



Macromolecular Nanotechnology

Synthesis of oligomeric silsesquioxanes functionalized with (β -carboxyl)ester groups and their use as modifiers of epoxy networks

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Abstract

A silsesquioxane functionalized with (β -carboxyl)ester groups was synthesized by reacting a silsesquioxane functionalized with secondary hydroxyls with a stoichiometric amount of an acid anhydride. The reaction could be carried out to completion as shown by FTIR spectra and SEC chromatograms. The carboxyl-functionalized silsesquioxane was composed of polyhedra with 8–11 Si atoms, containing two (β -carboxyl)ester groups per organic branch (from 16 to 22 carboxyl groups per molecule). It was a stable glassy product at room temperature and could be dissolved in a variety of organic solvents. It was used as a modifier of epoxy networks based on diglycidylether of bisphenol A (DGEBA) cured with 4-(dimethylamino)pyridine (DMAP). A complete reaction of epoxy groups was observed in a higher temperature range than in the formulation devoid of the functionalized silsesquioxane. This was explained by the reversible complexation of the tertiary amine with (β -carboxyl)ester groups. The addition of the silsesquioxane produced a decrease in the crosslink density explained by the presence of transesterification and chain transfer reactions, and a maximum in the elastic modulus measured at room temperature, explained by a combination of variations of cohesive energy density and the magnitude of β -relaxations.

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Keywords: Silsesquioxanes; Poly(silsesquioxanes); COOH-functionalized silsesquioxanes; Epoxy-acid reaction; Epoxy networks**1. Introduction**

Silsesquioxanes are usually synthesized by the hydrolytic condensation of organotrialkoxysilanes, $\text{RSi}(\text{OR}')_3$, performed in the presence of an acid or base as catalysts. The resulting n -mers have a

generic formula $\text{R}_n\text{Si}_n\text{O}_{1.5n-x}(\text{OH})_{2x}$, and may vary from polyhedra of formula $(\text{RSiO}_{1.5})_n$ ($n = \text{even number} \geq 6$), denoted as T_n or polyhedral oligomeric silsesquioxanes (POSS), to partially condensed (but completely hydrolyzed) species designed as $T_n(\text{OH})_m$, where $T = \text{RSiO}_{1.5-m/2n}$. The maximum value of m is equal to $2 + n$ representing a chain without intramolecular cycles.

The introduction of appropriate functionalities in the organic branch (R) has been used to obtain a

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large variety of organic–inorganic hybrid materials. In previous studies we have reported the one-step synthesis and characterization of narrow distributions of perfect and imperfect polyhedra bearing secondary hydroxyls in the organic branches (hydroxyl-functionalized silsesquioxanes, OH–SSO) [1–3], and their use as modifiers of epoxy networks [4,5]. On the other hand, carboxylic acids are useful functionalities to attach to silsesquioxanes to provide ion-exchange resins for scavenging heavy metals and organic amines [6], but also as multifunctional monomers to synthesize different types of cross-linked networks. A simple way to generate carboxylic acid functionalities is through the reaction of the secondary hydroxyls present in the OH–SSO, with acid anhydrides, leading to (β -carboxyl)ester groups (carboxyl-functionalized silsesquioxanes, COOH–SSO).

In this paper, the synthesis and characterization of oligomeric silsesquioxanes functionalized with (β -carboxyl)ester groups will be reported and their use as modifiers of epoxy networks will be analyzed.

2. Experimental

2.1. Synthesis of the silsesquioxane containing (β -carboxyl)ester groups

The organotriethoxysilane with secondary hydroxyls in the organic group was synthesized by reacting (3-aminopropyl)triethoxysilane (APS, Sigma, 98% purity) with phenylglycidylether (PGE, Aldrich, 99% purity), in a molar ratio PGE/APS = 2. The reaction was carried out in bulk, at 50 °C for 24 h under vacuum, attaining complete conversion [3]. The hydrolytic condensation was performed by dissolving 1 g of the resulting product in 1.5 ml tetrahydrofuran (THF) and adding HCOOH 85 wt% (molar ratios: HCOOH/Si = 3, H₂O/Si = 1.35). Formic acid acts both as a catalyst and as reactant, promoting the condensation through the formation of sililformates as intermediate species [7,8]. The reaction was carried out at 50 °C for 24 h allowing continuous evaporation of volatiles and leading to a silsesquioxane (OH–SSO) containing two secondary hydroxyls per organic branch (Fig. 1a).

Secondary hydroxyls were converted into (β -carboxyl)ester groups by reaction with a stoichiometric amount of 4-methyl tetrahydrophthalic anhydride (MTHPA, HY 918 Ciba) in a THF solution. The reaction was carried out at 50 °C for 24 h in closed

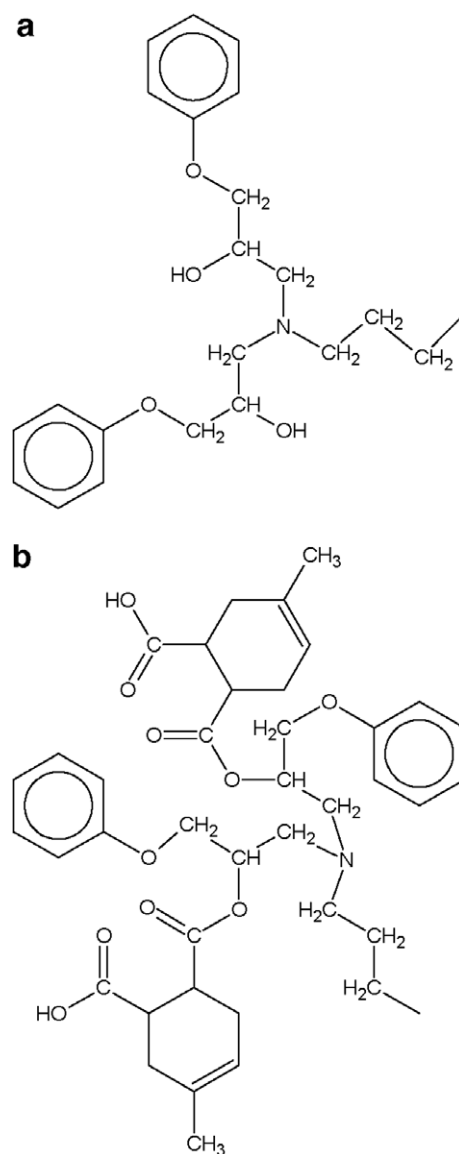


Fig. 1. Chemical structures of the organic branches of silsesquioxanes functionalized with: (a) secondary hydroxyls and (b) (β -carboxyl)ester groups.

tubes. Then THF was eliminated by heating at 80 °C for 2 h at atmospheric pressure, followed by another 2 h at the same temperature under vacuum. The resulting silsesquioxane (COOH–SSO) containing two (β -carboxyl)ester groups per organic branch (Fig. 1b), was ground and stored as a yellow glassy powder.

2.2. Epoxy networks modified by COOH–SSO

The epoxy monomer was based on diglycidylether of bisphenol A (DGEBA, Der 332 Dow, equiv-

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