



Chiral lactate-modified silica aerogels



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ABSTRACT

Silica-based aerogels containing L-lactic moiety were synthesized by a cogelation procedure of tetra-methoxysilane (TMOS) with lactate-modified aminopropyltrimethoxysilane L-CH₃CH(OH)CO–NH–(CH₂)₃Si(OMe)₃, followed by supercritical drying (SCD). Lactate-modified silica aerogels are semi-transparent yellowish monoliths possessing high specific surface area (up to 340 m²/g). L-lactate-containing lyogel and aerogel possess the optical activity inherent to L-lactic acid derivatives.

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1. Introduction

Aerogels (AGs) are unique engineered nanomaterials possessing an ultra-low density, high porosity and high specific surface area. AGs are widely used as effective thermal and acoustical insulators [1], sorbents [2–4], catalyst supports [5], optical materials [1,6], etc. Preparation of AGs is a multistage process typically including lyogel synthesis by a sol-gel technique, aging and washing with a desired solvent, followed by supercritical drying. Alcohols and carbon dioxide (CO₂) are the most conventional types of SCD fluids for aerogels preparation [7], while other solvents, including ethers, ketones and other organic compounds, can also be used [8–10].

Key functional properties of aerogels can be readily tuned by fairly simple procedures. For example, specific surface area and surface groups' composition are easily tailored by a choice of solvent used for SCD [7–9,11]; changes in hydrophobicity and transparency are usually achieved by silylation or fluorination of the AGs' surface hydroxyl groups [11–15].

Several unsolved problems still exist in AGs' chemistry and technology; for instance, low mechanical strength of the majority of aerogels notably limits the practical use of AGs. One challenging task in the aerogel chemistry is the introduction of chirality into AGs' network structure. Inducing chirality in porous materials is a topical challenge for many applications. Chiral aerogels could possibly be used as stereo-selective catalysts and catalyst supports, sorbents for separation of stereoisomers (e.g. in chromatography of chiral compounds). Until now, several attempts have been made to prepare chiral gels, but the optical activity of AGs has never been reported yet [16–21]. Terech et al. prepared chiral lyogel and xerogel from the D-form of 1,2-hydroxyoctadecanoic acid, while no attempts were made to synthesize corresponding aerogels [16]. L-isoleucine-based surfactant was used as a template for the synthesis of SiO₂ aerogel and xerogels in a number of works [17–19]. Chiral helical SiO₂ fibers were obtained as a result; however, the obtained materials showed neither optical activity nor the ability to separate the tartaric acid stereoisomers. Aerogel based on poly-L-lactic acid was prepared by SCD in CO₂, but its optical activity was not investigated [20]. Nanostructured peptide-based aerogels and cryogels were prepared by supercritical and freeze-drying procedures, but their optical activity was also not determined [21].

The present work is focused on the preparation of aerogels bearing a chiral L-lactic acid substituent with the aim of inducing

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chirality in amorphous AGs' structure. We decided to use L-lactate-acylated 3-aminopropyltrimethoxysilane (APTMS, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$) as a precursor for the preparation of chiral silica aerogels, as we have shown earlier that acetylated aminosilanes appeared to be a convenient and available starting material for the synthesis of functionalized aerogels [11]. We have also investigated the ability of L-lactate acylated aerogels to rotate the angle of linear polarized light. To the best of our knowledge, the lactate derivatives of APTMS-based aerogels and xerogels have not been studied yet and, as indicated above, no AGs' optical activity has been reported.

2. Materials and methods

2.1. Materials

L-methyl lactate (L-ML, Aldrich, 98%, optical purity 97%), tetramethylorthosilicate (TMOS, Acros, 99%), (3-aminopropyl) trimethoxysilane (APTMS, Acros, 95%), isopropanol (Acros, 99.5+%), methyl-*tert*-butyl ether (MTBE, Acros 99%), n-hexane (Acros, 97+%), ethyl acetate (Acros, 99.8%), HF (Acros, 40% aqueous solution) were used without further purification.

2.2. Synthesis of L-lactate-modified APTMS (1)

3 g (0.029 mol) of L-ML and 5.15 g (0.029 mol) of APTMS (the molar ratio L-ML:APTMS = 1:1) were placed into a stainless steel autoclave and heated at 120 °C for 12 h. The yellowish product obtained was evacuated (25 °C and 0.0067 MPa) to remove all volatile products.

The ^1H NMR spectrum (CDCl_3), δ_{H} (ppm): 0.38 m (2H, $-\text{CH}_2-\text{Si}-$), 1.11 and 1.16 2 d (3H, $^3J_{\text{HH}}$ 6.5 Hz $\text{CH}_3-\text{CH}(\text{OH})-$), 1.37 m (2H, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 2.98 m (2H, $-\text{CH}_2-\text{NH}-$), 3.3 s (9H, $\text{CH}_3-\text{O}-$), 3.91 and 4.16 two m (1H, $\text{CH}_3-\text{CH}(\text{OH})-$), 7.02 broad s (1H, $-\text{CH}_2-\text{NH}-$).

The ^{13}C NMR spectrum (CDCl_3), δ_{C} (ppm): 5.8 ($-\text{CH}_2-\text{Si}-$), 20.5 ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 22.2 ($\text{CH}_3-\text{CH}(\text{OH})-$), 40.5 and 40.8 ($-\text{CH}_2-\text{NH}-$), 49.3 and 49.9 ($(\text{CH}_3-\text{O})_3-$), 67.5 and 69.1 ($\text{CH}_3-\text{CH}(\text{OH})-$), 173.3 and 175 ($-\text{CH}(\text{OH})-\text{C}(\text{O})-$).

The bifurcation of some signals of NMR ^1H and ^{13}C spectra is explained by E-/Z-isomers of the amide group.

Mass-spectrum m/z: 219 ($\text{M}-\text{CH}_3\text{O}^+$), 179 ($\text{M}-\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3^+$), 130 ($\text{M}-\text{C}(\text{CH}_3\text{O})_3\text{Si}^+$), 121 ($\text{M}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{O})\text{CH}(\text{OH})\text{CH}_3^+$), 45 ($\text{M}-\text{C}(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NHC}(\text{O})^+$).

2.3. Preparation of amide-modified L-lactate silica lyogels (A-1 series)

8.1 g (0.053 mol) of TMOS and 3.35 g (0.013 mol) of (1) were mixed and cooled with 12 g (0.2 mol) of isopropanol in a polypropylene beaker. 4.8 g (0.265 mol) of de-ionized water and 0.332 g of 40% HF solution were mixed and cooled in another polypropylene beaker. The second solution was added to the first solution in one portion, stirred for several seconds, poured into cylindrical polypropylene containers, sealed and allowed to age for 24 h. The resulting lyogels were soaked in isopropanol, methyl-*tert*-butyl ether or ethyl acetate for 24 h to exchange the pore liquid for the solvent chosen. This procedure was repeated five times. The gels to be dried with supercritical hexane were first washed with isopropanol once a day during 3 days, then with hexane once a day during 3 days. The gels formed were placed into an autoclave for supercritical drying.

2.4. Supercritical drying

Supercritical drying was performed as follows. The gel sample, in a glass tube containing ~14–16 mL of an appropriate solvent, was placed into a stainless steel autoclave ($V \sim 40$ mL). The autoclave was sealed and heated to a temperature exceeding the critical temperature of the solvent. The heating rate was approximately 100 °C/h. For isopropanol, methyl-*tert*-butyl ether, ethyl acetate and hexane, the drying temperatures were 250–260 °C (the measured pressure in the autoclave at the beginning of the drying procedure reached 6.0–7.0 MPa), 240–250 °C (4.5–5.5 MPa), 265–275 °C (5–6 MPa) and 250–260 °C (4.2–5.2 MPa) respectively. After reaching the desired temperature (which was maintained for 30 min), the valve was opened; the pressure was evenly decreased to atmospheric pressure over 2 h. Then the hot autoclave was evacuated for 30 min, cooled to room temperature and opened. The overall duration of the procedure was 5 h 30 min.

Elemental analysis of **A-1-iPrOH** (%): Si 34.55, C 14.30, N 2.80, H 2.54.

2.5. Characterization of aerogels

The bulk densities of the samples were calculated by their mass to volume ratio.

The specific surface area of aerogels was determined by low-temperature nitrogen adsorption measurements with an ATX-06 analyzer (Katakon, Russia). Experimental values were plotted against P/P_0 according to the Brunauer, Emmett and Teller (BET) equation; the correlation coefficient, R , of the linear regression was not less than 0.9975.

High resolution ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX-200 spectrometer at the Larmor precession frequencies 200 and 188 MHz respectively, relative to TMS in CDCl_3 .

Mass-spectra were obtained on a FINNIGAN MAT INCOS 50 mass-spectrometer at 70 eV EI.

Infrared (IR) spectroscopy was performed on a Spectrum One (Perkin Elmer, USA) spectrometer in a 4000–350 cm^{-1} region (KBr pellets, 0.25–0.5% mass sample content).

X-ray diffraction measurements were conducted using a Bruker D8 Advance powder diffractometer ($\text{CuK}\alpha$ radiation) in a 10–80° 2θ range at goniometer rotation speed of 5° 2θ /min.

The microstructure of the samples was studied using a Carl Zeiss NVision 40 high resolution scanning electron microscope (SEM) at 1–5 kV acceleration voltage. Before the measurements, the samples were coated with a 5 nm Au/Pd conductive layer.

Transmittance spectra of a specially fabricated **A-1-iPrOH** sample having plane parallel surfaces (4 mm thick) were registered using an Ocean Optics QE65000 UV–vis spectrometer equipped with a DH 2000 halogen-deuterium light source.

The optical activity of the samples was measured with a PerkinElmer polarimeter (Mod. 341) at the wavelength $\lambda_{\text{Na}} = 589$ nm, $T = 20$ °C ($\pm 0.003^\circ$ accuracy).

Elemental analysis was performed on a Carlo Erba 1106 CHN analyzer (C, H). The content of Si was determined spectrophotometrically (Agilent Cary 100 spectrophotometer).

3. Results and discussion

To prepare lactate-modified aerogels (**A-1**), APTMS was preliminarily modified by methyl ester of L-lactic acid, leading to monomer **1**, followed by cogelation with TMOS (Scheme 1). The lyogels obtained were supercritically dried, using four solvents of different chemical nature (Table 1).

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