УДК 544.022.822

М. М. Жигайло, О. І. Демчина, Х. В. Демидова, І. Ю. Євчук
Відділення фізико-хімії горючих копалин
ІФОХВ ім. Л. М. Литвиненка НАН України

ДОСЛІДЖЕННЯ В'ЯЗКОСТІ ЗОЛЬ-ГЕЛЬ СИСТЕМ НА ОСНОВІ 3-МЕТАКРИЛОКСИПРОПІЛТРИМЕТОКСИСИЛАНУ ТА ТЕТРАЕТОКСИСИЛАНУ

Досліджено вплив різних чинників (температури, концентрації вихідних речовин і каталізатора золь-гель процесу) на реологічну поведінку золь-гель систем на основі органо-неорганічних прекурсорів – тетраетоксисилану (ТЕОС) та 3-метакрилоксипропілтриметоксисилану (МАПТМС) – методом віскозиметрії. Визначено час досягнення порогу перколяції, який відповідає початку гелеутворення у золь-гель системі. На основі вимірювання градієнтної залежності в'язкості за допомогою методу оптимізації у програмі ORIGIN 5.0 оцінено пружну і фрикційну компоненти в'язкості. Розраховано інтегральну енергію активації процесу гелеутворення у досліджуваних золь-гель системах.

Ключові слова: золь-гель система, 3-метакрилоксипропілтриметоксисилан, тетраетоксилан, динамічна в'язкість, градієнтна залежність в'язкості, енергія активації.

M. M. Zhyhailo, O. I. Demchyna, Kh. V. Demydova, I. Yu Yevchuk

INVESTIGATION OF VISCOSITY OF SOL-GEL SYSTEMS BASED ON 3-METHACRYLOXYPROPYLTRIMETHOXYSILANE AND TETRAETHOXYSILANE

The influence of various factors (temperature, concentration of the starting substances and catalyst of sol-gel process) on the rheological behavior of sol-gel systems based on organic-inorganic precursors – tetraethoxysilane (TEOS) and 3-methacryloxypropyltrimethoxysilane (MAPTMS) – by viscosimetry method was investigated. The time of achieving of percolation threashold, when gelation process in sol-gel system occurs, was determined. The elastic and friction components of viscosity were estimated on the basis of gradient dependence measurement using ORIGIN 5.0 optimization method. The integral activation energy of the gelation process in the studied sol-gel systems was calculated.

Key words: sol-gel system, 3-methacryloxypropyltrimethoxysilane, dynamic viscosity, gradient dependence of viscosity, activation energy.

Formulation of the problem. Membrane science and technology are the subject of interest of many researchers and are constantly considered as prior scientific and technical directions. Membranes of different types are widely used in alternative power engineering, electrodialysis, ion-exchange processes. Problems connected with the use of membranes in micro- and nanofiltration of organic media, in homogeneous catalysis and extraction processes in petrochemical, chemical and food industries are investigated intensively. A variety of areas for the practical application of membranes determines the requirements for their properties and stimulates the development of new membrane materials for targeted use [1, 2].

A lot of membranes are made on the basis of polymers and hybrid organic / inorganic materials, which ensures the achievement of desired chemical, physical and mechanical properties. Among the various methods of composite membranes synthesis sol-gel technology takes an important place. Sol-gel technology has a number of advantages: simplicity and accessibility, environmental friendliness, possibility of modifying of material properties by introducing modifying substances at the synthesis stage. That is why this method of synthesis is of a considerable interest.

One way of obtaining hybrid organic-inorganic membranes using of sol-gel technology is their formation from organic-inorganic precursors which contain organic functional groups and inorganic alkoxysilane groups, undergoing sol-gel transformation. 3-methacryloxypropyltrimethoxysilane is one of the promising starting materials for such syntheses because it contains methacrylic fragments capable to form C-C bonds in polymerization processes as well as alkoxysilane groups near the silicon atom which can form siloxane chains during sol-gel process. For the wider use of this precursor, it is necessary to study its rheological behavior under different conditions.

Analysis of recent research and publications. A significant number of publications indicates the growing interest of scientists in the use of 3-methacryloxypropyltrimethoxysilane (MAPTMS) in organic-inorganic hybrid syntheses. The authors [3] prepared hybrid organic-inorganic material containing carbon and siloxane chains by radical polymerization of MAPTMS followed by hydrolytic polycondensation using acid catalysis. As a result of condensation of poly(MAPTMS) of different molecular weights $M_n = 830 – 12000$, synthesized by polyaddition, transparent flexible gel films were obtained. The dependence between the structure of the obtained hybrid organic-inorganic films and their mechanical properties is established: the latter are largely determined by the carbon chain length (with increase of the carbon chain length, elasticity of the gel films increases, however, tensile strength and Young’s modulus decrease). The degree of cross-linking of siloxane chains also depends on the degree of polymerization: poly(MAPTMS) with a higher degree of polymerization forms gum-like hybrid materials, whereas at lower polymerization stages solid hard hybrids are obtained. Hydrolysability of poly(MAPTMS) decreases with increasing of the carbon chain length, which can be explained by steric barriers.

In [4] the results of the research on the synthesis of silicon-acrylic copolymer by emulsion copolymerization of acrylic acid (AC) and MAPTMS are presented. MAPTMS is used to create additional cross-links in the polymer matrix in order to provide the final product with improved physico-chemical properties. The process was studied at various temperatures (60–120 °C), molar ratio of the starting materials and concentrations of the reaction initiator – ammonium persulfate. This made it possible to find optimal conditions for the synthesis of a gel and powder products, which may be used in paint and varnish production.

In several works MAPTMS are used together with the most commonly used alkoxysilane – tetraethoxysilane (TEOS). When added to the sol-gel system based on TEOS, this organic precursor acts as a structural modifier. As a result of the influence of the modifier, the final siloxane network acquires the necessary properties (for example, hydrophobicity, flexibility). Thus, in [5] a mixture of MAPTMS and TEOS at molar ratio of 4 : 1 was used. Hydrolysis of a mixture of precursors was carried out in ethanol/water solution. Investigation of the sol-gel process of alkoxysilanes mixture by ^{29}Si NMR spectroscopy and FTIR spectroscopy allowed to optimize the duration of hydrolysis of both components and subsequently to prepare organic-inorganic hybrid materials – sol-gel coatings for metal surfaces.

The influence of MAPTMS : TEOS ratio on gelation rate in the process of obtaining of hybrid materials was the subject of interest of the authors [6]. Investigation of the mixtures of two alkoxysilanes with different times of adding of MAPTMS to the sol-gel systems TEOS – isopropano – water with base catalyst of hydrolysis allowed to reveile that the size and morphology of synthesized nanoparticles depend on the time of hydrolysis and condensation of TEOS. At a small period of time of sol-gel conversion up to the moment of adding of MAPTMS in nanoparticles organic fragments were detected, while at the same time, organic fragments in nanoparticles not detected before the addition of MAPTMS. Consequently, the way of the component introduction affects the size of the particles formed, the distribution of particles in size and their morphology.

A similar task was set by the authors [7]: they observed the change in gelation time in the sol-gel systems based on TEOS when MAPTMS was added to them. Hydrolyzed MAPTMS was introduced into a gel network and significantly influenced the process of structuring. The lower functionality of MAPTMS compared to TEOS, as well as the steric barriers of acrylate groups lead to a significant increase in gelation time.

Thus, the organic-inorganic precursor of the sol-gel process – MAPTMS – is increasingly used by researchers in the synthesis of composite materials, most often in combination with TEOS. However, the analysis of publications in this research area indicates that there are not enough publications devoted to the separate stages of the sol-gel transformation at the presence of MAPTMS. In particular, publications on the rheological research of the sol-gel systems of organic-inorganic precursors, which would allow to get the information necessary for the synthesis of composite materials of desired structure and properties, are rare.

In general, quantitative rheological studies were performed on the sol-gel systems based on precursor TEOS [8–9]. By monitoring the changes in viscosity and elasticity of the system near the gelation threshold, it was possible to observe the constructing of the spatial network during the sol-gel transformation of the TEOS solutions and the structural evolution of gels. Dependences of rheological properties of alkoxide solutions on concentration, molecular weight *etc.* determine the conditions necessary for obtaining a gel with a certain structure.

The authors [10] conducted experimental rheological studies of the sol-gel systems of TEOS in combination with other alkoxysilanes: 3-(2-aminoethylamino)propyltrimethoxysilane, 3-aminopropyltrimethoxysilane or 3-aminopropyltriethoxysilane. This study was focuses on the determining of the gelation time by measuring the gel viscoelastic response as a function of the shear rate and measuring of the gel elastic modulus immediately after gelation and its evolution within several hours of gelation. The measuring of the gelation time in systems with different ratios of additive / TEOS enabled to offer the mechanisms of nucleation and aggregation of particles in these sol-gel systems.

The publication [11] it is reported about the synthesis of the organic-inorganic hybrid composite based on cross-linked polyimide and silica by sol-gel process using the precursor TEOS. Two binding agents – mercaptopropyltrimethoxysilane and triethoxysilane – were used for compatibilization of organic and inorganic components of solution. The use of these additives allowed homogeneous phase morphology to be obtained. Properties of solutions were investigated by rheological and analytical methods.

The purpose of this work is to investigate the influence of various factors on the rheological behavior of the sol-gel systems on the basis of organic-inorganic precursors – TEOS and MAPTMS.

Experimental. For research the following reagents were used: 3-methacryloxypropyltrimethoxysilane (Aldrich) (MW 248.35; d^{25} 1.045; n_D^{20} 1.431; bp 190 ºC; 98 %), tetraethoxysilane (“Sfera Sim”) (MW 208.33; d^{20} 0.933; n_D^{20} 1.431; bp 169 ºC; 99 %), ethanol and orthophosphoric acid (85 %) of high purity, distilled water.

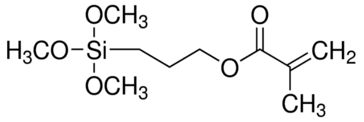
Solutions of the sol-gel precursors were prepared by mixing TEOS, MAPTMS, ethanol, water and orthophosphoric acid in the appropriate ratios at constant stirring on a magnetic stirrer (500 rpm) at different temperatures.

Rheological behavior of these systems was investigated using the rotary viscosimeter RHEOTEST 2.1 (VEB MLW, GDR), which is a two-system device: rheological characteristics can be determined using cylindrical or conical plate measuring devices. The investigated solutions were thermostated in a water bath connected to a liquid circulatory thermostat. For the solutions of the sol-gel precursors studied the dependences between the shear stress τ and the shear rate D_r were revealed. The increase in the shear rate was achieved by increasing the speed of the measuring cylinder or cone (in the case of gels) by tuning the reducer. Dynamic viscosity was determined by the ratio:

$$\eta = \tau / Dr, \qquad (1)$$

where η is the dynamic viscosity (Pa • s); τ is the shear stress (Pa); D_r is the shear rate (s^{-1}).

Results and discussion. As it was noted above, we choose for the study the sol-gel system based on two commercially available precursors: tetraethoxysilane $Si(OC_2H_5)_4$ with four ethoxyl groups near the Si atom and 3-methacryloxypropyltrimethoxysilane, which contains three methoxy groups and a methacryloxypropyl moiety covalently bonded with Si atom:



(2)

As a result of the sol-gel conversion, the alkoxysilanes are hydrolyzed, the hydrolysis products react in polycondensation reactions between themselves and with the starting materials, forming siloxane bonds (-Si-O-Si-). Nanosized products of alkoxysilane polycondensation are interconnected and form a silicon framework. These processes take place in parallel [5] and cause the growth of the viscosity of the sol-gel system.

The process of the structural changes in a system with sol-gel transformation occurs through the formation and evolution of fractal aggregates (the formation and growth of fractal aggregates before they collide with each other and link between themselves). At the point of gelation, adjacent clusters form a single 3D network. The gelation point corresponds to the percolation threshold, when a single cluster is formed in the entire volume of the sol, resulting in the losing of the sol mobility and its freezing, becoming a gel. The point of percolation is corresponded to such a concentration of formed macromolecules and their conformational size, at which the conformational volumes of macromolecules begin to overlap. This results in a sharp increase in the viscosity of the sol-gel system. Consequently, the state of gelation can be estimated by changing in the viscosity of the system in time.

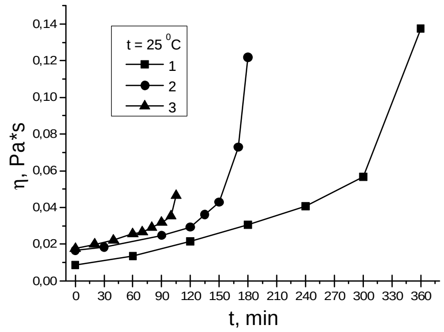
Dynamics of viscosity of the sol-gel systems was investigated at high angular rates of rotation of the working cylinder (ω = 4.05 rps). The following viscosity dependences are obtained:

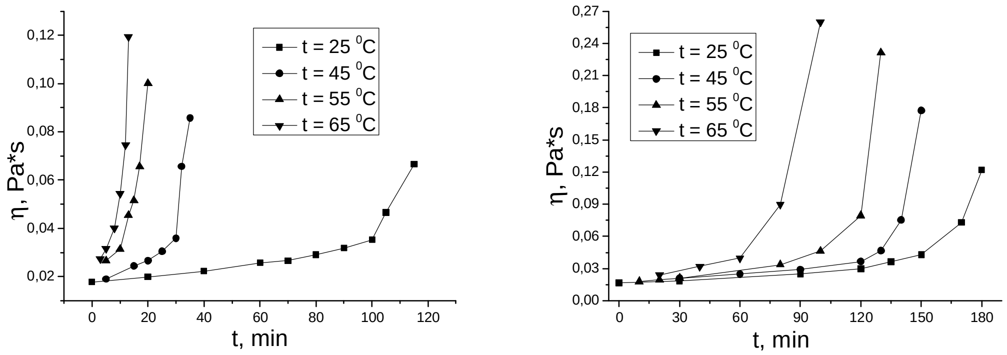
– on the temperature for the sol-gel systems of five different compositions;- on MAPTMS content;

– on the content of the sol-gel conversion catalyst – orthophosphoric acid.

Measured dependences are presented in Fig. 1–3.

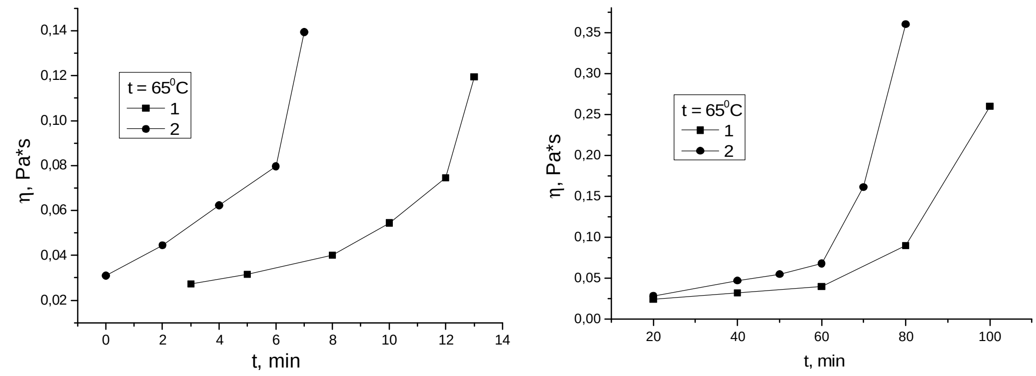
Fig. 1. The changes in the viscosity in time for the systems with different contents of TEOS and MAPTMS:
1 – MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O =
= 0.4:0.6:4:1.2:4 (mol);
2 – MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O =
= 0.25:0.75:4:1.2:4 (mol);
3 – TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.2:4 (mol)





a) *b)*

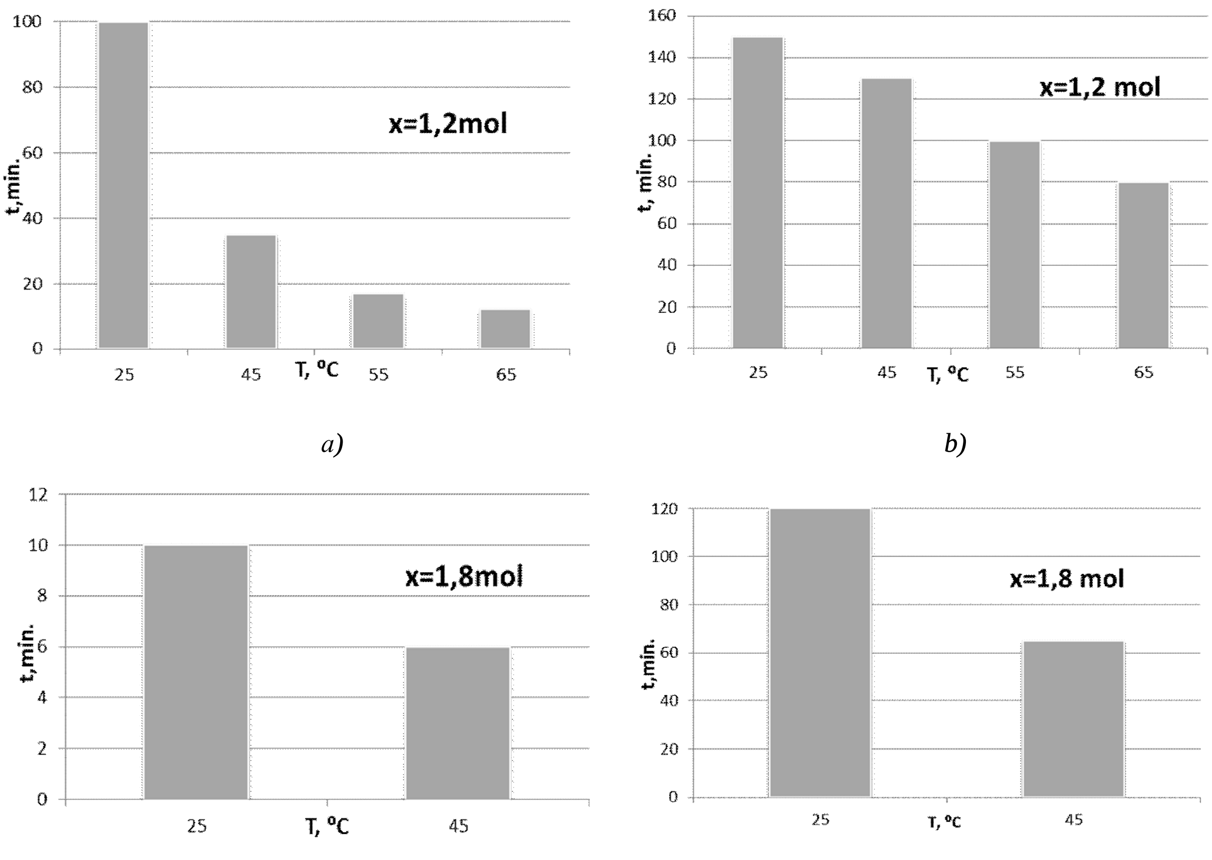
Fig. 2 . The dynamics of the viscosity at different temperatures: a – TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.2:4 (mol); b – MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = 0.25:0.75:4:1.2:4 (mol)



a) *b)*

Fig. 3. The dynamics of the viscosity for the systems with different H_3PO_4 content: a – 1 - TEOS:C_2H_5OH:H_3PO_4:H_2O= = 1:4:1.2:4 (mol); 2 – TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:6:0.8:4 (mol); –) 1 – MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O= = 0.25:0.75:4:1.2:4 (mol); 2 – MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = 0.25:0.75:4:1.8:4 (mol)

All obtained curves of the viscosity changes in time have a typical shape: they consist of a section with a very slowly increasing viscosity that corresponds to the processes of hydrolysis and condensation in the sol-gel systems, and the second section with a sharp increase in viscosity illustrating the processes of aggregation of formed macromolecules, which leads to the formation of a gel. By linearizing of the second sections, the time of achievement of the percolation threshold – t_p, which corresponds to the beginning of the conformational volumes of macromolecules overlapping, was determined. The obtained data are presented in Fig. 4.



a) *b)*

c) *d)*

Fig. 4. The time of achievement of the percolation threshold of the systems TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:X:4 (a, c) (mol) and MAPTMS:TEOS:C_2H_5OH:H_3PO_4 :H_2O = 0.5:0.75:4:X:4 (mol) (b, d)

Analyzing the data obtained, we can conclude that the composition of the sol-gel system has a significant influence on the rate of gelation. By varying MAPTMS concentration, it is possible to regulate the amount of silanol groups that participate in the sol-gel process. Adding MAPTMS to TEOS in the ratio of 1 : 3 leads to an increase in the time of the achievement of the percolation threshold from 100 *min* to 150 *min* (1.5 times), and at a ratio of 1 : 1.5 – up to 360 *min* (3.3 times). This can be explained on the one hand by the lower functionality of MAPTMS compared to TEOS (three methoxy groups in MAPTMS molecule, four ethoxy groups in TEOS molecule), and on the other hand by steric effects, since the large methacryloxypropyl group prevents the interaction of molecules in solution and thus slows down the reaction. This conclusion coincides with the publication data [7]. The authors [6], based on experimental results, assert that the addition of MAPTMS may even stop hydrolysis and condensation of TEOS. This is explained by the fact that MAPTMS shields the surface of silica particles formed as a result of TEOS sol-gel transformation. In [3] it was investigated that the sol-gel transformation of MAPTMS occurred in parallel with the radical polymerization of this precursor. It was found that the degree of polymerization affects the hydrolysis of MAPTMS – increasing the length of carbon chain of the formed macromolecules reduces hydrolysis, which also confirms a presence of a steric factor in the case of this precursor.

The sol-gel process catalyst – orthophosphate acid – has a noticeable effect on the characteristic time t_p of the achieving of the percolation point in these systems. So, with an increase in the catalyst content in the system MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = 0.25:0.75:4:X:4 mol from 1.2 to 1.8 mol, the time t_p decreases from 130 min to 120 min (at a temperature of 45°C). This indicates the catalytic nature of the reactions of hydrolysis and polycondensation; the rate of these processes determines the size and concentration of macromolecules, which affects the rate of gelation in general.

The dynamics of the viscosity of the studied sol-gel systems depends to a great extent on temperature. For comparison, let’s look on the temperature dependences of the gelation time in the temperature range of 25–65 °C for two systems: MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = = 0.5:0.75:4:1.2:4 (mol) and TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.2:4 (mol). As one can see, in the first case, the time t_p changed from 150 min to 70 min (2.1 times), and in the second case – from 100 min to 13 min (7.7 times).

Consequently, a significant change in the rate of the reactions of the precursor hydrolysis and hydrolysis products polycondensation from temperature causes the corresponding temperature dependence of the time of the achievement of percolation threshold in the system. The fact that gelation represents a unique extent of polycondensation allows for the use of the gelation time as the inverse rate of the reaction.

Thus the Arrhenius equation can be set equal to the inverse of the gelation time, as shown in eq:

$$1/t_p = A \exp(-E /RT), \tag{3}$$

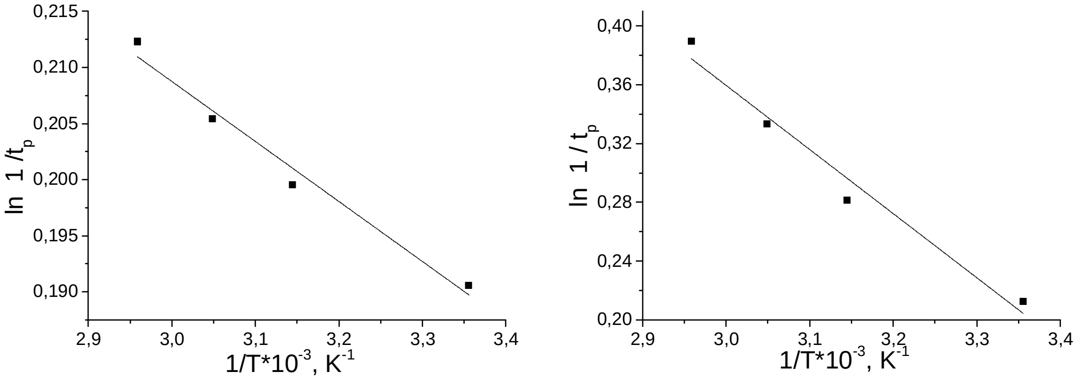
where E is the activation energy of the gelation process [12].

This technique has been used by many researchers to determine the activation energy of gelation for TEOS systems. Activation energies for gelation range from 40 to 70 kJ/mol (9.5–16.7 kcal/mol) depending on different factors [13].

The activation energy can not be ascribed to any particular reaction, as gelation depends in a complicated way on the rates of hydrolysis, condensation and diffusion of clusters.

The experimentally determined activation energy of the gelation process is 56,9 kJ/mol for the system: MAPMTS:TEOS:C_2H_5OH:H_3PO_4:H_2O = 0.5:0.75:4:1.2:4 (mol) and 25/5 kJ/mol for the system: TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.2:4 (mol). This activation energy can not be attributed to a particular reaction, since the gelation process depends on the rate of hydrolysis, condensation of alkoxysilane and the cluster diffusion by a complicated way. Nevertheless, it characterizes the process as a whole.

It is known that macromolecule solutions, which include the sol-gel system, are not Newtonian fluids, that is, their viscosity essentially depends on the gradient rate of the hydrodynamic flow. The measured rate of macromolecule solution depends not only on the frictional forces between the layers of the moving fluid, but also on the shear deformation of macromolecules. Accordingly, it is possible to distinguish conditionally frictional and elastic components of viscosity. The elastic component of viscosity determines the dependence of the measured viscosity of macromolecule solutions on the magnitude of the gradient of the hydrodynamic flow rate.



a) *b)*

Fig. 5. The temperature dependence of the gelation time in the sol-gel systems:
a – MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = 0.25:0.75:4:1.2:4 (mol);
b – TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.2:4 (mol) in the Arrhenius equation coordinates

The authors [14] using SARW (self-avoiding random walks) statistics, derived an equation that describes the gradient dependence of macromolecule solution viscosity η:

$$h = h_o + h_s \frac{1 - \exp(-b / w)}{1 + \exp(-b / w)}, \qquad (4)$$

where η_o is a frictional component of viscosity; η_s is an elastic component of viscosity; **b** is a coefficient that characterizes the segmental motion of macromolecules.

Thus, studying of the dynamics of the sol-gel system viscosity and its dependence on the angular rate ω of the rotation of the working cylinder allows to estimate the frictional and elastic viscosity components and to some extent evaluate the dynamic properties of macromolecules.

The gradient dependence of the sol-gel system viscosity was measured in the range of the working cylinder rates 0.5–243 rpm. Using the optimization method in ORIGIN 5.0 program the frictional and elastic viscosity components and the coefficient *b* for each composition of the sol-gel system and the conditions of the process were calculated. The examples of experimentally measured gradient dependences of the sol-gel system viscosity in the moment before the percolation threshold, as well as the calculated values of the frictional and elastic viscosity components and the coefficient *b* are shown in Table 1 and Fig. 6.

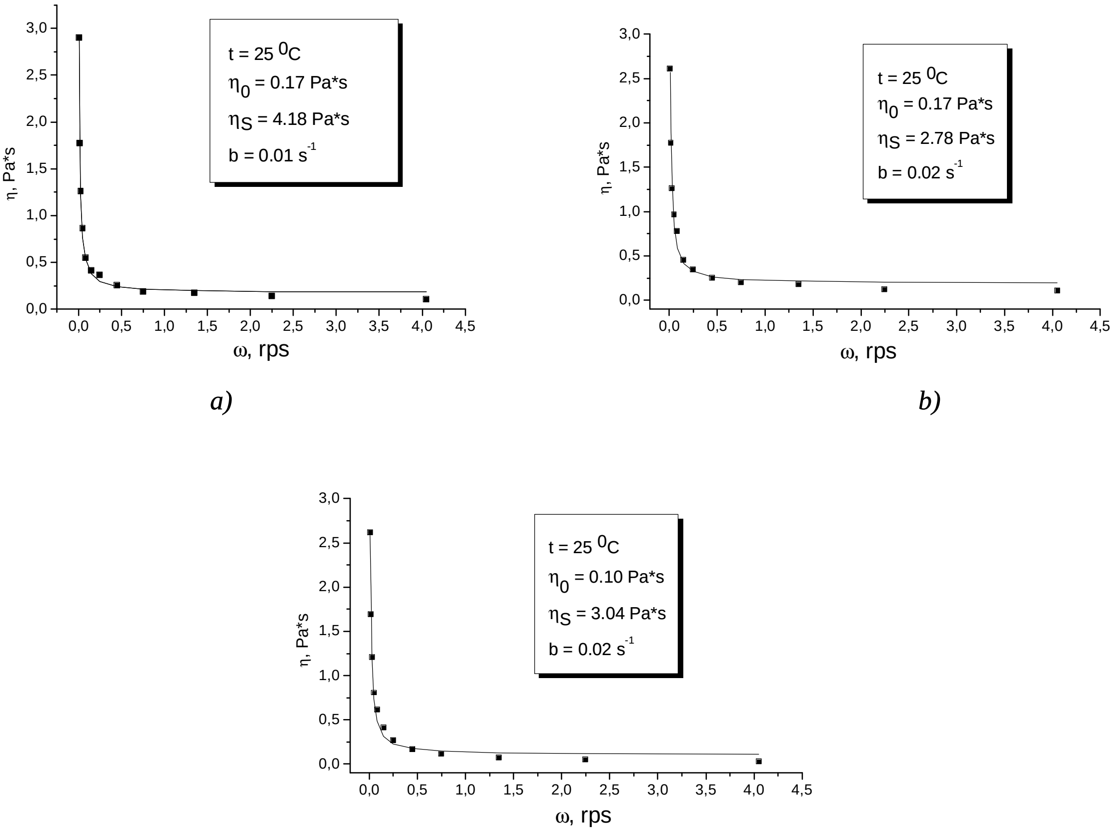
Table 1

The viscosity parameters of the investigated sol-gel system

№	Temp., °C	System composition	η_o, Pa*s	η_s, Pa*s	b, s^{-1}
1	2	3	4	5	6
1	25	MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = = 0.4:0.6:4:1.2:4	0.17	4.18	0.01
2	25	MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = =0.25:0.75:4:1.2:4	0.17	2.17	0.02
3	45	– “ –	0.19	2.18	0.05
4	55	– “ –	0.26	2.29	0.06
5	65	– “ –	0.29	2.40	0.07
6	45	MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = = 0.25:0.75:4:1.8:4	0.26	1.96	0.05

Continuation of table 1

1	2	3	4	5	6
7	65	– “ –	0.38	1.98	0.09
8	25	TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.2:4	0.10	3.04	0.01
9	45	– “ –	0.13	3.21	0.01
10	55	– “ –	0.15	3.42	0.02
11	65	– “ –	0.17	3.72	0.06
12	45	TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.8:4	0.13	3.56	0.02
13	65	– “ –	0.18	3.83	0.04



a) *b)*

c)

Fig. 6. The gradient dependences of viscosity of the systems with different TEOS and MAPTMS content:
a – MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = 0.4:0.6:4:1.2:4 (mol);
b –MAPTMS:TEOS:C_2H_5OH:H_3PO_4:H_2O = 0.25:0.75:4:1.2:4 (mol);
c – TEOS:C_2H_5OH:H_3PO_4:H_2O = 1:4:1.2:4 (mol)
(dots – experimental data, lines – values, calculated using eq.n (3))

The results of the calculation of η_o, ηs and b from the experimental curves of the gradient viscosity dependence, given in Table 1, show the dependence of these parameters both on the system composition, and on temperature and catalyst content. In all cases, the elastic component of viscosity is greater than the frictional one, which indicates a significant contribution to the segmental motion of macromolecules. With increasing temperature, we observe the growth of viscosity, and the elastic component changes more significantly. However, since during gelation a continuous change in the concentration of macromolecules in the system, as well as their conformations takes place, which has a complex effect on the segmental motion of macromolecules, the gradient dependence of viscosity of sol-gel systems requires further investigation.

Conclusions. The investigation of viscosity of sol-gel systems of various compositions based on precursors TEOS and MAPTMS allowed to determine the effect of the temperature, system composition and catalyst concentration on the time of percolation point achievement, when gelation occurs. This is of practical importance in the synthesis of organic-inorganic composites using the sol-gel process, since it allows to find the appropriate ratio of precursors and the conditions for sol-gel transformation. It was established that the replacement of the part of TEOS on MAPTMS slows down the gelation process. Studying of the gradient dependence of viscosity of sol-gel systems made it possible to determine the frictional η_o and elastic η_s components of viscosity of sol-gel systems, depending on the temperature and the initial composition of the system.

1. Терещенко Г. Ф., Орехова Н. В., Єрмилова М. М. Мембраны // Критические технологии. – 2007. – № 1(33). – С. 4–20. 2. Волков В. В., Мчедлішвілі Б. В., Ролдугін В. І., Іванчев С. С., Ярославцев А. Б. Мембрани і нанотехнології // Наноматеріали функційного призначення. – 2008. – Т. 3, № 11–12. – С. 47–99. 3. Yoshimoto Abe, Yuki Honda, Takahiro Gunji. Preparation and properties of silicon-containing polymer hybrids from 3-methacryloxypropyltrimethoxysilane // Appl. Organometal. Chem. – 1998. – 12. – P. 749–753. 4. Рубан О. В., Кисельова-Логінова К. В., Попов Є. В. Отримання кополімеру акрилової кислоти і 3-метакрилоксипропілтриметоксисилану методом емульсійної кополімеризації // Технологический аудит и резервы производства. – 2015. – № 3–4. – С. 17–23. 5. Amir A. El hadad, Diogenes Carbonell Violeta Barranco, Antonia Jimenez-Morales, Bianka Casal, Juan Carlos Galvan. Preparation of sol-gel hybrid materials from γ-methacryloxypropyl trimethoxysilane and tetramethyl orthosilicate: study of the hydrolysid and condensation reactions // Colloid Polym. Sci. – 2011. – 289. – P. 1875–1883. 6. Evelisy Cristina de Oliveira Nassor, Lilian Rodrigues Avila, Paula Fabiana dos Santos Pereira, Katia Jorge Ciuffi, Paulo Sergio Calefi, Eduardo Jose Nassar. Influence of the hydrolysis and condensation time on the preparation of hybrid materials // Materials Research. – 2011. – 14(1). – P. 1–6. 7. M.J. van Bommel, P.M.C. ten Wolde, T.N.M. Bernards. The influence of methacryloxypropyltrimethoxysilane on the sol-gel process of TEOS // Journal of Sol-Gel Science and Technology. – 1994. – Vol. 2, Iss. 1–3. – P. 167–170. 8. Sacks M. D., Sheu R. S. Rheological Properties of Silica Sol-Gel Materials // J. Non-Cryst. Solids. – 1987. – 92, 2. – P. 383–396. 9. Klein L. C., Garvey G. J. Soluble silicates, ACS Symp.Series No. 194, ed. Falcone J. S., Am. Chem. Soc., Washington, D.C. – 1982. – P. 293. 10. Christelle Alie, Rene Pirard, Jean-Paul Pirard. Preparation of low-density xerogels from mixtures of TEOS with substituted alkoxysilanes. II. Viscosity study of the sol-gel transition // J. Non-Cryst. Solids. – 2003. – 320. – P. 31–39. 11. Xenopoulos C., Mascia L. and Shaw S. J. Polyimide-silica hybrids derived from an isoimide oligomer precursor // J. Mater. Chem. – 2002. – 12. – P. 213–218. 12. Colby M. W., Osaka A. and Mackenzie J. D. Temperature dependence of the gelation of silicon alkoxides // Journal of Non-Crystalline Solids. – 1988. – 99. – P. 129–139. 13. Brinker C. J., Scherer G. W. Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing. San Diego: Academic Press. – 1990. – 908 p. 14. Medvedevskikh Yu. G., Voronov S. A., Zaikov G. E. Conformation of Macromolecules. Thermodynamic and Kinetic demonstrations. Nova Science Publishers, Inc. – N. Y., 2007. – 249 p.