. The integration ratio of T_3 to T_2 absorption peaks showed ~98% of T_3 structure, which indicated that obtained LCMPSQ was mostly consisted of the ladder-like siloxane structures.

FT-IR analysis also supported that the obtained LCMPSQ had a ladder structure. Figure 3 shows a broad and bimodal absorption peak ranged from 1000 to 1180 cm^{-1}, which originated from the stretching vibration of siloxane bond in the vertical (-Si-O-Si-R) and horizontal (-Si-O-Si-) direction of polysilsesquioxane [9].

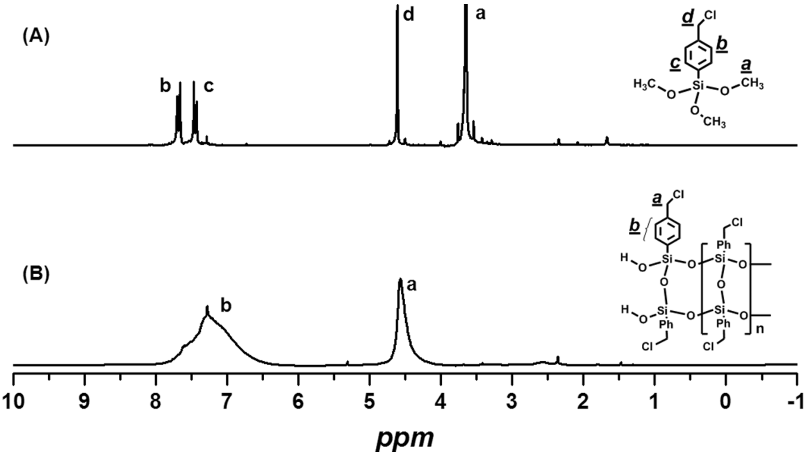


Figure 1. ^{1}H NMR spectra of CMPTMS (A) and LCMPSQ (B) in $CDCl_3$.

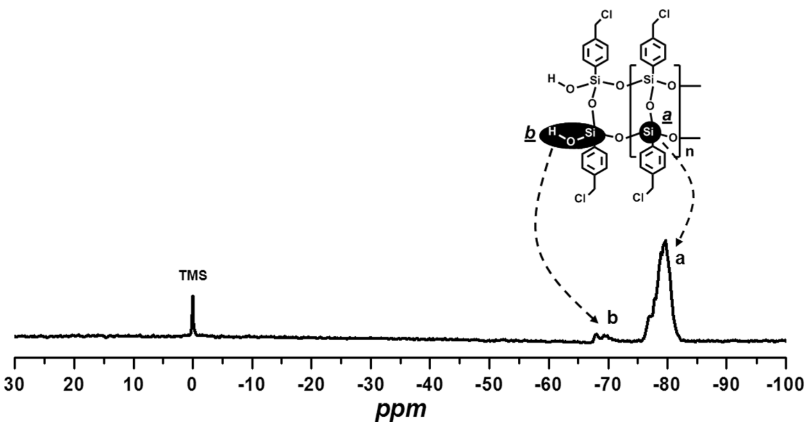


Figure 2. ^{29}Si NMR spectra of LCMPSQ in $CDCl_3$.

The peak top at 1150 cm^{-1} has been known to be the characteristic peak for the horizontal siloxane bond and was more preferentially formed, while the peak at 1040 cm^{-1} was attributed to the vertical siloxane bond. The peak top of the unsymmetrical absorption peak was much closer to 1150 cm^{-1}, which indicated that the LCMPSQ as macro-initiator had more horizontal siloxane structure, like a ladder structure [10].

X-ray diffraction (XRD) analysis was carried out to investigate more detailed structure of the LCMPSQ (Fig. 4) [11]. Obtained XRD spectra showed two characteristic diffraction peaks at 6.15° (a) and 20° (b), which were quite similar as typical ladder-like polysilsesquioxanes [12]. The first sharp peak (a) indicated the intermolecular periodic chain-to-chain distance ($d_1 = 14.4$ Å), thus the distance between two choromethylphenyl pendant groups through the ladder structured siloxane backbone, while the second diffused peak (b) indicated the average thickness of the siloxane backbone ($d_2 = 4.5$ Å).

Graft Polymerization from LCMPSQ Macroinitiator by ATRP Method. Obtained LCMPSQ was then used as a macroinitiator to polymerize styrene (St), *n*-butyl acrylate (*n*BA), and their comonomers in the presence of CuCl catalyst and

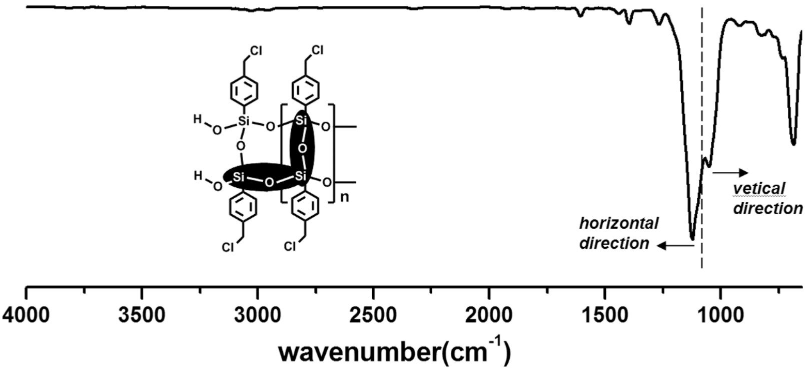


Figure 3. FT-IR spectrum of LCMPSQ.

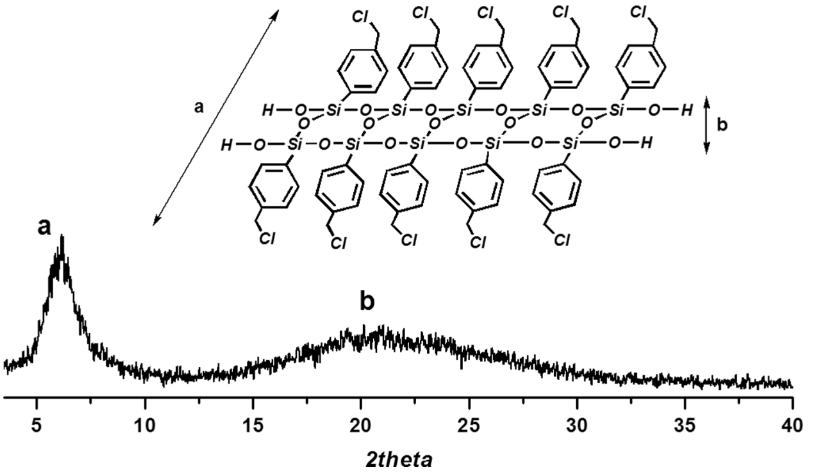
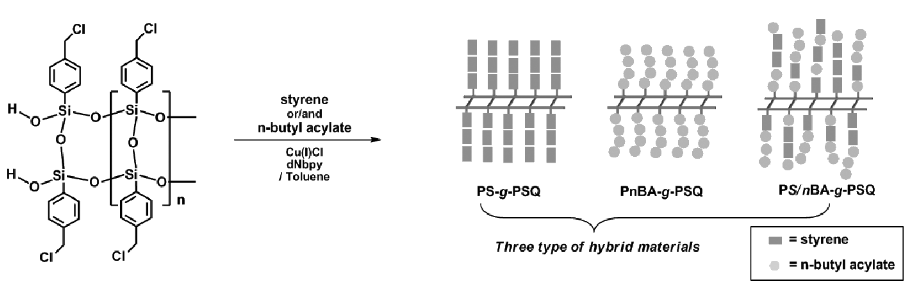


Figure 4. XRD pattern of LCMPSQ: periodic chain-to-chain distance (a) and thickness (b).

4, 4-di(5-nonyl)-2,2-bipyridine (dNbpy) ligand in toluene at 90°C, where the benzyl chloride groups along with the ladder-like polysiloxane backbone initiated the monomers to give the graft polymers brushed polysilsesquioxane (Scheme 2).

Styrene graft polymerization was first examined to synthesize a hybrid material with hard organic and hard inorganic segments (PS-*g*-PSQ). The LCMPSQ macroinitiator induced smooth graft polymerization of styrene until the conversion was lower than 50%, however the polymerization slowed thereafter (Fig. 5A). Figure 5B shows SEC curves of the LCMPSQ macroinitiator and the product obtained at different time intervals. The bimodal SEC curve of the LCMPSQ changed to a single unimodal SEC curve after graft polymerization, which was then shifted to high molecular weight with narrow polydispersity ($\mathrm{PDI} < 1.4$). However, the polymers obtained after 46.7% of the conversion showed a small amount of undesirable higher molecular weight shouldering in addition to main SEC peak. This is probably due to coupling reactions, which often occurred when in syntheses of branched polymers such as star polymer and graft polymer by ATRP [4].

As a second organic-inorganic hybrid material, relatively soft poly(*n*BA) was grafted to hard LCMPSQ by graft polymerization of the *n*BA (P*n*BA-*g*-PSQ). Figure 6A shows the polymerization was smoothly proceeded for 25 h (the conversion $> 90\%$). SEC curves of the obtained products at different time interval



Scheme 2. Synthetic diagram of hybrid material series using LCMPSQ as macroinitiator.

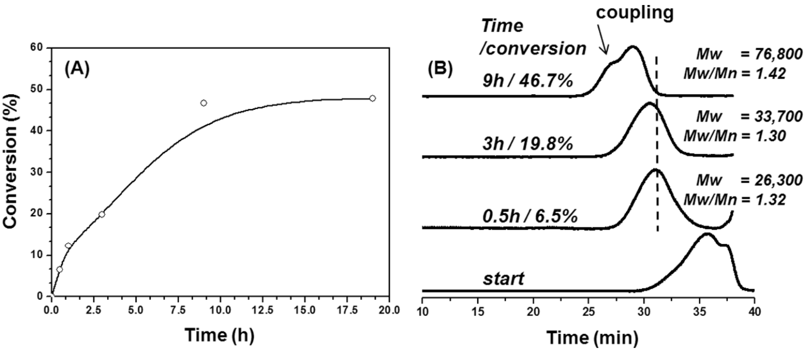


Figure 5. Graft polymerization of styrene from LCMPSQ (A) and GPC curves (B) of PS-*g*-PSQ obtained from CuCl/dNbpy catalytic system in toluene at 90°C.

showed similar behavior as the styrene graft polymerization, thus they shifted to high molecular weight with narrow polydispersity (PDI < 1.4) as the monomer was consumed (Fig. 6B). However, the coupling reaction was also occurred in this graft polymerization after 74.8% of the conversion. These results indicated that earlier stopping the polymerization was important to obtain well-defined graft polymers both in styrene and *n*BA polymerization by ATRP.

A series of hard-soft grafted random copolymers with the inorganic polysiloxane backbone were synthesized by copolymerization of styrene and *n*BA from the LCMPSQ macroinitiator. In these syntheses, different molar ratios of styrene and *n*BA were utilized for graft polymerization by ATRP (Table 1). The reaction was conducted for 8 h, because this reaction time was the maximum point at which no coupling reactions both in styrene or *n*BA graft homopolymerization. Obtained grafted copolymers showed narrow polydispersities (PDI < 1.4) regardless of the monomer molar ratio, but they were a slightly broader in higher styrene molar ratio (Table 1, Run 1). ^{1}H NMR analyses showed that the ratios of styrene and *n*BA in the graft copolymers corresponded well to the molar ratios of the monomers, especially in higher *n*BA molar ratio (Table 1, Run 3 and Figure 7C). These results indicated that control of monomer molar ratio could tune the physical property of the graft polymer such as hardness and softness, which may greatly affect the final properties of the hybrid material.

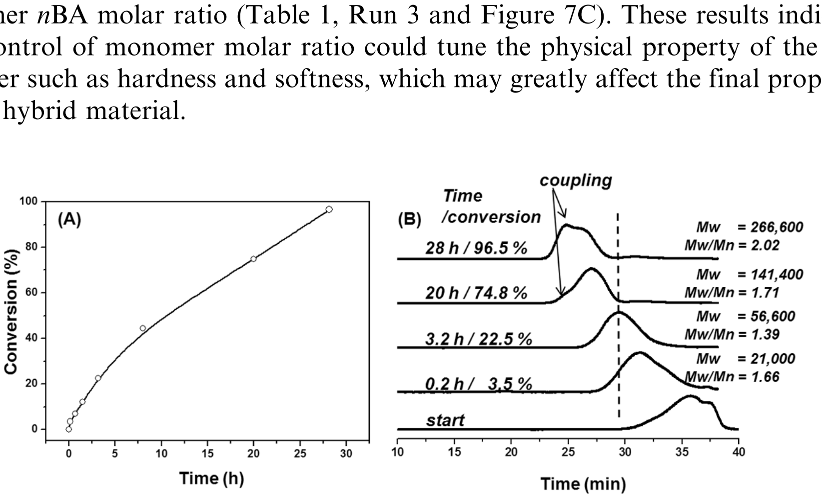


Figure 6. Graft polymerization of n-butylacylate from LCMPSQ (A) and GPC curves (B) of P*n*BA-*g*-PSQ obtained from CuCl/dNbpy catalytic system in toluene at 90°C.

Table 1. Graft copolymerization of styrene and *n*BA from LCMPSQ macroinitiator by ATRP

	Monomer ratio (mol %)		Conversion (%)		Integral ratio in graft polymer (^{1}H NMR)			
Run	*n*BA	Styrene	*n*BA	Styrene	*n*BA	Styrene	M_w (SEC)	M_w/M_n (SEC)
1	25	75	14	19	35	65	44,000	1.37
2	50	50	19	13	55	45	61,900	1.31
3	75	25	21	10	79	21	68,000	1.30

Figures 7 and 8 show ^{1}H NMR and FT-IR spectra of the final products of the grafted polymers: (A) polystyrene graft polymer (PS-*g*-PSQ), (B) poly(*n*BA) graft polymer (P*n*BA-*g*-PSQ), and (C) poly(styrene-*ran*-*n*BA) graft polymer (P*S*/BA-*g*-PSQ). All graft polymers showed their specific absorption peaks derived from polystyrene, poly(*n*BA), and their copolymers in addition to the absorption peaks of the LCMPSQ. Figure 7A and 7B showed specific absorption peaks (a) derived from the phenyl proton in the PS from 6.4 to 7.7 ppm and the absorption peaks (b) of the ethylene protons adjunction to the ester group in the P*n*BA at 4.1 ppm, respectively. These specific absorption peaks of the PS and the P*n*BA were mixed in the graft copolymer (Fig. 7C). In addition, Figure 8A and 8B showed specific absorptions at 3045 cm^{-1} (sp^2 C-H stretch), 1451 and 1500 cm^{-1} (aromatic C=C stretch) derived from the PS and 1732 cm^{-1} (C=O stretch) derived from the P*n*BA, respectively.

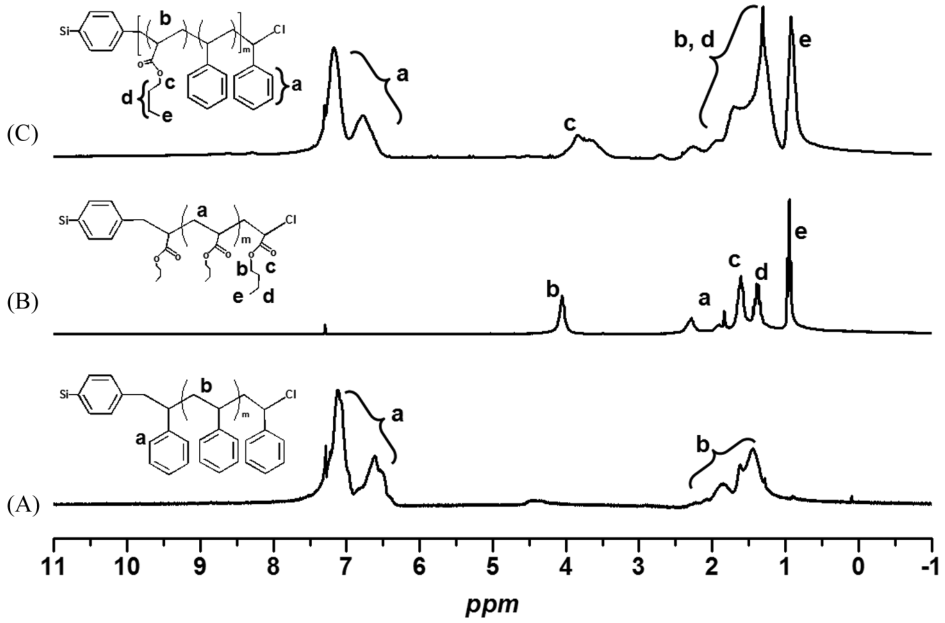


Figure 7. ^{1}H NMR spectra of synthetic hybrid materials: (A) PS graft polymer, (B) P*n*BA graft polymer, (C) PS-*ran*-P*n*BA graft polymer.

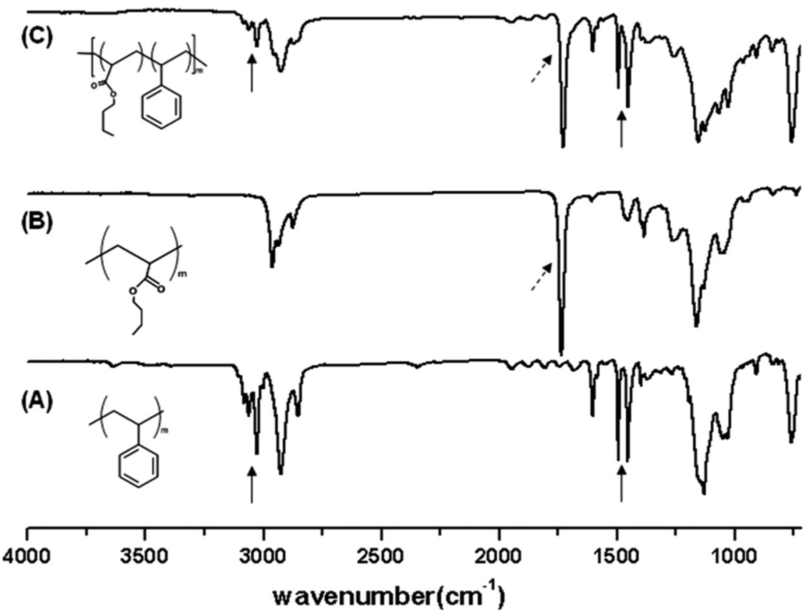


Figure 8. FR-IR spectrum of synthetic hybrid materials: (A) PS graft polymer, (B) P*n*BA graft polymer, (C) PS-*ran*-P*n*BA graft polymer.

Figure 8C showed their mixed absorption peaks derived from PS and P*n*BA. These results indicated that the graft polymerization from the LCMPSQ macroinitiator by ATRP was useful method to prepare well-defined hybrid materials with organic graft polymers.

Conclusion

We successfully synthesized ladder-like structured poly(chloromethylphenylsilsesquioxane) (LCMPSQ), which was used as a macroinitiator to polymerize styrene, *n*BA, their comonomers by Cu based living radical polymerization (ATRP). Obtained graft polymers polystyrene, poly(*n*BA) from the polysilsesquioxane backbone showed narrow polydispersities ($PDI < 1.4$) and their molecular weight was also precisely controlled by the reaction time. In addition, the graft copolymers with various ratios of styrene and *n*BA were obtained by change of the monomer ratio. In conclusion, graft polymerization by ATRP from inorganic polysilsesquioxane (LPSQ) promises to create various new hybrid materials and provide useful a wide range of physical properties for industrial development.

Acknowledgment

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