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$B(C_6F_5)_3$ catalyzed dehydrocarbon polycondensation of $PhSiH_3$ with $(MeO)_4Si$ as model polyfunctional comonomers in new route to hydrophobic silicone TQ resins

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ABSTRACT

Highly branched methoxy substituted phenylsilsesquioxane-silicate copolymers were obtained by dehydrocarbon polycondensation of phenylsilane ($PhSiH_3$) with tetramethoxysilane (TMOS) in toluene solution catalyzed by tris(pentafluorophenyl)borane [$B(C_6F_5)_3$]. This model reaction represents a new non-hydrolytic route to TQ silicone resins, which do not contain reactive and hydrophilic silanol groups and therefore, should be more stable and have better miscibility with some organic polymers. The soluble siloxane copolymers, which do not contain volatile oligomers, were obtained using the $PhSiH_3$:TMOS molar ratios below 0.9. The dehydrocarbon condensation is accompanied by metathetic exchange of hydrosilyl and methoxysilyl functions, which is responsible for the formation of links between units originating from the same comonomer. Competition between the dehydrocarbon condensation and metathesis is consistent with a mechanism involving the transient formation of a tertiary oxonium ion intermediate. ^{29}Si NMR analysis of the copolymer product proves that extensive cyclization occurs during the polycondensation, most likely leading to a significant proportion of ladder and cage like structures.

1. Introduction

Silicone resins are highly branched organosilicon polymers having a silicon–oxygen backbone bearing a great number of functional groups, mostly hydroxide and alkoxide, which give rise to cross-linking in an application process. The most common are copolymers of silsesquioxanes [1–5]. Among them copolymers with organic esters of orthosilicic acid are used. They are composed of silsesquioxane T units and Q units originating from tetraalkoxysilane [1–5]. Due to a combination of their unique useful properties, the silicone resins found a broad range of applications as protective coatings for electrical, electronic and optical devices [1–11]. They show many advantages over traditional organic resins such as high thermal stability, resistance to oxygen, water vapor, light, UV radiation and exhibit good optical and electrical properties. On the other hand their room temperature mechanical properties, in particular flexural, tensile and fracture properties, are inferior to other organic resins. The combination of silicone resins with organic materials, such as epoxides, polyesters and acrylates, provides a means to overcome these shortcomings [12–18].

Conventional silicone resins obtained by hydrolytic polycondensation of silicone monomers contain a large uncontrollable amount of hydroxyl groups, which make the silicone resins hydrophilic and poorly miscible with organic polymers [19,20]. The presence of hydroxyl groups, which have a great propensity to self-condensation, makes the silicone resins less stable on storage and may cause a premature cross-linking during application processes, in particular at elevated temperatures [2,20]. Considerable effort has been devoted to a synthesis of

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hydrophobic, hydroxyl-group free silicone resins. Hyperbranched ethoxy functional polysiloxanes were obtained by non-hydrolytic one-pot polycondensation of tetraethoxysilane with acetic anhydride using an organotitanium catalyst [21] or by hetero-functional polycondensation of isolated AB_3 monomers such as acetoxytriethoxysilane or triethoxysilanol [22,23]. These reactions either suffer from a troublesome synthesis of AB_3 type monomers or proceed slowly and must be performed at high temperatures using a considerably high concentration of catalyst. Other methods are based on a careful hydrolytic polycondensation between organotrialkoxysilanes and tetraalkoxysilanes [24–26]. These processes are difficult to control and preclude the formation of a polymer that is completely void of hydroxyl groups.

Our approach to synthesize hydrophobic siloxane resins is based on the hetero-functional polycondensation of monomers bearing silylalkoxy and silylhydride groups catalyzed by tris(pentafluorophenyl)borane ($B(C_6F_5)_3$). This reaction occurs rapidly at very low concentrations of catalyst and leads to a branched, hydroxyl-group free polymer. A by-product in this reaction is a volatile and chemically inert hydrocarbon, i.e. methane [27,28]. This polycondensation was successfully used for the synthesis of linear siloxane polymers [28–33] as well as branched siloxane oligomers of a special design [34]. Also, we have recently reported the application of this reaction to the preparation of DQ silicone resins [35]. This report is devoted to the synthesis of TQ silicone resins by $B(C_6F_5)_3$ catalyzed polycondensation of model SiH and SiOR polyfunctional monomers such as phenylsilane $PhSiH_3$ and tetramethoxysilane (TMOS).

It is worth to mention that free of hydroxyl groups QT resins are also attractive as precursors of silica materials as they undergo facile gelation in the presence of controlled amounts of water [24–26,36,37]. The gelation may occur in nonpolar and non-hydrolytic solvents and leads to the generation of hydrophobic gels that have recently gained great interest as low-*k* dielectric materials [38,39].

2. Experimental

2.1. Chemicals

Tetramethoxysilane (TMOS) (Aldrich) reagent grade, was distilled from sodium. $PhSiH_3$ (ABCR) reagent grade, was kept over calcium hydride and distilled. Purity of all substrates was checked by gas chromatography and was above 98%. Solvent, toluene (POCH – Polskie Odczynniki Chemiczne) was shaken with H_2SO_4, washed with water, then with a sodium carbonate solution, again with water, dried over $MgSO_4$, distilled over P_2O_5 and distilled again from sodium. Catalyst, reagent grade tris(pentafluorophenyl)borane (Aldrich) with a declared purity of 95% was either sublimed at 50 °C on a vacuum line or used without further purification.

A stock solution of $5 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ of the borane catalyst in toluene was prepared under nitrogen shortly before use.

3. Analytical methods

3.1. NMR spectroscopy

^{1}H NMR spectra were recorded on Bruker DRX 500 operating at 500 MHz. ^{29}Si NMR spectra were recorded in the presence of $Cr(acac)_3$ on the same instrument working at 99.36 MHz in the inverse gated pulse sequence mode with relaxation delay of 3 s, scan number 9.4 K, time domain 65.5 K and 90° pulse 15.00. The solvent was $CDCl_3$. Peak assignment was made using Refs [40,41].

3.2. Gas chromatography (GC)

Gas chromatography analyses were performed using a Hewlett Packard HP 6890 chromatograph equipped with a thermal conductivity detector and a HP1 capillary column $l = 30$ m, $d = 0.53$ mm. Further specifications include: helium carrier gas, flow rate 5 ml/min, detector temperature 250 °C, injector temperature 250 °C, column programmed in most cases: 3 min at 40 °C isoth., ramp from 40 °C to 240 °C at rate 10 °C/min. About 10–15 min at 240 °C isoth. *n*-Dodecane was used as the internal standard.

3.3. Gas chromatography–mass spectroscopy (GC–MS)

Mass spectra were recorded with a GC–MS Finningan MAT 95 instrument using the chemical ionization technique. The reactive gas (H^+ carrier) was isobutane at 10^{-4} Torr. The mass-spectrometer worked in tandem with the gas chromatograph that was fitted with a standard capillary column DB-1 $l = 30$ m. The temperature was programmed to fit to the corresponding chromatogram recorded on the HP-6890 instrument. Since ionization occurs under mild conditions, a fragmentation of analyzed species was limited. Siloxane oligomers give a strong M + 1 peak and/or its simple fragmentation product, which dominate over other fragmentation products.

3.4. Size exclusion chromatography (SEC)

Absolute average values of molar mass and polydispersity of siloxane resins were determined using an Agilent 1100 HPLC pump and a set of two PLGel 5 micron MIXED-C columns. An Optilab rEX interferometric refractometer and DOWN EOS laser photometer from Wyatt Technology were used as detectors. Methylene chloride was used as the eluent. The refractive index increment (dn/dc) was measured at 662 nm for the all copolymers and was determined to be 0.033–0.040.

3.5. Synthesis

The polycondensation reactions were performed in Schlenk type 25 ml reactor equipped with a magnetic stirrer and a three-way stopcock through which argon was flowing. Substrates, catalyst, a GC standard and solvent were introduced under nitrogen through this stopcock by means of a precision Hamilton syringe with a long needle.