Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2018, **28**, 102–104

Mendeleev Communications

Methyl trifluoropyruvate – a new solvent for the production of fluorinated organic resorcinol–formaldehyde aerogels

Sergey A. Lermontov,*[a] Alena N. Malkova,[a] Nataliya A. Sipyagina,[a] Alexey V. Semakov,[a] Alexander E. Baranchikov[b] and Vladimir K. Ivanov[b,c]

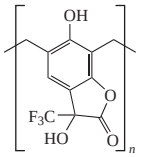
[a] *Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 524 9508; e-mail: lermontov52@yandex.ru*

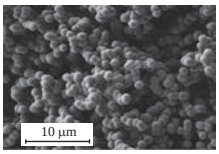
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

[c] *National Research Tomsk State University, 634050 Tomsk, Russian Federation*

DOI: 10.1016/j.mencom.2018.01.035

Resorcinol–formaldehyde aerogels obtained in methyl trifluoropyruvate (MTFP) possess a fluorinated matrix due to the mechanism of electrophilic substitution in the resorcinol moiety with the formation of C–C bond. The use of MTFP as a solvent also substantially accelerates the formaldehyde–resorcinol interaction.





Aerogels (AGs) are mesoporous solids with a set of unique properties such as low density and thermal conductivity, large specific surface area and high porosity.[1] Aerogels are typically used as thermal- and sound-insulating materials,[2] sorbents,[3–6] heterogeneous catalysts,[7] optical materials,[2,8] *etc*. At present, known types of AGs include inorganic (usually based on oxides – SiO_2, TiO_2, Al_2O_3, ZrO_2), carbon (pyrolized organic polymers) and organic ones based on agar, cellulose, polyisocyanates, polyacrylates or formaldehyde-containing resins [phenol–formaldehyde, melamine–formaldehyde, resorcinol–formaldehyde (RF)].[1,9,10]

Organic AGs are promising due to their extremely low thermal conductivity and high mechanical strength. RF AGs are the most studied among the organic ones.[11–13] The properties of RF AGs are similar to those of inorganic ones, including high porosity, large specific surface area, large pore volume and very low thermal conductivity, (*e.g*., they are better insulators than commercial glass fiber).[1] As a rule, RF AGs are more rigid, have greater strength and lower thermal conductivity (~0.012 W m^{-1} K^{-1}) than silica-based aerogels (0.016 W m^{-1} K^{-1}).[14–16] RF AGs can be used for effective separation of gases or liquids, and as precursors for the synthesis of carbon nanoparticles or carbon AGs (promising materials for energy storage).[1]

RF AGs are produced by the polycondensation of resorcinol with formaldehyde under alkali or acid catalysis conditions.[11–13,17–19] The pH of the reaction medium, the concentration and ratio of monomers (resorcinol/formaldehyde), the type of catalyst and the resorcinol/catalyst ratio are the key factors that determine the final characteristics of the products (*i.e*. their density, specific surface area, particle size and pore size distribution).

Resorcinol is used instead of phenol in the resin synthesis, since the rate of its interaction with formaldehyde is higher than that of phenol by a factor of 10–15, and it can react with formaldehyde at lower temperatures. Recently, we showed that the structural analogue of methyl trifluoropyruvate [MTFP, $CF_3C(O)C(O)OMe$], namely, hexafluoroacetone (HFA), enters into an electrophilic substitution reaction with a resorcinol-based AG to form a new C–C bond.[20] This allowed us to anticipate that the same interaction with MTFP can occur. The purpose of this work was to study the reaction of RF AG formation when MTFP is used as a solvent at the stage of gelation and aging, and to evaluate the possibility of introducing fluorine-containing fragments from MTFP to an RF AG.[†]

The recognized mechanism of RF resin formation includes formation of clusters linked by methylene groups (Scheme 1). When acids and bases are applied as catalysts, the rate of acid-catalyzed reaction is higher (several hours).[1]

When MTFP was used as a solvent, the reaction of resorcinol with formaldehyde was found to be very fast: it took 10–15 s in

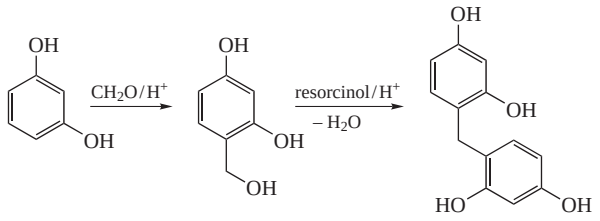
[†] Resorcinol (98%), formaldehyde (37 wt% aqueous solution), isopropanol (99.5%+), HCl (38 wt% aqueous solution), acetonitrile (99%+) purchased from Acros and methyl 3,3,3-trifluoropyruvate (97%, Aldrich) were used as received.

Synthesis of sols using acetonitrile as a solvent. A standard resorcinol : formaldehyde 1 : 1.5 molar ratio was applied in all cases.[19,20] First, resorcinol (1.1 g, 10 mmol) was dissolved in acetonitrile (8 ml) in a plastic beaker. Then, HCl (38%, 0.025 ml) and formaldehyde solution (1.1 ml, 15 mmol) were added, and the mixture was stirred for 10–20 min.

Synthesis of sols using methyl trifluoropyruvate as a solvent. A solution of resorcinol (0.28 g, 2.5 mmol) in deionised water (0.5 ml) was cooled in a plastic beaker to 3–5 °C. Then, formaldehyde (0.28 ml, 3.8 mmol) precooled to 3–5 °C was added, and the mixture was stirred for 15 s. After that, MTFP (1.5 ml, 15 mmol) precooled to 3–5 °C was added, and the mixture was stirred for 1–2 s.

Gelation of sols. Sols (3–5 ml) were poured into polypropylene syringes of 3 or 5 ml volume. When MTFP was used as a solvent, gels RF MTFP were formed within 3–5 s. In the case of acetonitrile, gels RF MeCN 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 were placed into an apparatus for supercritical drying in CO_2.

Treatment of lyogels with MTFP. The lyogel of RF MeCN (Table 1, entry 1) was additionally treated with MTFP (10 ml) for seven days at 50 °C. The sample was then washed with isopropanol, using the procedure described above, and supercritically dried in CO_2.



Scheme 1

the absence of a catalyst and afforded a pink gel. Elastic, yellow-brown monolithic materials were formed upon aging at 50 °C for 7 days and subsequent supercritical drying in CO_2. According to elemental analysis data, the fluorine content in the RF AG sample was 0.57 wt%. The solid-state ^{19}F NMR spectrum contained a signal with a chemical shift of –81 ppm, which implied the presence of CF_3 groups in the sample. In the IR spectra, such RF AG samples exhibited a band at 1820 cm^{-1}, which is characteristic of the C=O group. Thus, the reaction of resorcinol with formaldehyde in MTFP leads to the formation of fluorine-containing acylated AGs.

According to the reported data, the solvent used for gelation and supercritical drying plays an important role in the synthesis of inorganic and hybrid organic–inorganic AGs, and substantially determines the texture characteristics of the materials to be synthesized.[21–25] In particular, we found that when resorcinol reacted with formaldehyde in hexafluoroacetone, the properties of the AGs differed from those of formed in acetonitrile in the presence of an acid catalyst.

Supercritical drying in CO_2 was performed in an apparatus consisting of a high-pressure CO_2 pump (Supercritical 24, SSI), a 50 ml steel reactor (Thar Instruments Inc.) and a back pressure regulator BPR (Waters). The sample was washed with liquid CO_2 for 2 h at 20 °C and 15 MPa, then the reactor temperature was raised to 50 °C and the sample was additionally washed with supercritical CO_2 (15 MPa) for 2–2.5 h. The pressure in a heated autoclave was then evenly decreased to atmospheric one; the autoclave was cooled to room temperature and then opened.

Preparation of an adduct of resorcinol with MTFP. A solution of resorcinol (0.55 g, 0.005 mol) in acetonitrile (3 ml) was cooled to 3–5 °C in a plastic beaker and then added to MTFP (1.0 ml, 10 mol) precooled to 3–5 °C. The mixture was placed in a Teflon coated steel autoclave and heated for seven days at 50 °C. The product obtained was evacuated (25 °C, 6.7 kPa) to remove the volatiles. The oily residue was purified by reversed-phase preparative HPLC using a Gilson chromatograph, column Diasorb 130C16, Gilson 118 UV/Vis Detector, at 240 nm. The acetonitrile–water mixture (from 10 : 90 to 100 : 0 v/v) was used as an eluent.

The specific surface area and porosity of aerogels were determined by low-temperature nitrogen adsorption measurements using a Katakon ATX-06 analyzer. The specific surface area values were determined using a 5-point Brunauer, Emmett and Teller (BET) method at the nitrogen partial pressure (P/P_0) range of 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 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 in their geometric volume compared to that 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 ^{19}F NMR experiments were performed on a Bruker Avance III 400 spectrometer, with $CFCl_3$ as an external reference. The Larmor precession frequency was 376.5 MHz. ^{19}F NMR spectra were recorded using 9 μs pulse length, accumulating 64 repetitions for each spectrum. High-resolution ^1H, ^{13}C and ^{19}F NMR spectra of an adduct **B** of resorcinol with hexafluoroacetone sesquihydrate were recorded on a Bruker DPX-200 spectrometer (TMS and $CFCl_3$ as external standards, respectively) and its mass spectrum was obtained using a FINNIGAN MAT INCOS 50 mass-spectrometer at 70 eV EI.

Table 1 Texture characteristics and chemical composition of RF aerogels.[a]

Entry[b]	Sample	Density/ g cm^{-3}	S_{BET}/ m^2 g^{-1}	Elemental analysis data (wt%)		IR, ν/cm^{-1}	Solid state ^{19}F NMR, δ/ppm
				F	C		
1	RF MeCN	0.6	380±50				
2	RF MTFP	0.2	4±1	0.57	63.48	1816	–81
3	RF MeCN, treated with MTFP	0.6	400±40	3.89	59.99	1820	

[a] All the samples were aged at 50°C within 7 days after gelation. [b] To check the reproducibility each sample was synthesized in triplicate.

Figure 1 Appearance of the RF AGs synthesized in (*a*) acetonitrile and (*b*) MTFP.

To compare the characteristics of the RF AGs formed in various solvents, we synthesized AGs in MTFP, and under standard conditions (*i.e.* in acetonitrile with HCl as a gelation catalyst[17,20]). In fact, texture properties and the chemical compositions of AGs obtained in MTFP and in acetonitrile differed markedly. The former were elastic, sponge-like, yellow-orange materials, whereas the latter were rigid, brown-black monoliths (Figure 1, Table 1). The specific surface area and geometric density of AGs synthesized in MTFP were smaller by two orders of magnitude and by a factor of three, respectively, as compared with those of AGs synthesized in acetonitrile.

The data on nitrogen adsorption/desorption correlated with scanning electron microscopy (SEM) results (Figure 2). According to the SEM data, the RF AGs formed using acetonitrile consisted of nanoparticles 10–20 nm in size and contained pores up to 20 nm in diameter. The materials obtained in the presence of MTFP had a principally different structure: spheroidal, pore-free particles joined to form loose, chain-like aggregates, and the pore diameter reached several microns. AGs synthesized in acetonitrile or MTFP were hydrophilic, and they rapidly absorbed water without degradation. This high wetting ability is likely caused by the presence of several hydroxyl groups in each aromatic ring.

RF AGs obtained in MTFP demonstrated two interesting specific features. First, their texture characteristics could be significantly changed using a simple procedure. After gelation in MTFP, the aerogel samples had a specific surface area of ~4 m^2 g^{-1}, whereas gelation in MeCN, followed by processing in MTFP, increased this value by two orders of magnitude (up to 400 m^2 g^{-1}). The second feature is a very strong increase in the rate of formaldehyde–resorcinol interaction and RF resin formation: the process takes several seconds in MTFP *versus* several hours in acetonitrile. This can be caused by the specific ability of MTFP and formaldehyde to form the products of addition of a hydroxyl group (Scheme 2). The reacting CH_2 group in the intermediate product **X** is close to the *ortho*-position of the aromatic ring, which accelerates the electrophilic substitution

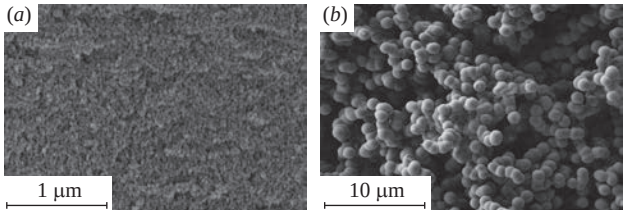
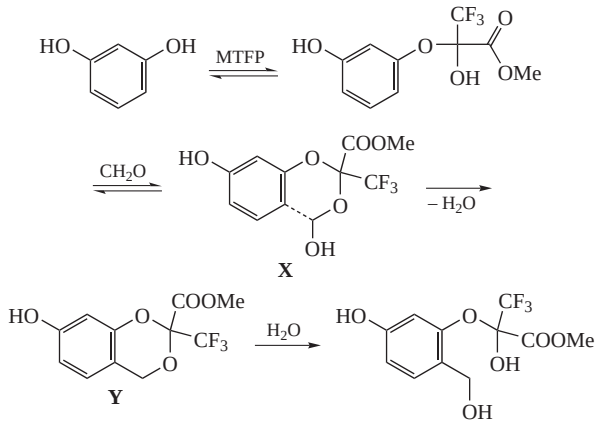


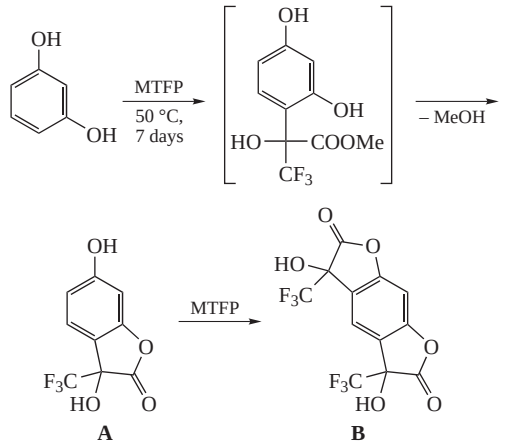
Figure 2 Microstructure of the RF AGs synthesized in (*a*) acetonitrile and (*b*) MTFP.

reaction. Intermediate product **Y** is the ketal of MTFP, which is easily hydrolyzed by water in an acid medium. This significant increase in the rate of aromatic substitution reaction is quite unusual, could not be predicted *a priori* and deserves a separate investigation.



Scheme 2

To understand the structure of the fluorinated AGs obtained, we performed the reaction of MTFP with resorcinol in the absence of formaldehyde, and found that a mixture of fluorine-containing products thus formed consisted of more than eight compounds. The ^{19}F NMR spectra of all products contained the signals of CF_3 groups (–0.5 to –4.5 ppm), and no signals of C(O)OMe groups were detected in ^{1}H NMR spectra. In the IR spectra, signals of C=O groups (1830 cm^{-1}) are observed for all products. According to the mass spectrometry data, the two main products had molecular masses 234 and 358, which allowed us to assume the structures **A** and **B** (Scheme 3). The proposed scheme can be used to explain both a significant number of the products formed (differences in the number of fluorinated fragments entering the resorcinol molecule, position isomerism, *cis-trans* isomerism), and the absence of an ester fragment in the products. Thus, our experimental results demonstrate that the RF AGs synthesized in MTFP contain a fluorinated benzofuranone fragment (Figure 3).



Scheme 3

In conclusion, the nature of the solvent used to synthesize RF resins substantially affects the characteristics of the RF AGs formed from them, *i.e.* their appearance, texture characteristics and chemical composition. In the synthesis using MTFP, the RF AG matrix undergoes electrophilic substitution with the formation of fluorine-containing fragments. The RF lyogels formed in acetonitrile can also be fluorinated by processing in MTFP. The proposed approach can be used to produce fluorinated AGs based on RF resins with a specific surface area up to 400 $m^2\ g^{-1}$.

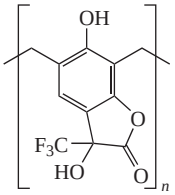


Figure 3 Fragment of the structure of the RF aerogel synthesized in the presence of MTFP.

This work was supported by the Russian Science Foundation (project no. 14-13-01150) (synthesis and investigation of texture characteristics of aerogels) and the program 'Fundamental Scientific Investigations for the Development of the Arctic Zone of the Russian Federation' (analysis of the mechanism of fluorine-modified aerogel formation).

References

1 *Aerogels Handbook*, eds. M. A. Aegerter, N. Leventis and M. M. Koebel, Springer, New York, 2011.
2 N. Hüsing and U. Schubert, *Angew. Chem. Int. Ed*., 1998, **37**, 22.
3 A. V. Rao, N. D. Hegde and H. Hirashima, *J. Colloid Interface Sci*., 2007, **305**, 124.
4 L. W. Hrubesh, P. R. Coronado and J. H. Satcher, Jr., *J. Non-Cryst. Solids*, 2001, **285**, 328.
5 J. G. Reynolds, P. R. Coronado and L. W. Hrubesh, *J. Non-Cryst. Solids*, 2001, **292**, 127.
6 K. Wörmeyer, M. Alnaief and I. Smirnova, *Adsorption*, 2012, **18**, 163.
7 W.-C. Li, M. Comotti, A.-H. Lu and F. Schüth, *Chem. Commun*., 2006, **16**, 1772.
8 C. A. Morris, M. L. Anderson, R. M. Stroud, C. I. Merzbacher and D. R. Rolison, *Science*, 1999, **284**, 622.
9 A. C. Pierre and G. M. Pajonk, *Chem. Rev*., 2002, **102**, 4243.
10 R. Fu, B. Zheng, J. Liu, M. S. Dresselhaus, G. Dresselhaus, J. H. Satcher, Jr. and T. F. Baumann, *Adv. Funct. Mater*., 2003, **13**, 558.
11 R. W. Pekala, *J. Mater. Sci*., 1989, **24**, 3221.
12 S. A. Al-Muhtaseb and J. A. Ritter, *Adv. Mater*., 2003, **15**, 101.
13 M. Schwan and L. Ratke, *J. Mater. Chem. A*, 2013, **1**, 13462.
14 L. W. Hrubesh and R. W. Pekala, *J. Mater. Res*., 1994, **9**, 731.
15 X. Lu, M. C. Arduini-Schuster, J. Kuhn, O. Nilsson, J. Fricke and R. W. Pekala, *Science*, 1992, **255**, 971.
16 B. E. Yoldas, M. J. Annen and J. Bostaph, *Chem. Mater*., 2000, **12**, 2475.
17 K. Chen, Z. Bao, A. Du, X. Zhu, J. Shen, G. Wu, Z. Zhang and B. Zhou, *J. Sol-Gel Sci. Technol*., 2012, **62**, 294.
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 and C. Rochas, *J. Non-Cryst. Solids*, 2001, **285**, 154.
19 R. Petričević, M. Glora and J. Fricke, *Carbon*, 2001, **39**, 857.
20 S. A. Lermontov, A. N. Malkova, N. A. Sipyagina, E. A. Straumal, A. E. Baranchikov, Kh. E. Yorov and V. K. Ivanov, *J. Fluorine Chem*., 2017, **193**, 1.
21 S. A. Lermontov, A. N. Malkova, L. L. Yurkova, E. A. Straumal, N. N. Gubanova, A. Ye. Baranchikov and V. K. Ivanov, *Mater. Lett*., 2014, **116**, 116.
22 S. Lermontov, A. Malkova, L. Yurkova, E. Straumal, N. Gubanova, A. Baranchikov, M. Smirnov, V. Tarasov, V. Buznik and V. Ivanov, *J. Supercrit. Fluids*, 2014, **89**, 28.
23 S. A. Lermontov, A. N. Malkova, N. A. Sipyagina, A. E. Baranchikov, D. I. Petukhov and V. K. Ivanov, *Russ. J. Inorg. Chem*., 2015, **60**, 541 (*Zh. Neorg. Khim*., 2015, **60**, 607).
24 S. A. Lermontov, N. A. Sipyagina, A. N. Malkova, A. E. Baranchikov, Kh. E. Erov, D. I. Petukhov and V. K. Ivanov, *Russ. J. Inorg. Chem*., 2015, **60**, 488 (*Zh. Neorg. Khim*., 2015, **60**, 549).
25 S. A. Lermontov, A. N. Malkova, N. A. Sipyagina, A. E. Baranchikov, D. I. Petukhov and V. K. Ivanov, *Russ. J. Inorg. Chem*., 2015, **60**, 1169 (*Zh. Neorg. Khim*., 2015, **60**, 1283).

Received: 5th May 2017; Com. 17/5242