Polymer 138 (2018) 255–266

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Simple and fast method for producing flexible superhydrophobic aerogels by direct formation of thiol-ene networks in $scCO_2$

Maxim N. Temnikov [a], [*], Yuriy N. Kononevich [a], [**], Ivan B. Meshkov [b], Mikhail I. Buzin [a], Viktor G. Vasil'ev [a], Galina G. Nikiforova [a], Aziz M. Muzafarov [a], [b], [***]

[a] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS), Moscow, 119991, Russian Federation
[b] N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences (ISPM RAS), Moscow, 117393, Russian Federation

ARTICLE INFO

Article history:
Received 15 December 2017
Received in revised form
19 January 2018
Accepted 23 January 2018

Keywords:
Flexible aerogel
Superhydrophobic
Thiol-ene click reaction
Polysiloxane

ABSTRACT

A new fast (about 1.5 h) and simple method for producing light-weight polymeric aerogels by radical thiol-ene click reaction direct in the $scCO_2$ media is described. A series of flexible, monolithic and superhydrophobic polysiloxane aerogels based on vinyl- and thiol-containing precursors have been synthesized by this method. The influence of precursor structure on the aerogel properties has been investigated. Bulk densities for synthesized aerogels were between 0.097 and 0.44 g cm^{-3} and skeletal densities of these aerogels were in the range of 1.171–1.215 g cm^{-3}. All investigated polysiloxane aerogels exhibit excellent thermal stability. The weight loss is observed to begin at about 300 °C in air and about 370 °C in argon for all samples. The compressive modulus of the aerogels ranged from 0.025 to 2 MPa. All samples have porosity in the range of 63–93% and a very low specific surface area. The developed method for producing aerogels by *Direct Sol-Gel* polymerization in *SuperCritical Fluid* (DSGSCF) seems to be interesting and perspective in the row of fast and cost-effective methods.

1. Introduction

Aerogels are porous materials with extremely low density, high specific surface area, large porosity and very low thermal conductivity [1–4]. These unique tunable properties of the aerogels allow them to find a wide range of various applications such as promising thermal insulating materials [5–8], catalysts [9–12], sensors [13], optical devices [14], absorbents [15–17], electrochemical devices [18], materials for oil/water separations [17,19,20] and aerospace materials [21,22], materials for high-performance fenestration applications [23]. At the first aerogels were obtained by Kistler in 1931 by the replacement of liquid component in gels by air using specific drying technique [24]. Since then many techniques for producing aerogels of different nature were developed.

There are several classes of aerogels: inorganic, organic and hybrid organic-inorganic. Among them the most popular aerogels are silica-based aerogels [15,25,26], non-silica inorganic aerogels [9,27,28], carbon aerogels [29,30], and polymer aerogels such as polysiloxane [31–33], polyurethane [34,35], polyurea [36], poly(vinylalcohol) [37], polydicyclopentadiene [38], polyimide [39], resorcinol-formaldehyde [40], cellulose [41] and metal-organic [42] aerogels.

For preparations of aerogels special methods which generally are based on sol-gel process with the next supercritical drying are used [30,43]. Practical applications of aerogels are limited due to high costs of preparation procedure of them. An exchange of a solvent in the gel by supercritical carbon dioxide ($scCO_2$) requires prolonged step of extraction that makes this approach expensive and less attractive. Along with traditional methods for producing aerogels several techniques, that are alternative to high-cost supercritical drying like a freeze-drying (FD) [11,44–46], ambient pressure drying (APD) [8,15,40,47–53], vacuum-drying (VD) [54,55], organic solvent sublimation drying (OSSD) [28] are also used. The main drawback of these methods is an increased density of aerogels in comparison with "classic" aerogels due to pore collapsing.

Another alternative method for obtaining aerogels is carrying out the process of gelation directly in $scCO_2$ (DSGSCF - "*Direct*

---

[*] Corresponding author.
[**] Corresponding author.
[***] Corresponding author. A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS), Moscow, 119991, Russian Federation.

E-mail addresses: temnikov88@gmail.com (M.N. Temnikov), kononevich.yuriy@gmail.com (Y.N. Kononevich), aziz@ineos.ac.ru (A.M. Muzafarov).

https://doi.org/10.1016/j.polymer.2018.01.067

Sol-Gel process in SuperCritical Fluid"). This approach favorably differs from the "classic" one because it does not have a high-cost process of supercritical drying. Earlier succeed examples of DSGSCF in $scCO_2$ as a solvent based on the polycondensation [56] and the hydrosilylation reaction [32,33] were shown. Despite the attractiveness of this approach a limiting factor of it is a complexity of process of control under pressure. Thus, development of new methods facilitating of carrying out of sol-gel process directly in $scCO_2$ media seems to be actual.

It is well known that $scCO_2$ is widely used as a solvent for carrying out free radical [57], ring-opening [58] and Lewis-acid catalyzed [59] polymerizations [60–64]. Although a lot of examples of the radical polymerization in $scCO_2$ are described in the literature there are no examples of obtaining aerogels by radical polymerizations at these conditions.

One of the promising type of reactions that is widely used for synthesis of new compounds, in particular in polymer chemistry, are "click reaction" [65]. A thiol-ene click reaction occupies a special place in the synthesis of monomers and polymers due to soft condition of carrying out and easy controlling [66,67]. Materials with promising properties are obtained at the combination of siloxane and thioether fragments by thiol-ene click reaction [68–71]. Thiol-ene click reaction was used for synthesis of bridged silsesquioxane precursors for preparation of aerogels based on them [52,54,72]. Taking into account the above the obtainment of polysiloxane aerogels by thiol-ene click reaction direct in $scCO_2$ media seems very interesting and perspective.

In this work we have described for the first time a new method of the fast synthesis of superhydrophobic polymeric aerogels by thiol-ene click reaction which is carried out directly in the $scCO_2$ media. The applying of this approach significantly decreases costs for producing aerogels by removing the drying step.

2. Experimental

2.1. Materials

2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, diethoxy(methyl)vinyl-silane, 3-mercaptopropyltrimethoxysilane, hexamethyldisiloxane and acetyl chloride were purchased from ABCR. Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich. All chemicals were used without further purification. All solvents were purified before use. Acetic acid was distilled over phosphorus pentoxide. Toluene and pentane were distilled over calcium hydride.

2.2. Synthesis

2.2.1. Synthesis of thiol-containing oligomer

A mixture of 3-mercaptopropyltrimethoxysilane (50 g, 0.254 mol), acetic acid (178.33 g, 2.972 mol), hexamethyldisiloxane (23 g, 0.142 mol) and acetyl chloride (0.5 g, 0.0064 mol) was stirred at refluxed for 24 h. Then toluene (200 mL) was added to the reaction mixture. After the washing by water the solution was dried by Na_2SO_4 and a solvent was removed by rotor evaporator. After drying in vacuo the product in 98% yield was obtained. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.17–0.07 (m, 9 H, Si-CH_3), 0.80–0.53 (m, 2.0 H, Si-CH_2-CH_2-CH_2-SH), 1.39–1.26 (m, 1.0 H, Si-CH_2-CH_2-CH_2-*SH*), 1.78–1.58 (m, 2 H, Si-CH_2-CH_2-CH_2-SH), 2.61–2.47 (m, 2 H, Si-CH_2-CH_2-CH_2-SH). GPC data: $M_n = 780$, $M_w = 840$, PDI = 1.08.

2.2.2. Synthesis of vinyl-containing oligomer

A mixture of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (10 g, 0.029 mol), hexamethyldisiloxane (1.08 g, 0.0067 mol) and sulfocationite Purolite was stirred at 90 °C for 24 h. After the reaction was completed the sulfocationite was filtered off. The polymer was obtained in 99% yield. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.08–0.13 (m, 3 H, Si-CH_3), 5.72–6.04 (m, 3.0 H, CH=CH_2). GPC data: $M_n = 2900$, $M_w = 5600$, PDI = 1.9.

2.2.3. General procedure for synthesis of aerogels

The general process of aerogels preparation that consists from five consecutive steps is presented on Fig. 1. In a first step all components including thiol-, vinyl-precursor, AIBN (0.1% of mass of components) and a small amount of pentane as a co-solvent were charged in a high-pressure still reactor (20 mL) (*1*). Then, at room temperature reactor was filled with CO_2 up to a pressure of 250 atm using CO_2 pump (SCF-24, Scientific systems Inc., USA) (*2*). After this the reaction mixture was dispergated in ultrasonic bath at 40 °C during 10 min (*3a*). The last procedure is required for solubilization of all components in $scCO_2$ that is critical important for obtaining high quality aerogels. In the next step the reactor was placed in an air oven and was maintained at 85 °C during 1 h (*3b*). It should be noted that at these conditions a pressure in the reactor increases to 750 atm. Then the reactor was cooled to 40 °C and CO_2 was carefully removed (*4*). In the last step the reactor was opened and aerogel was taken out (*5*).

2.3. Characterization

^1H NMR spectra were recorded on a Bruker Avance II spectrometer (300 MHz; Germany). Chemical shifts are reported relative to chloroform (δ = 7.25 ppm) for ^1H NMR. Infrared spectra were recorded on Bruker Equinox 55/S spectrometer (Germany). GPC analyses were performed in THF (1 mL/min) using a Shimadzu Prominent system equipped with RID-20A refractive index detector. The GPC columns (Phenogel) were calibrated with polystyrene standards (PSS).

The morphology of aerogels was characterized by scanning electron microscopy (SEM). The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 2–10 kV accelerating voltage and at working distance 8–10 mm. The morphology of the samples was studied taking into account possible influence of metal coating on the surface [73]. The target-

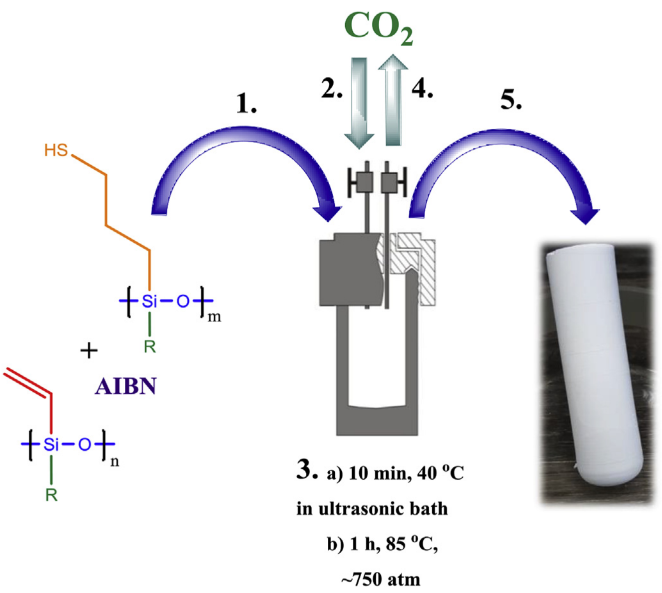

Fig. 1. Schematic representation of aerogels preparation direct in $scCO_2$.