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The Effect of the Co-Solvent on the Aerogel Formation Directly in Supercritical CO₂ Medium

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A series of flexible hydrophobic siloxane aerogels were obtained by the hydrothiolation reaction in supercritical CO₂ medium in the presence of a co-solvent. The effect of the co-solvent nature on the aerogel morphology and physico-mechanical properties were studied. n-Pentane, a propane/n-butane mixture, CH_2CI_2 , dimethyl ether (DME) and 1,1,2-trichloro-1,2,2-trifluoro-ethane were used as the co-solvents. The morphology of aerogel particles was studied by SEM. In the case of n-pentane, propane/n-butane mixture, CH_2CI_2 , or DME as the co-solvents, aerogels with a density of 0.18–0.21 g/

1. Introduction

Aerogels are porous materials with unique tunable properties such as low density, high specific surface area, high porosity and low thermal conductivity that make them promising materials for insulation, catalysis, sensor, as absorbents, and in other applications.^[1-6] Since their discovery until now, a lot of methods for the preparation of aerogels of various nature have been developed. One of the tasks of current interest is the development of new modern approaches and methods for aerogel synthesis that can significantly reduce the cost of production. The latter is one of the major stumbling blocks on the way to the widespread use of aerogels.

The traditional and most popular method for preparing aerogels involves a number of long stages where a gel is obtained followed by supercritical drying.^[7-9] Instead of the "classical" methods for producing aerogels, new more efficient and less energy-consuming methods have appeared. In general, these methods are similar and have such stages as preparation of a sol, a gel, and aging. The main difference lies in the drying stage. These methods currently became more popular because they allow fairly easy process scaling.

At the moment, five main alternative methods for producing aerogels of different nature are described in the literature. cm³ and an average particle size of 0.15-5.35 μm were obtained. Depending on the morphology, the mechanical properties of aerogels change in the range of 0.2–0.75 MPa (Young's modulus), 38–68% (compressibility) and 0.11–0.42 MPa (stress rupture). In the case of 1,1,2-trichloro-1,2,2-trifluoro-ethane as the co-solvent, the aerogel with an inhomogeneous structure was obtained. All the aerogels studied have a large water contact angle in the range of 142°-151°.

These are the FD ("Freeze-Drying"),^[10-13] OSSD ("Organic Solvent Sublimation Drying"),^[14] VD ("Vacuum-Drying"),^[15,16] APD ("Ambient Pressure Drying")^[17-26] and DSGSCF ("Direct Sol-Gel process in SuperCritical Fluid")^[27-30] methods. Each of them has its advantages and drawbacks. However, regardless of the method, the need for drying makes it a multi-step process and, consequently, increases its cost.

In our previous work it was shown that the use of hydrothiolation directly in supercritical carbon dioxide $(scCO_2)$ medium for polymer aerogel preparation seems an interesting and promising approach. It is a radical process that allows one to reduce the preparation time to 1–2 hours, which is the shortest time among all the methods described.^[30] Furthermore, it was shown that to obtain high quality aerogels by this method, it is necessary to use a small amount of a co-solvent, n-pentane in the study referred to.

Previously, mixtures of scCO₂ with various organic compounds such as acetone,^[31] ethanol,^[31] dimethyl ether,^[31,32] chlorodifluoromethane,^[33] and others were successfully used as the medium for the solubilization of polymers. The effect of increasing the solubility of compounds in scCO₂ is well known^[34-36] and finds application in the catalysis of oxidation reactions,^[37,38] nanocomposite formation,^[39] impregnation,^[40-42] chromatography^[43,44] and extraction.^[45-50]

In this article we focused on a study of the effect of a cosolvent on the process of aerogel preparation directly in $scCO_2$ medium by radical hydrothiolation. The properties of the aerogels obtained are also discussed. A number of most common co-solvents such as n-pentane, a propane/n-butane mixture, dichloromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and dimethyl ether that are well soluble in $scCO_2$ were used in the study. A copolymer with γ -mercaptopropylsilsesquioxane and trimethylmethoxy chains and a linear methylvinylsiloxane oligomer were used as the starting materials (Figure 1). The

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Figure 1. The thiol- (left) and vinyl-containing (right) precursors.

selection of these precursors is based on our previous results.^[30] It was shown that aerogels with the best properties were obtained from these precursors.

2. Results and Discussions

In our previous work we reported a fast method for producing of high quality polysiloxane aerogels directly in scCO₂ medium.^[30] The method involves creating a cross-linked network by hydrothiolation between vinyl and thiol multifunc-



Scheme 1. Synthesis of aerogels by hydrothiolation.



Figure 2. Photo of an aerogel obtained without a co-solvent.

tional precursors in $scCO_2$ according to Scheme 1. After the reaction is completed, CO_2 is decompressed and the aerogel is removed from the reactor.

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An important detail of this method is that a small amount of a co-solvent has to be used. The latter ensures that a homogeneous aerogel sample is obtained. If only supercritical CO_2 is used as the medium for the preparation of an aerogel sample without any co-solvents, aerogels with a high density (ca. 0.3 g/cm³ or higher) and a heterogeneous texture are formed (Figure 2).

A series of organic solvents such as n-pentane, a propane/ n-butane mixture, dichloromethane, 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113 brand) and dimethyl ether were selected as the co-solvents in this study.

n-Pentane was used as an efficient co-solvent in the previous study, so it was now chosen as a starting point.

A propane/n-butane mixture is a cheap commerciallyavailable gas product. Comparison of this mixture (b.p. (propane) = -42 °C, b.p. (n-butane) = -0.5 °C) with n-pentane (b.p. (n-pentane) = 36.1 °C) allows us to estimate the effect of the co-solvent's boiling point on the structure and properties of aerogels.

The utilization of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) as a co-solvent can be explained by its good solubility in supercritical CO_2 .

Dichloromethane (μ =1.5 D, b.p. 39.6 °C) was chosen as a co-solvent more polar than alkanes (μ =0 D).

Dimethyl ether (DME) (μ =1.3 D and b.p. -24 °C) is yet another polar co-solvent with low boiling point used in this study. In addition, DME is a green solvent.^[51-53] This distinguishes it from toxic halogenated co-solvents.

Aerogels were synthesized by the hydrothiolation "click"reaction between the corresponding thio- and vinylsilane derivatives by the method that we reported previously (Scheme 1).^[30] The procedure for the preparation of aerogels is simple and requires about 1 h. In all cases, 2 g of a co-solvent per a 20 mL reactor was used.

It was found that in all cases (Figure 3) except Freon-113 (Figure 4), homogeneous aerogels with similar density were obtained in the presence of various co-solvents.

As one can see from Table 1, varying the solvent nature leads to significant changes in the aerogel particle size and



Figure 3. Photo of aerogels obtained with various co-solvents: 1 - n-Pentane, 2 - Propane / n-butane, 3 - CH_2CI_2 , 4 - DME.



Figure 4. Photo of an aerogel obtained with Freon -113 as a co-solvent.

dispersity. Analysis of SEM micrographs gives us understanding of the processes that take place during the preparation of an aerogel. Figure 5 shows micrographs of aerogels 1–4 and Figure 6 shows micrographs of aerogel 5 divided into three parts (5.1, 5.2 and 5.3).

It can be seen from SEM micrographs that the particle size in all the aerogels is in the 0.15-8 μ m range, which is significantly larger than in the case of aerogels obtained by the classic sol-gel method. Probably, it can be due to the different mechanisms of network formation in these cases. In the case of the classic sol-gel method, an insoluble gel is formed with a high conversion of functional groups. In our case, only the initial components are well soluble in the scCO₂/co-solvent mixture. Further, as the molecular weight of the growing polymer increases, a colloid solution is formed. After that, the particles grow in a heterophase, which results in their larger size. This mechanism is similar to the dispersion polymerization mechanism.^[54,55] Figure 5 shows that the particles of aerogel 1 are smaller than those of aerogels 2 and 3. Probably this is related with the higher solubility of precursors in n-pentane than in the propane/n-butane mixture or dichloromethane. Aerogel 4 which was obtained with DME as a co-solvent has the lowest particle size. This fact is in good agreement with the mechanism of dispersion polymerization that occurs in the course of formation of a three-dimension network during hydrothiolation in supercritical CO₂ medium.

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A three-dimensional network can be formed in *two* possible ways. According to the *first* way in a "good" solvent, a large amount of particles is formed during the polymerization process before a colloid solution is formed. According to the *second* way, the polymer particles formed during the polymerization process segregate from the solution on an earlier stage to form a colloid solution.

In the first way, the number of particles is larger, however their poor stabilization after a dispersion solution is formed results in agglomeration. Accordingly, particles with a greater size dispersion are formed. In the *second* way, particles with lower dispersion are formed and the formation of a colloid at an earlier stage gives fewer particles with larger size. Thus, stabilization of particles in the colloid solution should result in the same particle size. It seems that both ways take place in the samples that we studied.

As one can see from the SEM micrographs for aerogels 1 and 2, the particle size dispersion is not high. However, on transition to more polar dichloromethane, the particle dispersion increases dramatically. This can be evidence of better stabilization of polymer particle growth by alkanes in the colloid solutions at comparable solubilities of the sol. On transition to DME, the co-solvent nature changes drastically. On the one hand, the solubility of the growing polymer becomes better, and on the other hand, the stabilization of particles in non-polar supercritical CO₂ occurs. As a result, an aerogel with the lowest particle size and relatively small dispersion is obtained.

Aerogel **5** was obtained with Freon - 113 as the co-solvent. This aerogel has a gradient structure that can be separated into three parts (Figure 4). A study of this sample by the SEM method shows that the particle sizes in the parts differ

Table 1. Properties of aerogels obtained with various co-solvents.											
No.	Co-solvent	Bulk density (g cm ⁻³)	Shrinkage (%)	Specific surface area (BET) (m^2g^{-1})	Contact angle (°)	Average particle size ^[c] (µm)	Degree of particle dispersity ^(d)				
1	n-Pentane	0.180	20	5.0 ^[a]	145 ± 5	3.5	0.75				
2	Propane / n- butane	0.180	20	1.0 ^[a]	$142\!\pm\!5$	5.0	0.67				
3	CH_2CI_2	0.176	17	3.7 ^[a]	151 ± 5	5.35	0.34				
4	DME	0.210	40	11.0 ^[b]	151 ± 2	0.15	0.50				
5.1	Freon-113	0.130	-	4.0 ^[a]	-	8.0	-				
5.2	Freon-113	0.190	-	4.0 ^[a]	-	4.5	-				
5.3	Freon-113	0.268	-	3.4 ^[a]	-	1.5	-				

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Figure 5. SEM images of aerogels 1–4 at different magnifications.

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Figure 6. SEM images of aerogel 5 divided into three parts at different magnifications.

significantly. On transition from 5.1 to 5.3, the particle size decreases (Figure 6).

The inhomogeneity of aerogel **5** can be due to the high density of Freon-113 co-solvent (1.56 g cm^{-3}). As a result, the polymer particles persist longer in the solution in the lower part of the reactor and they are stabilized by Freon-113 after separation. At the same time, there is almost no co-solvent in the upper reactor part and hence large particles are formed.

Thus, the size and dispersity of aerogel particles can be controlled. To do this, it is sufficient to change the nature of the co-solvent. It should be noted that the particle size and dispersity considerably affect the mechanical properties of an aerogel.

Mechanical properties. As one can see from Table 2, the particle size determines the mechanical properties of the aerogels obtained.

Young's modulus for samples 2 and 3 is 0.2 MPa. As the particle size decreases from 5.0 μ m to 3.0 μ m, Young's modulus increases to 0.35 MPa. Young's modulus of aerogel 4 that was produced with DME as the co-solvent amounts to 0.75 MPa, which is the largest value among all the samples studied. The increase in Young's modulus with a decrease in the particle size can be explained by tighter particle packing.

As one can see from Table 2, this value is 0.1, 0.16 and 9.0 MPa for aerogels 5.1, 5.2 and 5.3, correspondingly. The increase in Young's modulus by two orders of magnitude is probably due to the higher density and homogeneity of particles in the lower part of the aerogel (Figure 6). Conse-

quently, the particle size is inversely proportional to Young's modulus.

Figure 7 shows a series of 10 consecutive deformation cycles for aerogels 1–4. As one can see from the Figure, the hysteresis loop square that represents mechanical losses decreases from cycle to cycle for all the samples, and as a result, it reaches a limit and then remains nearly unchanged.

The collapse of a network node that does not have enough time to recover after the first cycle ensures a residual strain. Since deformations in the cycle is small (10 %), the increment of residual deformation decreases continuously in subsequent cycles until the residual strain no longer changes beginning from some cycle. After the completion of a cycle, the sample returns to the same initial height as in the previous cycle. Thereafter, the period of stationary deformation begins when the hysteresis loop area has a definite value and does not change from cycle to cycle, and residual deformation no longer increases. The settling of a steady state is favored by the presence of a network of chemical bonds. As a rule, a spatially cross-linked polymer that has no structural defects retains a minor permanent residual deformation in the stationary mode.

From the curves presented in Figure 7, yet another important characteristic of the deformation properties of polymers can be obtained. The area bounded by the stress and related deformation curve equals the work spent to deform the polymer. The larger the area of the hysteresis loop is, the more work is irreversibly spent on heating the sample.

Table 2 contains values of work expended on polymer deformation during the first and last cycles that were

Table 2. Mechanical properties of aerogels obtained with various co-solvents.												
No.	Co-solvent	Average particle size (µm)	Young's modulus (MPa)	A1 cycle (J) ^[a]	A10 cycle $(J)^{[b]}$	A1/A10 ^[c]	$\sigma_{\rm p}~(\text{MPa})^{\rm [d]}$	ε _p (%) ^[e]				
1	n-Pentane	3.5	0.35	0.006	0.003	2	0.21	50				
2	Propane / n-butane	5.0	0.20	0.002	0.0008	2.5	0.11	46				
3	CH ₂ Cl ₂	5.35	0.20	0.0008	0.0004	2	0.19	68				
4	DME	0.15	0.75	0.015	0.0091	1.65	0.42	38				
5.1	Freon-113	8.0	0.10	-	-	-	-	-				
5.2	Freon-113	4.5	0.16	-	-	-	-	-				
5.3	Freon-113	1.5	9.0	-	-	-	-	-				
[a] Α1· [d] σ _p -	work of the first load cy Breaking stress. [e] ε _n -Br	cle. [b] A10-work of the t eaking strain.	enth load cycle. [c] The ratio	o of A1 to A1	0.							

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Figure 7. Changes of the hysteresis loop upon repeated strains for aerogels 1-4 (red-loop of the first deformation cycle).

calculated using the software of the LLOYD Instruments testing machine. The losses in the first cycle depend largely on the sample, namely on the type of the co-solvent that was used for aerogel preparation. As one can see from Table 2, this parameter affects the amount of work both in the first and tenth cycles.

The smallest work in the first cycle among the samples studied corresponds to the polymer obtained in CH_2CI_2 because of the smallest stress that is developed during deformation. Probably, this parameter, like Young's modulus, is related with the packing density that is apparently the most friable in the case of maximum dispersion of the polymer particle size (Figure 5). One can see from Table 2 that with a decrease in the dispersity, the work expended for the first deformation increases. This relation is valid if samples with particle sizes of the same order are compared. In aerogel **4** with a particle size that is by an order smaller, which was obtained with DME as the co-solvent, the strain reaches the highest value and the work in the first cycle is the largest.

The A1/A10 ratio reflects the degree of imperfection in the network structure due to the number of chemical nodes in the network as well as the different sample morphology associated with packaging defects. For aerogels 1, 2 and 3 that were obtained with n-pentane, the propane/n-butane mixture and

 CH_2CI_2 as the co-solvents, the work in the first cycle is 2, 2.5 and 2 times, correspondingly, larger than the work in the tenth cycle. For the aerogel obtained with DME as the co-solvent, this ratio is 1.65. This suggests that the aerogel structure with the smallest particle size has the smallest defects.

The defects also affect the degree of shrinkage of samples after CO₂ decompression. In fact, for aerogels **1,2** and **3** this value is approximately the same, about 20% (Table 1). Aerogel **4** has a shrinkage of 40%. That is perhaps related with a fact that with the smallest packaging defectness, the system tends to the maximum compression. Defects lead to the formation of voids between the polymeric particles, which is expressed by smaller shrinkage of the sample and, at the same time, in its rougher texture (Figure 4). It is possible that the shrinkage value also increases if the particle size is even smaller (due to their better solubility and stabilization in the colloid solution).

Figure 8 and Table 2 show the results of uniaxial compression of samples.

As one can see from Table 2, aerogel 4 obtained with DME as the co-solvent has the greatest σ_p (0.42 MPa) while its ε_p (38%) is the smallest among all the samples. The highest deformation before the breaking develops in the sample is obtained with CH₂Cl₂ as the co-solvent (68%). This aerogel has the smallest shrinkage, the smallest dispersity and the highest





Figure 8. Strain-stress curve for uniaxial compression of samples.

particle size (Table 1). Aerogel **2** which was prepared with the propane/n-butane mixture as the co-solvent has the smallest strength because of a loose morphology.

Thus, the value of work, E, σ_p and ϵ_p can be affected by a number of factors depending on the aerogel preparation method: shrinkage, density, average particle size and dispersity. The average particle size is the most important parameter, which is primarily determined by the choice of the co-solvent type. As a result, aerogels with desired physico-mechanical characteristics can be obtained by adjusting the synthesis conditions.

Figure 9 displays the N_2 adsorption-desorption isotherms of sample 4 at 77 K. According to the IUPAC classification,^[56] the N_2 adsorption isotherms belong to Type II profile that in conjunction with a low specific surface area (which is close to



Figure 9. Representative $N_{\rm 2}\mbox{-}sorption$ isotherm (obtained at 77 K) of aerogel 4.

that calculated from geometry) indicates that the aerogel contains no micro- and mesopores and its globules have a smooth surface. This aerogel can be attributed to macroporous materials.

All the aerogels studied have a large water contact angle in the range of $142^{\circ}-151^{\circ}$ (Table 1). Probably, these high values are due to the texture of the samples. The difference between the water contact angles is probably due to the difficulty of obtaining a flat surface of the samples being studied.

3. Conclusions

Hence, comparison of the co-solvent nature with the properties of aerogels obtained directly in supercritical CO₂ medium allows us to estimate the efficiency of using such co-solvents in this process and to make an assumption about the mechanism of three-dimensional network formation under thiol-ene reaction conditions. It was shown that a change in the co-solvent nature significantly affects the mechanical properties of aerogels. These properties can be attributed to the average particle size of the samples. This parameter ranges within 0.15– 8 μ m for aerogels obtained with different co-solvents. The best mechanical properties were found for aerogel 4 that was obtained with DME as the co-solvent. Also, using environment friendly DME is preferably, as compared with other co-solvents. At the same time, aerogel 4 has the smallest particle size. All the aerogels studied have considerable hydrophobicity.

Supporting Information Summary

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Conflict of Interest

The authors declare no conflict of interest.

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A series of flexible hydrophobic siloxane aerogels were obtained by the hydrothiolation reaction in supercritical CO₂ medium in the presence of a co-solvent. The effect of the cosolvent nature on the aerogel morphology and physico-mechanical properties were studied. It was shown that a change in the co-solvent nature significantly affects the mechanical properties of aerogels. These properties can be attributed to the average particle size of the samples. Dr. M. N. Temnikov*, Dr. Y. N. Kononevich, A. Y. Popov, Dr. V. G. Vasil'ev, Prof. A. M. Muzafarov

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The Effect of the Co-Solvent on the Aerogel Formation Directly in Supercritical CO₂ Medium