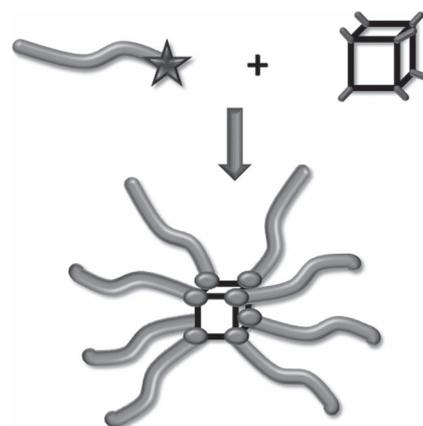


# Macromonomers as Well-Defined Building Blocks in the Synthesis of Hybrid Octafunctional Star-Shaped Poly(ethylene oxide)s

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The present work addresses the synthesis and the molecular and structural characterization of soluble macromolecular architectures based on functional poly(ethylene oxide) (PEO)s and octafunctional silsesquioxanes. The synthesis of a series of functional PEOs by deactivation, decorated with allyl groups at one chain-end, was considered first. PEO star-shaped polymers were prepared by coupling via hydrosilylation of  $\omega$ -allyl PEOs with octakis(hydridodimethylsiloxy)octasilsesquioxane ( $\text{HMe}_2\text{SiOSiO}_{1.5})_8$  ( $\text{Q}_8\text{M}_8^{\text{H}}$ ), in the presence of a “Speier” catalyst. The products were characterized by SEC,  $^1\text{H}$  NMR spectroscopy, light scattering, and MALDI–TOF MS to determine the molar masses and degree of functionalization. The star-shaped PEOs ( $\text{Q}_8\text{M}_8^{\text{PEO}}$ ) could be isolated from the raw reaction product and characterized. A functionalization close to the theoretical value was obtained.



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## 1. Introduction

Poly(ethylene oxide) (PEO) star-shaped polymers<sup>[1–3]</sup> are regarded as a particularly promising class of materials since they represent interesting models for physicochemical studies, variable building blocks for hydrogels,<sup>[4,5]</sup> or for amphiphilic networks that are of great interest for a wide range of biomedical and pharmaceutical applications. They can also serve as surface-modifying agents to improve the biocompatibility of surfaces designed for biomedical applications.<sup>[6,7]</sup> Several approaches based on the living anionic polymerization of oxirane have been developed to provide access to PEO stars covering a large range of molar masses and constituted of cores of different

chemical nature and functionalities.<sup>[1–3,8,9]</sup> Strategies based on the polymerization of well-defined monofunctional PEO macromonomers represent an interesting alternative to design PEO branched architectures.<sup>[10–12]</sup> Such polymers behave as branched or star-shaped polymers depending on the length of the backbone.<sup>[13,14]</sup> More recently, “click chemistry” was used in combination with controlled polymerization processes to enable access to PEO-based branched architectures.<sup>[15–18]</sup> The advantage of combinatorial chemistry was used to design a novel class of PEO-based branched amphiphilic materials with a unique potential of applications.<sup>[19]</sup>

Hybrid inorganic–organic materials, combining the behavior of organic polymers with physical properties of ceramics, have attracted increasing interest in recent years.<sup>[20–24]</sup> In the past two decades, polyoctahedral silsesquioxanes (POSS) constituted unique three dimensional nanometer-sized building blocks that can be used to create a large variety of hybrid macromolecular architectures.<sup>[23–26]</sup> Much interest has been devoted to hybrid materials based on POSS and PEO. PEOs, fitted at one chain with POSS<sup>[27]</sup> or star-shaped PEOs with a central octafunctional POSS core,<sup>[28]</sup> represent typical examples. Monosubstituted cube-shaped spherosilsesquioxanes with amphiphilic properties, combining the hydrophobic spherosilsesquioxane core with the hydrophilic oligo (ethylene oxide), were synthesized. Aggregation of the uncondensed amphiphile leads to micellar and vesicular structures.<sup>[27]</sup> Along the same line, new amphiphilic PEOs modified at the chain-ends with POSS entities<sup>[29]</sup> could be obtained and their dilute solution behavior examined. As mentioned above, octafunctionalized cubic silsesquioxanes were also used as nanosized reactive building blocks to yield PEO star-shaped polymers<sup>[28,30]</sup> or cross-linked PEO-based materials.<sup>[31]</sup> Star-shaped PEOs with silsesquioxane cores were established as an emerging class of new water-soluble materials characterized by enhanced thermal and thermomechanical stability, mechanical toughness, or optical transparency.<sup>[28]</sup> Their structural parameters and behavior were systematically investigated. However, most of the studies were limited to PEO chains of molar masses ( $\overline{M}_n$ ) of 2000 g mol<sup>-1</sup> or below. Therefore, the protection exerted by the PEO chain is not efficient and the solubility of the resulting star-shaped polymers poses problems. The main goal of the present work is to design new complex hybrid architectures based on PEO and to extend the domain of molar masses covered by the  $\omega$ -functional PEO precursors. The first part of the manuscript will be devoted to the synthesis and the

characterization of a series of  $\omega$ -allyl PEOs to be used in hydrosilylation reactions. The second part discusses the coupling of these  $\omega$ -allyl PEOs by hydrosilylation with octafunctionalized silsesquioxanes ( $Q_8M_8^H$ ) with the aim to access well-defined hybrid star-shaped PEO.

## 2. Experimental Section

The purification of the different products and the synthesis of  $\omega$ -allyl or  $\omega$ -undecenyl PEOs obtained by deactivation of the chain-end with allyl bromide or 11-bromo-1-undecene after modification with diphenylmethyl potassium (DPMK) as well as the synthesis of the octafunctional star-shaped poly(ethylene oxide)s ( $Q_8M_8^{PEO}$ ) from  $\omega$ -allyl PEOs via hydrosilylation with  $Q_8M_8^H$  in the presence of a “Speier” catalyst are discussed in Supporting Information (s.i.).

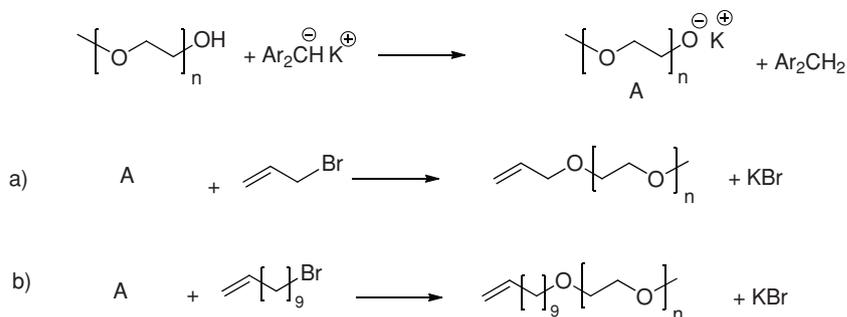
## 3. Results and Discussions

### 3.1. Synthesis of the PEO Macromonomers

A great variety of methods have been developed over the years to synthesize PEO macromonomers.<sup>[32–35]</sup> A detailed discussion of the different approaches to design PEO macromonomers is out of the scope of the present work. Briefly, two main approaches have been considered, either the initiator contains a polymerizable group, which is not affected by the polymerization reaction, or the living chain is capped with an electrophile containing a polymerizable group.

#### 3.1.1. $\omega$ -Allyl PEOs

In the present work, we selected an approach derived from the “chain-end functionalization” method to prepare the  $\omega$ -allyl PEOs starting from commercial PEOs after modification of the chain-ends with DPMK<sup>[36]</sup> followed by the addition of allyl bromide (Scheme 1a). The metalation can also be performed with potassium naphthalene.<sup>[27]</sup> This



**Scheme 1.** Schematical representation of the functionalization of  $\alpha$ -methoxy- $\omega$ -hydroxy PEOs with allyl bromide (a) or 11-bromo-1-undecene (b) after modification of the chain-end by reaction with a stoichiometric amount of DPMK.

**Table 1.** Molecular characteristics of the  $\omega$ -allyl PEOs obtained by deactivation with allyl bromide after modification of the chain-end with DPMK.

Reference	$\overline{M}_w^a)$ [g mol <sup>-1</sup> ]	$\overline{M}_n^b)$ [g mol <sup>-1</sup> ]	PDI <sup>c)</sup>	$\overline{M}_w^d)$ [g mol <sup>-1</sup> ]	$\overline{M}_n^e)$ [g mol <sup>-1</sup> ]	PDI <sup>f)</sup>	$f^g)$ [%]
PEOallyl1	1800	1750	1.03	1900	1800	1.05	92
PEOallyl2	1800	1750	1.03	1900	1800	1.05	93
PEOallyl3	1800	1750	1.03	1900	1800	1.05	93
PEOallyl4	5350	4900	1.09	5600	5100	1.10	95
PEOallyl5	11 100	10 000	1.11	11 300	10 200	1.11	96
EOallyl1*	–	–	–	9800	9050	1.08	96
EOallyl2	–	–	–	11 100	10 500	1.06	92
EOallyl3*	–	–	–	14 300	12 900	1.11	97

\*These sample were prepared by living anionic polymerization of ethylene oxide followed by direct deactivation of the alcoholate with allyl bromide as described in ref. [40]; <sup>a)</sup>Weight - average molar mass of the  $\alpha$ -methoxy- $\omega$ -hydroxy PEOs, measured by SEC, calibration with linear PEOs; <sup>b)</sup>Number - average molar mass of the  $\alpha$ -methoxy- $\omega$ -hydroxy PEOs, measured by SEC, calibration with linear PEOs; <sup>c)</sup>Poly dispersity index (PDI) of the  $\alpha$ -methoxy- $\omega$ -hydroxy PEOs ( $\overline{M}_w/\overline{M}_n$ ) determined by SEC; <sup>d)</sup>Number - average molar mass of the  $\omega$ -allyl PEOs, measured by SEC, calibration with linear PEOs; <sup>e)</sup>Weight - average molar mass of the  $\omega$ -allyl PEOs, measured by SEC, calibration with linear PEOs; <sup>f)</sup>PDI of the  $\omega$ -allyl PEOs ( $\overline{M}_w/\overline{M}_n$ ) determined by SEC; <sup>g)</sup>Yield of functionalization of the  $\omega$ -allyl PEOs measured by <sup>1</sup>H NMR (400 MHz) in CDCl<sub>3</sub> using an external standard (C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>); All the SEC measurements were conducted in THF ( $dn/dc_{PEO} = 0.062$  mL g<sup>-1</sup>).

procedure is preferable over the NaOH method because potassium initiators are much more efficient for the metalation and can be used at room temperature.<sup>[37]</sup>

PEO samples were obtained using DPMK for initiating the anionic polymerization of ethylene oxide, according to a well-established procedure,<sup>[38]</sup> followed by induced deactivation with allyl bromide. These syntheses are aimed to provide access to well-defined PEOs with molar masses higher than those of the commercial ones. The synthesis of such PEOs is also possible starting from allyl alcoholate as a initiator.<sup>[39]</sup>

After purification, the different reaction products were submitted to detailed characterization. It has to be established if every single molecule is modified with an end-standing double bond. The resulting functional PEOs were first characterized by size-exclusion chromatography (SEC) to verify the absence of the PEO precursor and of coupling products. Small PDI values, close to the precursor PEOs, were obtained by SEC (see Figure s.i.1, Supporting Information; and Table 1). In most cases the  $M_n$  values determined by SEC, and based on calibration with linear  $\alpha$ -hydro- $\omega$ -hydroxy PEOs, are in good agreement with the expected values. The slight increase in molar mass with respect to the PEO precursor is attributed to the presence of the unsaturation at one chain-end.

For the same samples, <sup>1</sup>H NMR measurements were performed in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>. A typical <sup>1</sup>H NMR spectrum measured in DMSO-*d*<sub>6</sub> is presented in Figure s.i.2 (Supporting Information). In addition to the signals of the methylene protons [CH<sub>2</sub> (4n - 2H),  $\delta = 3.65$  ppm, PEO chain except the first methylene group], the spectrum is

characterized by peaks assignable to the methoxy protons (initiator potassium methoxyethanolate). New peaks corresponding to the CH<sub>2</sub> = CH–protons appear (CH<sub>2</sub> = CH:  $\delta = 5.20$  ppm, CH<sub>2</sub> = CH:  $\delta = 5.90$  ppm) and the corresponding peak of the hydroxyl function (in the precursor polymer at 4.70 ppm) disappeared. By integrating the signals of the <sup>1</sup>H NMR spectra of the chain-end modified PEOs, the double bond content could be determined. The values are in good agreement with the expectation. The  $\overline{M}_n$  values of the  $\omega$ -allyl PEOs could also be obtained from <sup>1</sup>H NMR measurements and are close to the  $\overline{M}_n$  values measured by SEC. However, one has to be aware about the fact that, in particular for the 10 000 g mol<sup>-1</sup> molar mass sample, the accuracy of the determination of the functionality by <sup>1</sup>H NMR is questionable. This could be a possible explanation for the apparent lower functionalization yield in some cases.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI–TOF MS) has also been applied to analyze the different PEOs. Figure s.i.3a and 3b (Supporting Information) depict the MALDI–TOF MS spectra of an  $\omega$ -allyl PEO,  $\overline{M}_{n,SEC}$ , 1900 g mol<sup>-1</sup> and of its precursor, respectively. The signals between a *m/z* value of 1 772 and 1 816 with a characteristic shift of *m/z* 44 are unambiguously due to the PEO chain. The values calculated for the molar masses are in good agreement with the theoretical values. The difference in molar mass (of 40.18 g mol<sup>-1</sup>) corresponds exactly to the value of the allyl end group. Furthermore, no  $\alpha$ -methoxy- $\omega$ -hydroxy PEO is detectable. These different characterization results confirm that induced deactivation of metalated PEOs with allyl bromide indeed led to the expected  $\omega$ -allyl compound.

### 3.1.2. $\omega$ -Undecenyl PEO Macromonomers

$\omega$ -Undecenyl PEO macromonomers characterized by the presence of a hydrophobic spacer between the double bond and the PEO chain exhibit an enhanced amphiphilic character. They are therefore of great interest as versatile amphiphilic building blocks. The first attempt to synthesize  $\omega$ -undecenyl PEO macromonomers refers to an approach similar to that used for the synthesis of  $\omega$ -allyl functional PEOs (see also Scheme 1b and Supporting Information). This choice was motivated by the fact that these PEO macromonomers are fitted at one chain-end with a methoxy group (and not an OH function, which is always present at the chain-end of  $\alpha$ -undecene,  $\omega$ -hydroxy PEO macromonomers obtained by initiation). We must remember, that the main interests of these  $\omega$ -undecene PEO macromonomers lie in their use in coordination copolymerization with ethylene and, as well-defined build block, in the synthesis of star-shaped polymers by grafting via hydrosilylation onto POSS cores. In both cases, the OH function that is present at the PEO chain-end of macromonomers obtained by initiation may lead to side reactions. Two series of monofunctional PEO macromonomers were prepared with molar masses of 1750 and 4900 g mol<sup>-1</sup>, respectively. Their structural characteristics were determined by SEC, <sup>1</sup>H NMR spectroscopy, and MALDI-TOF MS to determine the molar masses and the degree of functionalization. The results are presented in Table 2 together with the experimental conditions.

It appears that for the PEO species prepared at room temperature, the functionalization yields are far from being quantitative. This is probably due to the occurrence of side reactions during the functionalization process. This

prompted us to perform a series of functionalization tests at lower temperatures. Decreasing the temperature from 25 to 10°C should limit the appearance of side reactions. It could be observed that the yield of functionalization is indeed higher, close to 65% for a PEO macromonomer with a molar mass of 4900 g mol<sup>-1</sup>. As PEO is well known to crystallize in THF at a temperature below 0°C, functionalization reactions at lower temperatures are not possible. It also seems that an increase in the molar mass of the PEO chain corresponds to an increase of the yield of functionalization. That can be explained by the increasing solvation effect of PEO chains as the molar mass increases. The characterization by MALDI-TOF MS confirms the presence of several distributions corresponding to the precursor polymer, the functionalized polymer, and side products (Figure 1).

Therefore, this approach should not be considered for the synthesis of well-functionalized PEO macromonomers decorated at one or at both chain-ends with undecene groups. Such polymers are, however, of significant interest for a wide range of applications. This stimulated the search for more efficient ways to design PEO macromonomers quantitatively fitted at least at one chain-end with undecene end groups (to be reported in a future manuscript).<sup>[40]</sup>

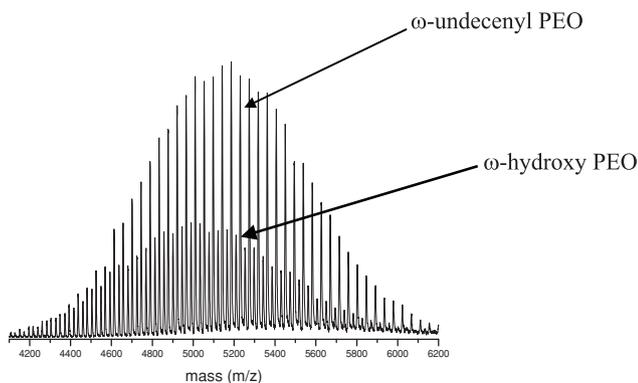
### 3.1.3. PEO Star-Shaped Polymers by Coupling of $\omega$ -allyl PEOs with Q<sub>8</sub>M<sub>8</sub><sup>H</sup>

As indicated in "Section 1," there is a growing interest for star-shaped PEOs. The present work proposes to study well-defined hybrid star-shaped PEOs, covering a much larger

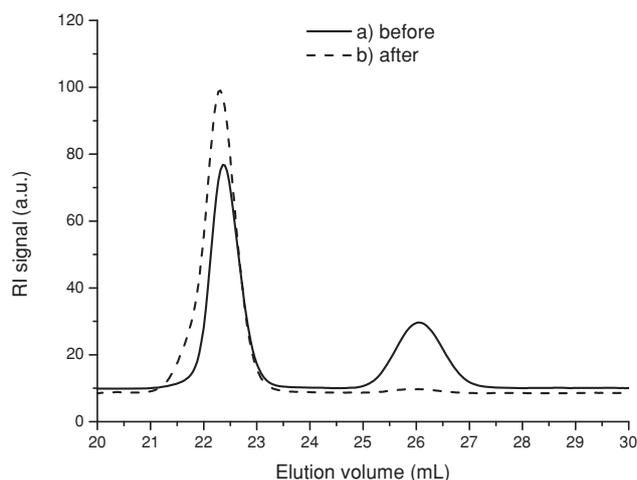
**Table 2.** Molecular characteristics of the  $\omega$ -undecenyl PEO macromonomers obtained by deactivation with 11-bromo-1-undecene after modification of the chain-end with DPMK.

Reference	$\bar{M}_w^a)$ [g mol <sup>-1</sup> ]	$\bar{M}_n^b)$ [g mol <sup>-1</sup> ]	PDI <sup>c)</sup>	$\bar{M}_w^d)$ [g mol <sup>-1</sup> ]	$\bar{M}_n^e)$ [g mol <sup>-1</sup> ]	PDI <sup>f)</sup>	Temp [°C]	$f^g)$ [%]
PEOund1	1800	1750	1.03	2000	1900	1.05	25	25
PEOund2	1800	1750	1.03	2000	1900	1.05	25	45
PEOund3**	1800	1750	1.03	1950	1900	1.03	25	48
PEOund4	5350	4900	1.09	5750	5050	1.14	25	38
PEOund5*	5350	4900	1.09	5050	4800	1.05	25	30
PEOund6**	5350	4900	1.09	5150	4900	1.05	25	45
PEOund7	5350	4900	1.09	5800	5100	1.13	13	65

These samples were prepared by deactivated with 11-bromo-1-undecene after modification of the chain-end with: \* Naphthalene Na or \*\* DPMNa; <sup>a)</sup>Weight - average molar mass of the  $\alpha$ -methoxy- $\omega$ -hydroxy PEOs, measured by SEC, calibration with linear PEOs; <sup>b)</sup>Number - average molar mass of the  $\alpha$ -methoxy- $\omega$ -hydroxy PEOs, measured by SEC, calibration with linear PEOs; <sup>c)</sup>PDI of the  $\alpha$ -methoxy- $\omega$ -hydroxy PEOs ( $\bar{M}_w/\bar{M}_n$ ) determined by SEC; <sup>d)</sup>Weight - average molar mass of the  $\omega$ -undecenyl PEO macromonomers, measured by SEC, calibration with linear PEOs; <sup>e)</sup>Number average molar mass of the  $\omega$ -undecenyl PEO macromonomers, measured by SEC, calibration with linear PEOs; <sup>f)</sup>PDI of the  $\omega$ -undecenyl PEO macromonomers ( $\bar{M}_w/\bar{M}_n$ ) determined by SEC; <sup>g)</sup>Yield of functionalization of the  $\omega$ -undecenyl PEO macromonomer measured by <sup>1</sup>H NMR (400 MHz) in CDCl<sub>3</sub> using an external standard (C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>); All the SEC measurements were conducted in THF ( $dn/dc_{PEO} = 0.062$  mL g<sup>-1</sup>).



**Figure 1.** MALDI-TOF MS of an  $\omega$ -undecenyl PEO macromonomer obtained by deactivation of the chain-end with 11-bromo-1-undecene after modification with DPMK.



**Figure 2.** SEC traces (RI detector) of  $Q_8M_8^{PEO}$ , (a) before fractionation and (b) after fractionation.

domain of molar masses than existing PEO/silsesquioxane star-shaped PEOs. The synthesis is based on the coupling via hydrosilylation of  $\omega$ -allyl functional PEOs with  $Q_8M_8^H$  fitted with 8 antagonist Si-H functions. The hydrosilylation was selected because this reaction is well known to provide a convenient route for the synthesis of functional materials.<sup>[41]</sup>

### 3.1.3.1. Preliminary Studies

It has been shown, that if an  $\omega$ -allyl PEO is reacted by hydrosilylation with  $Q_8M_8^H$ , chemical bonds are formed between the precursor chains and the silsesquioxane compound (Scheme 2).<sup>[28,42]</sup> The former becomes the branch and the latter the core of the star-shaped PEO named  $Q_8M_8^{PEO}$ .

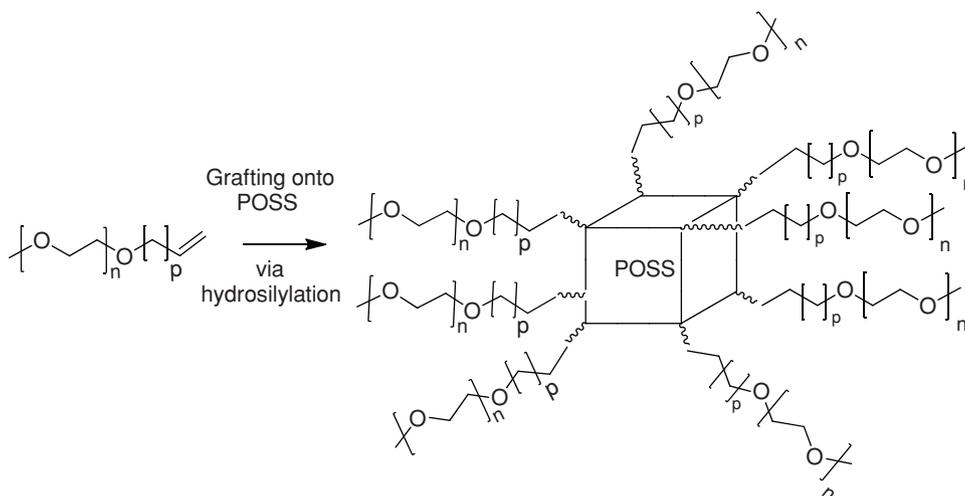
For these reactions, a platinum catalyst ( $H_2PtCl_6 \cdot 6H_2O / isoPrOH$ ) was selected whose efficiency

in hydrosilylation reactions is well established. This so-called “Speier” catalyst<sup>[43]</sup> is generally assumed to proceed by the Chalk-Harrod mechanism.<sup>[44]</sup> It is clear that side reactions cannot be entirely excluded.<sup>[37]</sup> Some attempts with the Karstedt catalyst are now under progress.<sup>[40]</sup>

A series of preliminary grafting experiments was carried out starting for  $\omega$ -allyl functional PEOs of molar masses ( $\bar{M}_n$ ) around 2000 and 5000  $g\ mol^{-1}$ , respectively, for a ratio with  $[ \omega\text{-allyl PEO} ] / [ Q_8M_8^H ]$  of 8 as described in Section 2 (see Supporting Information). The reaction was conducted at 75 °C for 15 h at a PEO concentration of 30 wt% and a platinum concentration of  $10^{-5}\ mol\ L^{-1}$ . The reaction products were characterized by three independent methods: SEC, IR, and  $^1H\ NMR$ . SEC with RI detection was used to evaluate the amount of PEO grafted onto the octafunctionalized silsesquioxane core. SEC with

multi-angle light scattering was used to determine the absolute molar mass of the reaction products. It has to be established whether or not all the  $\omega$ -allyl PEO chains have reacted with the antagonist functions of the octafunctionalized silsesquioxane core. A typical SEC trace is given in Figure 2a. This SEC reveals the presence of two peaks: a major one (attributed to the star-shaped PEO) and a second one corresponding to the unreacted  $\omega$ -allyl PEO.

In this experiment, an  $\omega$ -allyl PEO of an average



**Scheme 2.** Schematical representation of the synthesis of  $Q_8M_8^{PEO}$  stars by coupling via hydrosilylation monofunctional  $\omega$ -allyl ( $p = 1$ ) or  $\omega$ -undecenyl ( $p = 9$ ) PEO with  $Q_8M_8^H$  in the presence of a “Speier” catalyst.

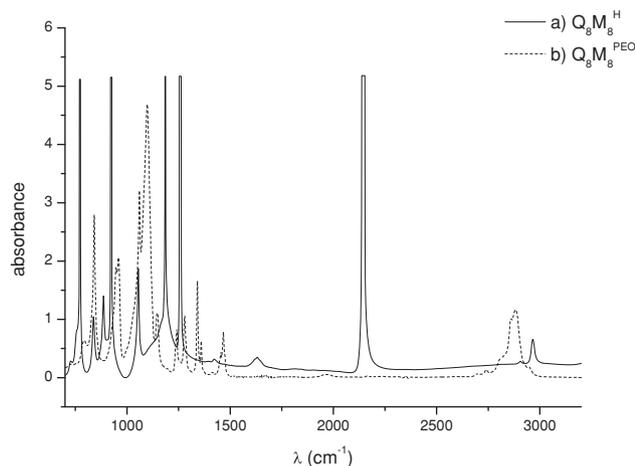


Figure 3. Infrared spectrum: (a)  $Q_8M_8^H$ , (b)  $Q_8M_8^{PEO}$ .

molar mass ( $\bar{M}_n$ ) of  $1900 \text{ g mol}^{-1}$  was selected. Considering a core functionalization value of 8, the number-average molar mass of the PEO star should be  $16\,200 \text{ g mol}^{-1}$ . Based on the calibration with linear PEOs, an apparent molar mass of  $11\,300 \text{ g mol}^{-1}$  is obtained for the former, which is lower than expected. 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. It appears for

the SEC results that the reaction product contains between 10 to 20 wt% of unreacted  $\omega$ -allyl PEOs. However, from the IR measurements made on the same samples (after the same reaction time), it can be concluded that most of the Si-H functions ( $2150 \text{ cm}^{-1}$ ) disappeared (Figure 3).

This result is in contradiction with the  $^1\text{H}$  NMR measurements, where the specific peak corresponding to unreacted Si-H (at 4.70 ppm) functions is still present in small amounts. A possible explanation for this phenomenon can be given by the characteristics of the IR-probe. Due to a self-absorbance of the diamond crystal in the Si-H region, the sensitivity of the measurements is significantly decreased.

### 3.1.3.2. Kinetic Studies of the Addition of the $\omega$ -allyl PEOs

This contradiction found in the studies mentioned above prompted us to investigate in more detail the grafting process with the help of  $^1\text{H}$  NMR spectroscopy to establish the influence of the  $[\omega\text{-allyl PEO}]/[Q_8M_8^H]$  ratio on the efficiency of the grafting process. We examined also the influence of the macromonomer and Pt concentration of the grafting yields for an  $[\omega\text{-allyl PEO}]/[Q_8M_8^H]$  ratio of 10. Initially, we performed a series of grafting experiments with different  $[\omega\text{-allyl PEOs}]/[Q_8M_8^H]$  ratios: 4, 8, and 10 at an  $\omega$ -allyl PEO concentration of 30 wt% and a platinum concentration of  $1 \times 10^{-5} \text{ mol L}^{-1}$ . The results of these studies are presented in Table 3.

Table 3. Molecular characteristics of the PEO star-shaped polymers obtained by grafting via hydrosilylation of  $\omega$ -allyl PEOs onto octafunctional silsesquioxanes ( $Q_8M_8^{PEO}$ ).

Reference	$\bar{M}_n^a)$ [g mol $^{-1}$ ]	$\bar{M}_{n,th}^b)$ [g mol $^{-1}$ ]	Macro $^c)$	$\bar{M}_{w,Star}^d)$ [g mol $^{-1}$ ]	$\bar{M}_{n,Star}^e)$ [g mol $^{-1}$ ]	PDI $^f)$	$\bar{M}_{w,Star}^g)$ [g mol $^{-1}$ ]	$f^h)$
SSPEO1	1900	16 200	22	13 600 $^i)$	12 400 $^i)$	1.08 $^i)$	17 000	–
SSPEO2 $^j)$	1900	16 200	23/25	13 500	12 500	1.08	17 000	8.9
SSPEO3 $^j)$	1900	16 200	18/4	12 200	11 300	1.08	–	–
SSPEO4	1900	16 200	22/3	13 400	12 300	1.09	15 500	8.2
SSPEO5	1900	16 200	29/3.7	12 900	11 800	1.09	–*	–
SSPEO6	1900	16 200	21/1	13 000	12 300	1.06	–	–
SSPEO7	4600	37 000	38/4	28 000	25 000	1.12	32 000	9.3
SSPEO8	4600	37 000	32	26 000	22 700	1.14	–**	–

Experimental conditions: solvent toluene, polymer concentration (30 wt%), Pt concentration:  $10^{-5} \text{ mol L}^{-1}$ , reaction temperature  $75 \text{ }^\circ\text{C}$ , reaction time 15 h; \*This sample is characterized by the presence in the raw samples of three peaks in RI detection (PEO macromonomer, the star-shaped PEO, and the coupling product corresponding probably to the reaction between Si-H groups of two stars). The main product could be isolated by repeated fractionation from raw reaction product; \*\*Fractionation of this sample was not efficient, this sample contained low concentrations of high molar mass PEO star resulting probably from coupling of two stars during the reaction (detected by SEC online light scattering);  $^a)$ Number - average molar mass of the  $\omega$ -allyl PEOs, measured by SEC, calibration with linear PEOs;  $^b)$ Number - average molecular mass of the PEO stars calculated taking into account the molar mass of the branch, the core and assuming a functionality of 8;  $^c)$ wt% of the residual PEOs in the raw reaction product/after purification;  $^d)$ Weight - average molar mass of the PEO stars, measured by SEC, calibration with linear PEOs;  $^e)$ Number - average molar mass of the PEO stars, measured by SEC, calibration with linear PEOs;  $^f)$ PDI determined by SEC in THF;  $^g)$ Weight - average molar mass determined by LS in methanol after fractional precipitation;  $^h)$ Functionality of the PEO star calculated from the ratio between the mass - average molar mass of the PEO star (measured by LS in methanol, after fractionation) and the molar mass of the precursor measured by SEC (RI);  $^i)$ Values determined on the raw sample by SEC based on calibration with linear PEOs;  $^j)$ These samples were purified by dialysis.

Samples SSPEO9 and SSPEO10 (not mentioned in Table 3) were prepared at an  $\omega$ -allyl PEO concentration of 15 wt% and a Pt concentration of  $2 \times 10^{-4}$  and  $1 \times 10^{-5}$  mol L $^{-1}$ , respectively. SEC studies performed with these samples revealed that the grafting reaction is not quantitative. The content of residual  $\omega$ -allyl PEO is higher than 60 wt%. The studies confirmed the influence of the polymer concentration in the reaction medium on the overall functionalization yield, already observed by other authors.<sup>[45,46]</sup> As a consequence, we decided to perform all the grafting reactions at much higher concentrations. These conditions were used to study the influence of the ratio  $[\omega\text{-allyl PEO}]/[\text{Q}_8\text{M}_8^{\text{H}}]$  on the grafting yield. The reaction products obtained in these reactions were systematically investigated by IR,  $^1\text{H}$  NMR, and SEC. It was found, that regardless the ratio  $[\omega\text{-allyl PEO}]/[\text{Q}_8\text{M}_8^{\text{H}}]$ , the characteristic peak at 2150 cm $^{-1}$  for the Si–H function disappeared (Figure 3). After reaction of the  $\omega$ -allyl PEO with the Si–H functions of  $\text{Q}_8\text{M}_8^{\text{H}}$ , the characteristic peaks of the double bond at 5.20 and 5.80 ppm disappeared as well

as the peak at 4.70 ppm, characteristic for the Si–H functions. The peak of the methyl group on the  $\text{Q}_8\text{M}_8^{\text{H}}$  entity at 0.25 ppm is shifted to higher fields (0.13 ppm). The  $^1\text{H}$  NMR spectra of the different reaction products are presented in Figure 4.

The peak associated to the Si–H functions is totally absent in the  $^1\text{H}$  NMR spectrum when the reaction is conducted with a ratio  $[\omega\text{-allyl PEO}]/[\text{Q}_8\text{M}_8^{\text{H}}]$  of 10 (Figure 4c). However, double bonds of  $\omega$ -allyl PEO could not be detected. This is not the case when the reaction is performed with a ratio of 8 (Figure 4b). The characteristic peak for the methyl group ( $\text{Si}(\text{CH}_3)_2$ ) is still present at 0.25 ppm, however, only in very small amounts. This peak is, as expected, more significant when the reaction is performed at a ratio  $[\omega\text{-allyl PEO}]/[\text{Q}_8\text{M}_8^{\text{H}}]$  of 4 (Figure 4a). From these results, it can be concluded that the NMR technique seems much more suited than FTIR to monitor the grafting reaction of  $\omega$ -allyl PEOs onto octafunctionalized silsesquioxane cores. These results led us to conduct all grafting reactions of  $\omega$ -allyl PEOs onto silsesquioxanes

with a molar ratio  $[\omega\text{-allyl PEO}]/[\text{Q}_8\text{M}_8^{\text{H}}]$  of at least 10. However, this implies that, even when all the Si–H functions have been coupled with the  $\omega$ -allyl PEOs, unreacted  $\omega$ -allyl PEO is still present in all grafting reaction products, which has to be removed from raw reaction products. The results of the reaction of a series of  $\omega$ -allyl PEOs, under the above-mentioned conditions, are reported in Table 3. A typical SEC trace of such a reaction product is given in Figure 2a. The efficiency of grafting was also evaluated by IR and  $^1\text{H}$  NMR. However, such measurements are of limited interest as they were performed on raw samples. Nevertheless, they can be helpful for preliminary experiments to define rapidly the optimal experimental conditions. The first major peak, present at a low elution volume, corresponds to the star-shaped PEO. The second peak, present in a small quantity at higher elution volume, corresponds to the  $\omega$ -allyl PEO, which was on purpose introduced in excess. Thus, the raw reaction product contains both the star-shaped PEO and the  $\omega$ -allyl PEO, which has to be removed. This is important as the presence of a linear PEO would affect the behavior of the star-shaped PEO. The above discussed results stimulated us to investigate different approaches to isolate the PEO star from the raw reaction

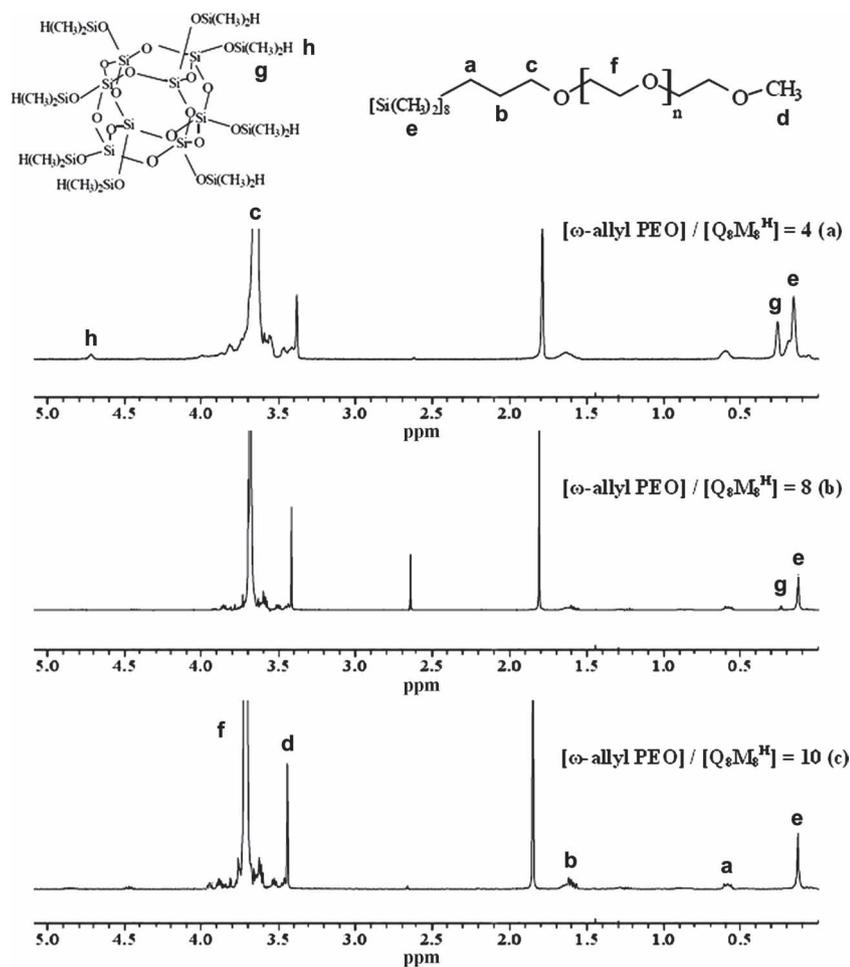


Figure 4.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ ) of the kinetics of the addition reaction of  $\omega$ -allyl PEOs onto  $\text{Q}_8\text{M}_8^{\text{H}}$  conducted at different  $[\omega\text{-allyl PEO}]/[\text{Q}_8\text{M}_8^{\text{H}}]$  ratios (4, 8, and 10).

product. Classical fractionation methods imply temperature manipulation. These methods revealed to be very efficient for the fractionation of noncrystalline polymers such as the isolation of cyclic polymers from raw reaction products.<sup>[47]</sup> However, it has been established that the fractionation of PEOs does not work if the  $\theta$  temperature is much below the crystalline melting point. However, advantage has been taken from the existence of a lower critical solution temperature (LCST) of PEOs to fractionate the raw products efficiently. It is also well known that the addition of salts lowers the LCST. By performing fractional precipitation in an aqueous solution of sodium carbonate, Merrill and co-workers<sup>[48]</sup> were able to isolate star-shaped PEOs obtained by the called “core-first” method,<sup>[49]</sup> characterized by bulky hydrophobic poly(divinylbenzene) “cores” from the raw reaction product. Some years ago, Gnanou and co-workers<sup>[50]</sup> prompted the development of the use of supercritical fluids for the fractionation of PEOs since this technique already constitutes an important method to fractionate broadly distributed polymers to quite narrowly distributed fractions. This procedure of fractionation proved to be particularly efficient compared with dialysis or SEC techniques. The first method takes much time and the latter provides access only to rather small amounts of fractionated PEO. Recently, Trimpin et al.<sup>[51]</sup> were able to achieve fractionation of mixtures of low molar mass PEOs (functionalized or not) using liquid adsorption chromatography at critical conditions combined with a MALDI-TOF MS characterization. Dialysis is known since many years as a possible separation method to remove undesired compounds from raw polymers in water by selective and passive diffusion through a semi-permeable membrane. This technique has been used successfully to remove unreacted homopolymers in block copolymers or PEO branches in star-shaped PEOs. We tested this approach to isolate our “POSS” stars from raw reaction product. The details concerning the fractionation are given in Supporting Information. As mentioned in that section, the main product, kept behind the membrane, was concentrated, recovered by precipitation, and characterized by SEC. From these measurements, it can be concluded that not all the  $\omega$ -allyl PEO could be removed even when the process was conducted over several weeks. The stability of the POSS/PEO stars in water over long periods may also be questionable. In some cases, we detected a shift of the reaction product peak toward higher elution volumes in the SEC curves after dialysis, that is, lower molar masses. A possible explanation may be the cleavage of the covalent bonds between the POSS core and the PEO chain in the presence of  $H_3O^+$ . This stimulated us to test other methods to isolate the star-shaped PEO from the raw reaction product. Although the efficiency of classical fractionation methods based on solvent/nonsolvent methods is questionable, we submitted our raw samples to

fractionation using toluene as a solvent and cyclohexane as precipitant as described in “Section 2” (see Supporting Information). Each fraction was allowed to settle for at least 24 h to provide adequate sedimentation of the precipitate. The samples were characterized independently by SEC (and online LS) to investigate the efficiency of the fractionation and grafting process and by IR and  $^1H$  NMR to verify the absence of Si-H functions. The successful isolation of the star-shaped PEO by fractional precipitation from the crude mixture was confirmed by SEC analysis. The efficiency of the fractionation procedure is illustrated in Figure 2a and b. The amount of “ungrafted”  $\omega$ -allyl PEO is vanishingly small. However, the star-shaped nature of the polymer characterized by a low elution volume has to be established, and its functionality determined. As star-shaped PEOs are known to exhibit a more compact structure in solution than the linear equivalent of the same absolute molar mass, the apparent molar mass values we obtained by SEC based on calibration with linear PEO are underestimated (Table 3). As a consequence, attempts were made to access the absolute molar masses of the PEO stars by SEC with online light scattering. These measurements showed significantly higher values than those obtained by SEC with RI detection. However, in most cases, they were much higher than the calculated values under the assumption of 8 chains grafted onto one silsesquioxane core. A possible explanation for this may be the formation of aggregates or covalent coupling reactions between two PEO star-shaped molecules due to the presence of unreacted Si-H functions. To overcome these problems, ethylene can be added at the end of the grafting reaction to transform the remaining unreacted Si-H functions into short alkanes following a procedure described in a previous publication.<sup>[27]</sup> Therefore, we did not pursue the studies on the molar determination of the PEO stars by SEC with online light scattering. The determination of the mass-average molar mass of PEO stars by classical light-scattering in methanol<sup>[52]</sup> revealed to be much more efficient to access the absolute molar mass of the PEO stars with a silsesquioxane core (Figure 5).

Selected values are provided in Table 3. In principle, the average number of branches of a star-shaped polymer is obtained from the ratio of the absolute weight-average molar mass, determined by light scattering, to the molar mass of the branch. It can be concluded from the data presented on Table 3 that, in most cases, the value of the functionality ( $f$ ) is close to its theoretical one, taking into account the limits of characterization techniques. The efficiency of the grafting of the  $\omega$ -allyl PEOs on the silsesquioxane cores was also verified by IR and  $^1H$  NMR spectroscopy. The intense peak of Si-H group at  $2150\text{ cm}^{-1}$  completely disappeared in the spectrum of the star. The  $^1H$  NMR spectrum shows the absence of the characteristic peaks for the double bond of the  $\omega$ -allyl PEO

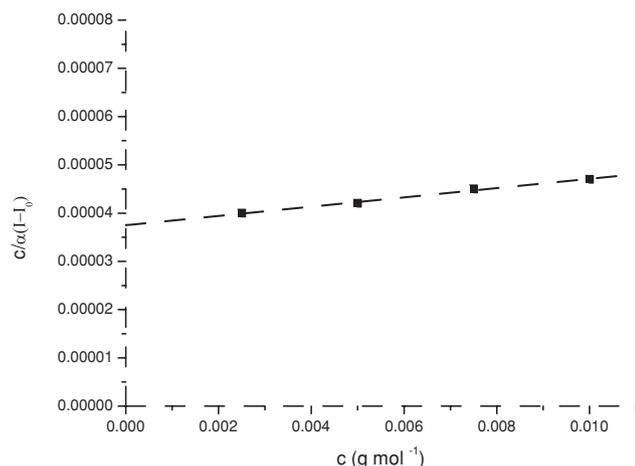


Figure 5. Light-scattering data of  $Q_8M_8^{PEO}$  measured in methanol.

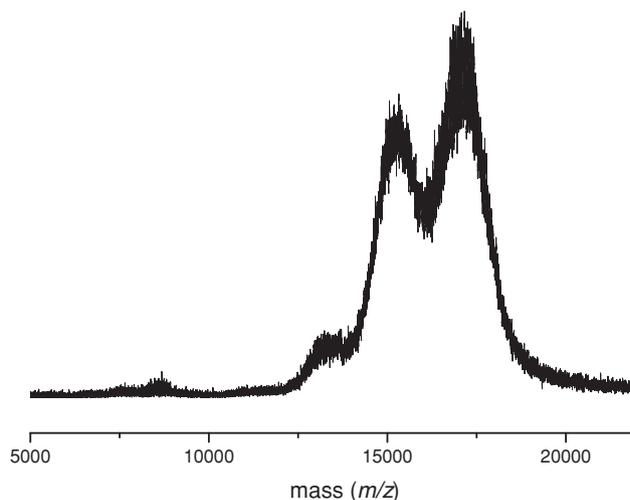


Figure 6. MALDI-TOF MS of  $Q_8M_8^{PEO}$ .

(peak at 5.80 and 5.20 ppm), which confirms the grafting onto the cage. In addition, the peak of the Si-H function (at 4.70 ppm) disappeared from the  $^1H$  NMR spectrum.  $^1H$  NMR spectroscopy was also used to determine the number of PEO chains attached to  $Q_8M_8^H$  average value of the functionality. By considering the ratio between the integrals of the peak of the methyl group at 0.13 ppm ( $Si(CH_3)_2$ ) (on the core) and the methylene group at 0.56 ppm ( $Si-CH_2-CH_2$ ) (originating from the  $\omega$ -allyl PEO), a functionality value close to 8 was calculated. In the first part of the present work, we have demonstrated the effectiveness of MALDI-TOF MS techniques to determine the molar mass and the functionality of  $\omega$ -allyl PEOs. MALDI-TOF MS was also used for the detailed investigation of the star-shaped PEO on both the raw sample (characterized by residual  $\omega$ -allyl PEO) and the star-shaped PEO after purification. Only few investigations were made on the determination of structural parameters of branched PEOs by that technique. The works on dendrimer-like PEOs<sup>[53]</sup> and Janus-Type dendrimer-like PEOs<sup>[54]</sup> constitute nice examples. More recently, Doycheva et al.<sup>[55]</sup> reported a detailed characterization by MALDI-TOF MS of PEO multiarm star-shaped polymers with a purely polyether structure. These samples were obtained by the so-called “core-first” method<sup>[1]</sup> using a hyperbranched polyglycerol-modified core as a multifunctional initiator for the anionic ring-opening polymerization of oxirane.<sup>[2]</sup> These MALDI-TOF MS measurements confirmed the performance of that technique to determine the molecular and structural characteristics of star-shaped PEOs. As a consequence, a detailed investigation by MALDI-TOF MS on sample SSPOE4 was performed on the raw grafting product and the purified one. The MALDI-TOF MS spectrum of the “pure” PEO star is presented in Figure 6.

These MALDI-TOF MS measurements corroborate the results obtained by SEC,  $^1H$  NMR analysis, and light-scattering measurements. As expected, the raw sample (not presented) is characterized by the presence of two peaks: a first one present at a  $m/z$  value of 2049 with a peak-to-peak mass increment of 44 (calculated 44.053 corresponding to the molar mass of one EO unit) and another peak of  $m/z$  value of 17 217 (with a shoulder at a maximum of 15 447). By taking into account the molar mass of the methoxy group and of the chain end (allyl-end group), the distribution of chains reflected in the MALDI-TOF MS spectrum could be perfectly assigned. The first peak appeared at  $m/z$   $(44.053n + 31.034(CH_3O) + 41.072(CH_2CHCH_2) + 22.990(Na))$  (where  $n$  is the degree of polymerization) and is attributed to the  $\omega$ -allyl PEO. The major peak corresponds to the star-shaped PEO with a molar mass value close to the value measured by light scattering in methanol, taking into account the accuracy of experimental techniques. This peak is characterized by a shoulder ( $m/z = 15 447$ ). This peak is related to a star-shaped PEO with only seven PEO branches. However, it is unclear whether this seven-armed PEO has been formed during the synthesis or results from a cleavage of the octafunctionalized star-shaped PEO. It is worth to note that the  $\omega$ -allyl PEO peak is absent in the purified product. This was already observed by SEC on the same sample. The peak corresponding to the star-shaped PEOs, in the purified grafting product, looks quite similar to the one observed for the raw product.

#### 4. Conclusion

The reaction of well-defined  $\omega$ -allyl PEOs via hydrosilylation with octakis(hydrido-dimethylsiloxy)octasilsesquioxane has been investigated in detail. This reaction was used

successfully for the synthesis of PEO star-shaped polymers, and the functional PEO precursors and the star-shaped samples were characterized accurately. They have been shown to exhibit, after fractional precipitation (for the star-shaped species), rather well-defined structures. The molar distribution is unimodal and quite narrow. The molar mass calculated under the assumption of a functionality of 8 for the core is close to the experimental value measured by light scattering in methanol. Hybrid PEO star-shaped polymers characterized by branches of molar masses up to 10 000 g mol<sup>-1</sup> could be obtained. The thermal properties of these hybrid PEO stars are currently under investigation using differential scanning calorimetry (DSC). Precise measurements concerning the dependence of the crystal structure (SAXS, WAXS) on the arm length as well as the nature of the core will also be made in the future. Further studies are now under progress to extend the hydrosilylation reaction to  $\omega$ -undecenyl PEO macromonomers. The synthesis of such macromonomers via chain-end modification of  $\omega$ -methoxy PEOs poses, however, some problems. The different approaches to design such well-defined  $\omega$ -undecenyl PEO macromonomers, based either on PEO chain-end modification or on living anionic polymerization of ethylene oxide, in the presence of the appropriate heterofunctional initiator will be presented and discussed in a forthcoming publication.<sup>[40]</sup>

## Supporting Information

Supporting Information is available from the Wiley online Library or from the author.

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