

SYNTHESIS, CHARACTERIZATION, AND THERMAL PROPERTIES OF BRIDGED POLYSILSESQUIOXANES–MOLECULAR NANOCOMPOSITES

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ABSTRACT

Polysilsesquioxanes (PSSQ) possesses excellent thermal stability and high transparency. In this study, three series of bridged PSSQ were synthesized by sol-gel method. They contain dipropylurea-bridged PSSQ, 1,6-bis(trimethoxysilyl)hexane bridged PSSQ, and 1,4-bis(trimethoxysilylethyl)benzene bridged PSSQ. Characterization of the structures, optical property, thermal stability and flame retardancy will be discussed in the study.

The changes of functional group (Si-O-Si) were monitored by FTIR. The characteristic peak is 1168–1104 cm^{-1} . The formations of Si-O-Si bond represent the occurrence of condensation. ^{29}Si NMR results show that T^3 (tri-substituted) and T^2 (di-substituted) are the dominant microstructure. This phenomenon indicates the formation of three-dimensional network. X-ray data reveal no existence of peaks. There is no structure of crystals, i.e., it is amorphous. TGA data shows that Td_{10} (the temperature at which 10 wt% weight loss of sample occurs) of dipropylurea-bridged PSSQ, 1,6-bis(trimethoxysilyl)hexane bridged PSSQ, 1,4-bis(trimethoxysilylethyl) benzene bridged PSSQ are 410°C, 506°C, 580°C, respectively. Results indicate these polymers possess excellent thermal stability. The char yields of dipropylurea-bridged PSSQ, 1,6-Bis(trimethoxysilyl) hexane bridged PSSQ, 1,4-bis(trimethoxysilylethyl) benzene-bridged PSSQ are 58.5 wt%, 70.7 wt% and 81.1 wt%, respectively. High char yields lead to excellent flame retardance. Theoretically, L.O.I. will achieve to 39.4~57.5. These three kinds of polysilsesquioxanes exhibit good flame retardance. There are no absorption occurred between 400 nm and 800 nm for these polymers, consequently, show excellent transparency. These polymers might have great potentials in waveguide applications.

Keywords: bridged polysilsesquioxanes, thermal stability, flame retardant, L.O.I., waveguide

1. INTRODUCTION

Hybrid materials lie at the interface of the organic and inorganic realms. These materials offer exceptional opportunities not only to combine the important properties from both worlds but also to create entirely new compositions with truly unique properties. Bridged polysilsesquioxanes (PSSQ) are a family of hybrid organic inorganic materials prepared by sol-gel technology of monomers that contain a variable organic bridging group and two or more trifunctional silyl groups [1-8].

PSSQ is one of the three dimensional oligomeric organosiliceous compounds of the general structural formula $(\text{RSiO}_{1.5})_n$, where n is an even number and R can be any of large number of groups (typically methyl, halogen, vinyl or phenyl). Each silicon is bound to an average of one and one half oxygens (sesqui-) and to one hydrocarbon group (-ane) [9-11]. The PSSQ can be prepared as gels, film, or fibers. The organic group, covalently attached to the trifunctional silicon groups through Si-C bonds, can be varied in length, rigidity, geometry of substitution, and functionality. Because the organic group remains an integral component of the material, the variability provides an opportunity to modulate bulk properties such as porosity, thermal stability, refractive index, optical clarity, chemical resistance, hydrophobicity, dielectric constant and so on. PSSQ possess high thermal stability and superior mechanical properties and electrical properties. These materials have attracted much attention and result in broad range of applications such as protective coating [12-13], insulating layer [14-15], photoactive materials [16], precursors as ceramics [17-18], etc.

In this study, three types of bridged PSSQ were synthesized by sol-gel method. These materials possess excellent thermal property. They will act as flame retardant for polymer since it contains silicon. In future study, it will be used to enhance the thermal properties and flame retardancy.

2. EXPERIMENTAL

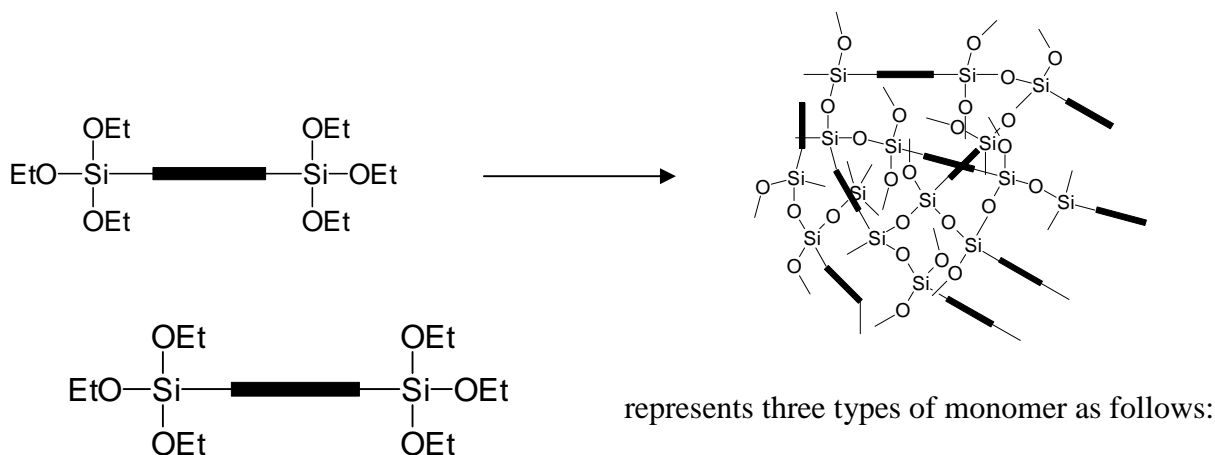
2.1 MATERIALS

3-aminopropyltrimethoxysilane (APTS), 3-isocyanatopropyltriethoxysilane (IPTS), 1, 4-bis (trimethoxysilyl) ethyl benzene, and 1, 6-bis (trimethoxysilyl)hexane were purchased from United Chemical Technologies, Inc. Bristol, PA, USA. Tetrahydrofuran (THF) was received from Tedia Co Farfield, Ohio.,USA..

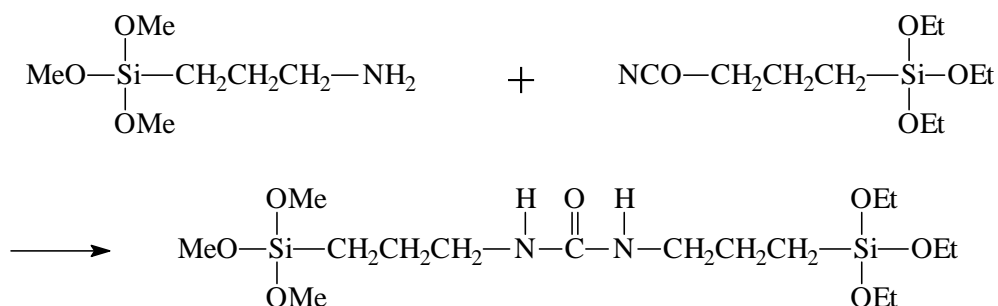
2.2 PREPARATION OF SAMPLES

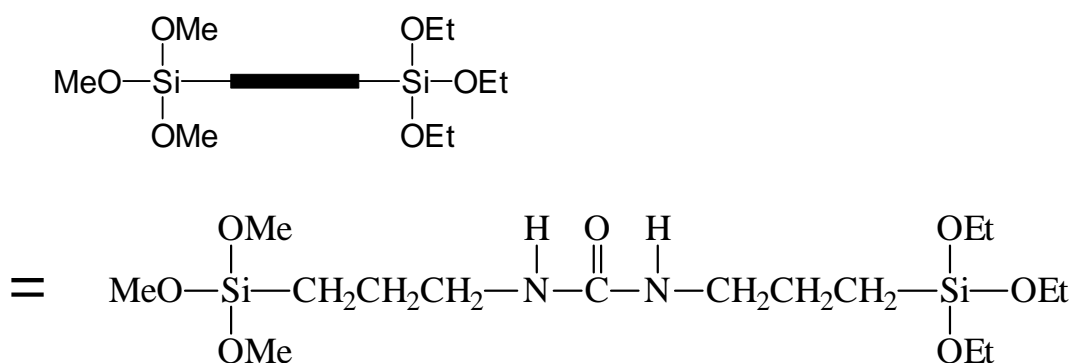
1.75 g, 3g and 3g of ATPS, 1.6-bis (trimethoxysilyl)hexane and 1.4-bis(trimethoxysilyl)ethylbenzen were placed into a 20ml sample bottle, respectively. 2.5 g of IPTS and 10 g THF were added into the sample bottle which contains IPTS. The reaction was monitored by FTIR. The mixtures were stirred until the characteractic peak of NCO group (2270 cm^{-1}) was disappeared. HCl was the catalyst used for hydrolysis. HCl was added until the PH value was 2. The solutions were cast into aluminum dishes to gel at room temperature. The wet gels were aged at room temperature for 48 hours, and then dried at 100°C for 24 hours. Samples were put in a vacuum oven at 200°C for 24 hours.

2.3 REACTION SCHEME

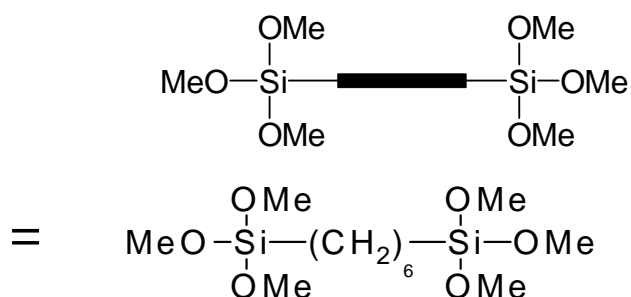


(1) Synthesis of dipropylurea-bridged PSSQ (Urea PSSQ)

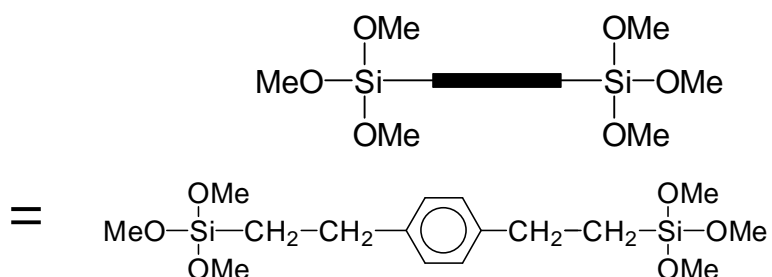




(2) Synthesis of 1.6-bis(trimethoxysilyl)hexane-bridged PSSQ (1.6-PSSQ)



(3) Synthesis of 1.4-bis(trimethoxysilylethyl)benzene-bridged PSSQ (1.4-PSSQ)



2.4 MEASUREMENTS

To identify the functional groups of monomers and nanocomposites, FTIR spectra were recorded between 4000-400 cm^{-1} with a resolution of 2 cm^{-1} on a Nicolet Avatar 320 FT-IR spectrometer, U.S.A. and then scanned more than 32 times. Thin films were prepared by the solution-casting method for monomer. The films were prepared, by mixing the finely ground solid sample with powered potassium bromide, and the mixture was pressed under high pressure at 8000-10000 kg/cm^2 . ^{29}Si NMR was performed by a Bruker DSX-400WB, Germany. The samples were treated at 180°C for 2hr and then ground into fine powder. Thermal degradation of hybrid was investigated by a thermogravimetric analyzer (Perkin Elmer TGA 7) from room temperature to 800 °C under nitrogen atmosphere. The measurements were conducted using 6-10mg samples. Weight-loss/temperature curves were recorded. UV/VIS spectra were tested on a Hitachi (Japan) U-3300 spectrophotometer and the sample was prepared as a thin film on a glass substrate by spin coating.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION

3.1.1 FTIR

The monomer of dipropylurea-bridged PSSQ was prepared from the reaction of APTS and IPTS. The NH_2 group of APTS will react with NCO group of IPTS. The reaction will generate urea linkage. Figure 1(a) shows the FT-IR spectra of the reaction between APTS and IPTS. The figure indicates the characteristic peak of NCO group of IPTS at 2270cm^{-1} disappears. This phenomenon reveals APTS has reacted with IPTS. The characteristic peak of Si-O-Si group of IPTS at $1104 \sim 1168\text{ cm}^{-1}$ indicates the condensation reactions occur. The characteristic peak of C=O group of IPTS at 1653 cm^{-1} and the characteristic peak of N-H group of IPTS at 3289 cm^{-1} show the formation of urea linkage.

1.6-PSSQ was synthesized from 1.6-bis(trimethoxysilyl)hexane using the sol-gel method. Figure 1(b) shows the FT-IR spectra of 1.6-PSSQ. The characteristic peak of Si-O-Si group of 1.6-PSSQ can be seen at $1104 \sim 1168\text{ cm}^{-1}$ which reveals the condensation reactions occur. The characteristic peaks at $820\sim 900\text{ cm}^{-1}$ are Si-OCH₃ group and the characteristic peaks at 2850 cm^{-1} are CH₂ group, respectively.

1.4-PSSQ was synthesized from 1.4-Bis(trimethoxysilylethyl)benzene using the sol-gel method. Figure 1(c) shows the FT-IR spectra of 1.4-PSSQ. The characteristic peak of Si-O-Si group of 1.6-PSSQ at $1104 \sim 1168\text{ cm}^{-1}$ reveals the condensation reactions occur. The characteristic peaks at $820\sim 900\text{ cm}^{-1}$, 1500 cm^{-1} and 2850 cm^{-1} are Si-OCH₃ group, CH₂ group and benzene group, respectively.

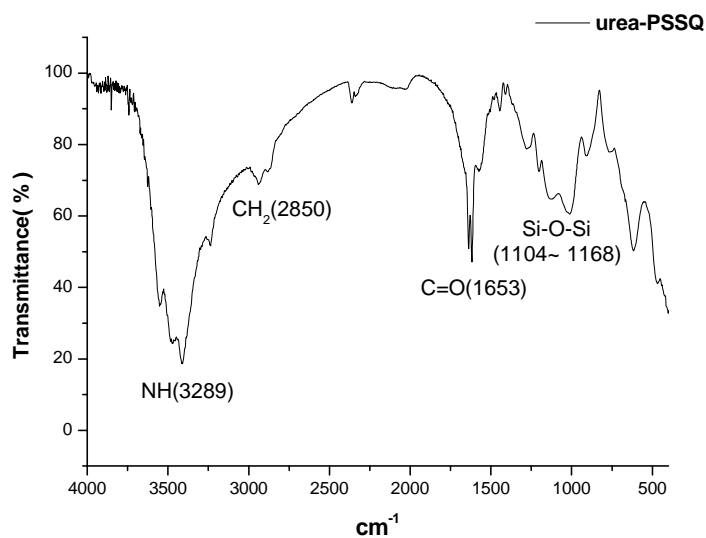


Figure 1(a) FTIR spectra of Urea-PSSQ

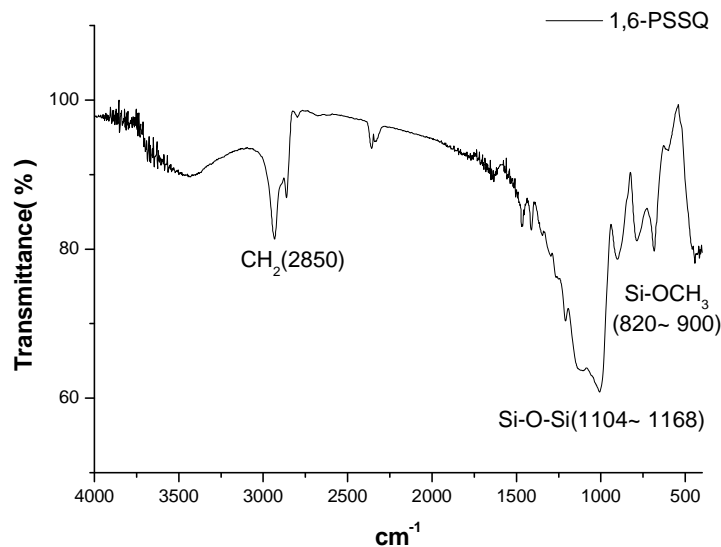


Figure 1(b) FTIR spectra of 1, 6-PSSQ

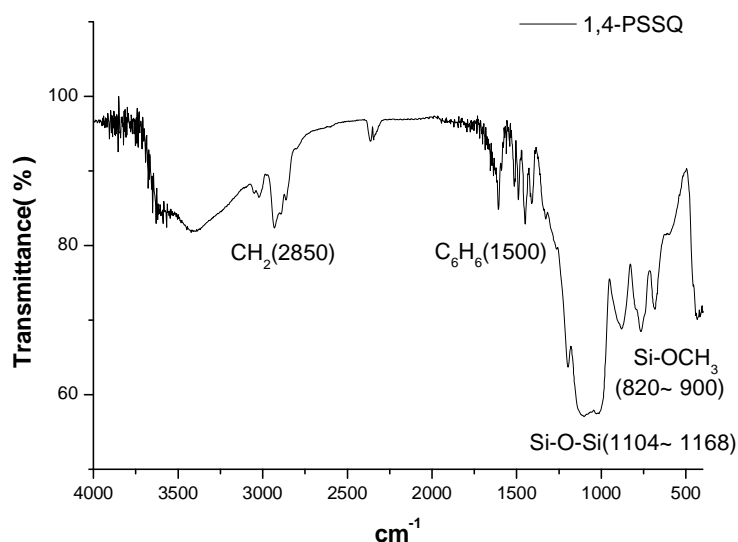


Figure 1(c) FTIR spectra of 1, 4-PSSQ

3.1.2 ²⁹SI SOLID STATE NMR

Figure 2 shows the curve of ²⁹Si solid-state NMR spectra of urea-PSSQ. Condensed siloxane species about urea-PSSQ in which silicon atoms through mono-, di and tri-substituted siloxane bonds are designated as T¹, T², T³, respectively. The chemical shifts at -58, -67 ppm of T², T³, respectively, are in good agreement with the literature values. Results revealed that, T², T³ are the major environments, ie, it formed the network structure. The curves of ²⁹Si solid-state NMR spectra of 1.6-PSSQ and 1.4-PSSQ behave the same trend as urea-PSSQ.

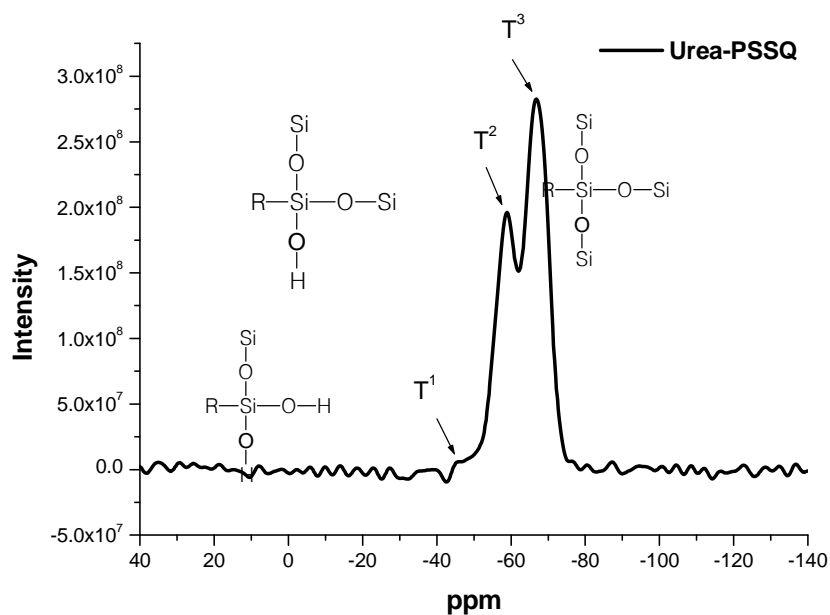


Figure 2 Typical ^{29}Si Solid State NMR spectrum of Urea-PSSQ

3.1.3 X-RAY DIFFRACTION PATTERN (XRD)

X-ray diffraction pattern of these bridge-PSSQ were shown in Figures 3. There are no obvious peaks shown in the XRD spectrum of bridged PSQ. This phenomenon shows that there are no crystalline regions in their structures. Results reveal the PSSQ posses amorphous structures.

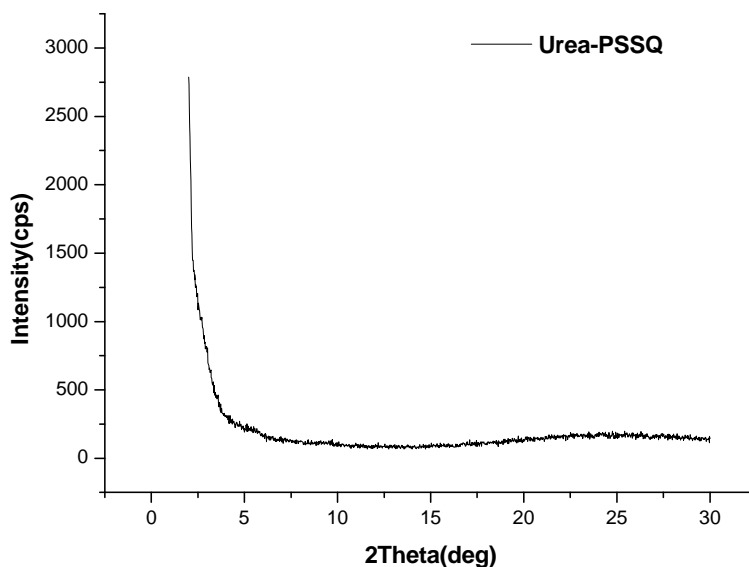


Figure 3 Typical X-ray spectra of Urea-PSSQ

3.2 THERMAL PROPERTIES

The dynamic thermogravimetric curves of PSSQ at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen are shown in Figure 4. Table 1 shows thermal characteristics of polysilsesquioxanes.

1,6-PSSQ and 1,4-PSSQ exhibit one-step decomposition while urea-PSSQ exhibits two-step decomposition. According to the figure, the T_{d10} (the temperature of degradation at which weight loss is 10%) of urea-PSSQ, 1,6-PSSQ and 1,4-PSSQ are 412°C , 507°C and 581°C , respectively. These bridged PSSQ show excellent thermal stability. The char yields of urea-PSSQ, 1,6-PSSQ and 1,4-PSSQ are 58.5 wt%, 70.7 wt% and 81.1 wt% at 800°C , respectively.

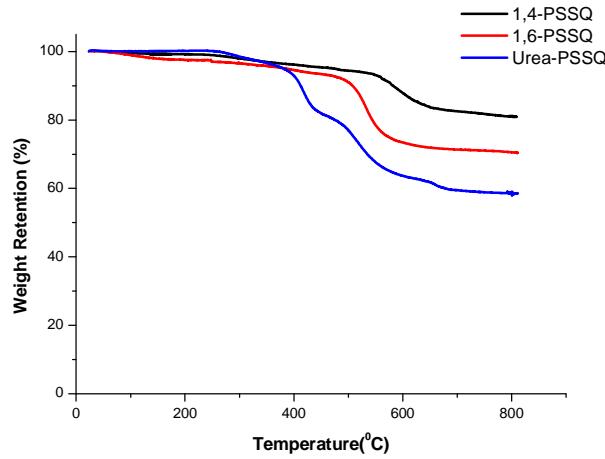


Figure 4 TGA of Urea-PSSQ、1,6-PSSQ、1,4-PSSQ

Flame resistance can be evaluated from the char residue on pyrolysis. A linear relationship between limiting oxygen index (LOI) for halogen-free polymers has been established by van Krevelen [20] and can be expressed as the following equation (1).

$$\text{L.O.I.} = 17.5 + 0.4\text{CR} \quad (1)$$

where CR is char yield in wt%

Increasing char formation can limit the generation of combustible carbon-containing gases, decrease the exothermicity due to pyrolysis reactions, as well as decrease the thermal conductivity of the surface of burning materials. A higher char yield will enhance the flame retardance. According to equation (1), the calculated LOI.s of 1,4-PSSQ, 1,6-PSSQ and urea-PSSQ are 39.4, 45.7 and 50.0, while the experimental LOI.s of 1 these PSSQs are 39.4, 45.7 and 50.0, respectively. The data show that these bridged PSSQ possess excellent flame retardance.

The integral procedure decomposition temperature (IPDT) proposed by Doyle [21] has been correlated the volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials [22-23]. IPDT was calculated from

$$\text{IPDT } (^{\circ}\text{C}) = A^*K^*(T_f - T_i) + T_i \quad (1)$$

$$A^* = (S_1 + S_2) / (S_1 + S_2 + S_3) \quad (2)$$

$$K^* = (S_1 + S_2) / S_1 \quad (3)$$

where A^* is the area ratio of total experimental curve defined by the total TGA thermogram, T_i the initial experimental temperature, T_f the final the initial experimental temperature. Figure 5 shows a representation of S_1 , S_2 and S_3 for calculating A^* and K^* .

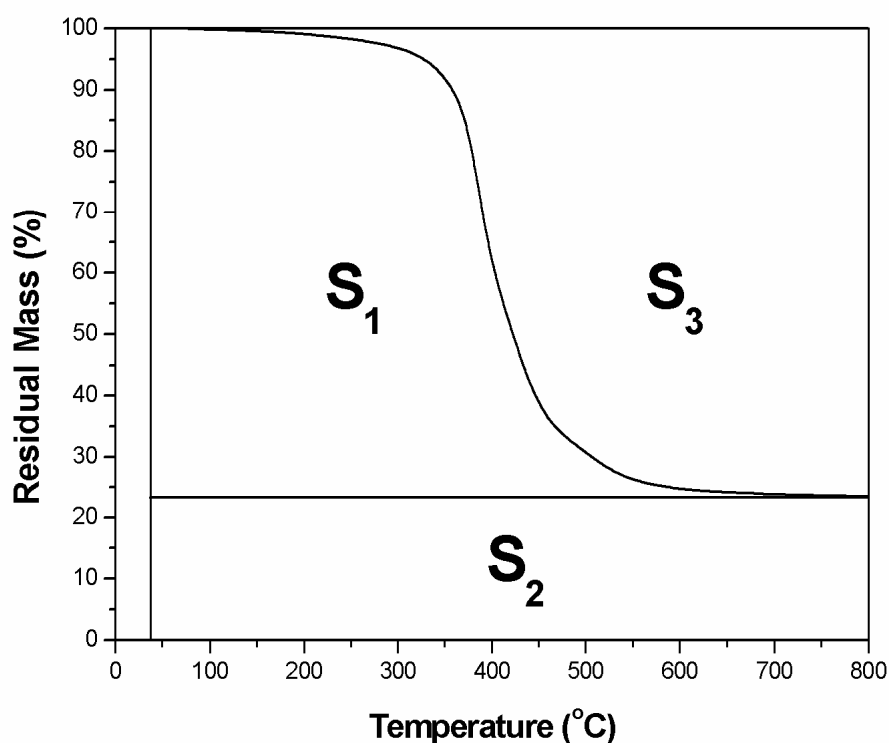


Figure 5 Schematic representation of S_1 , S_2 and S_3 for A* and K*

Table 1 Thermal characteristics of polysilsesquioxanes

SAMPLE NO.	T_{d10} (°C)	C.Y. at 800°C(%)	IPDT (°C)	LOI (cal.)	LOI(exp.)
Urea-PSSQ	410	58.5	2293	40.9	38
1.4-PSSQ	506	70.7	3371	45.8	45
1.6-PSSQ	580	81.1	5250	50	49

3.3 UV/VIS

Figure 6 shows the UV/VIS spectra measured for urea-PSSQ. There is no absorbance over a range of 400 ~ 800 nm. These phenomena revealed bridge PSSQ possess excellent optical transparency. This transmittance may be used as a criterion for the formation of a homogenous phase. The other PSSQs behave the similar trend. These polymers possess great potentials in waveguide applications.

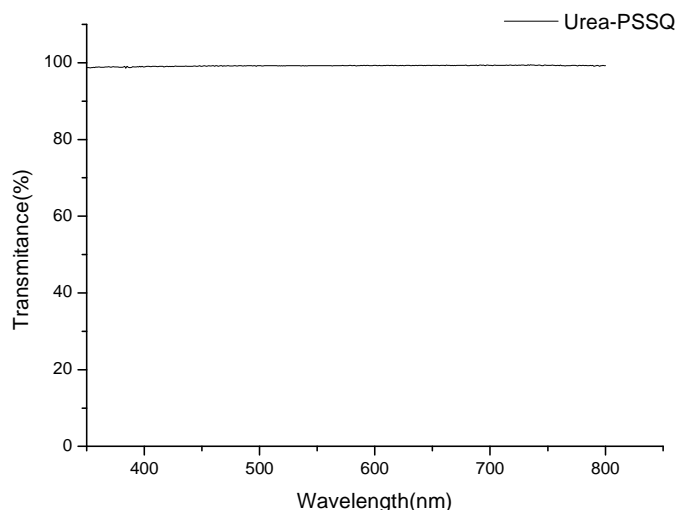


Figure 6 Typical UV/VIS of Urea-PSSQ

4. CONCLUSIONS

Three types of bridged PSSQ synthesized by sol-gel process have been demonstrated. TGA data show 1.4-PSSQ, 1.6-PSSQ and urea-PSSQ possess excellent thermal stability. L.O.I.s of these PSSQ are more than 26, and these bridged PSSQ possess excellent flame retardance. The UV/VIS spectra show that there is no absorbance over a range of 400 ~ 800 nm. These phenomena revealed bridged PSSQ possess excellent optical transparency. This transmittance may be used as a criterion for the formation of a homogenous phase. These polymers possess great potentials in waveguide applications.

REFERENCES

1. Small JH, Shea KJ, Loy DA. Arylene- and alkylene-bridged polysilsesquioxanes. *J Non-Cryst Solids*. 1993, 160, 3, 234-246
2. Loy DA, Jamison GM, Baugher BM, Russick EM, Assink RA. Alkylene-bridged polysilsesquioxane aerogels. Highly porous hybrid organic-inorganic materials. *J Non-Cryst Solids*. 1995, 186, 44
3. Oviatt HW, Shea KJ, Kalluri S, Shi Y. Applications of Organic Bridged Polysilsesquioxane Xerogels to Nonlinear Optical Materials by the Sol-Gel Method. *Chem Mater* 1995, 7, 3, 493
4. Graham AL, Carlson CA, Edmiston PL. Development and characterization of molecularly imprinted sol-gel materials for the selective detection of DDT. *Anal Chem* 2002, 74, 2, 458-467
5. Cerveau G, RJP Corriu, Framery E. Influence of the nature of the catalyst on the textural properties of organosilsesquioxane materials. *Polyhedron* 2000, 19, 307-313
6. Honma I, Nakajima H, Nishikawa O, Suqimoto T, Nomura S. Amphiphilic organic/inorganic nanohybrid macromolecules for intermediate-temperature proton conducting electrolyte membranes. *J Electrochem Soc* 2002, 149, A1389-A1392
7. Schaefer DW, Beaucage G, Loy, DA, Shea KJ, Lin JS. Structure of Arylene-Bridged Polysilsesquioxane Xerogels and Aerogels. *Chem Mater*, 2004, 16, 1402-1410
8. Lee TM, Ma CCM, Hsu CW, Wu HL. Effect of molecular structures and mobility on the thermal and dynamical mechanical properties of thermally cured epoxy-bridged polyorganosiloxanes. *Polymer* 2005, 46, 8286-8296

9. Yuan CY, Chen SY, Tang JC, Yang HC, Chen-Yang YW. Physical and electrochemical properties of low molecular weight poly (ethylene glycol)-bridged polysilsesquioxane organic-inorganic composite electrolytes via sol-gel process. *J Appl Polym Sci* 2007, 103, 2752-2758
10. Chen WY, Lin Y, Pramoda KP, Ma KX, Chung TS. Surface study of ladderlike polyepoxysiloxanes. *J Polym Sci, B: Polym Physic* 2000, 38, 138-147
11. Puyenbroek R, van de Grampel JC, Rousseeuw BAC, van der Drift EWJ.M. Functionalization of polysilsesquioxanes. *Polymer* 1994, 35, 3131-3132
12. Xing W, You B, Wu L. The microstructure and anticorrosion performance of phytic acid-catalyzed polysilsesquioxane coatings. *J Sol-Gel Sci and Techn* 2007, 42, 187-195
13. Gunji T, Iizuka Y, Arimitsu K, Abe Y. Preparation and properties of alkoxy(methyl)silsesquioxanes as coating agents. *J Polym Sci, A: Polym Chem*, 2004, 42, 3676-3684
14. Xie P, Zhang R. Functionalization and application of ladder-like polysilsesquioxanes *Polym Advan Techn* 1997, 8, 649-656
15. Linde HG. Interaction of polyamic acids and polyamic esters with copper and substituted polysilsesquioxane copolymers *J Appl Polym Sci*, 1992, 46, 353-361
16. Gu HW; Xie P; Shen, DY; Fu PF; Zhang JM; Shen ZR; Tang YX; Cui L; Kong B; Wei, XF; Wu Q; Bai FL; Zhang, RB. Photo-induced orientation of a film of ladderlike polysiloxane bearing dual photoreactive side groups. *Advan Mater*, 2003, 15, 1355-1358
17. Takamura N, Taguchi K, Gunji T, Abe Y. Preparation of silicon oxycarbide ceramic films by pyrolysis of polymethyl- and polyvinylsilsesquioxanes . *J Sol-Gel Sci Techn*, 1999, 16, 227-234
18. Abe Y, Gunji T. Oligo- and polysiloxanes. *Progress in Polymer Science*, 2004, 29, 149-182
19. Chiang CL, Ma CC M. Synthesis, characterization, and properties of novel ladderlike phosphorus-containing polysilsesquioxanes *J Polym Sci A: Polym Chem*, 41, 2003, 1371-1379
20. D.W.Van Krevelen, Some basic aspects of flame resistance of polymeric materials. *Polymer*, 1975, 16, 615-620
21. C.D. Doyle, Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis, *Analytical Chemistry* 1961, 33, 77-80
22. Jelena M, Ivan B, Sebastijan O, Hrvoje I., Marica I. Thermal degradation of epoxy-silica organic-inorganic hybrid materials. *Polym Dedra Stab.* 2006, 91, 122-127
23. Park SJ, Kim HC, Lee HI, Suh DH. Thermal stability of imidized epoxy blends initiated by *N*-benzylpyrazinium hexafluoroantimonate salt. *Macromolecules* 2001, 34, 7573-7575