



Short communication

Small-angle scattering investigation of silica xerogels and sonogels prepared with ionic liquid pyridinium tetrafluoroborate[☆]

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Abstract

Silica matrices were prepared via acid catalysed sol-gel processing augmented with sonocatalysis. As silica precursors, a mixture of tetra-functionalized alkoxide (TMOS) and three-functionalized alkoxide methyl-trimethoxysilane (MTMS) were employed. Ionic liquid *N*-butyl-3-methylpyridinium tetrafluoroborate ([bmPy][BF₄]), was used in various proportions, aiming to catalyse the sol-gel reactions, and to influence the mesoporous silica materials properties, serving as pore template. Small-angle neutron (SANS) and small-angle X-ray scattering (SAXS) techniques were used to explore the xerogels and sonogels microstructure evolution as a function of the IL/Si molar ratio. The results show a strong increase of the primary particle size under the influence of the ionic liquid. Ultrasonic agitation leads to further size increase by ca. 10%.

Keywords: silica, sol-gel processing, sonocatalysis, SANS, SAXS

I. Introduction

The sonochemical approach is widely used for the synthesis of a great variety of advanced inorganic materials. A strong ultrasound action (20–100 kHz) can induce chemical reactions or enhance their rates [1]. Sonication, being too weak for directly causing chemical effects, still can induce physical augmentations of ageing in the starting solutions [2]. Sonochemical techniques employ ultrasound to produce oxidative environment, via acoustic cavitations, due to the formation and collapse of microbubbles from acoustical wave induced compression/rarefaction [3–6].

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Ionic liquids (ILs) provide an interesting possibility to control the chemical contents of the collapsing bubble through the reduction of solvent vapour pressure [7]. It is known that the rates of sonochemical reactions can be increased by decreasing the vapour pressure of the solvent or by choosing a less volatile one [8,9]. ILs are usually more viscous and dense than other organic solvents and the cavitation should be more difficult to be produced under such conditions with the large cohesive forces [4,9]. Bubble collapse in liquids results in an enormous concentration of energy from the conversion of the kinetic energy of liquid motion into heat. Sonication is an alternative method to stimulate the hydrolysis of the alkoxides without using alcoholic solvents in the sol-gel process [10].

Ionic liquids can be used as reaction medium for synthesis of inorganic materials and have several advan-

tages, one of the less exploited ones being the self-organized structure of the neat ILs [11] as well as of their aqueous solutions [12,13]. The pre-organized structure of the ILs can serve as micro-compartment, or they can also be used as templates for porous nanomaterials, owing to their intrinsic high charge and polarizability [14,15]. The IL's properties as templating agent increase the thermal stability of particles [16]. The bulky hydrophobic cation can induce hydrophobicity and control the pore size in the materials [16]. Being used as solvents, their negligible vapour pressure prevents evaporation, and their high ionic strength increases the velocity of aggregation [17]. The ILs can increase the stability of polymeric gels by increasing the maturation time and diminishing the pore volumes. The collapse of the porous structure on ageing was shown to depend on the nature of the IL anion and to a lesser extent on the nature of silicon precursors [18].

We prepared nanostructured xerogels and sonogels with butyl-4-methylpyridinium tetrafluoroborate [bmPy][BF₄] ionic liquid, used as co-solvent and directing agent. The samples were synthesized in acidic conditions, with varying IL/Si molar ratios. Nitrogen adsorption, SANS and infrared results on these materials have been reported recently [19]. The particular choice of the precursors and ionic liquid was motivated by several considerations. Tetrafluoroborate anion shows an outstanding catalytic activity and leads to highly condensed silica networks [18]. Concerning the methyl-substituted silica precursors, TMOS is capable of undergoing a more rapid hydrolysis in comparison with TEOS [20]. Including methylsilane precursors in xerogel synthesis, like MTMS, can lead to textural improvements by modifying the hydrophobicity of the pore walls. Xerogels obtained from mixed TEOS/MTES or TEOS/isobutyltriethoxysilane precursors enhance the fluorescence emission of the immobilized porphyrins [21,22].

In the present communication, we use SAXS and SANS techniques to elucidate the influence of sonication and ionic liquid on the structure of the dry gels.

II. Experimental

Two series of samples (see Table 1): classic xerogels and sonicated gels were prepared and details are given in a previous paper [19]. In brief, 0.13 moles of TMOS, 1.15 moles of distilled water, 0.4 moles of acidic water

(adjusted to pH = 2.8 by addition of HCl) and 0.0162 moles of MTMS were mixed. The reaction mixture was mechanically stirred until a homogenous sol was obtained. Aqueous solution of [bmPy][BF₄] was added into the reaction mixture in an amount to obtain IL/Si molar ratios from 0.007 to 0.07.

One group of series (X) was left to gel and dry, while the parallel series (S) were subjected to ultrasonication using a VCX-T-750 apparatus with a titanium sonotrode, operating at 20 kHz and 750 W, starting from the addition of the first reactant into the reaction mixture, till the end of the synthesis process. The total transferred energy was 250 J/mL for each sample and during sonication the temperature increased from 25 to 60 °C. Finally, all samples were dried at 60 °C.

The small angle neutron scattering (SANS) measurements were performed at the *Yellow Submarine* diffractometer at the Budapest Neutron Centre [23]. The SAXS measurements have been made with a Rigaku instrument, using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocus X-ray tube (Osmic MicroMax 002) at the Institute for Macromolecular Chemistry in Prague. The samples in powder form have been measured at ambient temperature.

III. Results and discussion

Small angle X-ray and neutron scattering are methods of structural characterization on the nanometer scale. Both give information statistically averaged over a macroscopic volume without disturbing the sample structure. In SAXS the contrast is determined by the electron density, while in case of SANS the contrast is given by the neutron scattering length density difference between the different components of the material. Often one of the components can be regarded as “object” embedded in the homogeneous matrix of the second component. Dry silica gels consist of a network of solid silica containing pores of different sizes and forms, and the basic element of the solid network is the so-called primary unit, formed during the polycondensation [24]. The SANS and SAXS patterns of a given material can in general be different, due to the different contrasts between the constituent phases, which depend on the type of radiation. In our case, the system is regarded as being quasi two-phase, due to the low amount of ionic liquid dispersed in the silica matrix. Therefore, the two methods see essentially the same structure, apart from the difference in the absolute intensities.

The scattering intensity curves for xerogels and sonogels are shown in Figs. 1 and 2. The SAXS and SANS curves have a similar look. The q -range of the SAXS instrument was broader, therefore the increase of scattering at $q < 0.02 \text{ \AA}^{-1}$ can be seen only in the SAXS data. In general, for dry xerogels this part is described by a power law decay of the scattering curves, the power exponent being -4 for smooth surfaces of the large aggregates [25]. In the present case, only the IL-free samples

Table 1. Synthesis parameters

Xerogel samples	Sonogel samples	Molar ratio IL/Si	IL [mol]	TMOS [mol]	MTMS [mol]
0X	0S	0	0	0.13	0.0162
1X	1S	0.007	0.0011	0.13	0.0162
2X	2S	0.018	0.0026	0.13	0.0162
3X	3S	0.034	0.005	0.13	0.0162
4X	4S	0.053	0.0078	0.13	0.0162
5X	5S	0.07	0.0104	0.13	0.0162

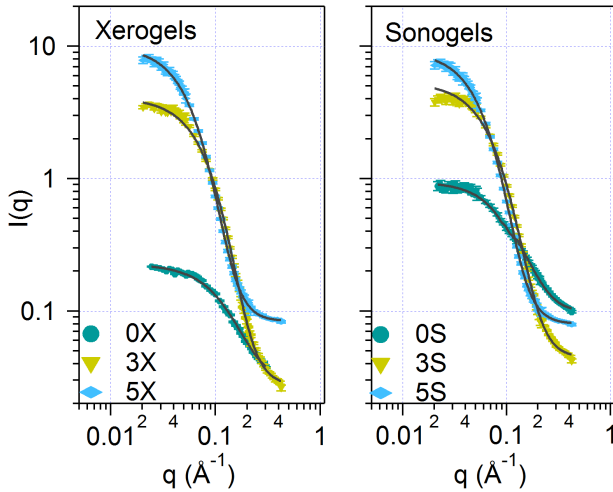


Figure 1. SANS curves for xerogels and sonogels (the solid lines are fits by Eq. 1 without the power law term)

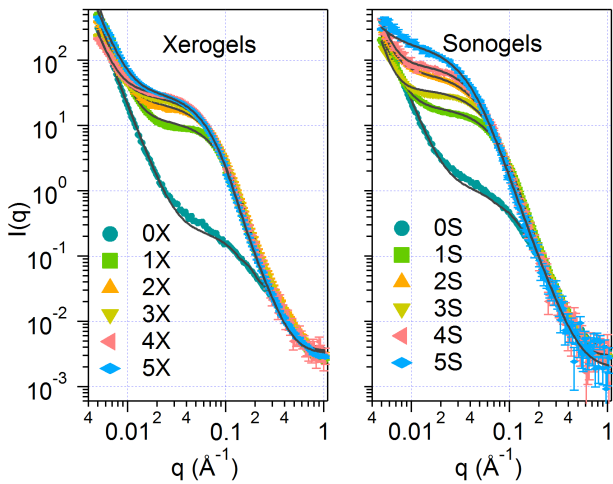


Figure 2. SAXS curves for xerogels and sonogels (the solid lines are fits by Eq. 1)

show a power-law behaviour over a sufficiently large range, while for the other samples it is shifted to smaller q , which prevented the accurate determination of the slope.

For revealing the inner structure of the gel, the medium and high q -ranges are interesting, as they contain information about the size and the size distribution of the constituent primary particles, and the character of their surfaces. The broad plateau in the q -interval 0.01 – 0.05 \AA^{-1} corresponds to the size of the primary particles, which form in the initial phase of the condensation reaction. Various theoretical models can be used to describe the behaviour of small-angle scattering from structures consisting of nanometer sized particles. The simplest models are the assemblies of mono- or polydisperse particles of spherical or other shapes, with or without interactions [25,26]. Here we use model of polydisperse spherical particles for describing the SANS spectra, and for the SAXS spectra a power law function is added for taking into account the structural organization of the agglomerated particles on the secondary level. A

flat background term is added to account for incoherent scattering and other material and instrument related contributions:

$$I(q) = \frac{K_1}{q^p} + K_2 \int V(r)^2 P(q, r)^2 D(r_0, r) dr + bg \quad (1)$$

Here, K_1 , K_2 are scale factors related to the number density and contrast of the particles, $P(q, r)$ is the form factor of a sphere, $D(r)$ is the size distribution, taken as Schulz-Zimm type, and bg is a constant background term. The model curves are displayed with the experimental data points in Figs. 1 and 2. The fitting is reasonably accurate, despite of some systematic deviations between the data and the model curves. Several other models have also been tested, which gave similar agreement with the data, but contained more free parameters. We consider, that the presented model describes the structure of the gels with a precision that allows us to use the fitted parameter values to derive conclusions on the structure and trends observed within these series of samples.

Figure 3 shows the dependence of the mean particle size on the amount of IL and the type of synthesis. The results show that the size of the primary particles grows by increasing the amount of IL. The sizes do not differ much upon applying ultrasound. The numerical values, and the trends obtained in the SANS and SAXS data agree in general. An important information, obtained from the SAXS data, is that the change of the primary particle size is rather sharp: the samples with the lowest amount of added ionic liquid already exhibit a strong increase of size, and thereafter, in the studied region of ionic liquid concentrations, this increase continues gradually.

The influence of IL on the primary particle size can

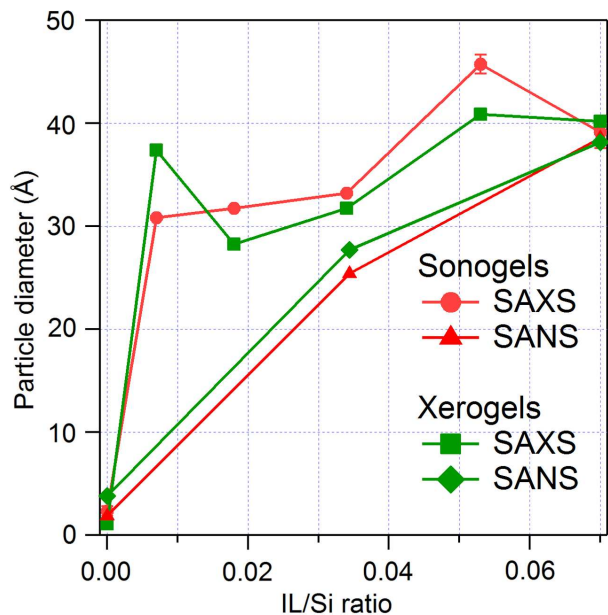


Figure 3. Mean particle sizes as measured by SANS and SAXS

be attributed to the apparent slowing down of the polycondensation reactions in the presence of IL co-solvent, leading to the formation of larger particles. In details, during condensation of the silica oligomers, they adsorb to the polar groups of the IL aggregates, similarly to the condensation of silica in the presence of long alkyl chain cationic surfactants [27]. The self-association of the IL molecules, induced by their hydrophobic aromatic and alkyl groups, brings about a cooperative character of the condensation of the silica, resulting in larger silica aggregates, i.e. primary particles in the sol-gel terminology [28].

The main conclusion of this study is therefore the strong influence of addition even of a small amount of ionic liquid on the kinetics of the sol-gel process. Comparing the primary particle sizes for the xerogels and sonogels, the latter show somewhat larger size. Though this difference is only 10%, it is in agreement with the observations of a recent comparative study of zirconia xero- and sonogels [26].

IV. Conclusions

Xerogels containing short chain ionic liquid were prepared by ultrasonication and characterized by small-angle scattering techniques. The ionic liquid used as co-solvent plays both catalytic and pore templating role. The growth of the primary particles in the initial stage of the sol-gel process is promoted by the presence of the ionic liquid. The polar and self-associated ionic liquid molecules act as condensation centres during the polycondensation process. The ultrasound treatment had only a minor effect on the dry gel structure, resulting in an increase of the particle sizes by less than 10%. The present data provide further information about the influence of using ionic liquid co-solvent and ultrasonic activation on the structure and properties of the prepared xerogels.

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