

STRUCTURE AND BIREFRINGENCE PROPERTIES OF SiO₂-THIOPHENES XEROGELS SYNTHESIZED BY SOL-GEL-TEMPLATE

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Abstract The ceramic tubular substrates of SiO₂-thiophenes as a ceramic membrane were prepared successfully by the combining method of sol-gel-template process. The organic precursor of 2,5-bis(trimethoxysilyl)terthiophene was used as a template agent and tetraethoxysilane (TEOS) was used as organic or inorganic silicon source. The gel formations of alkoxides are taken by condensation and polymerizations of TEOS with the catalyst ammonium fluoride, after mixing with the precursor. Characterizations were taken by NMR solid, SEM and XR-powder diffraction. The results showed that surface morphologies of its membranes are defect-free, and the bond-linking structure has been formed between silicate and template agent. The (SiO₂) membrane prepared from TEOS has amorphous phase. The studies reveal that the silicone is mainly in tetrahedral coordination and combining with terthiophene units as a nanostructure to form lamellar structure. The optical birefringence properties of SiO₂-thiophenes hybrid aerogels in the visible range strongly depend on amount of organic unit's modifier. The higher transparency is observed for aerogels having higher content of alkoxysilane (TEOS), and than for the higher birefringence, normally observed for aerogels containing higher quantity of thiophenes units.

KEYWORDS: Sol-gel-template, mesoporous, SiO₂-thiophene hybrids, lamellar structure, birefringence

Introduction

Preparation of ceramics via sol-gel processing from alkoxysilane containing motif organic precursor is very widely used for development of new materials with certain characteristic of optical applications. The alkoxysilane functions were partially hydrolyzed and condensed as the matrix formation (Brinker and Scherer, 1990).

The alkoxysilane that usually used are tetramethoxysilane Si(OMe)₄, more commonly known as TMOS and tetraethoxysilane, Si(OEt)₄, known as TEOS. Both compounds have become a notorious chemical precursor in two important and widely used applications: (a) the preparation of inorganic materials by sol-gel methods (Brinker and Scherer, 1990) and (b) the formation of SiO₂ films deposited by chemical vapor deposition (Sherman, 1987).

The preparation of ceramics via sol-gel processes were carried out by the base concepts of solid NMR spectra. The solid siliceous materials were analyzed with ²⁹Si-CP MAS NMR. The most likely structures of siliceous gels materials are as the matrices of -(Si-O₄)-Si- which sequenced by T (tertiary), and for the porous aerogels are sequenced by Q (quaternary).

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The pure aerogel product has NMR spectra dominant as Q^4 , absolutely pure as aerogels or technical terminology is called as ceramics (Brinker and Scherer, 1990). This research has studied about effect of organic motif on microstructure and birefringence phenomena's, in the matrices of ceramics formed via sol-gel processing. TEOS has been chose in this research observation as a matrixes or template source due to less reactive than TMOS. The motif organic terthiophenes are bisilylated to use as precursor (Corriu *et al.*, 1994; Kancono, 2003; Kancono and Senin, 2006).

Methodology

Chemical are used: TMOS and TEOS from Aldrich, 1% NH_4F in H_2O as catalyst and syntheses product's of hybrid precursor 2,5-bis(trimethoxysilyl)terthiophene (= BTS3T) (Shahrul *et al.*, 2005), dimethylformamide (DMF) and tetrahydrofurane (THF). Materials and equipment: teflon, non-silicone glue and polarization microscope.

The first synthetic methods of sol-gels processing are used to observe with SEM and XRD. In the reaction tube in the oil basin at $60^\circ C$, add the precursor 2,5-bis(trimethoxysilyl)terthiophene and TEOS in present of catalyst 1% NH_4F/H_2O by the variation mole ratio as sample : (a) 1:4, (b) 1:6 and (c) 1:8. Than observed time by time their gels formation (jellification time). After that mixture formed sol-gels, than ageing for 24 hours at $100^\circ C$. Gels formed divided in two parts: one is non washing as sample (A) and another one is washing with diethylether as sample (B), and both of these parts sample (A) and (B) are continued to sintering separately at $150^\circ C$ for 4 hours. The two products are grained separately for the analyses of SEM and powder X-Ray observation.

The second synthetic method is based on a molecular chemistry approach in order to observe the birefringence phenomenon. In the teflon cell's with thickness pores $15 \times 10^{-6} \mu m$ injected mixtures of precursor 2,5-bis(trimethoxysilyl)terthiophene and TEOS in present of catalyst 1% NH_4F/H_2O by the variation mole ratio: (a) 1:4, (b) 1:6 and (c) 1:8, than observe for each 5 hours by polarization microscope.

Results and Discussion

Results of the first experiment are preparation of aerogel (ceramics), characterization product are shown in Fig. 1 (a) and (b). Spectra's of ^{29}Si -CP MAS NMR shown that the most likely structures of the matrices $-(Si-O_4)-Si-$ were dominant as Q^3 than Q^4 (aerogels), but still leaved of the formation T^2 and T^3 . The first product prepared by BTS3T/TEOS (1:4) is not absolutely pure as aerogels or ceramics. The second product BTS3T/TEOS (1:6) with matrices of $-(Si-O_4)-Si-$ form were dominant as Q^2 , Q^3 than Q^4 , where T^2 and T^3 disappeared have formed absolutely as pure aerogels.

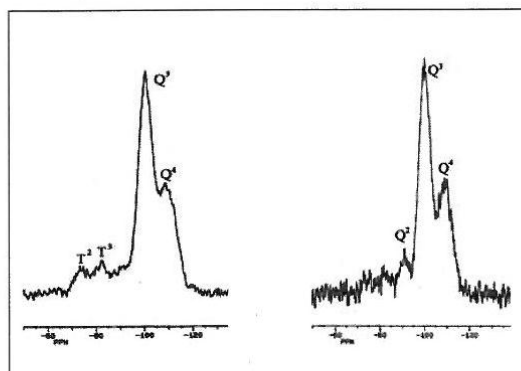


Figure 1. (a) Spectra ^{29}Si CP MAS NMR of BTS3T/TEOS (1:4); (b) Spectra ^{29}Si CP MAS NMR of BTS3T/TEOS (1:6)

Figure 2 shows the powder X-Ray diffractogram with certain pattern of intensity as the absorbance of energy on the characteristic materials. The parabolic curve determined are the formation of the repeated sequence of matrices with the certain layer distance on tubular structure of SiO₂. This phenomena suggested that the TEOS are totally formed of matrices as aerogels backbone, whereas the precursors BTS3T formed as terthiophene-bridged silsesquioxane net-work; $[O_{1.5}Si-(C_4H_2S)_n-SiO_{1.5}]_n$. That's are understood that TEOS are more favorable substrate in polymerization reactions due to the ability to eliminate ethylene and ethanol as neutral products via cyclic mechanisms, so that reacted more dominant as matrices.

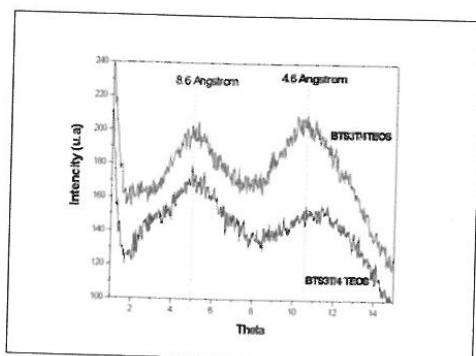


Figure 2. X-Ray Diffractogram of BTS3T/TEOS (1:4) and (1:6)

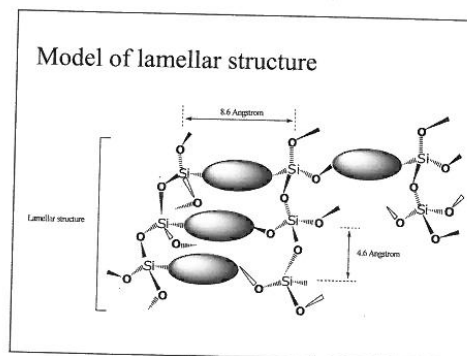


Figure 3. Modification structure BTS3T/TEOS (1:4) and (1:6) as the lamellar structure

Figure 3 displays the modification structure of the products, according combination analyses of the ²⁹Si-CP MAS NMR and X-RD, it is concluded that terthiophene-bridged silsesquioxane formed in the product shown two picks characteristics. The pick 4.6 angstroms as a distance between two organic precursors (terthiophene as a template) and the pick of 8.6 angstroms as distance between the two matrices layer of O-Si-O. These aerogel products were prepared via sol-gel with more quantity of alkoxy silane, shown the same picks in the same position. These phenomena's are concluded that the ordered microstructures in these solids organizations most probably can modified as the lamellar structure (Kancono, 2003; Kancono and Senin, 2006).

Results of the second experiment; the microstructure studied of solids organization and birefringence are characterized by SEM and polarization microscopy. Figure 4 shows that products with quantity variation of TEOS have aggregates particles as molecular building with certain sphere contains of silica and thiophenes unites. In the SEM and TEM observation shown there share of cloud particles as the primary particles of about diameter $\Phi = 10 \mu m$. That particles would then form the secondary particles with diameter of $\Phi = 40 - 60 \mu m$ as the agglomeration. Figures 5 (a) and (b) show the birefringence phenomena as the effect of terthiophene on anisotropic organizations molecular structure. The effect is more dominant on the microscopic behavior, in that they are weaker in higher quantity of SiO₂ matrices.

Table 1 indicates the agglomeration ratio element contain, that composition ratio of principle element in the BTS3T/TEOS product's have spheres rich in silicon. The higher quantity of SiO₂ matrices, will fully protect sulfur existence in terthiophenes unites. These matrices has amorphous phase with pore size of 4.2 to 6.0 nm (Kancono, 2003; Kancono and Senin, 2006).



Figure 4. Morphology of BTS3T/TEOS (1:4) by SEM

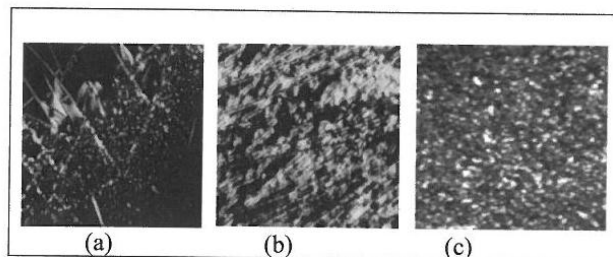


Figure 5. Micrograph polarization BTS3T/TEOS by ratio of (a) 1:4, (b) 1:6 and (c) 1:8

Table 1. Yields of microanalyses composition ratio of principle element in the sol-gel formed by BTS3T/TEOS

Washing sol-gels by (ratio mixtures)	Calculation ratio of		Experiment data's	
	Si/S	Si/C	Si/S	Si/C
BTS3T/TEOS (1:4)	3.33	0.83	3.57	1.00
BTS3T/TEOS (1:6)	6.00	1.5	6.21	1.80
BTS3T/TEOS (1:8)	11.33	2.83	11.72	3.40

Table 2 shows the birefringence data that have been recorded on the products prepared with different mole ratio of terthiophene and alkoxy silane. Birefringence in the ratio of BTS3T/TEOS (1:8) has detection limit of 1.06×10^{-3} . On the result reported before (Kancono, 2003; Kancono and Senin, 2006), pure oligothiophene (mole ratio of 1:0) shown a maximum isotropic birefringence on 9×10^{-3} . So that, in this product, isotropic values is significantly differences by $1/8$ (9×10^{-3}) or decreases every 1.125×10^{-3} per mole SiO_2 formed. According to SiO_2 matrices formed, one can concludes that the higher quantity of alkoxy silane are the weaker of birefringence.

Table 2. Birefringence value of the gel prepared by BTS3T/TEOS

Ratio of SiO_2 gel prepared by	Value of birefringence (Δn)
BTS3T/TEOS (1:4)	2.15×10^{-3}
BTS3T/TEOS (1:6)	1.50×10^{-3}
BTS3T/TEOS (1:8)	1.06×10^{-3}

Conclusion

Ceramic's materials based on SiO_2 gels and terthiophenes units have been synthesized via sol-gels-template processing. The spheres as SiO_2 matrices have been formed in the average diameter of $10 \mu\text{m}$

and rich in silicon. The matrices fully protected existence of sulfur in terthiophenes unites. The lesser quantity of alkoxy silane, the lesser units of thiophenes will be formed.

The structure of formed silsesquioxane terthiophene-bridged, $[O_{1.5}Si-(C_4H_2S)_n-SiO_{1.5}]_n$ have a layer distance of about 4.6 and 8.6 Å. The microstructure of SiO₂ in the presence of oligothiophenes gave an effect on the characteristic pattern of lamellar structure.

The effect of terthiophenes unites on SiO₂ gels formed on the birefringence are the higher quantity of terthiophenes units are more stronger of their birefringence. The birefringence phenomena's will decrease with the increase quantity of alkoxy silane. The values differences are decreased every 1.125×10^{-3} units per mole of SiO₂, whereas the optical transparency of SiO₂ gels formed are increase.

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