

TOWARDS NEW HYBRID STAR-SHAPED OR CROSSLINKED MATERIALS BASED ON MACROMONOMERS AND SILSESQUIOXANES

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Introduction

In recent years inorganic-organic compounds have emerged as an important category of new materials. The interest in their development resulted from the fact that they combine the unique behavior of organic polymers with the good physical properties of ceramics.¹ They represent a new class of materials characterized for example by enhanced thermal and thermomechanical stability, mechanical toughness² or optical transparency. Octafunctionalized cubic silsesquioxanes are often used as nanosized building blocks in such materials, leading novel hybrid nanocomposite structures.³ One of us reported the synthesis and the properties of monosubstituted cube-shaped spherosilsesquioxanes with amphiphilic properties, combining the relatively hydrophobic spherosilsesquioxane core with hydrophilic oligo(ethylene oxide) segments.⁴ The main aim of the present work is to discuss the synthesis of hybrid macromolecular architectures constituted of poly(ethylene oxide) (PEO) or polystyrene (PS) or poly(styrene-*b*-isoprene) (PS-*b*-PI) chains and spherosilsesquioxane core or crosslinking points. The synthesis and the characterization of a series of PEO or PS macromonomers fitted, at one or both chain ends, either with allyl or with undecenyl end-groups will be presented first. The second part will be devoted to the coupling, via hydrosilylation, of these PEO, PS, or PS-*b*-PI macromonomers with octa(dimethylsiloxy)-octasilsesquioxanes (Q₈M₈^H). The final section discusses the synthesis of networks based on bifunctional PEO and octafunctional silsesquioxanes.

Experimental part

Materials. All procedures were performed under argon using standard Schlenk techniques. The α,ω - or ω -hydroxy PEOs (FLUKA) were dissolved in DMSO, filtered, precipitated in diethyl ether and dried. Octa(dimethylsiloxy)-octasilsesquioxane (Q₈M₈^H) (Aldrich) was used without further purification. Styrene and isoprene monomers were pre-dried over CaCl₂ and then distilled over sodium, under reduced pressure. Butyllithium (*sec*-BuLi) was synthesized by reacting 2-chlorobutane with lithium in cyclohexane. 11-bromo-1-undecene was distilled under vacuum with CaH₂. Cyclohexane, toluene and THF were purified by conventional methods and collected in previously dried burettes.

Characterization. Molar masses and molar mass distributions were determined by SEC with refractive index (RI) detection or SEC combined with online light scattering (LS) at room temperature on a Waters apparatus equipped with five PL gel columns. Standard linear polystyrenes (PS) were used for calibration. Yields of functionalization were determined by ¹H NMR spectroscopy on a Bruker 400 apparatus using CDCl₃ as solvent at 25°C and C₂H₂Cl₄ as an internal standard. All macromonomer samples were analyzed by matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF MS) on a Bruker Reflex II apparatus. The measurements of the uniaxial compression modulus were made with home built, fully automated equipment.

Synthesis of macromonomers. The method of preparation of the macromonomers has been described extensively elsewhere.^{5,6}

Synthesis of star-shaped polymers. Typically star polymers based on silsesquioxanes has been prepared by dissolving ten mol equivalent of macromonomers and one mol equivalent of silsesquioxane cage in toluene. The reaction mixture was heated to 75°C, and 2 μ L of 13.6 wt.-% solution of Karstedt's catalyst were added. The reaction was kept going on at 75°C for 15 h

Fractionation of star-shaped polymers. Fractional precipitation was carried out in a constant bath temperature, using solvent/non solvent system in a conventional pear-like vessel. A typically fractionation of PEO star was carried out as follows: the raw reaction product was dissolved in toluene (solution at 1

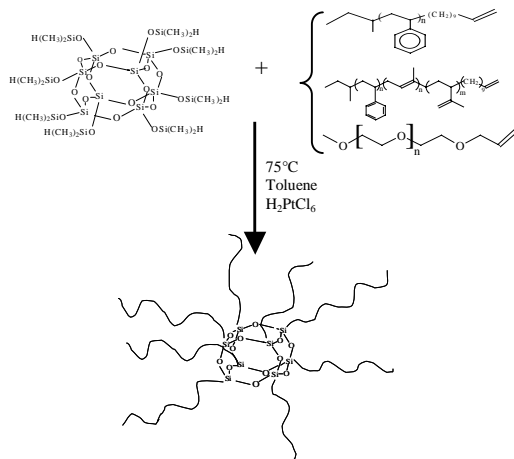
wt.-%, T=30 °C). Cyclohexane was added until precipitation takes place. At that point the solution was heated to 50 °C, and gets clear again. Then temperature was decreased to 30°C, and the solution was kept at that temperature during 24 hours to allow good separation of the two phases. The lower phase should contain mainly the star polymer and the upper one the unreacted or residual macromonomer. The fractions were analyzed by SEC with online light scattering. The lower phase was recovered, the resulting solid polymer was dissolved again and then fractionated to get the pure star polymer

Hydrogel Synthesis. The syntheses of PEO hydrogels have been described elsewhere.⁷ In short bifunctional PEO macromonomers (with molar masses (M_n) equal to 3000, 6600, 10600, 16000 g.mol⁻¹) were used in the synthesis of hydrogels. The crosslinking reactions were performed in toluene at different macromonomer concentrations (20, 30 or 40 wt.-%) with the same procedure reported in the case of star polymers described previously.

Results and Discussion

Synthesis of macromonomers. Series of ω -allyl PEO, α,ω -allyl PEO, ω -undecenyl PS or PS-*b*-PI macromonomers with various molar masses extending from 1900 to 50000 g.mo⁻¹ were synthesized, and they were submitted to appropriate characterization to assess molar mass, molar mass distribution and functionality (**Table 1**). Well-defined species with narrow molar mass distributions and free of coupling products (no shoulder on SEC curves) were obtained. The yield of functionalization determined by ¹H NMR was always close to 95 %. The samples were also analyzed by MALDI-TOF MS.

Star-shaped polymers. Well-defined ω -allyl PEO, ω -undecenyl PS or PS-*b*-PI macromonomers, obtained by anionic deactivation reactions⁶ were reacted via hydrosilylation with octa(dimethylsiloxy)octasilsesquioxanes. Characterization of the samples involved comparison of the molar mass of the star-shaped polystyrene with that of the individual branch, the macromonomer precursor. From SEC online light scattering experiments it was possible to determine the average number(s) of branches of the star. The f values for the different samples are close to eight.



Scheme 1. Synthesis of the star-shaped polymers.

PEO/Silsesquioxanes star polymers. Different grafting experiments were carried out by varying the molar mass of the ω -allyl PEO macromonomer from 1900 to 10000 g.mol⁻¹. The SEC diagram of the raw reaction product (**Figure 1a**) is characterized by the presence of two peaks: a major one attributed in principle to the star-shaped polymer and a second one corresponding to unreacted PEO macromonomer. Based on calibration with linear PEOs, an apparent molar mass of 11000 g.mol⁻¹ is obtained for the former. This value is lower than expected. However, it is well established that star-shaped polymers, owing to their higher segment density, which implies a smaller hydrodynamic volume, exhibit higher elution volumes than the linear equivalent.

Figure 1b depicts the SEC trace of the same sample after fractionation. As it can be seen, this sample is almost free of precursor PEO macromonomer. Accurate characterization of purified $Q_8M_8^{PEO1900}$ star by static light scattering in methanol and field-flow fractionation (F.F.F.) demonstrates the efficiency of the method: the molar mass of the star-shaped molecules ($M_{w,LS} = 16500 \text{ g.mol}^{-1}$, $M_{w,F.F.F.} = 15600 \text{ g.mol}^{-1}$) is very close to the expected value ($M_{w,th} = 16000 \text{ g.mol}^{-1}$).

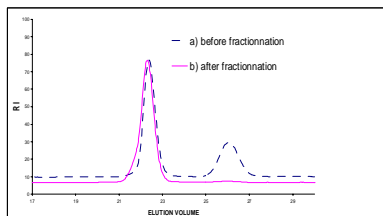


Figure 1. Typical SEC curves of a PEO / silsesquioxane star ($Q_8M_8^{PEO1900}$)

PS and PS-*b*-PI / Silsesquioxane star-shaped polymers. Well-defined ω -undecenyl PS or PS-*b*-PI macromonomers obtained by anionic deactivation reactions with molar masses extending from 10000 and 50000 g.mol^{-1} were reacted via hydrosilylation with octa(dimethylsiloxy)octasilsesquioxanes. Some characteristic data are given in **Table 1**

Table 1. Molecular characterization of PS and PS-*b*-PI / silsesquioxane stars.

Precursor Macromonomer	$M_n^{(a)}$	$M_w^{(a)}$	$M_w^{(b)}$	$I_p^{(a)}$	$f \phi$
ω -Und PS2100	13600	14700	17500	1.07	7.9
ω -Und PS- <i>b</i> -PI4000	88000	98500	140000	1.12	8.1
ω -Und PS- <i>b</i> -PI34000	198000	228000	300000	1.15	8.8

a) Measured by SEC in THF (with linear PS standard calibration)

b) Measured by SEC in THF with online light scattering.

c) $f \phi$ = Number of arms grafted, calculated by dividing the absolute molar mass of star polymer determined by SEC online LS to precursor molar mass measured in THF

The approach was extended to the synthesis of janus type architectures in which both PS and PI chains were grafted to the octafunctional silsesquioxane core. The morphologies of these macromonomer based star-shaped polymers were compared to those of polymacromonomers obtained by coordination polymerization of PS-*b*-PI macromonomers type architectures in which both PS and PI chains were grafted to the octafunctional silsesquioxane core.⁷

Hydrogel characterizations. The crosslinking by formation of bridges between individual PEO chains is well known to represent an efficient way to insolubilize PEO chains in aqueous or in organic solvents. Irradiation of water solutions of PEO chains was until recently the most commonly used method to design PEO networks in water. Crosslinking can also be achieved upon reaction of a linear dihydroxy PEO of controlled molar mass with a stoichiometric amount of a plurifunctional isocyanate⁸. Homopolymerization of bifunctional PEO macromonomers has been shown to be an interesting alternative to yield PEO hydrogels directly in water.⁹ In the following the properties of PEO hydrogels resulting from coupling via hydrosilylation of α,ω -allyl PEO macromonomers¹⁰ with $Q_8M_8^H$ will be discussed. It is well established that the degree of equilibrium swelling is related to parameters, which are experimentally accessible: the volume segment concentration upon crosslinking and the average molar mass of the elastics chains. The weight degree of equilibrium swelling in toluene or dioxane (Q_w) decreases with increasing macromonomer concentration. (**Figure 2**)

However, the value of the uniaxial compression modulus increases with increasing macromonomer concentration. (**Figure 3**) This demonstrates that the

density of elastically effective chains is essentially influenced by the macromonomer concentration.

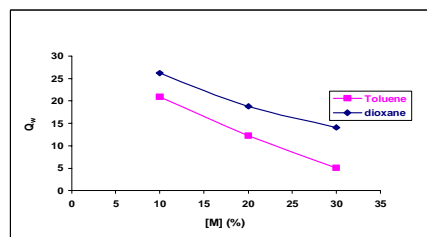


Figure 2. Evolution of the weight degree of equilibrium swelling (Q_w) versus PEO macromonomer ($M_n=10000 \text{ g.mol}^{-1}$) concentration for PEO / silsesquioxane networks swollen to equilibrium in toluene or dioxane.

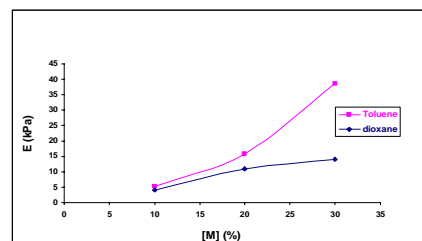


Figure 3. Evolution of uniaxial compression modulus (E_G) versus PEO macromonomer concentration ($M_n=10000 \text{ g.mol}^{-1}$) for PEO / silsesquioxane networks swollen to equilibrium in toluene or dioxane.

Conclusion

Reaction of well-defined macromonomers via hydrosilylation with octa(dimethylsiloxy)octasilsesquioxanes has been very successful for the synthesis of octafunctional PEO, PS, or PS-*b*-PI star shaped molecules. The SEC profiles showed sharp monomodal molar mass distributions, and the molar masses determined by SEC online LS are close to the expected values. Fractional precipitation proved very efficient to remove the residual macromonomer. Hydrogels arising from bifunctional PEO macromonomers have been also obtained using the same octafunctional silsesquioxane and the influence some parameters on their physico-chemical behavior were made.

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