

Full Length Article

Facile synthesis of fluorinated resorcinol-formaldehyde aerogels



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ABSTRACT

In this paper, we have tried to use some unconventional solvents for the preparation of resorcinol-formaldehyde (RF) aerogels. The nature of the gelation solvent is found to greatly influence the properties of RF aerogels, e.g., to affect the specific surface area. Fluorination of aerogels' matrix is shown to take place upon synthesis of lyogels in the hexafluoroacetone medium. Fluorination proceeds by the mechanism of electrophilic substitution reaction in a resorcinol cycle with a formation of a C—C bond. Unprecedented acceleration of the reaction of formaldehyde with resorcinol to form the RF-resin matrix under the action of hexafluoroacetone is observed. The results presented provide the first example of organic aerogels fluorination by electrophilic substitution reaction.

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1. Introduction

Aerogels are porous solid materials possessing unique properties, including very low bulk density, low thermal conductivity, large specific surface area and high porosity [1]. Aerogels can be used as thermal and acoustic insulators [2], sorbents [3–6], supports for heterogeneous catalysts [7], optical materials [2,8], etc.

Currently, several types of aerogels are known [1], including:

- inorganic aerogels (typically, oxide aerogels, SiO₂-, TiO₂-, Al₂O₃-, ZrO₂-based aerogels, among others);
- carbon aerogels (pyrolyzed organic polymers);
- organic aerogels (aerogels based on agar-agar, cellulose, polyisocyanates, polyacrylates, and on formaldehyde-containing resins (phenol-formaldehyde, melamine-formaldehyde, resorcinol-formaldehyde, etc.) [1,9,10].

Organic aerogels are promising materials for various industrial applications due to their excellent thermal and mechanical properties. Resorcinol-formaldehyde (RF) aerogels, first reported by Pekala [11], are the most studied materials among organic aerogels [11–13]. Resorcinol (1,3-dihydroxybenzene, C₆H₄(OH)₂) is used instead of phenol for the synthesis of phenol-formaldehyde

resins analogs because it is about 10–15 times more active in electrophilic substitution reactions than phenol, and therefore it can react with formaldehyde at lower temperatures, forming products of substitution and condensation. RF aerogels possess similar properties to inorganic aerogels, including high porosity, specific surface area and pore volume, as well as low thermal conductivity (for instance, RF aerogels are better thermal insulators than commercial fiber glass) [1]. RF aerogels are stiffer and stronger and have a lower thermal conductivity (~0.012 W/mK) than silica aerogels (0.016 W/mK) [14–16]. Resorcinol-formaldehyde organic aerogels can be used for the separation of gases or liquids, thermal insulation and sorption of contaminants [1]. Moreover, RF aerogels are widely used as precursors for the preparation of nanoparticulate carbon or carbon aerogels, which are regarded to be promising energy storage materials [1].

Resorcinol-formaldehyde aerogels are synthesized by base- or acid-catalyzed polycondensation of resorcinol with formaldehyde [11–13,17–19]. Reaction mixture pH, concentration and ratio of monomers (resorcinol/formaldehyde), the catalyst type and resorcinol/catalyst ratio are the key factors determining the final characteristics (density, specific surface area, particle size, pore size distribution) of RF aerogels.

Resorcinol is a very reactive substance readily participating in aromatic electrophilic substitution reactions. It easily undergoes nitration, sulfation, acylation, etc. The alkylated resorcinol moiety is a part of the RF matrix, so such aerogels are potentially prone to electrophilic attack. Nevertheless, we could not find any

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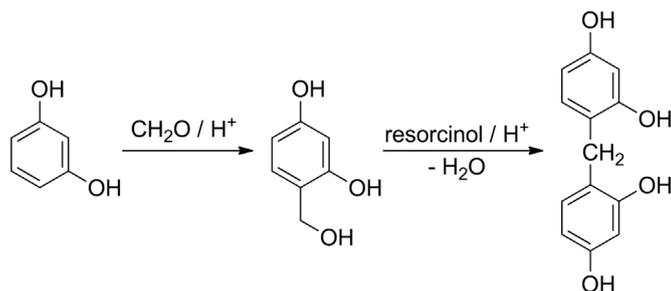
information concerning the modification of RF aerogels matrix by electrophilic substitution reactions.

In our current work, we have found that RF aerogels readily react with hexafluoroacetone (HFA), which leads to an introduction of fluorinated HFA-based moieties into the resorcinol cycle by the mechanism of the Friedel-Crafts reaction. To the best of our knowledge, this is the first example of fluorinated organic aerogels synthesis.

2. Results and discussion

Formation of resorcinol-formaldehyde resins is generally a two-stage process. At the first stage, resorcinol reacts with formaldehyde, affording hydroxymethylated products. At the second stage, substituted resorcinols condense with each other to form clusters of nanometer size, which are crosslinked by methylene ($-\text{CH}_2-$) groups to form a gel (Scheme 1). Both stages need acid or base catalysis, acid-catalyzed reaction being faster [1].

We decided to perform the RF aerogels synthesis in hexafluoroacetone sesquihydrate- $(\text{CF}_3)_2\text{CO}\cdot 1.5\text{H}_2\text{O}$ -a liquid derivative of gaseous hexafluoroacetone. HFA hydrates are acidic ($\text{p}K_a = 6.58$) [20] and dissolve both resorcinol and formaldehyde. Some reactions of HFA with aromatic compounds have been discussed in literature [21], so we expected HFA to react with resorcinol as well. For comparison purposes we have also synthesized RF aerogels by a standard procedure, using acetonitrile CH_3CN as a solvent and HCl as a gelation catalyst [17].



Scheme 1. xxx.

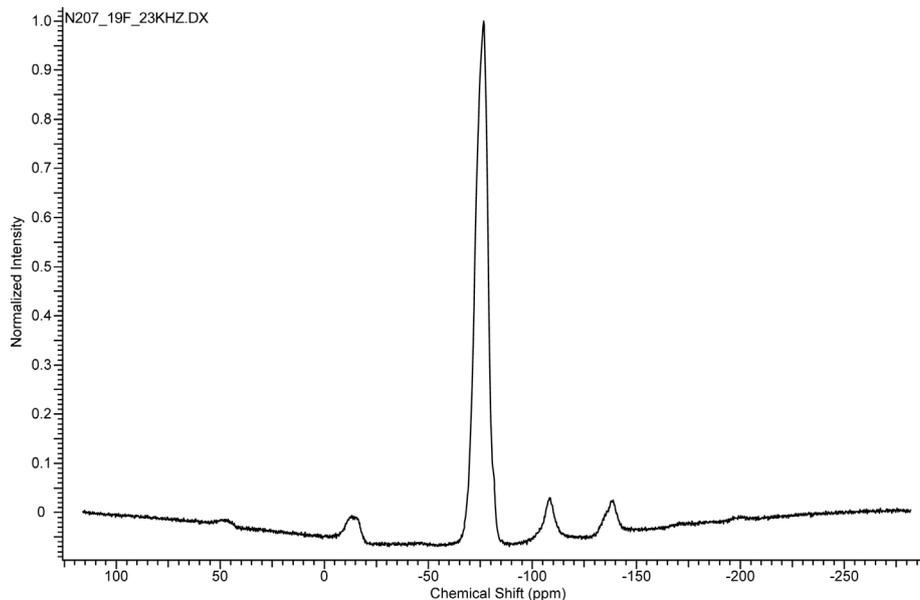


Fig. 1. ^{19}F NMR spectrum of the D-HFA aerogel sample aged at 50°C and dried supercritically in CO_2 .

In both cases, RF aerogels were prepared with a resorcinol: formaldehyde molar ratio = 1:1.5 at two different solvent loadings in precursor lyogels. In the first one, 8 mL of the solvent and 1.1 g (0.01 mol) of resorcinol were used. The samples from the corresponding series were denoted hereafter by the symbol **D** (dense). In the second procedure, 38 mL of the solvent and 1.1 g (0.01 mol) of resorcinol were used. These samples are denoted hereafter by the symbol **L** (light). Hereafter the following notation is used – L-samples gelated in HFA are denoted as L-HFA; D-samples gelated in acetonitrile are denoted as D-AcN, etc.

We have found that HFA $\cdot 1.5\text{H}_2\text{O}$, when used as a solvent for RF aerogels preparation, dramatically changed their texture properties and chemical composition compared to aerogels prepared by a conventional method in acetonitrile.

2.1. Fluorination of RF aerogels by HFA

We have found that when RF lyogels prepared in hexafluoroacetone are aged at 50°C , the introduction of fluorine-containing moieties occurs, leading to a modification of the primary aerogel matrix. The fluorine content in the D-HFA sample aged at 50°C reaches 7.4 wt.%. ^{19}F NMR spectrum of this sample shows the presence of one major fluorine-containing product after $50^\circ\text{C}/7$ days aging (Fig. 1), while the sample aged at 20°C is fluorine free.

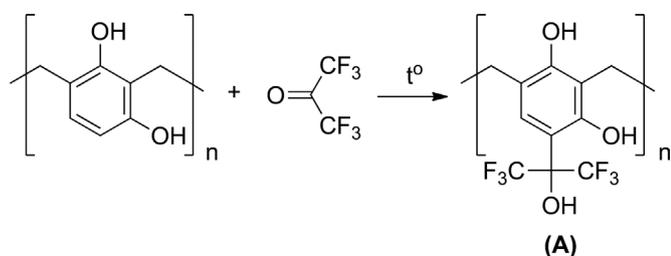
The chemical shift value (-75 ppm) indicates the presence of CF_3 -groups in the major fluorinated sample.

We propose the following interpretation of these results. HFA irreversibly reacts with resorcinol moiety in lyogel to form fluorinated benzyl alcohol **A** as a product of a conventional Friedel-Crafts substitution reaction (Scheme 2).

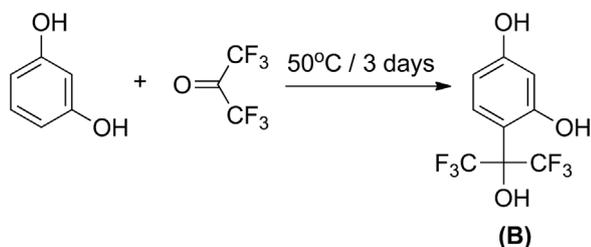
To confirm this supposition we performed a reaction of resorcinol with HFA $\cdot 1.5\text{H}_2\text{O}$ in the absence of formaldehyde and found that a substitution product **B** was formed in a good yield (73%) (Scheme 3).

The position of the $-(\text{CF}_3)_2\text{COH}$ substituent (ortho- and para- to phenolic resorcinol groups) is consistent with the general rules of electrophilic aromatic substitution and with the results of HFA reaction with other aromatic compounds [21].

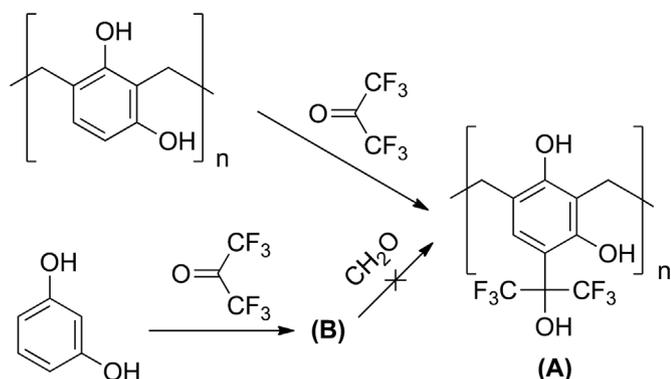
To determine the sequence of reactions leading to aerogel fluorination by HFA (Scheme 4a or b), we performed the reaction of product **B** with formaldehyde under the gelation conditions and



Scheme 2. xxx.



Scheme 3. xxx.



Scheme 4. xxx.

found that an appropriate gel was not formed. The opposite situation was observed when a preformed L-AcN lyogel sample (Table 1, entry 6) was heated in the presence of HFA at 50 °C. Under these conditions the formation of a fluorinated aerogel **A** (Table 1, entry 8) occurred (Scheme 4). Thus we can conclude that the

reaction of HFA with preformed RF aerogels or its oligomeric precursors takes place, resulting in a formation of a fluorinated benzylic alcohol.

To the best of our knowledge, this is the first example of fluorine modification of RF aerogels by electrophilic aromatic substitution reaction. This finding gives a path to a modification of RF aerogels matrix by other conventional organic reactions.

2.2. Influence of HFA on texture properties of RF aerogels

We have shown earlier that solvent used for gelation and supercritical drying plays a very important role in the synthesis of inorganic and hybrid organic-inorganic aerogels [22–26], while the influence of a gelation solvent on the properties and structure of resorcinol-formaldehyde aerogels is still virtually not studied.

Aerogels prepared in HFA·1.5H₂O are sponge-like soft yellow materials, while samples prepared in AcN are stiff brown-black monoliths (D-series) or brown semitransparent and flexible monoliths (L-series) (Fig. 2).

D-series aerogels (both HFA and AcN) show rather small shrinkage upon supercritical drying (approximately 7%). The

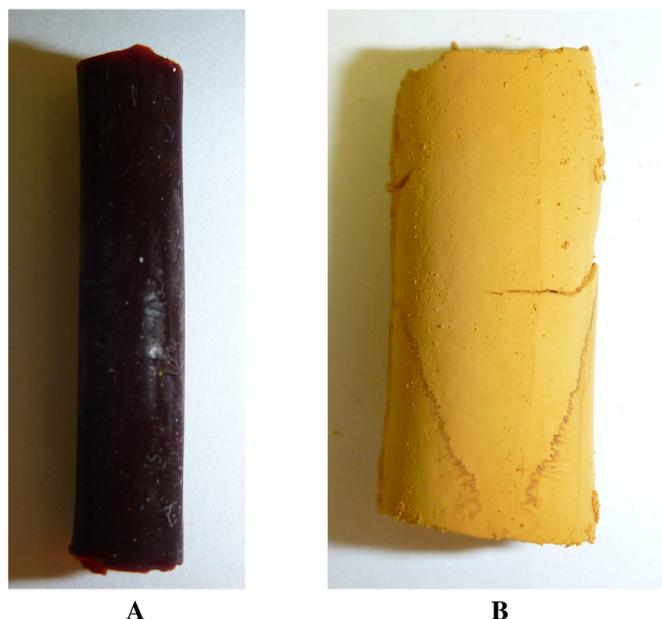


Fig. 2. D-AcN (A) and D-HFA (B) aerogels aged at 50 °C and dried supercritically in CO₂.

Table 1
Preparation conditions and textural characteristics of RF aerogels.

Entry	Sample	Aging conditions	Bulk density, g/cm ³	S _{BET} , m ² /g	Results of elemental analysis, wt.%
1	D-HFA	50 °C, 7 days	0.21	20	Fluorine 7.42, Carbon 54.64
2	D-HFA	20 °C, 7 days	0.17	10	no Fluorine
3	L-HFA	50 °C, 7 days	0.07	20	Fluorine 2.37, Carbon 63.04
4	D-AcN	50 °C, 7 days	0.6	380	
5	D-AcN	20 °C, 7 days	0.68	300	
6	L-AcN	20 °C, 7 days	0.15	520	
7	L-AcN	50 °C, 7 days	0.14	420	
8 ^a	6 + HFA	50 °C, 7 days	–	370	Fluorine 3.62, Carbon 54.34

^a L-AcN sample aged at 20 °C (entry 6) treated by HFA (see Section 4.3).

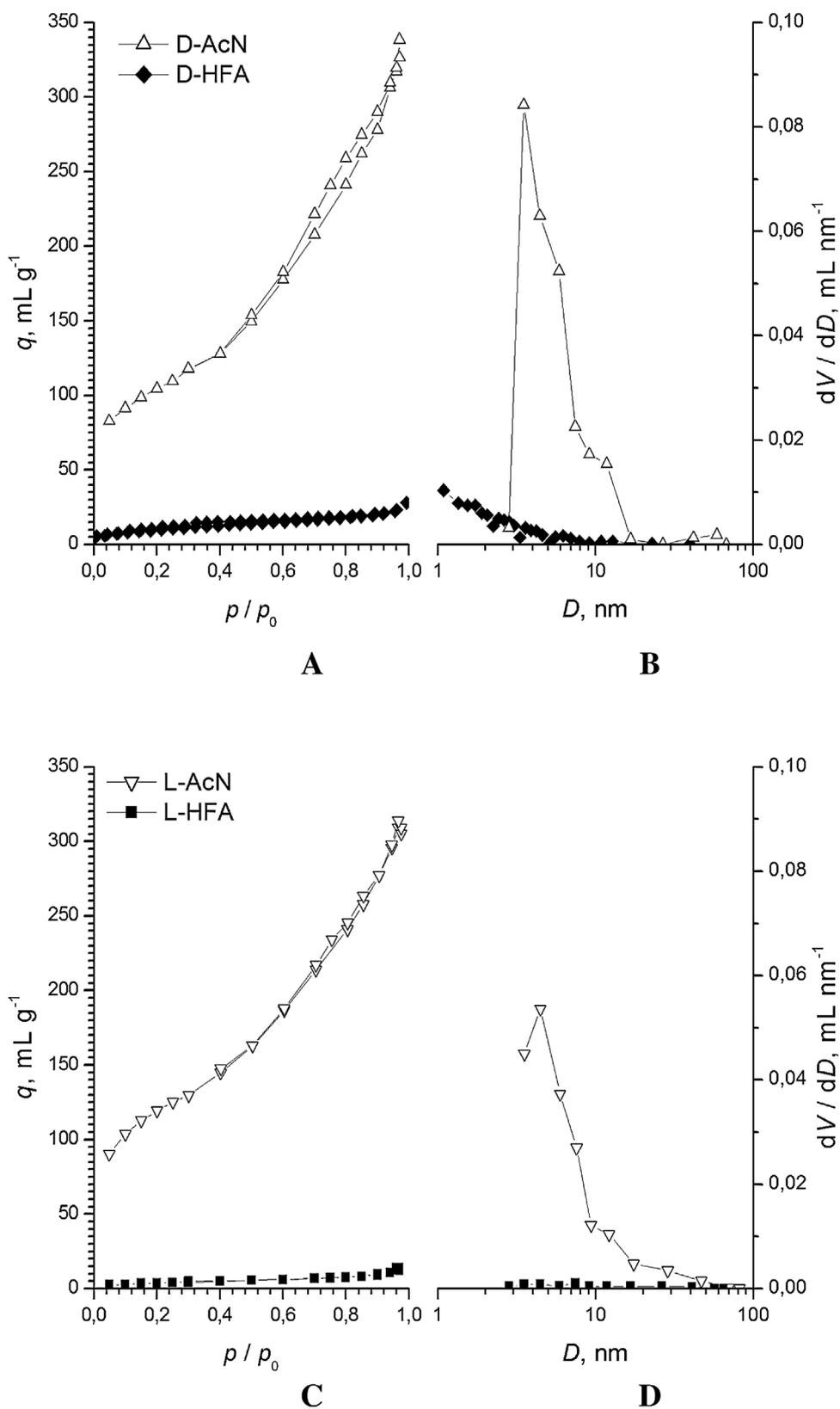


Fig. 3. Full adsorption-desorption isotherms (A) and pore size distributions (B) for D-AcN and D-HFA aerogels aged at 50 °C and dried supercritically in CO₂. Full adsorption-desorption isotherms (C) and pore size distribution (D) for L-AcN and L-HFA samples aged at 50 °C.

shrinkage of L-series aerogels is higher – 16% for HFA and 34% for AcN.

The major characteristics of the prepared samples of resorcinol-formaldehyde aerogels are summarized in the Table 1.

The data presented in the Table 1 reveal the following trends:

– The increase in the solvent content in lyogels (both D and L series) expectedly leads to a decrease of aerogels' density.

– The properties of aerogels prepared in HFA differ significantly from the AcN aerogels – they have an order of magnitude smaller specific surface area.

– HFA samples aged by heating at 50 °C (entry 1, 3) contain fluorine; the sample aged at 20 °C (entry 2) is fluorine free.

Elemental analysis data confirm the presence of fluorine in the samples heated with HFA. The degree of fluorination is not high – the 6F to C ratio (6F means two CF₃ groups in the fluorinated moiety) even in the most fluorine-rich sample (D-HFA, 50 °C, entry 1) is ≈1:70. This means that approximately one tenth of aromatic cycles bears the (CF₃)COH substituent. Two factors can be responsible for the low degree of fluorination:

a. a rather low reaction temperature (50 °C). It is highly anticipated that stronger heating would lead to a stronger fluorination, provided that it will not cause the destruction of the aerogel skeleton; (aromatic alkylation reactions are reversible).

b. *ortho*- and *para*- positions, which are favourable for electrophilic substitution, are sterically hindered by OH and –CH₂- groups, thus preventing the introduction of bulky CF₃–C(OH)–CF₃ substituents.

Fig. 3 shows full adsorption-desorption isotherms (A) and pore size distributions (B) for D-AcN and D-HFA samples aged at 50 °C, and full adsorption-desorption isotherms (C) and pore size distributions (D) for L-AcN and L-HFA samples aged at 50 °C.

The adsorption-desorption isotherms (Fig. 3) reveal a strong influence of a gelation solvent on aerogels' texture characteristics. The HFA-series samples have extremely low specific adsorption (*q*) values and show a practically total absence of micro- and

mesopores, while AcN samples exhibit the presence of relatively small pores (<20 nm). Full adsorption-desorption isotherms of AcN samples are of the IV type, with narrow hysteresis loops close to the H1 type, which is characteristic for cylindrical both ends open pores.

Nitrogen adsorption data correlates well with scanning electron microscopy data presented in Fig. 4.

SEM images indicate that the D-AcN sample aged at 50 °C consists of nanometer-sized particles interconnected to form a highly porous structure, while the D-HFA sample aged at 50 °C consists of relatively large (approximately 0.5 μm), nearly spherical particles, forming loose aggregates. The surface of the spheres seems to be non-porous, while it is covered by less than 100 nm size bumps.

Both AcN and HFA series aerogels are hydrophilic and absorb water drops quickly, the presence of several hydroxy-groups in each aromatic ring being the reason for high hydrophilicity.

Preparation of RF aerogels in HFA has several interesting features. The first one is that the texture characteristics of fluorinated RF aerogels can be dramatically changed by a very simple procedure. Upon gelation in HFA we obtained samples with *S*_{sp} ≈ 10–20 m²/g, while gelation in AcN followed by HFA treatment, leads to a specific surface area increase by an order of magnitude up to 370 m²/g.

The second intriguing feature is an unprecedented acceleration of the reaction of formaldehyde with resorcinol, leading to a formation of RF resins – the process took seconds in HFA vs hours in AcN as a solvent. Such enhancement of the substitution and condensation rates cannot be explained by the fact that HFA hydrates have acidic properties – the p*K*_a of HFA·1.5H₂O (6.58) is two orders of magnitude weaker than even p*K*_a of acetic acid. In our opinion, the possible reason is in the specific ability of HFA and formaldehyde to form addition products with hydroxyl-containing compounds. For phenols, the reaction mechanism can look as follows (Scheme 5).

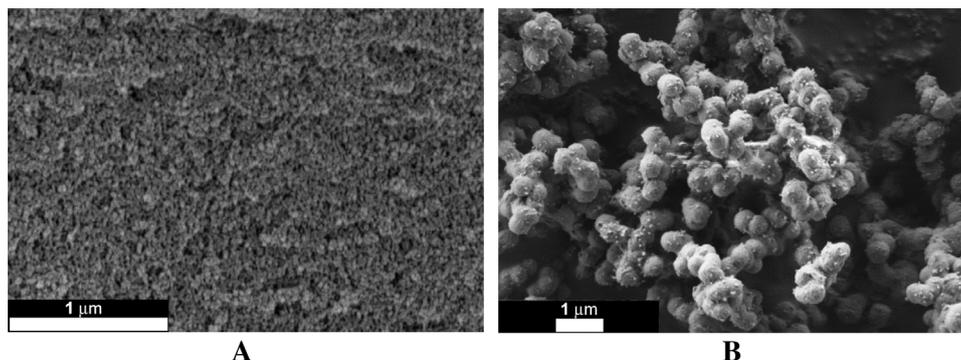
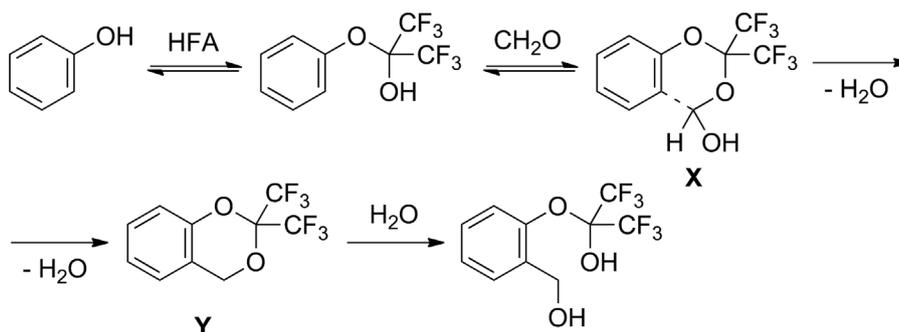
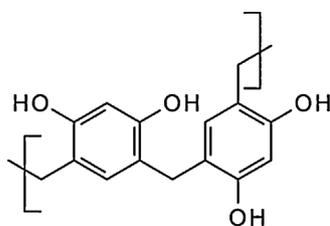


Fig. 4. Microstructure of D-AcN (A) and D-HFA (B) aerogel samples aged at 50 °C and dried supercritically in CO₂.



Scheme 5. xxx.



Scheme 6. xxx.

In the intermediate product **X**, the reacting CH_2 -group is located close to an ortho-position of the aromatic ring, due to a formation of a six-membered transition state increasing the rate of electrophilic substitution reaction. The intermediate product **Y** is the HFA ketal that is readily hydrolyzed by water in acidic media. To confirm the necessity of HFA coordination with the OH-group we performed the reaction of resorcinol dimethylether (1,3-dimethoxybenzene) with formaldehyde in HFA·1.5H₂O and found that only a tarry product was formed upon heating at 50 °C during a seven-day period, while no gel was formed.

Such a dramatic enhancement of the aromatic substitution reaction rate is quite unusual; it could not be predicted *a priori* and deserves special investigation.

The most intriguing feature of RF aerogels prepared in HFA is their unusual microstructure (see Fig. 4B). We suppose that the spherical shape of aerogel particles is connected with a liquid–liquid phase separation in the system prior to gelation. This may occur, for example, due to the very fast reaction of resorcinol with formaldehyde, resulting in low molecular weight resol-type compounds (Scheme 6).

These resol-type oligomers can merge into insoluble spherical droplets due to H-bonding [27]. Upon completion of the cross-polycondensation, the solid spherical particles are formed.

The effect observed could also be due to the fact that the reaction of substituted benzyl alcohol with resorcinol to form the methylene bridge (see Scheme 1) is a typical Friedel-Crafts reversible alkylation. This means that the depolymerization-repolymerization process can actually take place upon the soaking of aerogels in highly polar solvents, e.g. HFA, leading to the formation of larger aerogel particles, a process which is similar to a well-known Ostwald ripening.

3. Conclusions

The nature of the gelation solvent significantly influences the resorcinol-formaldehyde aerogels characteristics, such as appearance, texture properties, etc.

The most pronounced effect is seen when HFA·1.5H₂O is used as a gelation solvent: the specific surface area drops an order of magnitude compared to gels prepared in AcN.

It is shown that fluorination occurs in HFA·1.5H₂O when the lyogel is formed. The fluorination of RF aerogels prepared in AcN can also be achieved by their heating in HFA. Fluorination occurs by the mechanism of an electrophilic substitution reaction in a resorcinol cycle.

4. Experimental

4.1. Materials

Resorcinol (98%, Acros), formaldehyde (37 wt.% solution in water, Acros), isopropanol (99.5%+, Acros), acetonitrile (99+%, Acros),

hexafluoroacetone sesquihydrate ($\text{CF}_3\text{COCF}_3 \cdot 1.5\text{H}_2\text{O}$) (98%, Acros) were used as received.

4.2. Preparation of gels

4.2.1. Preparation of sols

4.2.1.1. Acetonitrile as a solvent. 1.1 g (0.01 mol) of resorcinol was dissolved in 8 or 38 mL of acetonitrile in a plastic beaker, then 0.025 mL of HCl (38%) and 1.1 mL (0.015 mol) of formaldehyde solution were added and the mixture was stirred for 10–20 min.

4.2.1.2. Hexafluoroacetone sesquihydrate acted as a solvent. A solution of 1.1 g (0.01 mol) of resorcinol in 8 or 38 mL of hexafluoroacetone sesquihydrate kept in a plastic beaker was cooled to 3–5 °C. Then, 1.1 mL (0.015 mol) of formaldehyde was added and the mixture was vigorously stirred for 2–5 s.

4.2.2. Gelation of sols

Sols (3–5 mL) were poured into polypropylene syringes of 3 or 5 mL volume. When hexafluoroacetone sesquihydrate was used as a solvent the gels were formed within 10–15 s. In the case of acetonitrile the gels were formed after 5–6 h at 20 °C. Upon formation the gels were left to age as described in Table 1. The resultant aged gels were soaked in isopropanol for 24 h in order to exchange the pore liquid for the solvent. This procedure was repeated five times. Then the gels that were formed were placed into an apparatus for supercritical drying in CO₂.

4.3. Treatment of lyogels with HFA

The lyogel of L-AcN (Table 1, entry 6) was additionally treated with hexafluoroacetone sesquihydrate (10 mL) for seven days at 50 °C. Next, the sample was washed by isopropanol by the procedure described above and supercritically dried in CO₂.

4.4. Supercritical drying

Supercritical drying in CO₂ was performed in an apparatus consisting of a high-pressure CO₂ pump (Supercritical 24, SSI, USA), a steel 50 mL reactor (Thar Instruments Inc., USA), and a back pressure regulator BPR (Waters, USA). The sample was washed with liquid CO₂ for 2 h at 20 °C at a pressure of 15 MPa, then the reactor temperature was raised to 50 °C and the sample was additionally washed with supercritical CO₂ (15 MPa) for 2–2.5 h. The pressure in a heated autoclave was then evenly decreased to atmospheric pressure, the autoclave was cooled to room temperature and opened.

4.5. Preparation of an adduct of resorcinol with hexafluoroacetone sesquihydrate (B)

A solution of 1.1 g (0.01 mol) of resorcinol in 8 mL of hexafluoroacetone sesquihydrate was placed in a Teflon coated steel autoclave and heated for three days at 50 °C. The product obtained was evacuated (25 °C and 6.7 kPa) to remove volatile products. After a solvent removal the product obtained was purified by dissolution-precipitation from an acetone/water mixture to give the waxy substance **B**.

¹H NMR (200 MHz, Me₂SO-d₆): δ_H 6.24 (dd, 1H, 3J_H–H = 8.8 Hz, 4J_H–H = 2.45 Hz, arom. H), 6.3 (d, 1H, 4J_H–H = 2.45 Hz, arom. H), 7.07 (d, 1H, 3J_H–H = 8.32 Hz, arom. H). ¹³C NMR (200 MHz, Me₂SO-d₆): δ_C 78.7 (m, 2J_C–F = 30.3 Hz, C–(CF₃)₂), 104.0 (arom. C), 108.0 (arom. C), 123.5 (q, 1J_C–F = 288.3 Hz, CF₃), 129.7 (arom. C), 157.6 (arom. COH), 160.0 (arom. COH). ¹⁹F NMR (200 MHz, Me₂SO-d₆): δ_F –74 (s, CF₃).

EIMS, 70 Ev, m/z (rel. int.): 276 (35) [M]⁺, 207 (60) [M-CF₃]⁺, 137 (100) [M+H-2CF₃]⁺.

4.6. Characterization of aerogels

The specific surface area and porosity of aerogels were determined by low-temperature nitrogen adsorption measurements with a Katakon ATX-06 analyzer. The specific surface area values were determined using a 5-point Brunauer, Emmett and Teller (BET) method at the relative pressure range of $P/P_0 = 0.05–0.25$; the correlation coefficients of the corresponding linear regressions in the coordinates of the BET equation were not less than 0.9975. Pore volume distributions were determined according to the Barrett, Joyner and Halenda (BJH) method, by the analysis of a desorption branch of an adsorption-desorption isotherm (28 points). Prior to measurements, samples were flushed with a dry helium flow for 30 min at 100 °C.

The bulk densities of the samples were calculated by their mass to volume ratio. Aerogels' shrinkage was estimated by the change of their geometric volume compared to the geometric volume of wet gels.

The microstructure of the samples was studied using a Carl Zeiss NVision 40 scanning electron microscope (SEM) at 1 kV acceleration voltage without any coating of their surface with a conductive layer.

Solid state ¹⁹F NMR experiments were performed on a Bruker Avance III 400 spectrometer with CFCl₃ as external reference. Larmor precession frequency was 376.5 MHz ¹⁹F NMR spectra were recorded using 9 μs pulse length, accumulating 64 repetitions for each spectrum.

High-resolution ¹H, ¹³C and ¹⁹F spectra of an adduct of resorcinol with hexafluoroacetone sesquihydrate (product **B**) were obtained on a Bruker DPX-200 spectrometer with TMS and CFCl₃ as external references respectively.

Mass spectrum of the product **B** was obtained on a FINNIGAN MAT INCOS 50 mass-spectrometer at 70 eV EI.

Elemental analysis was performed on a Carlo Erba 1106 CHN analyzer (C, H) and fluorine was determined spectrophotometrically (Carry 100 spectrophotometer).

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References

- [1] M.A. Aegerter, N. Leventis, M.M. Koebel (Eds.), *Aerogels Handbook*, Springer, N. Y., Dordrecht, Heidelberg, London, 2011 (932 p.).
- [2] N. Hüsing, U. Schubert, *Aerogels – airy materials: chemistry, structure, and properties*, *Angew. Chem. Int. Ed.* 37 (1998) 22–45.
- [3] A.V. Rao, N.D. Hegde, H. Hirashima, Absorption and desorption of organic liquids in elastic superhydrophobic silica aerogels, *J. Colloid Interface Sci.* 305 (2007) 124–132.
- [4] L.W. Hrubesh, P.R. Coronado, J.H. Satcher Jr., Solvent removal from water with hydrophobic aerogels, *J. Non Cryst. Solids* 285 (2001) 328–332.
- [5] J.G. Reynolds, P.R. Coronado, L.W. Hrubesh, Hydrophobic aerogels for oil-spill clean up – synthesis and characterization, *J. Non Cryst. Solids* 292 (2001) 127–137.
- [6] K. Wörmeyer, M. Alnaief, I. Smirnova, Amino functionalised silica-aerogels for CO₂-adsorption at low partial pressure, *Adsorption* 18 (2012) 163–171.
- [7] W.-C. Li, M. Comotti, A.-H. Lu, F. Schüth, Nanocast mesoporous MgAl₂O₄ spinel monoliths as support for highly active gold CO oxidation catalyst, *Chem. Commun.* 16 (2006) 1772–1774.
- [8] C.A. Morris, M.L. Anderson, R.M. Stroud, C.I. Merzbacher, D.R. Rolison, Silica sol as a nanoglue: flexible synthesis of composite aerogels, *Science* 284 (1999) 622–624.
- [9] A.C. Pierre, G.M. Pajonk, *Chemistry of aerogels and their applications*, *Chem. Rev.* 102 (2002) 4243–4265.
- [10] R. Fu, B. Zheng, J. Liu, M.S. Dresselhaus, G. Dresselhaus, J.H. Satcher Jr., T.F. Baumann, The fabrication and characterization of carbon aerogels by gelation and supercritical drying in isopropanol, *Adv. Funct. Mater.* 13 (2003) 558–562.
- [11] R. Pekala, Organic aerogels from the polycondensation of resorcinol with formaldehyde, *J. Mater. Sci.* 24 (1989) 3221–3227.
- [12] S.A. Al-Muhtaseb, J.A. Ritter, Preparation and properties of resorcinol-formaldehyde organic and carbon gels, *Adv. Mater.* 15 (2003) 101–114.
- [13] M. Schwan, L. Ratke, Flexibilisation of resorcinol-formaldehyde aerogels, *J. Mater. Sci. A* 1 (2013) 13462–13468.
- [14] L. Hrubesh, R. Pekala, Thermal properties of organic and inorganic aerogels, *J. Mater. Res.* 9 (1994) 731–738.
- [15] X. Lu, M. Arduini-Schuster, J. Kuhn, O. Nilsson, J. Fricke, R. Pekala, Thermal conductivity of monolithic organic aerogels, *Science* 255 (1992) 971–972.
- [16] B. Yoldas, M. Annen, J. Bostaph, Chemical engineering of aerogel morphology formed under nonsupercritical conditions for thermal insulation, *Chem. Mater.* 12 (2000) 2475–2484.
- [17] K. Chen, Z. Bao, A. Du, X. Zhu, J. Shen, G. Wu, Z. Zhang, B. Zhou, One-pot synthesis, characterization and properties of acid-catalyzed resorcinol/formaldehyde cross-linked silica aerogels and their conversion to hierarchical porous carbon monoliths, *J. Sol Gel Sci. Technol.* 62 (2012) 294–303.
- [18] S. Berthon, O. Barbieri, F. Ehrburger-Dolle, E. Geissler, P. Achard, F. Bley, A.-M. Hecht, F. Livet, G.M. Pajonk, N. Pinto, A. Rigacci, C. Rochas, DLS and SAXS investigations of organic gels and aerogels, *J. Non Cryst. Solids* 285 (2001) 154–161.
- [19] R. Petricevic, M. Glora, J. Fricke, Planar fibre reinforced carbon aerogels for application in PEM fuel cells, *Carbon* 39 (2001) 857–867.
- [20] W.J. Middleton, R.V. Lindsey, Hydrogen bonding in fluoro alcohols, *J. Am. Chem. Soc.* 86 (1964) 4948–4952.
- [21] B.S. Farah, E.E. Gilbert, J.P. Sabilia, V. Perhalo ketones, The reaction of perhaloacetones with aromatic hydrocarbons, *J. Org. Chem.* 30 (1965) 998–1001.
- [22] S.A. Lermontov, A.N. Malkova, L.L. Yurkova, E.A. Straumal, N.N. Gubanova, A. Ye Baranchikov, V.K. Ivanov, Diethyl and methyl-tert-butyl ethers as new solvents for aerogels preparation, *Mater. Lett.* 116 (2014) 116–119.
- [23] S. Lermontov, A. Malkova, L. Yurkova, E. Straumal, N. Gubanova, A. Baranchikov, M. Smirnov, V. Tarasov, V. Buznik, V. Ivanov, Hexafluoroisopropyl alcohol as a new solvent for aerogels preparation, *J. Supercrit. Fluids* 89 (2014) 28–32.
- [24] S.A. Lermontov, A.N. Malkova, N.A. Sipyagina, A.E. Baranchikov, D.I. Petukhov, V.K. Ivanov, Hexafluoroacetone: a new solvent for manufacturing SiO₂-based aerogels, *Russ. J. Inorg. Chem.* 60 (2015) 541–545.
- [25] S.A. Lermontov, N.A. Sipyagina, A.N. Malkova, A.E. Baranchikov, Kh.E. Erov, D.I. Petukhov, V.K. Ivanov, Methyltrimethoxysilane-based elastic aerogels: effects of the supercritical medium on structure-sensitive properties, *Russ. J. Inorg. Chem.* 60 (2015) 488–492.
- [26] S.A. Lermontov, A.N. Malkova, N.A. Sipyagina, A.E. Baranchikov, D.I. Petukhov, V.K. Ivanov, Hydrophobicity/hydrophilicity control for SiO₂ based aerogels: the role of a supercritical solvent, *Russ. J. Inorg. Chem.* 60 (2015) 1169–1172.
- [27] E. Christ, C. Blanc, A. Al Ouahabi, D. Maurin, R. Le Parc, J.-L. Bantignies, J.-M. Guenet, D. Collin, P.J. Mésini, Origin of invariant gel melting temperatures in the c-T phase diagram of an organogel, *Langmuir* 32 (2016) 4975–4982.