

Morphology of porous glasses. Colloid-chemical aspect

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A summarizing of the results of complex study of pore morphology of porous glasses has been carried out taking into consideration the dissolved secondary silica state in the systems *alkali borosilicate glass – a leaching solution*. An influence of the composition and phase structure of an initial glass, and their leaching conditions, on the colloid-chemical characteristics of the porous glasses has been shown. The polymodal micro porous substructure and meso porous one, the size and a form of the pores and secondary silica particles as well as the fractal dimensions of their aggregates, the coefficients of structural resistance and tortuosity of the pores has been discussed.

Keywords: phase-separated glass, porous glass, structure, porosimetry, transmission electron microscopy, small angle X-ray scattering.

1. Introduction

The high-siliceous porous glasses (PGs) represent the channel membrane nanosystems, having the thermal, chemical and microbiological stabilities combined with adjustable structural characteristics. At present these glasses are the promising materials for the use in advanced separation and nanofluidic technologies, particularly, as the basic matrices for the electrokinetic micropumps for lab-on-a-chip systems [1, 2]. In connection with this new perspective application, a creation of PG plates with the controllable colloid-chemical characteristics and optical properties is extremely important. As well as many other, the specific properties of PGs are caused very largely by morphology and the parameters of their pore structure [3, 4]. As it is known, the PGs possess a complicated structure [5]. They are formed by the spongy SiO₂ skeleton representing a silica framework of the initial two-phase alkali borosilicate (ABS) glass, and by the finely dispersed particles of hydrated secondary silica, which fill the spongy skeleton cavities (macropores) corresponding to the liquation channels. The colloid-chemical structure of secondary silica depends on the factors which have an influence on the processes of silica dissolution and polymerization [6]. Those include the composition of the initial glass, the regime of its thermal treatment,

and the conditions of two-phase glass leaching (*i.e.*, the composition, concentration and temperature of leaching solution, and a ratio between the glass surface and the solution volume [4, 6, 7], duration of the leaching process [8, 9]), and following rinsing in water [10].

Evidently, in order to find an optimum procedure for manufacturing PGs, it is necessary to know the influence of these factors on the PG structure parameters, which are caused by secondary silica behavior. The present work is devoted to generalization of the results of the PG porous structure investigations depending on the secondary silica state inside porous space.

2. Techniques

The objects of the investigation were plates of the $R_2O-B_2O_3-SiO_2$ ($R = Na, Na+K$; $R_2O \approx 7$ mol%) glasses with/without additives of PbO , or $|F|$ and P_2O_5 (Tab. 1), which were thermally treated at 500–700 °C until reaching the phase equilibrium. The porous glasses were produced by leaching of the phase-separated alkali borosilicate (ABS) glasses in 0.1–4 M HCl solutions with/without 0.1–2 M KCl at different temperatures (from the room temperature up to the solution boiling temperature) with following washing in water and drying at 120 °C [4].

Table 1. Molar ratio of B_2O_3/SiO_2 and a quantity of the additives in the alkali borosilicate glasses under study.

Glass	Molar ratio B_2O_3/SiO_2 in a glass ($R_2O \approx 7$ mol%)	Additive (as-analysed quantity, mol%)
1	0.3	Al_2O_3 (0.1)
2	0.3	P_2O_5 (0.2) $ F $ (0.5)
3	0.6	K_2O (3.8)
4	0.6	Al_2O_3 (1.0) PbO (1.2) K_2O (2.9)

Determination of the silica molecular forms in acid-salt solutions was carried out by the kinetic spectrophotometric technique with a subsequent calculation of the distribution of silica over the molecular forms [11]. The PG pore parameters were investigated by the classical adsorption methods (BET, mercury porosimetry) [12] and by new methods based *i*) on a computer simulation of the kinetics of gas desorption measured by mass spectrometry from a porous material into high vacuum and *ii*) on the analysis of the equilibrium isotherms of gas desorption at low pressures [13–15], as well as by transmission electron microscopy (TEM) [16], small angle X-ray scattering (SAXS) [17], the electrochemical methods [4].

3. Experimental results and discussion

It has been revealed that the leaching solutions contacting with the ABS glasses contain the both polymeric and weakly associated silica forms [11, 18, 19]. The monomer and oligomer forms of silica are the primary products of this interaction. Addition of KCl salt to leaching solution and increase of its concentration in the solution result in the change of the ratio between the weakly associated forms and the polymer ones of silica (*e.g.*, Fig. 1). This factor plays a vital role, as the character of distribution of the secondary silica particles in PG's pore space determines their structure parameters [5] and the type of silica macro-scale inhomogeneities [20]. The correlation between a fraction of weakly structured silica in the leaching solution and a pore specific surface area of PGs is characteristic for all glasses under study [11, 18]. The probable reason of this can be the following: the formation of the PGs structure is caused by the polymerization of secondary silica, which underlies the complicated processes of coagulation and gelation of silica [21]. These processes can occur upon a collision of silica particles with a sufficiently low surface charge. The presence of electrolytes decreases the surface charge of the silica particles, and hence, favors their aggregation. Therefore, addition of the KCl salt to the HCl solution should lead to the rapid silica polymerization with the formation of a weakly structured silica gel. Within certain KCl concentration range (for example, from 1.4 to 2.1 M in the case of Glass 1 [11]) the total polymerization of weakly structured silica is observed throughout the solution, due to the contact of low-molecular silica with the solid phase of high-silica PG. As the KCl concentration in the leaching solution increases, its critical concentration reaches the value above which the coagulating effect is weakened or discontinued. The processes described above influence the structural parameters of

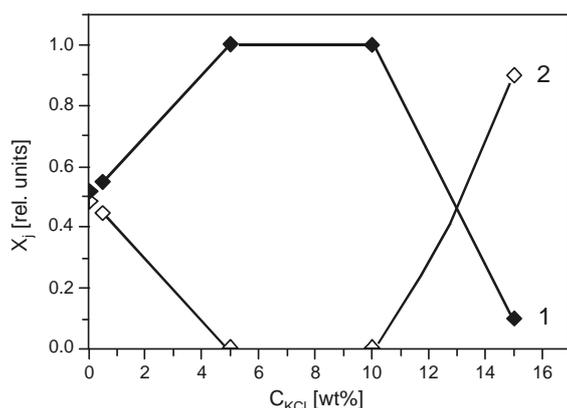


Fig. 1. Dependencies of the ratio X_j between the portions of weakly structural forms (1) and polymer forms (2) of silica in the leaching solutions contacted with the plates (thickness values are 2.0 mm, and 3 mm) of two-phase Glass 1 thermal treated at 550 °C vs. a concentration of KCl salt in the 3 M HCl solution.

T a b l e 2. The parameters* of the pore structure of the porous glass plates obtained by through leaching of the thermal treated at 550 °C alkali borosilicate glasses in the 3 M HCl solutions with/without 1.4 M KCl addition.

Leaching solution	Glass 1		Glass 2		Glass 3		Glass 4	
	HCl	HCl + KCl	HCl	HCl + KCl	HCl	HCl + KCl	HCl	HCl + KCl
Specific surface area S [m^2/g]	260	360	31	360	95	96	330	366
Pore volume V [m^3/g]	0.160	0.150	0.130	0.150	0.265	0.257	0.349	0.340
Porosity W [cm^3/cm^3]	0.26	0.24	0.23	0.24	0.37	0.36	0.43	0.43
Mean pore radius r [nm]	1.7	1.5	7.2	1.5	5.1 + 6.7	5.2	2.9	2.3
Coefficient of structural resistance β	19.9	21.6	14.3	21.6	4.9	6.2	6.2	6.6
Coefficient of tortuosity $\chi = \sqrt{W\beta}$	2.3	2.3	1.8	2.3	1.3	1.5	1.6	1.7

*The parameters S , V , and r were determined from the water vapor adsorption and desorption isotherms at 15–18 °C (for PGs obtained from Glasses 1, 3, and 4) and by mercury porosimetry (for PG obtained from Glass 2) [22, 23]. The β values were calculated from the data on electroconductivity of the PGs after 7-day contact with 0.1 M HCl solution [4, 23, 24].

T a b l e 3. Composition of unstable phase of the two-phase glasses and the characteristics of the porous glasses obtained by leaching in 3 M HCl boiling solution.

Glass	Thermal treatment temperature [°C]	Composition of the unstable phase before leaching [mol%]				Parameters of porous glass*		
		Na ₂ O	K ₂ O	B ₂ O ₃	SiO ₂	Specific surface area [m^2/g]	Pore volume [cm^3/g]	Mean diameter of mesopores [nm]
1	700	10.9	—	27.3	61.8	137	0.152	3.7
1	550	15.0	—	38.9	46.1	123	0.174	4.9
3	550	~15	~15	~59	~26	111	0.332	14.1

*The data were determined from the equilibrium adsorption and desorption isotherms of nitrogen at 77.5 K [13].

PGs. The data presented in Tab. 2 show that some structure parameters of PGs manufactured by glass leaching in acid-salt solutions are changed in comparison with the pure acid solution, especially in case of enriching the unstable phase of an initial two-phase glass with silica (Glass 1) [19, 22–24]. Namely, a decrease of mean pore radius value and an increase of specific surface area of PGs are observed. But for all that the pore volume of PGs does not practically change in most cases. It is possible to believe that at an introduction of KCl salt in the acid solution, the rate of silica gel formation decreases and the polymer network from the small silica particles is forming at the expense of weakly associated silica forms.

The computer simulation of the kinetic curves of gas diffusion at 77.5 K, which was performed in the framework of diffusion diagnostics [13–15], allows us to discover that the PGs under study have a through-out mesoporous structure with mean pore diameters ranging from 4 to 15 nm (Tab. 3). The structure is formed by the gaps between the secondary silica particles in the liquation channels and also by the parts of the liquation channels that are free from the secondary silica particles. Besides, a microporous substructure with pore sizes ranging from 0.35 to 2 nm is

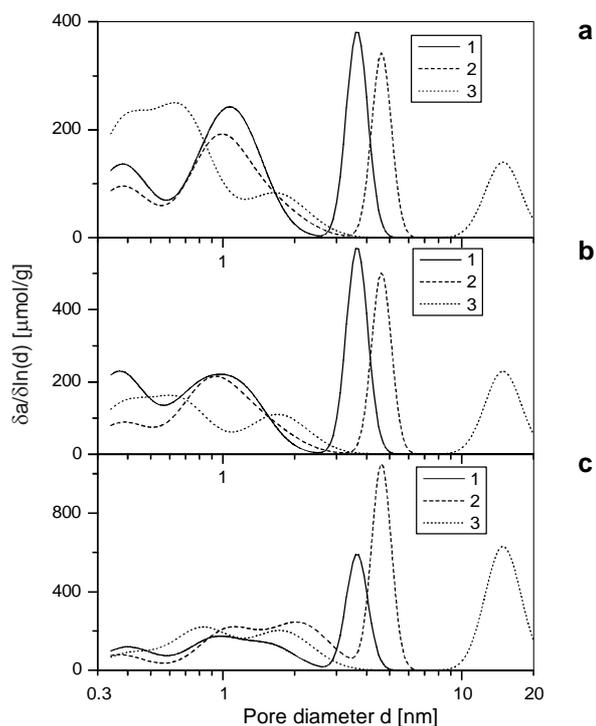


Fig. 2. Pore diameter distributions for the porous glass plates (thickness is 2.0 mm), which were produced by leaching of two-phase Glass 1 (curves 1, 2) and Glass 3 (curve 3) in the 3 M HCl boiling solutions according to the data of diffusion diagnostics method [13] with the use of nitrogen (a), oxygen (b), and argon (c) as diffusants. Temperature of glass thermal treatment: curve 1 – 700 °C; curves 2 and 3 – 550 °C.

inherited in these PGs (Fig. 2). This microporous substructure is formed by ultra micropores of molecular sizes (presumably, inside the silica skeleton) and also by medium- and large-sized micropores, which can be formed in the regions of silica particle contacts.

The data presented in Tables 2 and 3 demonstrate the influence of the initial ABS glass composition and the regime of its thermal treatment on the PG porous structure. It can be seen that a decrease in the pore volume V and the total specific surface area S_{spec} , and the mean radius r of mesopores correlate with a decrease in the alkali and boron oxide contents and an increase in the silica content of the unstable phase composition of the initial two-phase glasses. Hereby, the volume of the micropores is increasing [13]. Such changes of the unstable phase composition result not only from the changes of the initial glass composition (Glass 1 and Glass 3) but also from an increase of the temperature of glass thermal treatment of the same Glass 1 (Tab. 3). In case of the lead-containing Glass 4, the hetero-coagulation of the negatively charged secondary silica particles at their interaction with positively charged hydrolytic forms of lead salts in the solution inside a pore space likely takes place [23]. Owing to that, the PG produced from Glass 4 is characterized by a considerably smaller radius of the pores and their larger specific surface as compared to the PG which is obtained from the basic Glass 3 (Tab. 2). In case of Glass 2, the presence of fluoride-ions in the pore solution can promote dissolution of secondary silica during a glass leaching [25] that is resulting in formation of the PG with a large-sized pore structure. That is stimulated by a formation of the structural $\text{Na}^+[\text{F}^-\text{BO}_{3/2}]$ groupings in Glass 2, which is accompanied by a substantial loosening of the glass network [26].

Results of the PG conductivity measurements [4, 23, 24] have shown that the higher is the molar $\text{B}_2\text{O}_3/\text{SiO}_2$ ratio in glass, the lower are the values of the structural resistance coefficient β and the tortuosity coefficient χ of the PGs (Tab. 2). Simultaneously, at the identical $\text{B}_2\text{O}_3/\text{SiO}_2$ ratio and closely related porosities one can see different β and χ values as, for example, for PGs produced from Glass 1 and Glass 2 that gives the basis to estimate the change of secondary silica state inside pore space. Namely, in case of PG from Glass 2 both the amount and packing density of the secondary silica particles are small in comparison with Glass 1. During a long contact of PGs with dilute electrolyte (HCl, KCl) solutions, a degree of the β value decrease is more, than $\text{B}_2\text{O}_3/\text{SiO}_2$ ratio in glass is less. This occurs due to the removal of secondary silica from the pore-confined space, which is in accordance with the results of measurements of a silica amount in the solution contacting with glass [27].

One can see the influence of the acid concentration in the leaching solution on the PG structure parameters in Fig. 3 [15]. The differential curves of the distributions of the mesopores volumes over the mesopores diameters for PG samples obtained by leaching the Glass 1 in the 1 M and 3 M HCl solutions exhibit two peaks (Fig. 3a). The main peaks observed in the pore size range 3.6–4.6 nm correspond to the mesopores formed by the gaps between secondary silica particles in the liquation channels. The second peaks located in the pore size range 17–21 nm can be assigned

to the diameters of the liquation channels that are free from the secondary silica particles. These pore sizes correlate with the dimensions of the liquation channels (25–50 nm) according to a study by TEM method [16]. In the pore size range of 0.35–1 nm the polymodal microporosity is revealed (Fig. 3b). The main broad peak with the maximum at ~ 0.6 nm corresponds to the micropores in the regions of silica particle contacts and is observed for all PGs with a globular structure of mesopores.

An increase of the acid concentration in the leaching solution influences on PG structure as follows [15]. The total specific surface area of the pores decreases, for the most part, at the expense of the mesopores. The decrease of S_{spec} values of

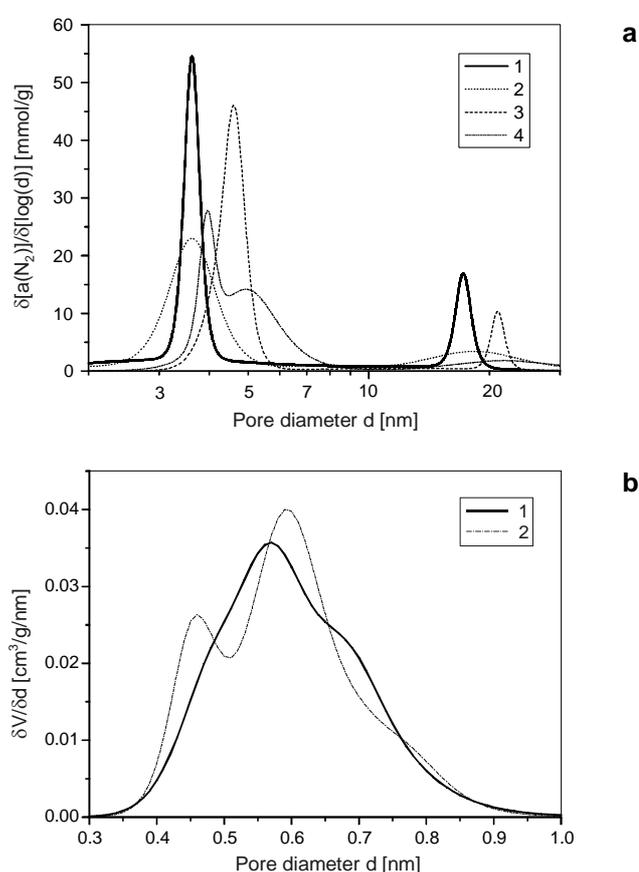


Fig. 3. Differential curves of the distribution of the mesopores volumes over the mesopores diameters obtained from the adsorption (2, 4) and desorption (1, 3) isotherms of nitrogen at 77.5 K (a) and of the micropore volumes over the micropore diameters calculated from the equilibrium isotherms of nitrogen and oxygen desorption at low partial pressures (b) [15] for the porous glass plates (thickness is 2.0 mm), which were produced from Glass 1 thermal treated at 550 °C by leaching of it in the HCl boiling solutions. Concentration of HCl solution: 1 M (curves 1 and 2 – a, curve 1 – b) and 3 M (curves 3 and 4 – a, curve 2 – b).

micropores is insignificant. The total pore volume decreases owing to the decrease of the V values of both mesopores and micropores. The dimensions of the mesopores increase (in accordance with the first peak in the size distribution curves given in Fig. 3a). A more complete clearing of the liquation channels from the secondary silica particles occurs (in accordance with the second peak in the size distribution curves given in Fig. 3a). The distribution of the micropore volumes over the micropore diameter becomes broader due to the appearance to the mode associated with the smallest micropores (ultra micropores) with the molecular size of ~ 0.5 nm (Fig. 3b). The width of the peaks in the mesopore size distribution curves obtained from the equilibrium nitrogen adsorption isotherms (Fig. 3a, curves 2 and 4) is larger than that determined from the desorption isotherms (Fig. 3a, curves 1 and 3). This most likely corresponds to the following: the diameter of the entrance in the pores received from desorption isotherms, is less dispersal in the sizes than the diameter of the internal pore volumes received from adsorption isotherms. It specifies that the form of the pores comes closer to spherical-and-cylindrical or to bottle-shaped one. It should be noted that the water vapor adsorption-desorption isotherms measured for studied PGs at 15–18 °C exhibit a hysteresis loop in the range $p/p_s = 0.3–0.7$ [22, 23]. This indicates that capillary condensation occurs in the mesopores [5]. And such shape of the isotherms is also characteristic of the bottle-shaped pores [5, 12]. But the presence of the bottle-shaped pores is revealed also in the micropore range [13].

The decrease in the S_{spec} values of mesopores and few decreases in the mesopores volume with an increase in the HCl concentration can point to the corresponding increase in the dimensions of secondary silica particles or to an increase of their packing density inside the liquation channels. These well founded assumptions are at one with the results of study of the structural transformation of secondary silica inside PGs with the help of TEM and SAXS methods [17], according to which an increase of leaching acid solution concentration is accompanied by both a decrease of the filling of their macropores (*i.e.*, liquation channels) by secondary silica sol and an increase of the amount and packing density of the chained structures, which are formed through gel formation and coalescence processes of secondary silica particles inside the macropores. It has been shown that for the PGs produced in particular from Glass 1 the various scattering sources, namely, the bottle-shaped pores, cylindrical and spherical pores and particles, and their aggregates can be a part of the PG's porous space structure. Such information about the scatterers can be obtained from the values of the mass-fractal dimension D and/or surface fractal dimension D_{surface} [28, 29], which are characterized by the slope of the I_s-s dependencies (see, for example, Fig. 4). For densely packed spheres in d -dimensional Euclidean space $D = d$; $D = 1$ for spheres arranged in a line in any space of dimension $d > 1$; for aggregates built up of chains of spheres the fractal dimension $1 < D < d$ is nonintegral and lies between 1 and 3. For any spatial dimension the function $p(r)$ goes as $\sim r^{d-1}$ for small r . In the region where the Porod's law is satisfied, the incident beam begins to interact with the individual particles of the aggregate and are scattered by the surface ($D_{\text{surface}} = 4$).

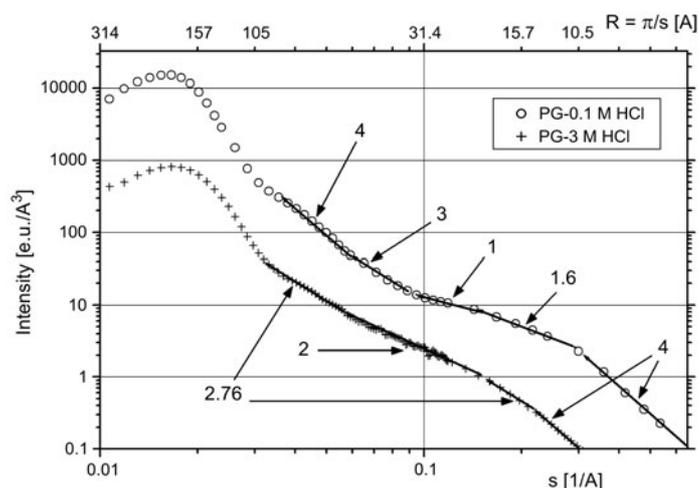


Fig. 4. Dependencies of scattering intensity $I(s)$ on wave vector s drawn on a log–log scale (with s plotted on the lower axis, and $R = \pi/s$, on the upper axis) for the porous glass plates (thickness is 0.5 mm) produced by leaching of thermal treated at 550 °C Glass 1 in boiling solutions with 0.1 M HCl concentration (PG-0.1 M) and 3.0 M HCl concentration (PG-3 M). The mass-fractal dimensions ($D = 1-3$) and surface fractal dimension ($D = 4$) are specified.

As it is seen from Fig. 4, the dimensions $D_{\text{surface}} = 4$ are typical for the regions of $R \leq 1$ nm and $R > 8$ nm. The incident beam can be scattered by surface of the finest particles of secondary silica and/or the ultra micropores in a silica skeleton (in the case of the least R values) and by surface of the silica skeleton, adjoining with exempted liquation channels (in the region with $R > 8$ nm).

An increase in the scattering intensity, which is accompanied to $D = 2.76$, can evidence of the densification (enlargement) and the ordering of scattering aggregates (*i.e.*, the pores, and silica particles). The interval of R sizes, which the value $D = 2$ corresponds to, is characterized by numerous oscillations. Similar oscillations can indicate the formation of branched structures with extended linear segments. At the detailed analysis of the intensity dependences in this interval a few segments with $D = 1$, which is characteristic of the spheres extended in a line, are founded. Those, for example, can be the oriented structures formed by the secondary silica particles inside pore space. Structures of such type have been revealed by TEM investigations of PGs [17]. At a significant decrease of the acid solution concentration, these characteristic regions with $D = 1; 1.6$ are more extended, but they are in the field of smaller R values.

4. Summary

In present work the following issues have been considered: the contributions from different molecular species of secondary silica to its total amount in the acid leaching

solution contacted with the phase-separated alkali borosilicate glass; an influence of the two-phase glass composition and the conditions of glass leaching on the secondary silica state and, consequently, on the structure parameters of the porous glass obtained.

The morphology of the porous glass has been investigated by independent complementary methods, such as the classical porosimetry methods (Brunauer–Emmett–Teller (BET) analysis, and mercury porosimetry) and new methods based on an analysis of the kinetic and equilibrium isotherms of gas desorption at 77.5 K under low partial pressures, as well as by a modified classical adsorption method under medium and high pressures; and also by transmission electron microscopy, small angle X-ray scattering, the electrochemical method of membrane conductivity.

It was shown that a relative fraction of weakly associated silica species and polymeric ones in the leaching solutions contacted with the phase-separated alkali borosilicate glasses depends on both the glass and the solution compositions. A correlation between the fraction of weakly structured silica and the value of the specific surface area of the pores has been marked.

An influence of the conditions of porous glass manufacturing on their morphology has been demonstrated. The polymodality of both the mesoporous structure and the microporous substructure of the porous glasses prepared by through acid leaching of the phase-separated alkali borosilicate glasses has been established. It has been revealed that the presence of the bottle-shaped pores is characteristic not only for the mesopore range, but also for the micropore range.

A probability of formation of the aggregates and oriented chained structures formed by the secondary silica particles inside pore space of the porous glasses has been demonstrated.

Acknowledgements – The measurements of the porous glass structure were realized in collaboration with the colleagues from the Faculty of Chemistry of Moscow State University (Dr. V. Kreisberg) and from the Department of Colloid Chemistry of Saint Petersburg State University (Prof. L. Ermakova and Prof. M. Sidorova). The study of the porous glasses by SAXS method is carried out by Dr. T. Vasilevskaya. Our work was supported by the Russian Foundation for Basic Research (projects no. 04-03-32165a and no. 08-08-00733a) and by the Department of Chemistry and Material Science of the Russian Academy of Sciences (The Programme FI OXNM-02, no. 02.1.29).

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*Received September 18, 2007
in revised form November 17, 2007*