

## TEMPERATURE INFLUENCE ON THE GELATION PROCESS OF TETRAETHYLORTHOSILICATE USING SOL-GEL TECHNIQUE

Wesam A. A. Twej

Department of Physics, College of Science, University of Baghdad. Baghdad- Iraq.

### Abstract

In this work the gelling time of silica alkoxide obtained by sol-gel process has been investigated. The Investigations are made with three variable parameters: water to TEOS molar ratios (1.4, 2, and 10), different pH values and reaction temperatures (25, 40 and 55 °C). The study shows that, the reaction temperatures have different effects on the gelling time according to other sol-gel preparation parameters. The values of the activation energy ( $E_a$ ) were estimated to be approximately the same in the studied range of initial hydrolysis ratio 1.4, 2, 10, slightly varying around 21.2  $\text{kJ}\cdot\text{mol}^{-1}$ , when the recipes derived under tightly closed cover. While under open recipe and with R-ratio equal to 1.4,  $E_a$  rises to 37.2  $\text{kJ}\cdot\text{mol}^{-1}$ .

### تأثير درجة الحرارة على عملية التحول الى حالة الجل لمادة التتراثيل اورثوسيليكات باستخدام تقانة سول - جل

وسام عبد علي تويج

قسم الفيزياء, كلية العلوم, جامعة بغداد, بغداد - العراق.

### الخلاصة

تم في هذا البحث دراسة زمن التحول الى حالة الجل لمادة الكيل السليكا المتكونة باستخدام تقانة Sol-Gel . اجريت هذه الدراسة عند ثلاث نسب مولارية (ماء:التترايثوكسي) 1.4 و 2 و 10. وتحت عدة قيم pH واجري التفاعل عند ثلاث درجات حرارية ( 25 و 40 و 55 ) °C . لقد بينت الدراسة ان لدرجة حرارة التفاعل تأثيرات مختلفة على زمن التحول الى حالة الجل اعتمادا على معاملات التفاعل الاخرى. عند اجراء التفاعل في حاويات محكمة الاغلاق كانت قيمة طاقة التفاعل المحسوبة تقريبا ثابتة وهي بحدود 21.2  $\text{kJ}\cdot\text{mol}^{-1}$  لكل النسب المولارية للماء الى المادة الاساسية TEOS (1.4, 2, 10), بينما ارتفعت قيمة هذه الطاقة الى 37.2  $\text{kJ}\cdot\text{mol}^{-1}$  عند اجراء التفاعل في حاويات مفتوحة الاغطية وذلك للوصفة ذات النسبة المولارية 1.4 فقط.

### Introduction

Over the last decade, hybrid nanometric materials, synthesized by sol-gel method using tetraethylorthosilicate (TEOS) have been

extensively studied [1-4]. These materials present distinct optical, magnetic and electronic properties due to their small size. The sol-gel method, is a very important and attractive

synthesis procedure, since it can be performed at low temperatures, with high homogeneity and purity of the resulting materials [5–8]. This method allows preparing hybrid xerogel nanometric materials, with the control of several physical properties.

In the sol-gel process, the reaction rate of transfer the reactant phase from sol to gel state  $K$  is expressed as the reciprocal of gelling time  $t_g$ , where,

$$t_g = 1/ K$$

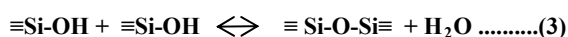
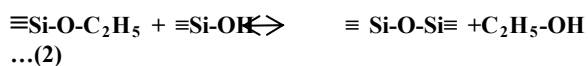
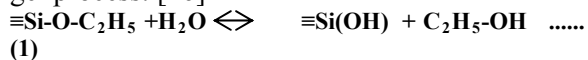
The reason for studying reaction rate, and then gelling time, is to understand how chemical reactions occur. By noting how the rate of a reaction is affected by changing conditions, we can sometimes learn the details of what is happening at the molecular level[9]. However, a little change in the parameters conditions of the synthesis, such as temperature, solvent, catalyst or silane amount, can produce great modifications in the final properties of the materials [10–13].

The rate of any given reaction may be affected by three factors;

1. Concentration of reactants, which represent R-molar ratio in sol-gel process.
2. Concentration of catalyst, which represent pH value in sol-gel process.
3. Temperature at which the reaction occur.

Usually reactions speed up when the temperature increases, reaction during cooking go faster at high temperature.

To fasten the hydrolysis and subsequently the condensation reactions, basic as well as acidic catalytic systems could be added [14, 15]. Three reactions are generally used to describe the sol-gel process: [16]



The basic sol-gel reaction, described in the above equations, consists of two chemical reactions, hydrolysis and condensation. The condensation reaction can occur in two ways, either two partially hydrolyzed molecules or nonhydrolyzed and partially hydrolyzed can be linked together in a condensation reaction that liberates water or alcohol, respectively. As the reaction proceeds, the number of Si-O-Si bonds

increases in a process called polymerization, which produces a macroscopic gel [16-18]. In this study we shall concentrate on the influence of reaction temperature.

### Temperature influence via gelation process

Heat is one of the fundamental factors that influence the rates of chemical reactions. Sol-gel process parameters, such as gelling time, were correlated to variables of the initial stage of the process, such as pH, temperature and hydrolysis ratio.

For a reversible physical gel, the transition of a gel-junction is a first order function of temperature. This implies that organized junctions are formed during the sol-gel process. [19]

Because gelation represented a specific extent of reaction, the temperature dependence of the time to gel should be described by the Arrhenius equation[19] The Arrhenius equation in logarithmic form is;

$$\ln K = \ln a - E_a / RT$$

or by replacing  $K$  with  $1/ t_{gel}$  and with some arrangements the Arrhenius equation can be written as:

$$\ln ( t_{gel} ) = A + E_a / RT \dots (4),$$

where  $A$  is a constant,  $R$  is the ideal gas constant and  $T$  is the absolute temperature. The activation energy  $E_a$  of the gelation can be calculated from the slope of the plot of  $\log t_{gel}$  against  $1/T$  [9].

From the collision theory, which is a theory that assumes that, for reaction to occur reactant molecules must collide with an energy greater than some minimum value and with the proper orientation. The minimum energy of collision required for two molecules to react is called activation energy ( $E_a$ ).

Now the reaction rate depends on three parameters;

$$K = Z P f$$

where

$Z$  is the collision frequency which is a first order function of temperature,  $P$  is the fraction of collisions that occur with the reactant molecules properly oriented and it is independent of temperature,  $f$  is the fraction of

collisions having energy greater than the  $E_a$ , and can be written as[9],

$$f = \exp(-E_a/RT)$$

from the above equation one can see that  $f$  decreases with the increase of  $E_a$ . Because the rate constant depends on  $f$ , this means that reaction with large  $E_a$  have small rate constant and reactions with small  $E_a$  have a large rate constant.

The apparent activation energy of the cross-linking leading to the gelation is calculated from the gelling times at various temperatures. For TMOS tetramethylorthosilicate it was found to be approximately  $139 \text{ kJ mol}^{-1}$  and independent on hydrolysis ratio. [19]

### Chemical procedure

The best sol-gel solution procedure, which was developed experimentally throughout the work, is briefly described as follows. The best chemical composition is shown in table1. Either this exact mixture or a proportional mixture may be used. Three hydrolysis ratios  $R = 1.4, 2$  and  $10$  and five pH values, ranging from  $3$  to  $10$ , were investigated due to gellibility zone while the mole ratio of ethanol to Si was kept at  $4$  for all recipes. The solution was mixed with a vigorous stirring at temperature range varied from  $25$  to  $55 \text{ }^\circ\text{C}$ . All chemicals were measured out carefully using a graduated plastic pipette into an Erlenmeyer flasks. First the catalysis, water and ethanol mixture is added slowly to the TEOS ethanol mixture according to the recipes mentioned in table 1.

The mixture is allowed to mix at a medium speed for one hour in the Erlenmeyer flask using a magnetic stirrer. It is best to mix it at a speed such that the solution does not excessively splash up onto the walls of the flask. Immediately after the chemicals are mixed, the

Table 1: Total prepared solution recipes.			
Reactant	Sample type		
	R 1.4	R 2	R 10
TEOS ml	1	1	1
Water ml	1.4	2	10
Ethanol ml	4	4	4
PH	3, 4, 7, 9, 10	3, 4, 7, 9, 10	3, 4, 7, 9, 10
Temperature $^\circ\text{C}$	25, 40, 55	25, 40, 55	25, 40, 55

recipe was divided into two main parts; one was kept without any cover ( open system) and the

other was kept in high tightly sealed cover (closed system). Then each of the two main parts was divided into three parts, each part was kept in the oven at fixed temperatures  $25, 40, 55 \text{ }^\circ\text{C}$  (see table.1). Then  $0.5 \text{ ml}$  of N,N-dimethylformamide was added to each recipe (to prevent final product cracks) as a drying control chemical additive (DCCA). It is important that the newest possible solution is always used since the older solutions tend to crack more during densification.

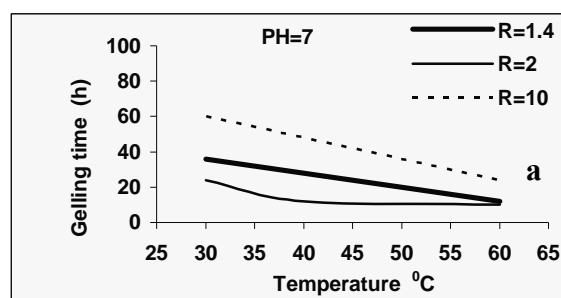
The following chemical materials were used in this work; (TEOS) (Purity > 98%) supplied by Schuchardt, Germany; Ethanol was of Analytical grade, (Purity 99.9%) supplied by Gainland Co., U.K.; N,N-dimethylformamide; hydrochloric acid(0.15 M HCl 37%) supplied by Aldrich company; ammonia( $\text{NH}_3$ ) supplied by BDH limited, Poole, England; Deionized water.

### Results and discussion

The temperature at which the measurements were performed is one of the most important factors influencing the time required to transfer sol to gel. The hydrolysis occurred within  $10 \text{ s}$  and was marked by bubbling of the solution [20]. The size of separated silica particles within the sol increased as the temperature increased. On the other hand, keeping the temperature constant, the particle size also increases as pH increases from neutral to basic environment [20]. The small gelling time of the gel held at relatively high temperature might be attributed to the onset of the aggregation of the particles, according to their size, in the earlier stage in such a gel because of the higher possibility of the particle collision at this relatively high temperature.

### Temperature effect

Regarding to the pH value, it can be seen from Figure (1);



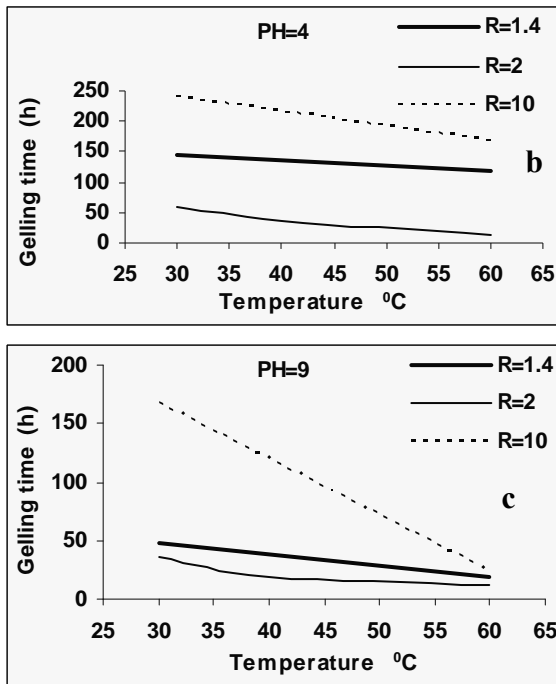


Figure 1: Gelling time as a function of temperature for several values of R-ratio a- pH=4, b- pH=7 and c- pH=9.

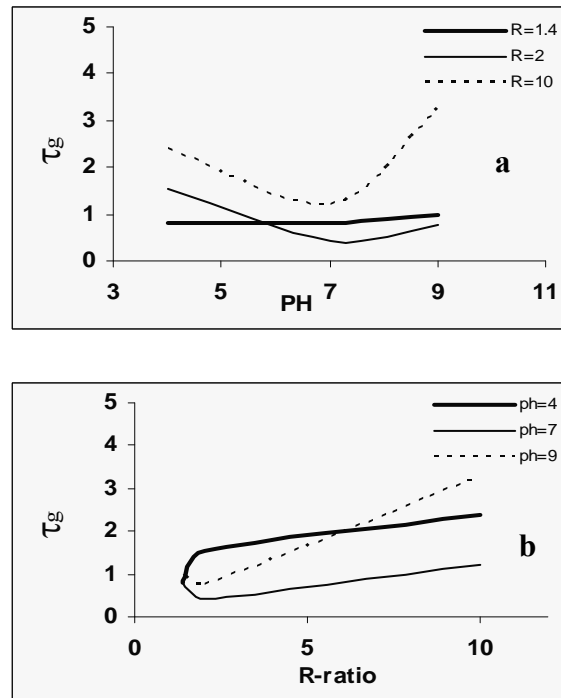
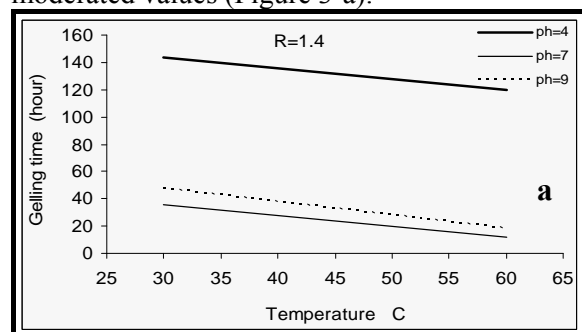


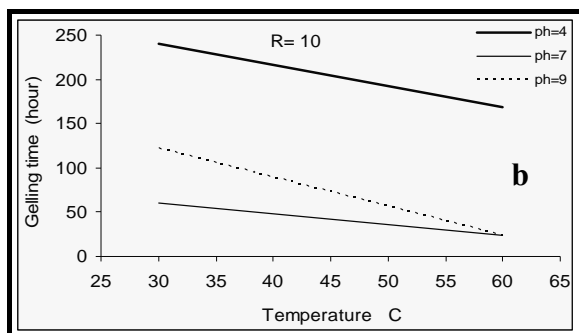
Figure 2:  $\tau_g$  gelling time ratio as a function of a) pH, b) R-ratio.

that the effect of the physical parameters, particularly temperature of reaction are little at acidic and noncatalyzed recipe (pH = 4 & 7) for low R ratio values and noticeable but still of low effect at large R values. While at basic environment the reaction temperature has noticeable effect for low R values and dramatic effect on the gelling time for large R values.

The growth of free primary particles would be easier than those in the aggregated secondary particles [14]. The aggregation takes place faster at 55 °C than at 40 °C and 25 °C, because increasing the temperature increases the particles kinetic energy ,i.e. increases the particles speed, and thus increases the probability of collisions and aggregation. This may lead to increase the number of secondary particles with time, Thus, in general, reduces the gelling time as the reaction temperature increases. On the other hand, the difference in the capillary force because of the increase of the viscosity, which yield from the evaporation of the alcohol as well as water at different reaction temperatures (i.e. the capillary force is a function of viscosity which is function of temperature) may also lead to this variation in the gelling time.

On the other hand the ratio of the gelling time value for any recipe at high reaction temperature (55 °C) to its value at low temperature (30 °C), which we denoted as  $\tau_g$  ( gelling time ratio), can be plotted as a function of R- ratio to give a good certification to the previous indication, as shown in Figure(2-a). Under stoichiometric ratio (R= 1.4) the reaction temperature has a little influence on the gelling time, where the gelling time have low and moderated values for neutral and basic environment (pH 7 and 9), while under acidic environment (pH4) have high and moderated values (Figure 3-a).





**Figure 3: Gelling time as a function of temperature for several value of pH, a) R = 1.4 , b) R = 10.**

At high R value ( $R=10$ ) in both acidic and basic reaction environment the reaction temperature affects the gelation process strongly, and this may be attributed to the reverse reaction of equation (3) where the solubility of silica increases as the R-ratio increases. While at neutral environment the reaction temperature has a little effect. As a result of vaporization of ethanol and water the volume of the solution at gelling time is about 30% of the volume of the original solution, in the open system recipes.

At reaction temperatures of 25 °C and 40 °C the evaporation rate of ethanol is larger and faster than that of water. While at 55 °C, which is relatively high temperature, the evaporation of alcohol and water together occur approximately in the same rate.

Therefore if  $R=1.4$  (alcohol condensation) and as mentioned before (equation 2) , we have alcohol condensation which means large ratio of water used in preparation will be converted to alcohol as well as the rate of water within the pores is decreased.

At large R values, such as  $R=10$ , the behavior of pH4 and pH7 are just like that at low R-ratio, while at pH 9 the effect of reaction temperature on increasing the gelling time is clear, Figure(2-b, 3-b). These observations indicate that the network formation proceeded faster with increasing of temperature.

### Activation energy calculation

There are some discussions in the literature regarding the apparent activation energy for the gelation reaction calculated from the gel time for TMOS at different temperatures. [21]

The Arrhenius equation plots for our system are shown in Figure 4. The values of  $E_a$  were estimated to be approximately the same in the studied range of initial hydrolysis ratio 1.4, 2 and 10. It is slightly varying around

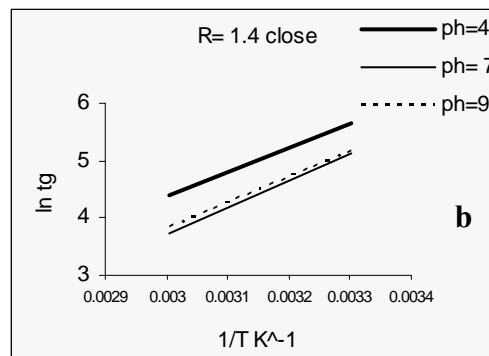
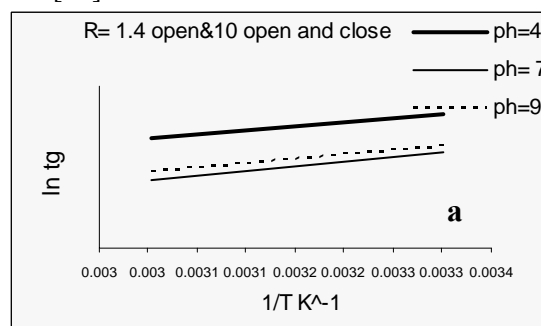
21.2  $\text{kJ}\cdot\text{mol}^{-1}$  , when the recipes derived under tightly closed cover, where the evaporation was prevented. This implies that  $E_a$  of the gelation does not depend on hydrolysis ratio.

The activation energy values of close recipe, for R equal to 2 and 10, are still approximately within their open value. While under the stoichiometric ratio, with R equal to 1.4 and close recipe,  $E_a$  rises to 37.2  $\text{kJ}\cdot\text{mol}^{-1}$  , see Figure(4).

Colby et al. [22] have reported the effects of temperature on the formation of silica gels derived from TMOS and TEOS with HF and HCl as catalysts. They found that the apparent activation energy attributed to the process of polymerization is around 40  $\text{kJ}\cdot\text{mol}^{-1}$  for HF and 49  $\text{kJ}\cdot\text{mol}^{-1}$  for HCl in the case of TMOS. This evolution of gelation time versus temperature is found in chemically crosslinking systems.

The same type of linearization has been verified for crosslinking and gelation in chlorobutyl elastomer systems [21] and titanium oxide based gels [23].

It was postulated that the increased viscosity may reduce the ability of the nucleus to reorient during hydrolysis reaction and reducing also the diffusion coefficients of reactive species within the solution, and further reduces the hydrolysis rate.[15]



**Figure 4:  $\ln$  gelation time  $t_g$  as a function of inverse of temperature  $1/T$  at three pH values and two hydrolysis molar ratio; a)  $R=1.4$  open,  $R=10$  open and closed, b)  $R=1.4$  closed.**

It was observed that the gelation time is inversely related with the gelation temperature and it is in accordance with other results found in the literature. [24]

### Conclusion

At higher temperatures gelation occurs faster, resulting in a shorter time to gel. The trend of these results is analogous to that of other studies for other precursor. [21, 25] The operation variables, viz. pH and hydrolysis ratio, affects dramatically the gel time. The apparent activation energy of the gelation reaction is determined directly from gel time measurement at different temperatures. It rise from 21 kJ mol<sup>-1</sup> in open recipe to 37 kJ mol<sup>-1</sup>, when the process driven under close system recipe.

### References

- Boury, B.; Chevalier, P.; Corriu, R.J.P.; Delord, P.; Moreau J.J.E. and Chiman, M.W. **1999**. Hybrid organic-inorganic xerogel access to meso-microporous silica by thermal and chemical treatment. *Chem. Mater.*, **11**:281-291.
- Yamada, N.; Yoshinaga I. and Katayama, S. **1998**. Processing and properties of inorganic-organic hybrids containing various inorganic components. *J. Sol-Gel Sci. Technol.*, **13**(1-3):445-449.
- Lev, O.; Wu, Z.; Bharathi, S.; Glezer, V.; Modestov A.; Gun, J.; Rabinovich L. and Sampath, S. **1997**. Sol-Gel materials and electrochemistry, *Chem. Mater.*, **9**:2354-2375.
- Loy, D.A. and Shea, K.J. **1995**. Bridged polysilsesquioxanes highly porous hybrid organic-inorganic material. *Chem. Rev.*, **95**:1431-1442.
- Foussaier, O.; Menetrier, M.; Videau J. J. and Duguet, E. **2000**. Polydimethylsiloxane-based ormosil microstructure: correlation with compressive behavior. *Mater. Lett.*, **42**(5):305-310.
- Lev, O.; Tsionsky, M.; Rabinovich, L.; Glezer, V.; Sampath S.; Pankratov, I. and Gun, J. **1995**. Organically modified Sol-Gel sensor, *Anal., Chem.*, **67** (1): 22 A -30A.
- Hench, L.L. and West, J.K. **1990**. Sol-Gel Process, *Chem. Rev.*, **90** :33-72.
- Schubert, U.; Sing, N.H. and Lorenz A. **1995**. Hybrid Inorganic-organic materials by sol-gel processing. *Chem. Mater.*, **7**: 2010-2027.
- Ebbing, D.D.; Gammon S.D.; and Ragsdale, R. O. **2003**. *Essential of General Chemistry. Sixth Edition*, Houghton Mifflin Co. , New York. pp 453-457.
- Choi D. G. and Yang, S. M. **2003**. Effect of two-step sol-gel reaction on the mesoporous silica structure, *J. of Colloid and Interfacial Science*, **261**:127-132,
- Caykara T. and Guven, O. **1998**. Effect of preparation on thermal properties of poly(acrylic acid) silica composites, *J. Appl. Polym. Sci.*, **70** (5): 891-895.
- Robert, J.; Corriu P. and Leclercq, D. **1996**. Recent development of molecular chemistry for sol-gel processes, *Angew. Chem.*, **35** (13-14):1420-1436.
- Loy, D.A.; Beach, J.V.; Baugher, B.M.; Assink, R.A.; Shea, K.J.; Tran J. and Small, J.H. **1999**. Dialkylene carbonate-bridged polysilsesquioxanes. hybrid organic-inorganic sol-gels with a thermally labile bridging group. *Chem. Mater.*, **11**:3333-3341.
- Iler, R. K. **1979**, *The Chemistry of Silica*, Wiley, New York., pp 172-177.
- Stoeber, W.; Fink A. and Bohn, E. **1968**. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.*, **26**:62-69.
- Brinker J.C. and Scherer, G.W. **1990**. *Sol-Gel Science*, Academic Press, New York. pp 2-8.
- Mosquera, M. J.; Bejarano, M.; De la Rosa-Fox, N. and Esquivias, L. **2003**. Producing crack-free colloid-polymer hybrid gels by tailoring porosity. *Langmuir*, **19**(3):951-957.
- Brinker, C.J.; Hurd, A.J. and Ward, K.J. **1988**. Fundamentals of Sol-Gel thin film formation. in: Makenzie, J.D. and Ulrich, D.R. (Eds), *Ultrastructure Processing of Advanced Ceramics*. Wiley. New York. pp. 223-240.
- Guizard, C.G.; Julbe, A.C. and Ayrál, A. **1999**. Design of nanosized structures in sol-gel derived porous solids. Application in catalysts and inorganic. *J. Mat. Chem.*, **9**:55.
- Yasumori, A. and Yamane, M. **1988**. Effect of temperature and time on The structural evolution of alkoxy-driven gel. in: Makenzie, J.D. and Ulrich, D.R. (Eds.), *Ultrastructure Processing of Advanced Ceramics*. Wiley. New York. pp. 355-366.

21. Gough L.J. and Smith,I.T. **1960**. A Gel point method for estimation of overall apparent activation energies of polymerization. *J. Appl. Polym. Sci.*, **3**: 362-364.
22. Colby,M.; Osaka,W. A. and Mackenzie,J. D. **1986**. Effect of temperature on formation of silica gel. *J. Non-Cryst. Solids* , **82**(1-3):37-41.
23. Ponton,A.; Barboux-Doeuff S. and Sanchez,C. **1999**. Rheology of Titanium Oxide Based Gels: Determination of gelation time versus temperature. *Coll. Surf. A : Physicochem. Engng Asp.*, **162** (1-3):177-192.
24. Al-Wattar,A. J.; Chiad,B. T.; Twej W. A. A. and Al-Awadi, S. S. **2006**. Development of temporal spectroscopic properties for Xerogel matrices doped with Rhodamine 6G dye. *Cen. Eur. J. of Physics*, **4** (3):1-8.
25. Pavan,F. A.; Hoffmann,H. S.; Gushikem, Y. Costa T.M.H. and Benvenuto, E. V. **2002**. The gelation temperature effects in the Anilinepropylsilica Xerogel Properties, *Materials Letters*, **55**: 378–382.