*Macromol. Symp.* **2010**, 291–292, 43–49 DOI: 10.1002/masy.201050506

# New Trends in Poly(ethylene oxide) or Polystyrene Macromonomer Based Networks Exhibiting Silsesquioxane Cross-Linking Points

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**Summary:** Poly(ethylene oxide) (PEO) hydrogels and polystyrene (PS) networks were synthesized in toluene by coupling α,ω-diallyl PEO or α,ω-diundecenyl PS macromonomers with octafunctional silsesquioxanes via hydrosilylation in the presence of a "Speier" catalyst. Their equilibrium swelling degree and uniaxial compression modulus could be controlled by the synthesis parameters, i.e. the solvent, the macromonomer molar mass and the macromonomer concentration.

**Keywords:** cross-linked materials; hydrogels; hydrosilylation; macromonomers; silsesquioxanes

## Introduction

Numerous methods have been developed to synthesize cross-linked polymeric networks.[1,2] These methods can be classified into three groups: methods involving free radical copolymerization of two monomers,[3] including macromonomers,[4] methods employing formation of bridges between existing linear or branched chains by vulcanization, peroxidation, or irradiation,[5,6] and those based on chemical reactions involving bifunctional polymers bearing living anionic or other functions at the chain ends.[7–9] In the last method, the average length of the precursor polymer can be chosen arbitrarily, and determined precisely. The precursor chains become the elastic chains of the network, and the functionality of the core is given by that of the interconnecting low molar mass compound.

Hybrid inorganic-organic materials, combining the unique behavior of organic polymers with the good physical properties of ceramics, have attracted increasing interest in recent years.[10] Octafunctionalized cubic silsesquioxanes are often used as nanosized building blocks and have gained increasing interest as cross-linking points in networks.[11]

The aim of the present work is to design and study a new type of complex hybrid cross-linked architecture based on poly(ethylene oxide) (PEO) or polystyrene (PS) macromonomers and octafunctional silsesquioxanes. The synthesis and characterization of α,ω-diallyl PEO and α,ω-diundecenyl PS macromonomers will be discussed first. The second part concerns the cross-linking process of these macromonomers via hydrosilylation. The final part examines the dependence of some physico-chemical properties of the resulting networks on macromonomer molar mass and concentration.

## Experimental Part

### Materials

### Solvents, monomers, initiators, deactivating or coupling agents

Toluene, tetrahydrofuran (THF) and cyclohexane were purified by conventional methods. Allyl bromide and 11-bromo-1-undecene (Aldrich) were distilled before use and were kept under dry argon. Octa(hydridodimethylsiloxy)octasilsesquioxane ($Q_8M_8^H$) (Aldrich) was used without further purification. Diphenylmethyl

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potassium and potassium naphthalenide were synthesized according to well-established procedures. The "Speier" catalyst[12] ($H_2PtCl_6{}^*H_2O$) (Aldrich) was used in isopropanol at a 13.6 wt.- % of Pt.

### Synthesis of $\alpha,\omega$-diallyl PEO Macromonomers

The hydroxyl functions of $\alpha,\omega$-dihydroxy PEOs (FLUKA), with number-average molar masses, $M_n$, equal to 6150 or 10100 g mol$^{-1}$, were transformed into alcoholates by addition, at room temperature, of a stoichiometric amount of diphenylmethyl potassium (the stoichiometry being determined by colorimetry) which provoked the viscosity of the reaction medium to increase, due to the formation of associations between chain ends. Subsequently, allyl bromide or 1-bromo-11-undecene was added in a slight excess to the living polymer solution.[13] The required amount corresponds to the total number of active sites present in the medium. The resulting macromonomers were centrifuged, filtered, precipitated twice from their THF solution into diethylether and characterized by size exclusion chromatography (SEC) and NMR spectroscopy.

### Synthesis of $\alpha,\omega$-diundecenyl Polystyrene Macromonomers

The $\alpha,\omega$-diundecenyl PS macromonomers were synthesized by anionic polymerization of styrene as described earlier.[14] Briefly, they were prepared by anionic polymerization in THF using potassium naphthalenide as initiator at $-60\,°C$. 11-bromo-1-undecene was added at $-78\,°C$ to the living PS solution in a slight excess. The reaction solution was stirred overnight at room temperature, and was then filtered and precipitated in methanol. This method provided four PS macromonomers with $M_n$ values of 5000, 10000, 20000 and 30000 g mol$^{-1}$.

### PEO Network Synthesis

The bifunctional PEO macromonomers were cross-linked via hydrosilylation using a stoichiometric ratio ([allyl]/[SiH] = 1), in the presence of a "Speier" catalyst, in toluene at 75 °C at different macromonomer concentrations (20, 30 or 40 wt.-%).[13] In most cases, the gel point was reached rapidly. After extraction of the soluble materials, the gels were placed in toluene or dioxane and were left to swell.

### PS Network Synthesis

A series of PS networks were prepared by end-linking the bifunctional PS macromonomers. The cross-linking reactions were performed via hydrosilylation using a stoichiometric ratio ([undecenyl]/[SiH] = 1), in the presence of a "Speier" catalyst, in toluene at 50 °C at different macromonomer concentrations (20, 30 and 40 wt.-%). After extraction of the soluble materials, the gels were placed in toluene or cyclohexane for swelling.

### Analysis and Characterization

Macromonomer molar masses and molar mass distributions were determined by SEC using refractive index detection (linear PS or PEO calibration) or using (online) light scattering detection. The yields of functionalization were determined by $^1H$ NMR spectroscopy on a Bruker 400 apparatus. The networks, free from non-connected chains, were characterized in terms of their swelling behavior and uniaxial compression moduli according to well-established procedures.[15,16]

## Results and Discussion

### $\alpha,\omega$-diallyl PEO Macromonomers

The $\alpha,\omega$-diallyl PEO macromonomers were obtained starting from linear commercial $\alpha,\omega$-dihydroxy PEOs of well-defined molar mass and exhibiting sharp molar mass distributions as described in the Experimental Part. They were characterized by SEC and by $^1H$ NMR spectroscopy. The molar masses of the resulting macromonomers were slightly higher than those of their precursors, the increase corresponding to the introduction of the polymerizable terminal entities. The polydispersity indices (*PDI*s) were close to those of the precursor chains and the yield of functionalization determined by $^1H$ NMR was almost quantitative. The molecular characteristics of these macromonomers are given in Table 1.

### $\alpha,\omega$-Diundecenyl Polystyrene Macromonomers

The $\alpha,\omega$-diundecenyl PS macromonomers were prepared as indicated in the Experimental Part. They were submitted to characterization to assess molar mass, molar mass distribution and functionality. Well-defined species with narrow molar mass distributions and free of coupling products (no shoulder detected on the SEC peak) were obtained. Experimental and theoretical molar masses were in good agreement with each other. The yield of functionalization calculated by $^1$H NMR was almost quantitative. The molecular characteristics of these macromonomers are given in Table 2.

### Synthesis and Characterization of PS and PEO Networks

The PS and the PEO networks synthesized via hydrosilylation (Scheme 1) were submitted to detailed physico-chemical characterization to access the volume degree of equilibrium swelling ($Q_v$) and the uniaxial compression modulus ($E_G$).

This study was performed in order to establish the influence of the preparation conditions on the properties of the final networks, and to test existing theories. In all cases, the networks have to be freed from any soluble materials i.e. macromonomer precursor chains non-connected to the network structure. Once free of soluble material, the networks were submitted to physico-chemical characterization. The method for the determination of $Q_v$ has been described elsewhere.[15] Briefly, the relation to calculate $Q_v$ from the measured weight degree of equilibrium swelling $Q_w$ ($Q_w = (\text{Weight}_{\text{dry gel}} + \text{Weight}_{\text{solvent}})/\text{Weight}_{\text{dry gel}})$) is $Q_v = 1 + (Q_w - 1)\ v_s / v_o$, where $v_s$ and $v_o$ are the specific volumes of the solvent and the dry gel (equal to that of linear PEO). The uniaxial compression modulus ($E_G$) is determined as:

$$F/S_g = \nu RTQ_v\,(\Lambda_x - \Lambda_x^{-2})$$

***Table 1.***
Molecular characteristics of the $\alpha,\omega$-diallyl PEO macromonomers.

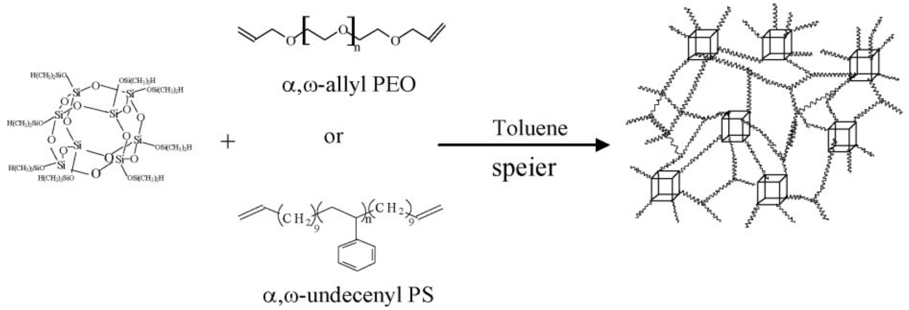
| Reference | $M_{n,prec}$ a) g mol$^{-1}$ | $M_n$ b) g mol$^{-1}$ | $PDI_{prec}$ c) | $PDI_{al.}$ d) | $f$ e) (%) |
|---|---|---|---|---|---|
| PEO1 | 6100 | 6150 | 1.09 | 1.09 | $\geq 95$ |
| PEO2 | 10000 | 10100 | 1.16 | 1.16 | $\geq 95$ |

a)Number-average molar mass of the PEO precursor measured by SEC.
b)Number-average molar mass of the $\alpha,\omega$-diallyl macromonomer measured by SEC.
c)Polydispersity index of the PEO precursor determined by SEC.
d)Polydispersity index of the $\alpha,\omega$-diallyl macromonomer determined by SEC.
e)Yield of functionalization measured by $^1$H NMR in $CDCl_3$ using an external standard ($C_2H_2Cl_4$).

***Table 2.***
Molecular characteristics of the $\alpha,\omega$-diundecenyl PS macromonomers.

| Reference | $M_{n,\ th.}$ a) g mol$^{-1}$ | $M_{n,SEC}$ b) g mol$^{-1}$ | $M_{w,SEC}$ c) g mol$^{-1}$ | $PDI$ d) | $f$ e) % |
|---|---|---|---|---|---|
| PS1 | 5000 | 5200 | 5900 | 1.15 | $\geq 95$ |
| PS2 | 10000 | 9900 | 11600 | 1.17 | $\geq 95$ |
| PS3 | 20000 | 18500 | 22000 | 1.19 | $\geq 95$ |
| PS4 | 30000 | 28600 | 32300 | 1.13 | $\geq 95$ |

a)Theoretical number-average molar mass calculated from the ratio [Monomer converted]/[initiator].
b)Experimental number-average molar mass measured by SEC.
c)Experimental weight-average molar mass measured by SEC.
d)Polydispersity index determined by SEC.
e)Yield of functionalization measured by $^1$H NMR in $CDCl_3$ using an external standard ($C_2H_2Cl_4$).



***Scheme 1.***
Schematic representation of the synthesis of the PS and the PEO networks.

where $F/S_g = \sigma$ corresponds to the uniaxial force exerted per unit area of the hydrogel, $S_g$ is the section area of the gel in the swollen state, $\nu$ the number of elastic chains per unit volume of dry gel, $E_G$ is the uniaxial compression modulus, ($E_G = \sigma\ (\Lambda_x - \Lambda_x^{-2})$, and $\Lambda_x = L_x/L_0$, $L_0$ and $L_x$ are, respectively, the length of the sample before compression and at each step of the uniaxial compression process. The measurements of uniaxial compression modulus were made as follows: a cylindrical sample, about 1.5 to 2 cm in length and 1.3 to 1.5 cm in diameter, was placed between two disks in a solvent bath. The influence of several experimental parameters, such as the macromonomer concentration and the molar mass of the macromonomer precursor, on $Q_v$ and $E_G$ was examined for both the PEO and the PS networks.

### PEO Networks

The amount of extractable polymer, $Q_v$ and $E_G$ of the different PEO hydrogels were systematically measured in toluene and in dioxane. Some results are presented on Table 3 and in Figure 1 and call for the following comments:

- The amount of extractable material, between 2 and 10 wt.-% for gels with molar mass of 6150 g mol$^{-1}$, and 7 and 20 wt.-% for gels with molar mass of 10100 g mol$^{-1}$, is higher than for gels obtained by classical end-linking procedures.[17] For a given concentration, it increases with precursor molar mass, and for a given molar mass, it decreases with increasing macromonomer concentration.
- For a given macromonomer molar mass, $Q_v$ increases with decreasing macromo-

***Table 3.***
Physico-chemical characteristics of the PEO/silsesquioxane networks.

| Reference | $M_n$ a) G mol$^{-1}$ | [M]b) wt.-% | $\varepsilon$c) | $Q_v$d) | $E_G$e) Pa | $E_G$f) Pa |
|---|---|---|---|---|---|---|
| GPEO1 | 6150 | 20 | 20.7 | 28.1 | 8100 | 3500 |
| GPEO2 | 6150 | 30 | 12.9 | 18.6 | 22500 | 8900 |
| GPEO3 | 6150 | 40 | 7.7 | 15,6 | 55000 | 17000 |
| GPEO4 | 10100 | 20 | 10.3 | 18.8 | 15700 | 11000 |
| GPEO5 | 10100 | 30 | 3.8 | 14,1 | 38600 | 14000 |
| GPEO6 | 10100 | 40 | 2.6 | 12.7 | 103400 | 25800 |

a)Number-average molar mass of the PEO macromonomer.
b)wt.-% of PEO macromonomer to be cross-linked.
c)$\varepsilon$ is the percentage of extractable polymer (wt.-%).
d)Volume equilibrium swelling degree measured in dioxane.
e)Uniaxial compression modulus measured in toluene.
f)Uniaxial compression modulus measured in dioxane.

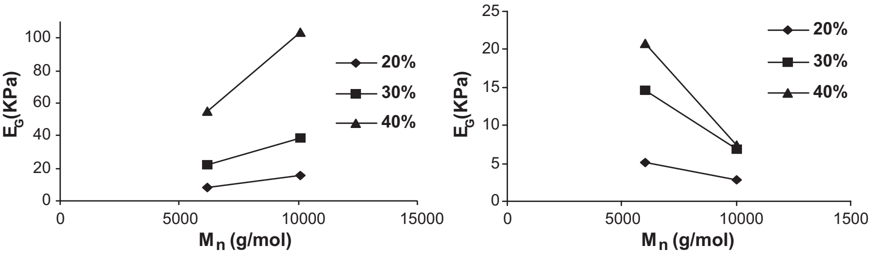


***Figure 1.***
Dependence of the uniaxial compression modulus, $E_G$, on the PEO macromonomer molar mass for networks prepared and swollen to equilibrium in toluene (left), and prepared and swollen to equilibrium in dioxane (right).

nomer concentration while $E_G$ increases, whatever the polymerization solvent. This demonstrates that the density of elastically effective chains (governing the mechanical properties) is essentially influenced by the macromonomer concentration. The higher the PEO concentration and the higher the concentration of polymerizable units, the higher the probability of reaction.

- For a given macromonomer concentration, it appears that $E_G$ increases with increasing macromonomer molar mass. This conclusion is in contradiction with observations generally made for gels prepared by end-linking under identical conditions.[18–20] However, one has to consider the fact that our PEO hydrogels were prepared in toluene. It is well established that PEO, and, especially long PEO chains, might crystallize in toluene whereupon additional cross-linking points may be formed.

As a consequence, the uniaxial modulus should increase. This prompted us to perfom a series of synthesis and characterization of PEO silsesquioxane networks in dioxane, a solvent in which crystallization of PEO chains does not take place, at least at room temperature. $E_G$ values measured in dioxane for networks prepared in dioxane are given in Table 3 (above) and the dependence of $E_G$ on molar mass is presented in Figure 1 below.

### PS Networks

The measured swelling ($Q_v$) and mechanical ($E_G$) properties of PS/silsesquioxane networks equilibrated in toluene and cyclohexane are plotted in Figures 2 and 3. Figure 2 (right) shows that the $Q_v$ values of the PS networks, swollen to equilibrium in toluene or cyclohexane, increase with increasing the molar mass of the macromonomer precursor chains, as expected. For a given precursor PS molar mass, $Q_v$, measured in both toluene and

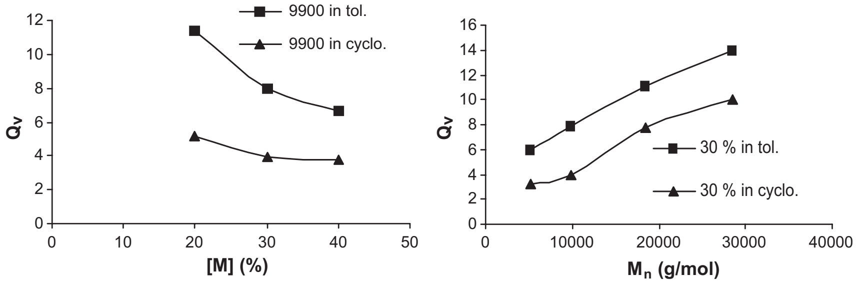


***Figure 2.***
Dependence of the volumetric degree of equilibrium swelling in toluene and cyclohexane of the PS networks, $Q_v$, on macromonomer concentration (left) and macromonomer molar mass (right).

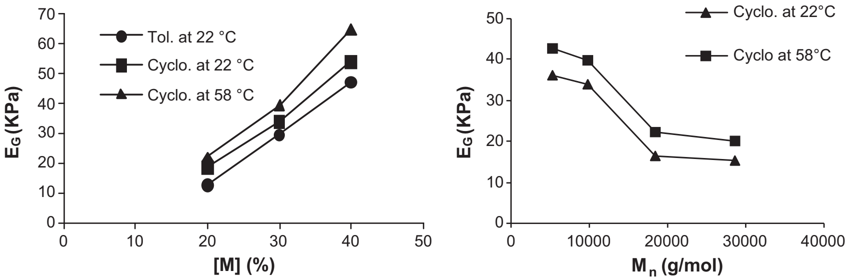


***Figure 3.***

Dependence of the uniaxial compression modulus $E_G$ of the PS networks on macromonomer concentration for a macromonomer precursor with $M_n = 9900\,g\,mol^{-1}$, and on molar mass for macromonomer concentration = 30 wt.- %.

cyclohexane, increases with decreasing macromonomer concentration (Figure 2, left). However, this increase is less pronounced for swelling in cyclohexane than in toluene, as the latter is a good solvent for PS, whereas the former is a theta solvent at 34.5 °C.

Figure 3 shows the dependence of the $E_G$ values of the PS networks on the concentration and molar mass of the PS precursor chains. When the molar mass of the PS chains rises from 5000 to 30000 $g\,mol^{-1}$, the $E_G$ values of the networks decrease, as expected (Figure 3, right). On the other hand, when the concentration of the macromonomer precursor increases, $E_G$ also increases (Figure 3, left). This demonstrates that the density of elastically effective chains is essentially influenced by the macromonomer concentration. Subsequently, we examined the influence of temperature on the gel properties at equilibrium swelling in cyclohexane. The values of $E_G$ measured at 58 °C are higher than those at 22 °C. This can be due to a structural rearrangement of the elastic chains of the PS networks in cyclohexane (Figure 3).

## Conclusion

PS and PEO networks could be obtained by coupling well-defined α,ω-diallyl PEO and α,ω-diundecenyl PS macromonomers, respectively, with octafunctional-silsesquioxanes via a hydrosilylation reaction. The influence of the molar mass and concentration of the precursor chains, the solvent, and the temperature, on the swelling and mechanical properties of both types of networks was thoroughly investigated and the results were discussed.

*Acknowledgements:* The authors thank C. Foussat, Y. Guilbert and A. Rameau for their skillful help with polymer characterization. They also acknowledge the CNRS and the French Ministry of Education for financial support.

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