Synthesis of new types of polysiloxane based surfactants

Josef Bauer, Nicola Hüsing and Guido Kickelbick*

*Institut für Anorganische Chemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria.
E-mail: kickelgu@mail.zserv.tuwien.ac.at*

New types of amphiphilic polysiloxane diblock copolymers containing a pure polysiloxane backbone were prepared by the functionalization of poly(dimethylsiloxane)-*block*-poly-(methylvinylsiloxane) copolymers, synthesized by 'living' anionic ring opening polymerisation of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^v) and hexamethyl-cyclotrisiloxane (D_3).

Amphiphilic block copolymers find widespread technological applications especially as non-ionic polymeric surfactants. The coexistence of the dissimilar segments, which show a different solubility in a specific solvent, produces unique properties because of their ability to self-organize at interfaces and in solution and thus modify interfacial properties and enhance compatibility or separation.[1] Typically, purely organic back-bones are found in this type of surfactant, nevertheless inorganic polymer segments, especially polysiloxanes show properties that are advantageous, such as biocompatibility, robustness, flexibility *etc.*[2] Although polysiloxanes have superior proper-ties compared to common organic polymers their controlled formation as block copolymers is nearly unexplored.

In recent years the interest in amphiphilic block copolymers has grown especially due to their surface activity and their lyotropic behaviour.[3] Amphiphilic block copolymers with a hydrophobic polysiloxane part are predominantly known in combination with organic hydrophilic blocks such as poly(eth-ylene oxide) or polymethacrylates.[4] As far as we know there is only one example in literature citing a block copolymer with a pure polysiloxane backbone bearing carboxyl groups pendant to the polysiloxane chain.[5]

In this paper we present the formation and post-functionaliza-tion of block copolymers of poly(dimethylsiloxane) (PDMS) and poly(methylvinylsiloxane) by 'living' anionic ring opening polymerisation.

Valuable precursors for a post-functionalization are silane-bonded vinyl groups. For the preparation of a vinyl-function-alized block *via* anionic ring opening polymerisation a cyclic monomer with a sufficient reactivity is needed. The only commercially available monomer that fulfils this demand is 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^v). D_4^v did not show satisfactorily polymerisation initiated by butyllithium with the usual donor solvents (THF, DMF, DMSO, HMPA). Therefore another initiator with a higher basicity, *i.e.* trimethylsilylmethyllithium, $(CH_3)_3SiCH_2Li$, was used to trans-form the carbanionic acids into the silanolate species.[6] Usually polymerisations of unstrained cyclic siloxanes, such as cyclo-tetrasiloxanes or larger rings, are more difficult due to the presence of intra- and intermolecular reactions of the active ends leading to an equilibrium reaction between the ring, an oligomeric, and a polymeric species. It was shown that the equilibrium is shifted to the polymeric species if additives able to separate the ion pair between the oxidic end group and the lithium ion are added to the reaction solution. Typical additives are ethylenediamine, diglyme, cryptands and crown ethers like 12-crown-4.[7]

Block copolymers from 'living' ring opening polymer-isations are obtained by using a polymer as macroinitiator and extending it with a second monomer. For the PDMS-*block*-poly(methylvinylsiloxane) we observed that the extension of a

PDMS chain with poly(methylvinylsiloxane) only leads to the addition of up to five monomeric units until the final equilibrium between polymeric and ring species is reached, while the polymerisation of D_4^v first allows for a much better control of the equilibrium. Therefore, the polymerisation of vinylmethylcyclotetrasiloxane was initiated with trimethylsilyl-methyllithium in a first step and the chain was extended by PDMS in a second step[8] (Scheme 1). With this procedure block copolymers with polydispersities around 1.40 and block lengths up to 10.000 with varying poly(methylvinylsiloxane) content were obtained (Table 1).

The resulting block copolymers have purely hydrophobic properties but the vinyl groups can easily be transformed into a variety of other functional groups. The double bonds of the methylvinylsiloxane blocks were modified either by hydro-silation[9] or by epoxidation.[10] In the latter case further modification reactions of the polyepoxide block were carried out[11] (Scheme 2).

The hydrosilation of the double bonds with Karstedt's catalyst at 70 °C worked quantitatively as confirmed by the disappearance of the vinylic protons in ^{1}H NMR. $HSi(OEt)_3$, $HSi(OMe)_3$ and $HSi(CH_3)_2Cl$ were used for this reaction to obtain a functionalized polysiloxane block. While the trialk-oxysilane groups can be hydrolysed and used for cross-linking reactions, the chlorosilanes are able to react with a variety of nucleophiles, like alcohols, carboxylic acids, *etc.*
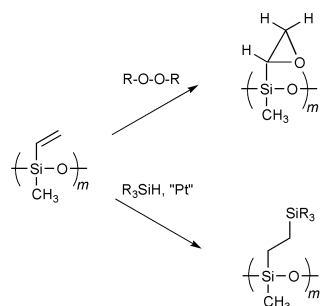
Another possibility of the double bond functionalization is the epoxidation[12] followed by the subsequent ring opening of the oxirane ring. The epoxide was quantitatively formed by a selective oxidation of the double bonds with *m*-chloroperoxy-benzoic acid (MCPBA) in methylene chloride or toluene proved by ^{1}H NMR. SEC measurements of the epoxidised samples showed that only a small amount ($< 4\%$) of high molecular weight (cross-linked) polymer was formed. The cross-linking was almost quantitatively suppressed by working in high dilutions.[13] The obtained epoxide was opened with different mono- or difunctional nucleophiles, such as hydroxide ions, diamines, diols, dicarboxylic acids, hydroxy-functionalized ethers and carboxylic acid chlorides (Scheme 3). These reactions resulted in the formation of a hydroxide group at one carbon atom and the coupling product with the nucleophile at
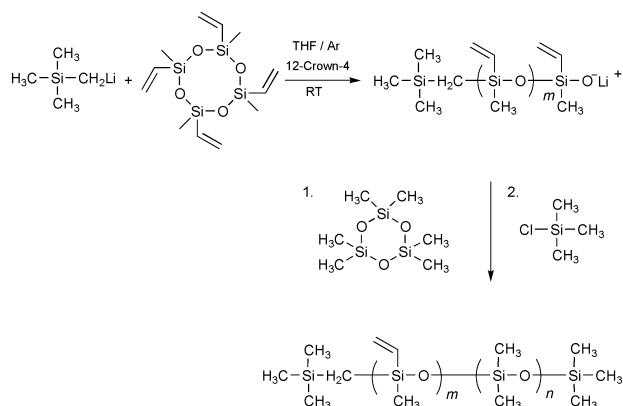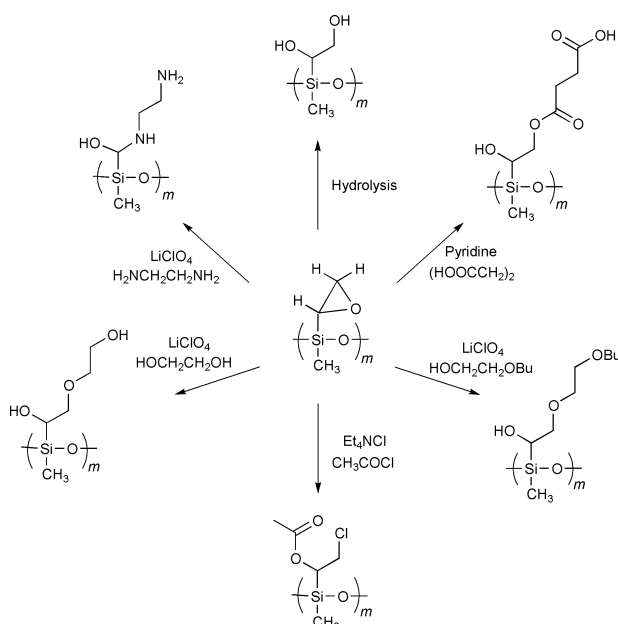

Scheme 1

Table 1 Selected data of typical PD$_4^v$-*b*-PD$_3$ block copolymers prepared

Sample	M_n (M_w/M_n) (PD$_4^v$-block)	m	n	M_n (M_w/M_n) (PD$_4^v$-PD$_3$-diblock)	Ratio by ^{1}H NMR (PD$_4^v$/PD$_3$)	Ratio by SEC (PD$_4^v$/PD$_3$)
1	2840 (1.36)	33	96	9940 (1.46)	0.38	0.40
2	1900 (1.36)	22	22	3520 (1.38)	0.86	0.85
3	1730 (1.21)	20	82	7840 (1.36)	0.25	0.28
4	1480 (1.14)	17	50	5190 (1.31)	0.35	0.40

Scheme 2

the other. Modification of the epoxide block by reaction with amines or alcohols was catalysed by LiClO$_4$. Nucleophilic attack of the epoxide by the nucleophile on the more hindered carbon atom (SiCH=CH$_2$) was not observed in ^{1}H NMR spectra which indicates an almost quantitative attack on the terminal methylene carbon atom. In the case of modification with oxalic acid the reaction was performed in *N,N'*-dimethylformamide to dissolve the reactant and additionally catalysed by pyridine. Hydrolysis of the epoxidised block copolymers leads to the corresponding 1,2-diol side groups and may either be acid- or base-catalysed. Epoxide opening worked quantitatively, which was proved by ^{1}H NMR (disappearance of the signals of the epoxide protons at 2.2, 2.7 and 2.9 ppm). The processing parameters of the ring opening reactions allow for the preparation of different materials. High dilution of the block copolymers in the solvent during the ring opening leads to linear polymers while cross-linked hydrogels are formed in low dilution. To completely suppress cross-linking reactions using multifunctional nucleophiles a large excess of reactants is necessary and harsh purification conditions should be avoided. For a total prevention of cross-linking reactions it is advisable to use monofunctional protected ring opening agents and remove

the protecting groups afterwards. Additional advantages of this procedure are simpler purification and analyses. In those cases in which hydroxy groups are formed during the ring opening or other functionalities are present, no elution in the SEC experiments was obtained due to interaction with the column material. This was avoided by protection of the free functional groups.

In summary new methylvinyl-substituted polysiloxane diblock copolymers were prepared by 'living' anionic ring opening polymerisation. The vinyl group was used for a further functionalization to obtain silicon alkoxide substituted or amphiphilic block copolymers with a variety of functional groups.

Scheme 3

Notes and references

1 P. Alexandridis, U. Olsson and B. Lindeman, *Langmuir*, 1998, **14**, 2627.
2 P. R. Dvornic and R. W. Lenz, *High temperature siloxane elastomers*, ed. P. Dvornic and R. W. Lenz, Hüthig & Wepf, Verlag, 1990.
3 S. Förster and M. Antonietti, *Adv. Mater.*, 1998, **3**, 195.
4 H.-W. Haesslin, *Makromol. Chem.*, 1985, **186**, 357.
5 M. Scibiorek, N. K. Gladkova and J. Chojnowski, *Polymer Bulletin*, 2000, **44**, 377.
6 R. P. Quirk and D. E. Kester, *J. Organomet. Chem.*, 1977, **127**, 111.
7 J. Chojnowki, K. Ròzga, W. Foruniak and A. Kowalewska, *Makromol. Chem., Makromol. Symp.*, 1993, **67**, 183.
8 Typical procedure: to a solution of D$_4^v$ in THF (CH$_3$)$_3$SiCH$_2$Li was added. The amount of the lithium compound was chosen depending on the target molecular weight of the poly(methylvinylsiloxane)

$$[I] = \frac{[M]_0}{DP}$$ ([*I*] = initiator concentration; [*M*]$_0$ = monomer

concentration; *DP* = degree of polymerisation). After stirring the solution at rt for 1 h 12-crown-4 was added. Propagation progress was determined during the polymerisation by taking samples, quenching the reaction with chlorotrimethylsilane at various reaction times and determining the molecular weights by size exclusion chromatography (SEC) analyses. By adding D$_3$ to the 'living' polymer the PDMS-blocks were formed. The diblock copolymers were quenched by chloro-trimethylsilane and analysed by SEC and NMR measurements. SEC was performed using a Waters 717 autosampler, 515 HPLC pump, 2410 RI detector and Styragel columns in THF at 40 °C at a rate of 1 ml min^{-1} applying linear polystyrene standards. The DP of each block was calculated by the SEC results of homopolymer and diblock copolymer and compared with the results of the composition determined by ^{1}H NMR. ^{29}Si NMR analyses allowed the determination of the sequence distribution of repeat units, which showed no random copolymerization of D$_4^v$ and D$_3$.
9 Y. Chang, Y. C. Kwon, S. C. Lee and C. Kim, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, 1999, **40**, 269.
10 F. Macchia, P. Crotti and M. Chini, *Tetrahedron Lett.*, 1990, **31**, 4661.
11 A. Hassner, in *Small Ring Heterocycles*, ed. A. Weissberger and E. C. Taylor, John Wiley & Sons, New York, 1976.
12 General procedure: MCPBA was dissolved in toluene and dried over Na$_2$SO$_4$. Depending on the block length of the poly D$_4^v$ block, a calculated amount of the solution was added to the block copolymer. The resulting mixture was stirred overnight at rt. The organic layer was extracted with an aqueous sodium bicarbonate solution and deionised water several times. The organic layers were collected and dried over Na$_2$SO$_4$. Afterwards the solution was filtered and evaporated.
13 K. Udipi, *J. Appl. Polym. Sci.*, 1979, **23**, 3301.