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Hybrid networks derived from isosorbide by means of thiol-ene photoaddition and sol–gel chemistry

C. Lorenzini, D.L. Versace*, C. Gaillet, C. Lorthioir, S. Boileau, E. Renard, V. Langlois**

Institut de Chimie et des Matériaux Paris Est UMR 7182, CNRS – Université Paris-Est Créteil, 2-8, Rue Henri Dunant, 94320 Thiais, France

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ABSTRACT

New bridged silsesquioxanes derived from isosorbide were synthesized, according to the sol–gel process, by acidic or basic hydrolysis and condensation of a bis-trimethoxysilyl precursor. The latter was prepared by thiol-ene photoaddition of 3-(trimethoxysilyl)-1-propane thiol on diallyl isosorbide ether synthesized by a phase-transfer-catalyzed reaction of allyl bromide with isosorbide. The structure of those hybrid networks prepared according to a sol–gel process was investigated by ^{29}Si solid-state NMR and X-ray diffraction experiments. Acid hydrolysis leads to the formation of randomly branched structures while basic catalysis promotes the creation of clusters. The anisotropic character of the hybrid networks was evidenced by cross polarized optical light observations (birefringence), demonstrating an organization at the micrometric-scale. These hybrid networks derived from isosorbide showed a thermal stability up to 360 °C.

1. Introduction

Sol–gel chemistry promoted the emergence of the so-called hybrid materials, and the design of new organosilsesquioxanes combining inorganic fragments covalently bonded by organic moieties which allow the control of well-defined three-dimensional networks. These materials offer exceptional opportunities to create entirely new compositions with unique properties. They appear as a promising family of materials for a variety of advanced technologies [1,2] due to the processing versatility and the synthesis conditions. The properties of the resulting hybrid solids can be tuned by the introduction of appropriate organic functional groups into the silicate network through covalent linkages.

In this context, bridged silsesquioxanes have been rapidly developed as potentially applicable hybrid materials in many areas of interest, such as in heterogeneous catalysis, electrochemically active solids, extracting solids for lanthanides and actinides, and materials for optics and opto-electronics. These functional hybrid silicates synthesized by “sol–gel” processing of monomers containing an organic bridging group joining two trialkoxysilyl groups, constitute a particular class of materials with uniformly mixed organic and inorganic moieties at the molecular level [3,4]. The commonly used synthetic routes for the elaboration of such precursors proceed through different strategies: for instance a coupling reaction between trialkoxychlorosilane and lithiated oligomers [5], hydrosilylation of allyl ether end groups of oligomers with trialkoxysilane [5], treatment of a diol or a diamine with 3-(isocyanatopropyl)trialkoxysilane [6,7], or thiol-ene addition of 3-(trialkoxysilyl)-1-propane thiol to the terminal double bonds of precursors [8–12]. The organic fragment, covalently bonded to the trialkoxysilyl groups, can be modified in functionality, length, geometry and rigidity. This determines its contribution to the properties of the cross-linked hybrid materials which can present both nanometric and micrometric-scale organization in the solid-state, according to the nature and the geometry of the organic units [13]. Until now, only linear organic spacers presenting rigid, semi-rigid or flexible geometries (mono-, bi-, terphenyl, diphenylallene, oligothiophenes, alkyl chains or urea groups…) have been studied [13,14]. In all the investigations, self-organization at the nanometric scale was checked by X-ray diffraction studies and evidenced at a microscopic scale by birefringence measurements with the exception of the flexible aliphatic spacers $(CH_2)_n$ [15]. It is worth noticing that this nanometric organization was driven in solution by the concomitant effect of the irreversible Si–O–Si bond formation that brings the organic units close to each other, and the weak interactions between the organic moieties such as Van der Waals, π–π stacking or H-bonding formation with suitable substituents like urea [16] or urethane groups, or by both. In contrast, the

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* Corresponding author. Tel.: +33 (0)1 49 78 12 28; fax: +33 (0)1 49 78 12 08.
** Corresponding author. Tel.: +33 (0)1 49 78 12 17; fax: +33 (0)1 49 78 12 08.
E-mail addresses: versace@icmpe.cnrs.fr (D.L. Versace), langlois@icmpe.cnrs.fr (V. Langlois).

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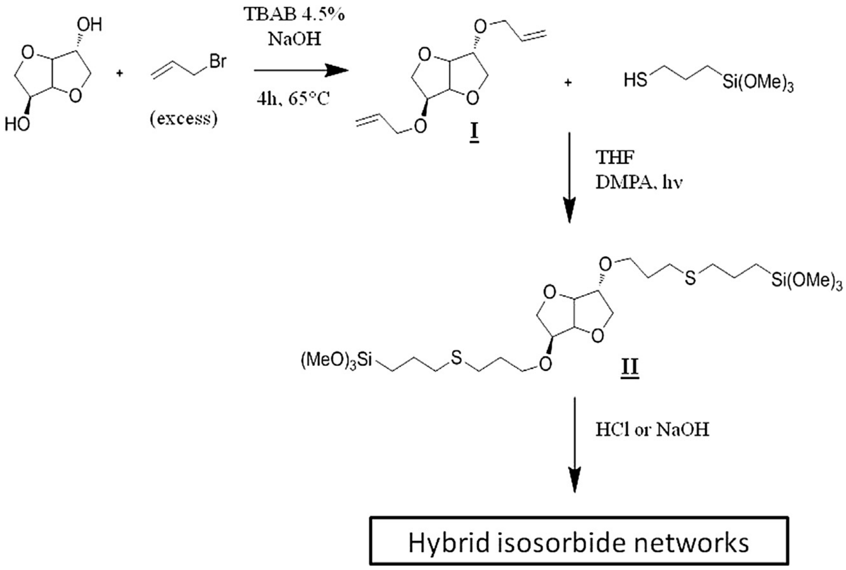

Scheme 1. General way of synthesis of hybrid isosorbide networks.

micrometric-scale organization takes place during aging in the solid-state. Densification of the Si—O—Si framework and reorganization of the micrometric aggregates induce stresses that are released by the formation of cracks leading, upon propagation, to a birefringence phenomenon [13].

The originality of this paper lies in the use of a chiral, birefringent and bio-based unit as an organic bridge between two trimethoxysilyl groups for the preparation of a novel "natural" and nano/microstructured bridged silsesquioxane material with interesting optical properties.

Biobased polymers, especially agricultural commodity-based polymers, have been explored during the last few years as an alternative to reduce the amount of petroleum consumed in the chemical industry. A molecule of high importance in this context is isosorbide, which is a 1,4:3,6-dianhydrohexitol derived from glucose, produced at an industrial scale. The attractive features of this compound are linked to its rigidity, chirality and non-toxicity. Because of the presence of two functional hydroxyl groups that allows further chemical modification, isosorbide has been used to synthesize or modify polycondensates [17–20]. Isosorbide has been investigated as a sustainable replacement for diol monomers, especially bisphenol A, that are used in nearly all types of commercially available polymers, such as polyesters, poly(ester amide)s, polycarbonates, polyurethanes, and polyethers. Crosslinking of bio-based polymers, derived from isosorbide, has been widely used in order to enhance their thermal and mechanical properties [21–24]. Among the precursors derived from isosorbide implied in polymer synthesis, diallyl isosorbide ether has been used to prepare the corresponding diglycidyl ether as a monomer for epoxy resins [20]. Similar epoxy resins were obtained from isosorbide diglycidyl ether prepared by reaction of isosorbide with epichlorohydrin, using several amines or anhydrides as curing agents [20,21]. Isosorbide diglycidyl ether was also used as a precursor for the synthesis of a dimethacrylic monomer which can find applications as a dental restorative material [25]. Networks with good thermal properties were synthesized by combining diallyl isosorbide ether with tri or tetrathiols by means of thiol-ene photoaddition [26]. Finally, it must be mentioned that side-chain cholesteric elastomers have been obtained by hydrosilylation of polymethylhydrogenosiloxane with α,ω- divinyl chiral precursors derived from isosorbide, thus acting as crosslinkers [27–29].

To the best of our knowledge, the formation of hybrid networks based on diallyl isosorbide ether modified by a 3-(trialkoxysilyl)-1-propane thiol has not been examined yet. The aim of the present work was to develop new bio-based and sol–gel processable systems (incorporating isosorbide units) with birefringence properties. Diallyl isosorbide ether (**I**) was first prepared by a reaction involving allyl bromide and isosorbide under phase transfer catalysis conditions in the presence of tetrabutylammonium bromide TBAB (Scheme 1). The second step consists in the functionalization of the diallyl isosorbide ether according to a photoinitiated radical addition of 3- (trimethoxysilyl)-1-propane thiol to the allyl bonds of (**I**) performed in the presence of a photo-initiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA, Irgacure 651), according to a "click" thiol-ene reaction, leading to a precursor bearing trimethoxysilyl end groups (**II**). Evidence of the photoinitiated radical addition was demonstrated by Real-Time Fourier Transform Infrared Spectroscopy (RT-FTIR) and ^{1}H NMR. Hybrid networks were formed by hydrolysis and condensation of the terminal methoxy groups under acidic or basic conditions, according to the "sol–gel" process. The resulting structures were analyzed by ^{29}Si solid-state NMR to evaluate the degree of condensation and by XRD analysis to determine the organization at the nanoscopic-scale. Thermal stability of those hybrid materials was examined by Thermal Gravimetry Analysis (TGA) and the optical properties were evaluated through birefringence experiments indicating the isotropic or anisotropic character of the hybrid solids.

2. Experimental part

2.1. Materials

Allyl bromide (99%) and 3- (trimethoxysilyl)-1-propane thiol (95%) were purchased from Aldrich. Tetrabutylammonium bromide (TBAB, >98%) and hydrochloric acid (37%) were obtained from Fluka. Methylene chloride and tetrahydrofuran (THF) were purchased from Carlo Erba, and were used without further purification. Isosorbide (99%) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, Irgacure 651) were kindly supplied by Roquette Frères (Lestrem, France) and BASF Company respectively.

2.2. Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II NMR spectrometer, working at 400 MHz (^{1}H) and 100 MHz (^{13}C)