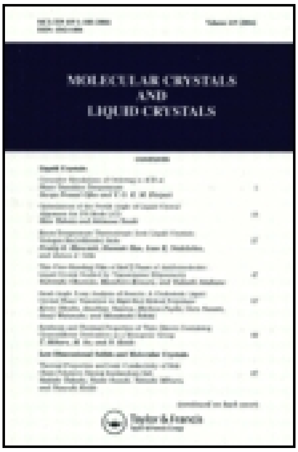

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Synthesis and Characterization of Azido-Substituted Ladder-like Polysilsesquioxanes and their Click Chemistry

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Synthesis and Characterization of Azido-Substituted Ladder-like Polysilsesquioxanes and their Click Chemistry

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A novel organic-inorganic hybrid-type ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) and ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) were synthesized through azidation of ladder-like poly(p-chloromethyl)phenylsilsesquioxane (LPCMPSQ) and ladder-like poly(propylchloro)silsesquioxane (LPPCSQ). The ladder-like structure of the synthesized LPBAzSQ and LPPAzSQ compounds, full substitution of azide groups, and their click chemistry with various functional groups was characterized by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, FT-IR, GPC. This new approach for functionalization of ladder-like silsesquioxanes has allowed for insertion of polar functional groups that have yet be examined in silsesquioxane chemistry.

Keywords Polysilsesquioxanes; ladder-like silsesquioxanes; azidation; click reactions; click chemistry

Introduction

Polysilsesquioxanes $(RSiO_{3/2})_n$ comprise a class of inorganic-organic hybrid materials exhibiting excellent properties such as thermal stability, low dielectric constant, good mechanical properties, chemical resistance, and even biocompatibility [1–4]. Such properties, arising from its rigid siloxane backbone, have advanced these materials to applications not limited to semiconductor devices [4], OLEDs [5], molecular silicas [6], nano-patterning in lithography [7], and drug delivery [8]. There are three structural classes of polysilsesquioxanes which include sol-gel processed random-branched, cage-type polyhedral oligomeric silsesquioxanes (POSS), and double-stranded ladder-like silsesquioxanes. Today, much of silsesquioxane research has centered on cage silsesquioxanes, because of their well-defined, unique three-dimensional structure. However, ladder-like silsesquioxanes [9–13] offer further advantages in being a polymeric analogue in having a greater number of functional groups for post-functionalization.

However, post-functionalization of the R groups of polysilsesquioxanes has been known to be a tedious process. Sol-gel derived random branched structures have remaining

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Si-OH groups which are sensitive to acidic, basic, and acqueous conditions, making them incompatible to be further chemically modified. Furthermore, cage structures and ladder silsesquioxanes, while chemically stable, are limited by the –R groups available as trialkoxy or trichloro monomers [14]. Even elementary functional groups such as hydroxyl or amine groups are problematic as monomers are not available as in the case of hydroxyl groups, or ladder silsesquioxane synthesis tedious, in the case for amine groups [11]. As such, a universal method for post-functionalization of polysilsesquioxanes is to be desired, with the chemistry involved to be able to cover a wide range of functional groups, especially polar functional groups.

The azide-alkyne ‘click’ reaction is considered today as one the most powerful tools in polymer chemistry [15–17]. The utility in being able to functionalize polymers in high yields with high stereospecificity has allowed for further chemical modification and design of new polymeric geometries [18]. Moreover, the extremely high tolerance to a vast number of functional groups has made it one of the most popular methods of polymer post-functionalization [15]. While studies of click-chemistry with cage silsesquioxanes have been reported previously [19–23], we report the first azido-functionalized ladder silsesquioxane and click reactions therein.

In this study, two types of ladder silsesquioxanes: ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) and ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) were synthesized through azidation of ladder-like poly(p-chloromethyl)phenylsilsesquioxane (LPCMPSQ) and ladder-like poly(propylchloro)silsesquioxane (LPPCSQ). These azido-functionalized ladder polysilsesquioxanes were then clicked with various terminal alkynes groups, exemplifying the utility of click chemistry in silsesquioxane research and for the introduction of new functional groups that have yet to be realized in ladder silsesquioxanes.

Experimental

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. ^{1}H, ^{13}C ^{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 pallets.

Materials

(p-chloromethyl)phenyltrimethoxysilane (Gelest, 95%), chloropropyltrimethoxysilane (Gelest, 95%), and N,N,N’,N’,N”-pentamethyldiethylenetriamine, PMDETA (Aldrich, 99.9%) were vacuum distilled before use. Tetrahydrofuran (THF) (J.T baker, 99.8%) and Toluene (J.T. Baker, 99.8%) were distilled from metal sodium with benzophenone before use. Potassium carbonate (K_2CO_3) (sam-jun) was dried overnight under vacuum at 50 °C. Sodium Azide (Dae-Jung), CuBr (Aldrich, 99.999%), 3,3-dimethyl 1-butyne (Aldrich, 98%), propargyl alchohol (Aldrich, 99%), propargyl amine (Aldrich, 99%), and all other solvents of HPLC grade were used as received.

Synthesis of Ladder-like Poly[(p-chloromethyl)phenylsilsesquioxane] (LPCMPSQ) and Ladder-like Poly[chloropropylsilsesquioxane] (LPCPSQ). 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. And then, vacuum distilled (ρ-chloromethyl)phenyltrimethxysilane (0.04 mol, 9.87 g) or chloropropyltrimethoxysilane (0.04 mol, 7.95 g) was added dropwise via syringe under nitrogen and the reaction kept for stirring at room temperature for 72h. 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. Afterwards, deionized water was removed and M.C solution was dried overnight from $MgSO_4$. The M.C solution was filtered to remove anhydrous $MgSO_4$ and then M.C was evaporated at 40°C. Final white powder (6.8g, 96% yield) was obtained after vacuum drying at 40°C.

Azidation of Ladder-like Poly[(p-chloromethyl)phenylsilsesquioxane] (LPCMPSQ) and Ladder-like Poly[chloropropylsilsesquioxane] (LPCPSQ). In a 100 ml round-bottomed flask, LCMPSQ (0.34 g, 0.33 mmol) or LCPSQ (6.2 g, 0.33 mmol) were charged with 50 ml of DMF. To this solution, sodium azide (2 g, 30 mmol) was added. The reaction mixture was stirred at 40°C for 72 hr. Extraction with M.C. and brine several times, followed by precipitation in deionized water yielded the desired products ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) and ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) in good yield ($<$95%).

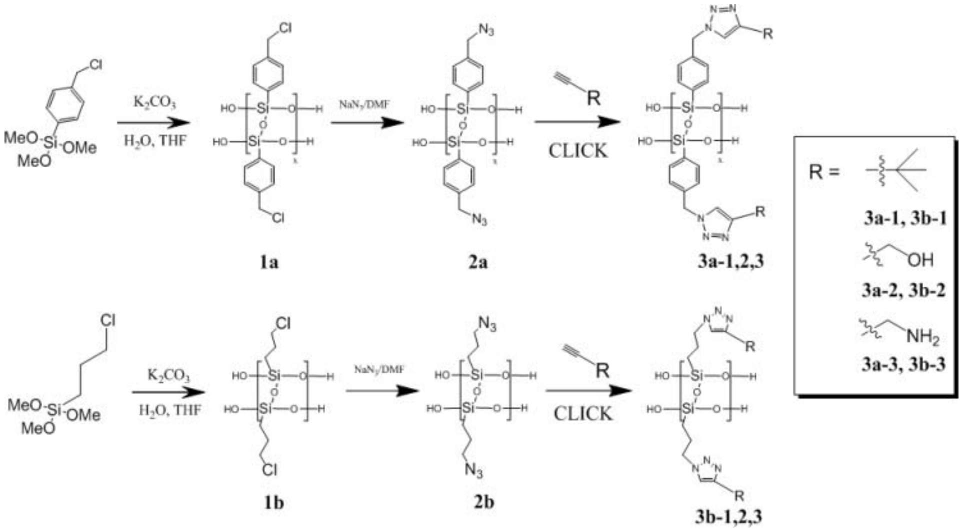
Click Reactions with ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) and ladder-like poly(propylazide) silsesquioxane (LPPAzSQ). Using an inert Schlenk line, LPBAzSQ (0.4 g, 2.3 mmol azide groups) or LPPAzSQ (0.3 g, 2.3 mmol azide groups) were charged in a 100 ml flask, along with CuBr (0.33 g, 2.3 mmol), PMDETA (0.49 ml, 2.5 mmol) and Toluene (20 ml). After stirring for 20 minutes, the reaction mixtures were cooled to −78°C by dry ice-acetone bath, and the corresponding alkynes (2.5 mmol) were added under Argon. Then, the reaction solution was slowly warmed to room temperature and left for 48 hr. After reaction, the solution was passed through an alumina column and precipitated in cold hexane. The clicked products were vacuum dried at 40°C.

Results and Discussion

Synthesis of ladder-like poly(p-chloromethyl)phenylsilsesquioxane (LPCMPSQ) **1a** and ladder-like poly(propylchloro)silsesquioxane (LPPCSQ) **1b** were carried out following a modified literature procedure [5]. The detailed synthetic route for ladder compounds, azidation, and click chemistry are detailed in Scheme 1.

^{1}H NMR spectra (Fig. 1) of LPCMPSQ and LPPCSQ showed the complete disappearance of methoxy groups and silanol groups, indicating full hydrolysis and full condensation of the monomers. Broad peaks assigned to the alkyl and aromatic protons indicated that the structure was of a polymeric nature, substantiated by GPC results (non shown) giving a weight averaged molecular weight of 11,100 and 20,000 with PDI values of 2.4 and 4.0 for LPCMPSQ, LPPCSQ, respectively. Moreover, azidation of the chloro groups to azo groups showed a 2 ppm downfield shift for both ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) (**2a**) and ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) (2b).

Full conversion of chloro groups to azide groups were further characterized by ^{13}C NMR (Fig. 2). The methylene protons in the alpha position relative to the chloro groups located at 46 ppm and 48 ppm for LPCMPSQ, LPPCSQ respectively, fully disappeared and



Scheme 1. Synthetic Scheme for Clicked Ladder-like Silsesquioxanes

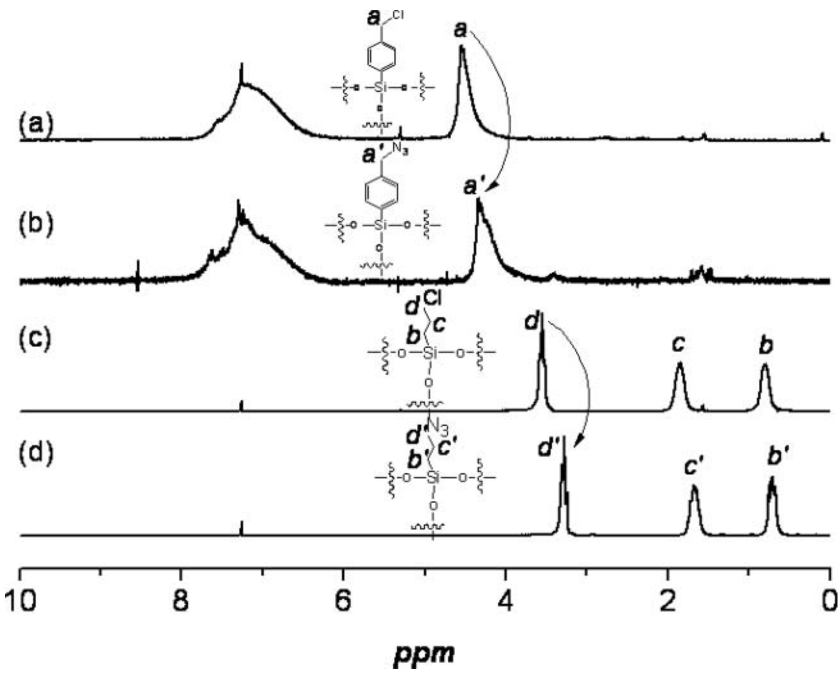


Figure 1. ^{1}H NMR Spectra for (a) poly(p-chloromethyl)phenylsilsesquioxane (LPCMPSQ) **1a**, (b) ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) **2a**, (c) ladder-like poly(propylchloro)silsesquioxane (LPPCSQ) **1b**, and (d) ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) **2b**

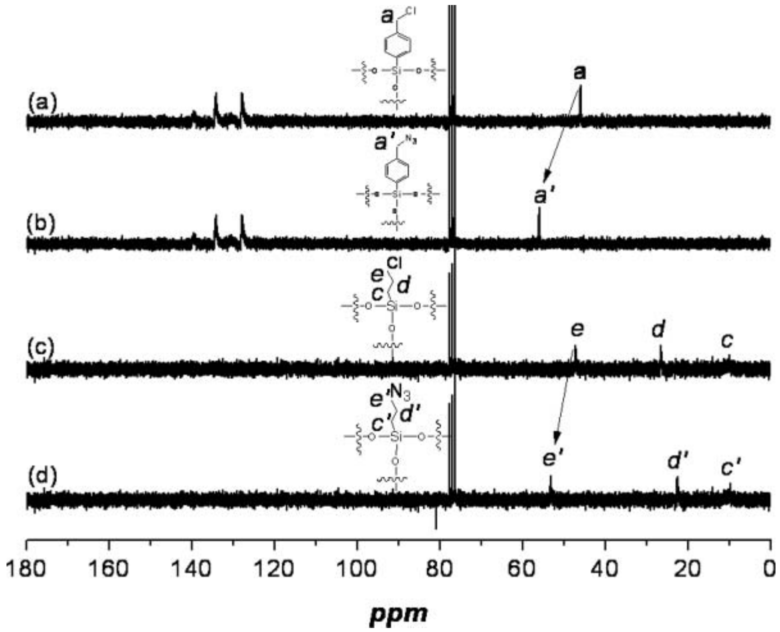


Figure 2. ^{13}C NMR Spectra of (a) poly(p-chloromethyl)phenylsilsesquioxane (LPCMPSQ) **1a**, (b) ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) **2a**, (c) ladder-like poly(propylchloro)silsesquioxane (LPPCSQ) **1b**, and (d) ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) **2b**

shifted to 53 ppm and 52 ppm after azidation to yield LPBAzSQ, LPPAzSQ respectively. These results, along with the ^{1}H NMR results indicated that full conversion of chloro groups to azo groups had occurred.

FT-IR spectrum (Fig. 3) of the synthesized ladder compounds and azido-substituted compounds showed characteristics peaks at 1150 cm^{-1} and 1040 cm^{-1} which were assigned to the horizontal and vertical stretching modes for the siloxane bonds of the ladder structured silsesquioxanes [12]. Also, the lack of peaks at 3500 cm^{-1} indicated that the structure had minimal Si-OH silanol groups, characteristic of high molecular weight ladder materials [11,13]. Moreover, the azido-substituted ladder-like poly(benzylazide) silsesquioxanes LPBAzSQ and LPPAzSQ (Fig. 3b,d) showed a sharp peak at 2200 cm^{-1}, assigned to the azide –N_3 groups.

^{29}Si NMR spectra (Fig. 4) of the azido-substituted ladder silsesquioxanes, **2a and 2b**, showed an entirely T3 structure [R-Si(OSi-)$_3$] for both compounds. The T3 peak for ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) **2a** was assigned to the broad peak centered at −77 ppm, while the T3 peak for ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) **2b** was assigned to the peaks centered at −68 ppm. The T3 peaks for ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) **2b** were observed to be multiplicative, due to the large PDI (4.0). These peaks were in good agreement with those T3 peaks reported previously [14].

Click reactions with propargyl alcohol, propargyl amine, and 3,3-dimethyl 1-butyne yielded the 1,2,3 triazole adducts in good yield >95%. ^{1}H NMR spectra (Fig. 5) showed that the presence of the unsaturated proton at 7.8 ppm assigned the proton at the 5′ position of the triazole moiety. Moreover, the representative proton peaks for amine –NH_2 were found

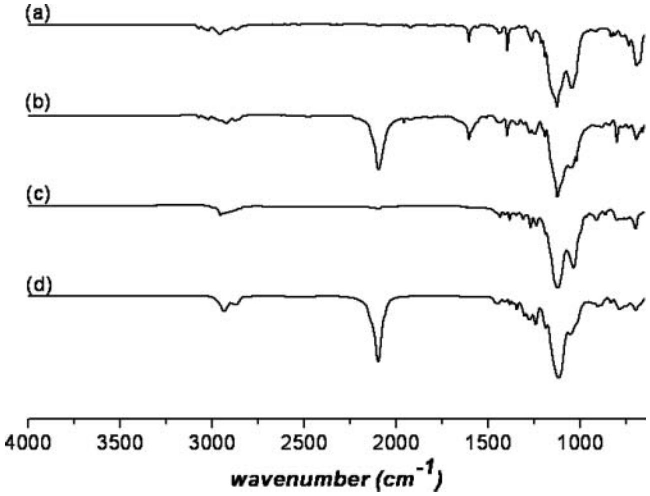


Figure 3. FT-IR Spectra of (a) poly(p-chloromethyl)phenylsilsesquioxane (LPCMPSQ) **1a**, (b) ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) **2a**, (c) ladder-like poly(propylchloro)silsesquioxane (LPPCSQ) **1b**, and (d) ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) **2b**

at 8.4 ppm and 8.7 ppm for compounds **3a-3**, **3b-3**, respectively, as well as the hydroxyl –OH proton peak at 3.565 ppm and 3.55 ppm for compounds **3a-2**, **3b-2**, respectively. 100% conversion of the azide groups to triazole groups were confirmed by the complete disappearance of the protons alpha to the azide groups.

The introduction of the hydroxyl and amine groups into ladder silsesquioxanes via click chemistry was also confirmed by FTIR (Fig. 6). Clicked adducts shown in Fig. 6 (b),

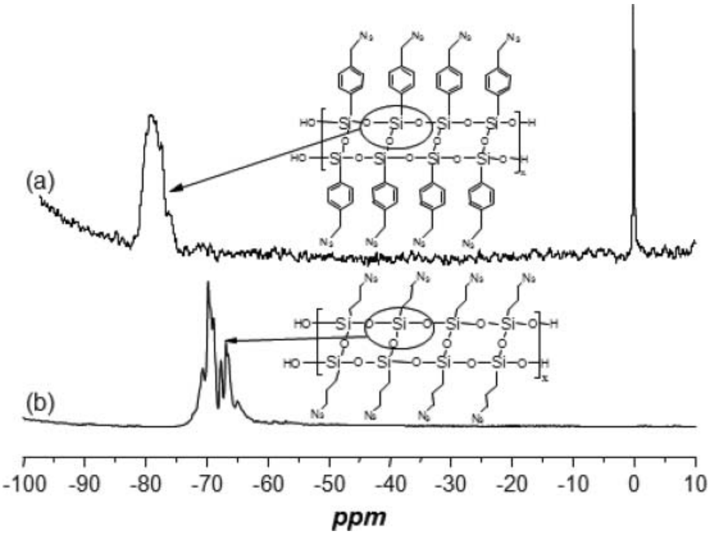


Figure 4. ^{29}Si NMR Spectra of (a) ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) **2a** and (b) ladder-like poly(propylazide) silsesquioxane (LPPAzSQ) **2b**

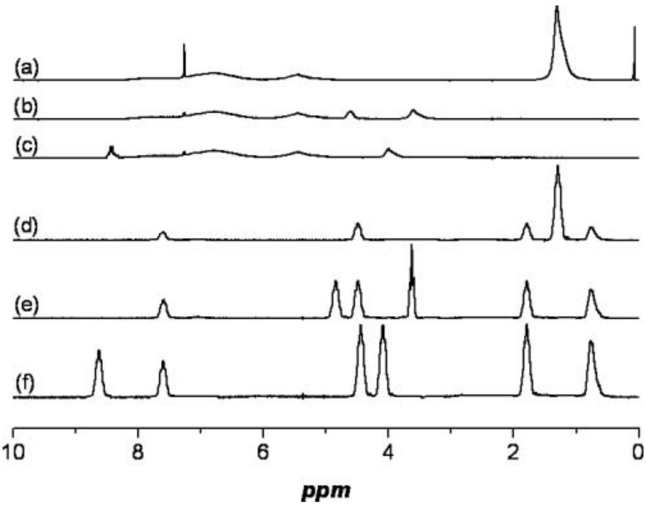


Figure 5. ^{1}H NMR Spectra of Clicked Products (a) **3a-1** (b) **3a-2** (c) **3a-3** (d) **3b-1** (e) **3b-2** (f) **3b-3**

(c) showed the presence of hydroxyl groups assigned to the broad peak at 3500 cm^{-1}, while amine peaks shown at 3200 cm^{-1}, while the characteristic horizontal and vertical siloxane peaks at 1150 cm^{-1} and 1040 cm^{-1} remained constant. These results, coupled with ^{1}H NMR results showed that the click reaction was successful in introducing hydroxyl and amine groups into ladder silsesquioxanes.

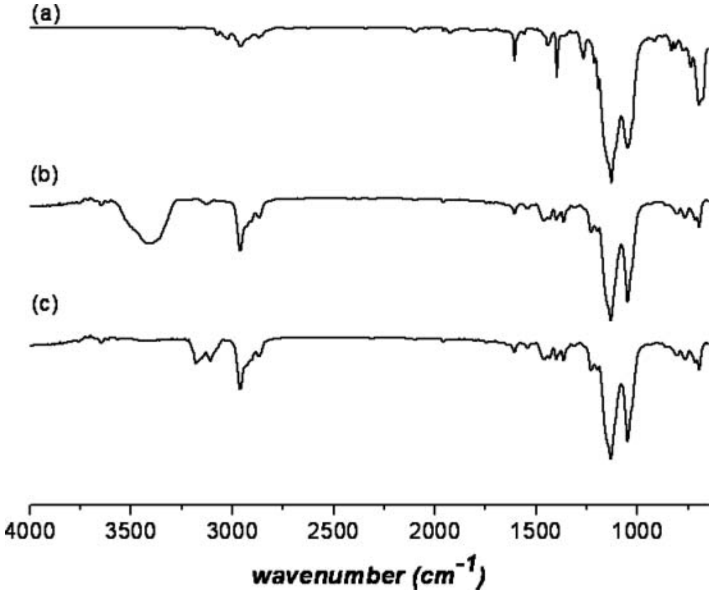


Figure 6. FTIR Spectra of Clicked Adducts (a) **3a-1** (b) **3a-2** and (c) **3a-3**

Conclusion

Novel azido-substituted ladder silsesquioxanes were synthesized via azidation of ladder-like poly(p-chloromethyl)phenylsilsesquioxane (LPCMPSQ) and ladder-like poly(propylchloro)silsesquioxane (LPPCSQ) to yield ladder-like poly(benzylazide) silsesquioxane (LPBAzSQ) and ladder-like poly(propylazide) silsesquioxane (LPPAzSQ). These hybrid polymers were subjected to click reactions using Copper catalyst for the introduction of elementary, polar, functional groups such as hydroxyl and amine. This approach will allow for the introduction of more novel functional groups that have yet to be realized in silsesquioxane chemistry.

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