Functional Silicones and Silicone-Containing Block Copolymers

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Motivation

Silicones or polysiloxanes are certainly one of the most interesting classes of polymers. They are of remarkable significance both in academical and industrial research since decades, and the areas in which silicones find application are exceptionally manifold. Silicones are used in such different field as electronics and personal care products, structural engineering and textiles or medicine and sports equipment. Nevertheless, current research keeps developing new silicone inventions that aim towards novel kinds of silicone applications, most of them concerning products that demand high tech performance.

Silicones divide themselves from all other kinds of polymers through a set of unique properties. They show extremely high dynamic and equilibrium flexibility, which leads to outstanding surface properties and the lowest glass transition temperatures of all polymers. The fact that silicones retain their flexibility over a broad temperature range makes them especially advantageous with regard to low temperature devices. They are also remarkably stable towards high temperature, oxidation and reduction. Moreover, silicones are predestined for biomedical applications because they are bioinert, transparent and highly permeable for oxygen.

However, because of the fact that silicones are so different and unique in their features, the study of their properties and, more importantly, the molecular cause for the same is still ongoing. Most of the known concepts of polymer chemistry that have been developed for other hydrocarbon-based polymers usually cannot be applied to silicones, which makes the properties of new silicone-based materials unpredictable to a certain extent.

Despite a large number of benefical properties, silicones suffer from some major drawbacks that limit their application. The most significant factor in this context is their strong hydrophobicity. Wettability is a crucial point for some applications, especially those regarding biomedical devices. As contact with water is essential for a material to be compatible with biological systems, enhancing the hydrophilicity of silicones and silicone-based materials is one of the dominating subjects of polysiloxane-related research nowadays.

In order to obtain silicone-based materials in a well-defined fashion, the modification of polysiloxanes by covalent addition of other polymers or smaller molecules that provide different, even contradictory features compared to silicones, is the method of choice.

The objective of this thesis is to combine polysiloxanes with different polymeric structures in the form of graft or block copolymers to obtain materials that consist of a new combination of beneficial features. Two major ways are followed to reach this goal.

Polysiloxanes can be synthesized and subsequently modified (i) by the attachment of small molecules that change the properties of the silicone in such a way that it becomes more hydrophilic, but under the premise that this does not go together with a loss of the silicone-specific features. This can be done by adding hydrophilic sidechains to a polysiloxane. Polyethers like poly(ethylene glycol) or hyperbranched polyether-polyols are suitable in this regard. In order to assure that the silicone properties retain, these side groups can be attached to only one part of the polysiloxane backbone, which results in a block copolymer that consists of a common polysiloxane and a second block of the modified structure. (ii) Polysiloxanes can be equipped with functional groups that are capable of initializing polymerization of a different monomer (macroinitiator approach). For example, hydroxyl groups are used to initiate the ring opening polymerization of cyclic esters, or ATRP macroinitiators can be synthesized to add a second block via controlled radical polymerization. Stimuli responsive polymers like poly(oligoethylene glycol methacrylate) (POEGMA) can be added via this route to create “smart” siloxane-containing block copolymers that respond to certain stimuli.

An important premise for all synthetic routes is to achieve the targeted structure in a process as simple as possible, because facile availability of the material is crucial with regard to industrial applicability of the invented products.

Concerning characterization of the synthesized macromolecules, emphasis is put on their (temperature dependent) aggregation behavior, which can be investigated by several microscopic and scattering methods, their behavior at the interface between silicone oils and water and their thermal properties.

Abstract

In **Chapter 2.1.** of this thesis a new type of hydrophilic silicones was synthesized in a remarkably easy way via a “grafting-to”-approach. Starting from different Si-H-functionalized polydimethylsiloxanes, silicones with hydrophilic grafts or amphiphilic ABA-triblock copolymers were obtained using hydrosilylation chemistry to connect the hydrophilic structure to the silicone. The hydrophilic parts of the polymer consist of either glycerol side-chains or hyperbranched polyglycerol units. Therefore, this sidechains contain at least two and (more likely) up to about 13 hydroxyl groups. Polymers were characterized by ^{1}H- and ^{29}Si-NMR- as well as IR-spectroscopy. Glass transition temperatures and solubility of the polymers were analyzed and found to be in linear correlation to their hydrophilicity. This parameters can be readily tuned by variation of the number of Si-H bonds in the poly(dimethylsiloxane)-co-poly(methylhydrosiloxane)-copolymers and the character of the sidechain.

Chapter 2.2. presents a facile approach towards the synthesis of a new type of block copolymer with a backbone that solely consists of silicon-oxygen bonds was developed. The overall silicone-based block copolymers are built up of a nonfunctional, hydrophobic block of poly(dimethylsiloxane) (PDMS) and a second block of variable functionality. Their synthesis involves only two steps. Starting with the ring-opening polymerization of hexamethylcyclotrisiloxane (D3) to form the PDMS, a second functionalizable block is added by subsequently adding tertamethyl-teravinylcyclotetrasiloxane ($D4^{V}$) to the living polymerization. Polymers of different molecular weights between 4000 and 9000 g/mol and different block length ratios were obtained with narrow polydispersities. In the second reaction step, various functional molecules that carry a silicon-hydride bond can be attached to the methyvinylsiloxane block by hydrosilylation. The well-defined products were characterized by ^{1}H and ^{29}Si NMR spectroscopy, DOSY NMR analysis and SEC.

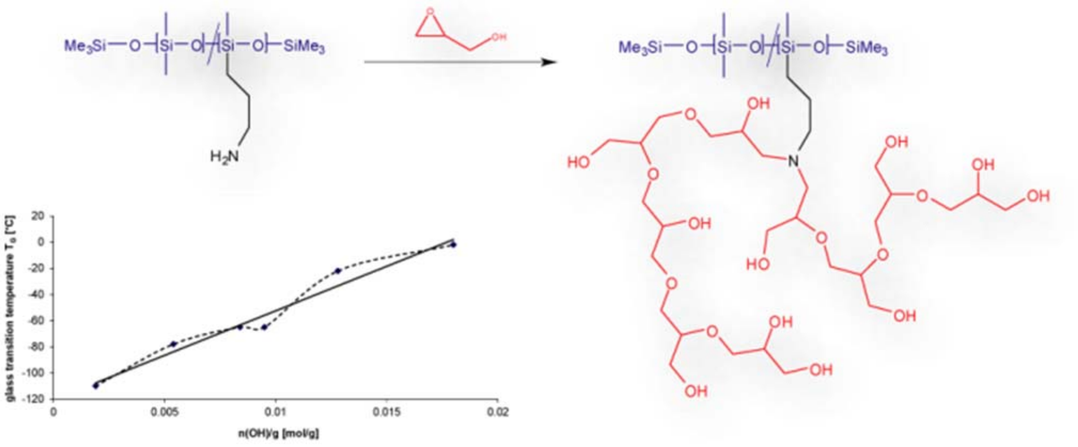
In **Chapter 2.3.**, AB- and ABA-type block copolymers consisting of poly(dimethylsiloxane) and poly(lactide) segments have been developed. The synthesis was carried out using hydroxyl end-functionalized poly(dimethylsiloxane)s, prepared via anionic or cationic ring-opening polymerization (ROP), as a macroinitiator for the ring-opening polymerization of the dilactide. Block-length ratios were calculated from ^{1}H NMR and were in the range of 1:9 to 9:1 (PDMS:PLLA) and molecular weights between 1.000 and 36.000 g/mol were synthesized,

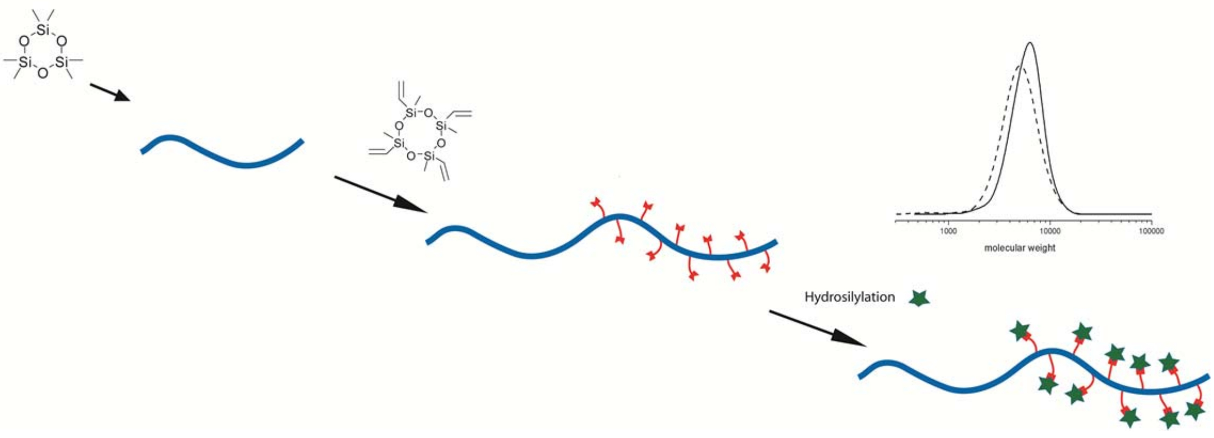
obtaining PDIs of 1.2 to 1.3. Thermal properties were analyzed by DSC measurements and the bulk structure and surface morphology of the different polymers was investigated by use of AFM and TEM analysis. Both PLLA- and PDLA-based block copolymers have been prepared and were demonstrated to form stereocomplexes. Materials derived from stereocomplexation of the poly(lactide) blocks offer potential for application in the field of thermoplastic silicone elastomers.

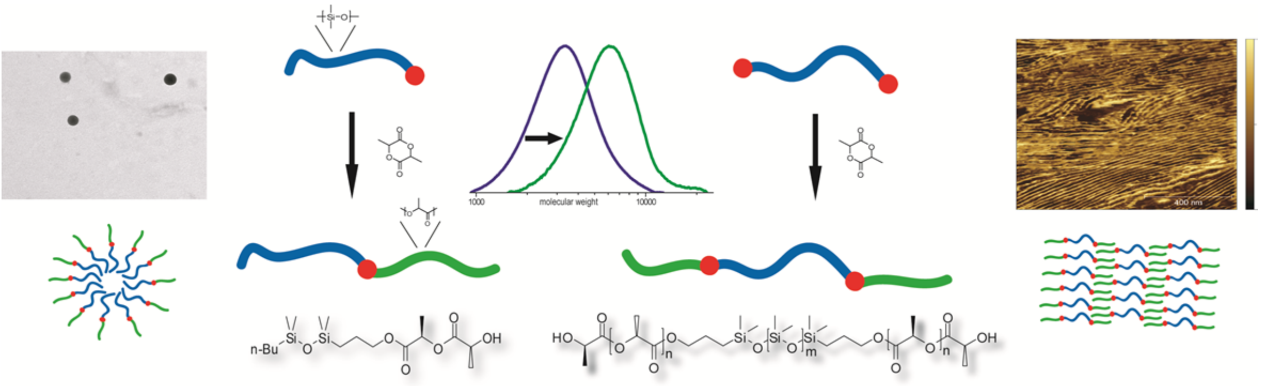
In **Chapter 2.4.**, silicone-containing amphiphilic block copolymers have been synthesized by combination of anionic ring-opening polymerization of hexamethyltrisiloxane (D3) and atom transfer radical polymerization (ATRP) of oligo(ethyleneglycol) methacrylate. The firstly synthesized poly(dimethylsiloxane) was converted into an ATRP macroinitiator using hydrosilylation chemistry. The resulting block copolymers show narrow polydispersities of 1.3 to 1.4 and were analyzed by ^{1}H NMR spectroscopy. Interfacial properties were investigated using spinning drop tensiometry, showing that the block copolymers are powerful surfactants. Measurements at different temperatures revealed interesting effects on surface properties, which tend to be significant only at concentrations below the polymers critical micelle concentration.

An interesting new class of thermoresponsive block copolymers of poly(oligoethyleneglycol-methacrylate) and poly(lactide) Is presented in **Chapter 2.5.**. They were synthesized by use of a bifunctional initiator, from which the POEGMA block is firstly synthesized via ATRP in acetonitril and the second subsequently by ring-opening polymerization of dilactide, using the POEGMA-block as a macroinitiator. The LCST of the POEGMA-block was tailored by random copolymerization of two different OEGMA monomers and was adjusted to about 40°C. Successful synthesis was proven by NMR analysis and SEC measurements that show narrow molecular weight distributions over a broad size-range. Nile Red was incorporated into previously formed micelles and could be released upon temperature stimulus. Moreover, a trifunctional initiator was synthesized and used to create an in-chain functionality of the copolymer, which was successfully addressed by rhodamine B via click reaction.

Graphical Abstract



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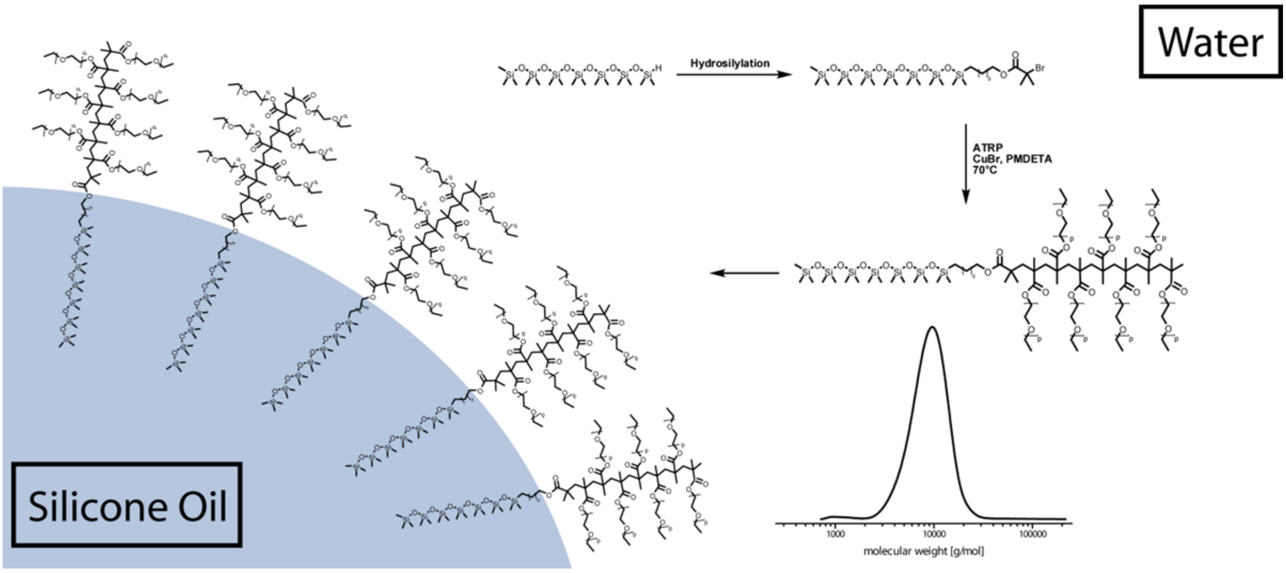
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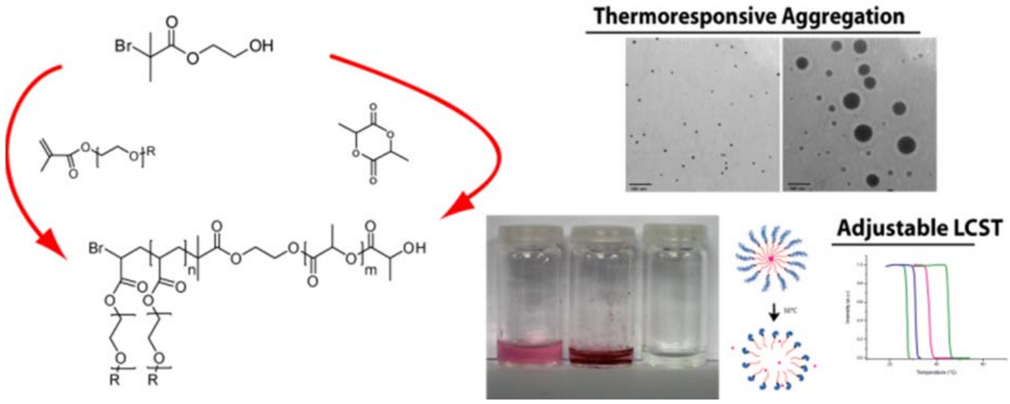
Thermoresponsive Aggregation
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1. Introduction

Silicones and Silicone-Containing Polymer Structures – Synthesis and Applications

1.1. Silicones and Their Properties

Polysiloxanes (IUPAC) or silicones are macromolecules that consist of a backbone of alternating silicon and oxygen atoms. Two alkyl moieties are attached to the tetravalent silicon in the chain. In case of the most popular and common polysiloxane, poly(dimethylsiloxane) (PDMS), these organic side chains are simply methyl groups. With this structure, silicones represent a unique hybrid of organic and inorganic components.

While silicones were firstly used as extremely temperature- and weather-stable isolators for electricity cables, the variety of different silicone products nowadays is remarkably manifold. Cosmetics, electronics, and sport products are only a few examples that demonstrate their miscellaneous application. But also water-repellent textiles, automobile parts, or the building industry in general profit from the silicones' characteristics. Furthermore,- they work either as foam stabilizers or defoaming agents in paints and foams. Referring to a rather recent usage, it is essential to mention polysiloxane based material playing an important role in clinical and medical applications, where they serve as casting compounds in dental medicine, as surgical short-time implants, or function as parts of medical devices such as artificial cardiac valves or cardiac pacemakers. **Figure 1** gives an overview of the different fields of silicone applications.

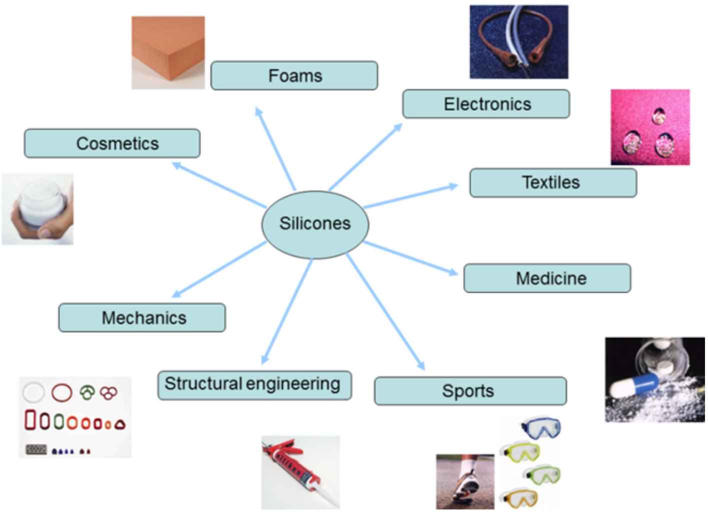


Figure 1. Overview of silicone applications

Research on polysiloxanes and novel silicone-containing materials is still ongoing, whereas current attempts mostly focus on the combination of silicones and other materials in order to combine the unique silicone-specific properties with those of other polymers. The industrial market for silicones has constantly been growing up to the present day. Reaching a market volume of 10.3 billion US$ in 2007, the still increasing demand for silicone products has brought it to a value of 13.5 billion US$ in 2010.[1]

Polysiloxanes exhibit a number of unique and extraordinary features that strongly distinguish them from all other kinds of known polymers. Their special character is the basis for manifold applications concerning various fields, in which they sometimes even show seemingly contradictive behavior. To name just a few examples, they can be used as water repellents as well as dewatering agents, can function as emulsifiers or de-emulsifiers, as foam stabilizers or anti-foaming agents. Therefore, silicones have extensively been being studied with regard to chain conformation, reactivity, thermodynamics, and other aspects for years and are still object of detailed studies to date.[2,3] Their molecular structure is shown in detail in **Figure 2.**

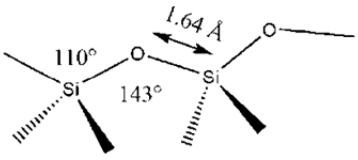


Figure 2. Section of a PDMS chain labeled with bond lengths and angles

The most obvious differences of polysiloxanes compared to other polymers are their bond lengths and angles. With 1.64 Å, the Si-O bond is longer than the C-C bond.[4] The Si-O-Si bond angle exceeds the normal tetrahedral value of 109.5 by far, whereas the O-Si-O angle conforms to the usual value of 110° approximately. The inequality of the backbone angles plays a crucial role with respect to chain conformation, an aspect that will be discussed in detail later on. More significant than the actual bond angles, is their high flexibility. The bonds in polysiloxanes are so flexible that they are even able to pass through the planar 180° state.[3] A further effect that contributes to the extremely high flexibility of the polysiloxane chain is the fact that the oxygen atoms of the polymer backbone are not encumbered by any side groups or atoms. Moreover, the torsional barrier for free rotation is very low for all bonds of the silicone backbone, which allows high mobility of all atoms. Silicone chains prefer a planar all trans state, which is favored by van der Waal's interaction between its organic side chains. Combined with its unequal bond angles, it causes the chain to approximate a series of closed polygons with a closed figure after 11 repeat units.[5] This configuration is also expected to be one of the basic reasons for the properties of silicones in general, since it inhibits the chains to arrange in the normal “zig-zag” conformation as other polymers do and thus impedes a close packing.[6]

In terms of thermodynamics, equilibrium flexibility as well as dynamic flexibility is very high for silicones. High equilibrium flexibility causes a low melting point, which is due to a high conformational randomness in the amorphous state. This is the reason for the low melting point of siloxane polymers, like PDMS (-40°C).[7,8] Several concepts have been pursued to increase the melting point of polysiloxanes by developing structures that cause higher rigidity of the silicone chain. Such attempts include the synthesis of ladder-like polymers as well as the addition of rigid and bulky groups, like aromatic units, either within the polymer backbone or in the form of side groups.[8-11] Dynamic flexibility represents the ability of a polymer chain to rotate around its backbone bonds. Therefore, a high dynamic flexibility stands for the potential to retain mobility and flexibility even at very low temperatures, which in fact directly correlates with the glass transition temperature of the material. Consequently, the high dynamic flexibility of the polysiloxane chains provides them the lowest glass transition temperature of all known polymers. The most popular silicone PDMS exhibits a glass transition of -125°C. The high influence of the dynamic flexibility of silicones also becomes visible considering the change of the materials´ viscosity at low temperatures. Unlike other polymers, polysiloxanes display only very slight changes in their viscosity over a broad range of temperatures.

Another very valuable feature of silicones is their remarkably high gas permeability, which can also be related to the unique combination of a polar but very flexible polymer backbone. Taking special advantage of the high oxygen permeability of polymethacrylate, contact lenses can be considered as the most popular and successful application. Contact lenses present a good compromise between permeability and wettability. Recent products are made of a polymethacrylate that carries bulky siloxane sidechains. The monomer that is used in this materials is called TRIS (Tris(trimethylsiloxy)silyl-propyl-methacrylate). The use of polysiloxanes in contact lenses thus reveals a further very important feature of silicones, namely their outstanding transparency.

Silicones are especially suitable for biomedical purposes, since they are fully inert toward biological systems. This is due to the fact that the active centers of enzymes are not able to accept siloxane structures and thus cannot convert siloxane-based molecules at all. Silicones are remarkably stable materials and are not sensitive towards oxidation or reduction. As silicones are water repellent, they are also stable against hydrolysis. Additionally, silicones are considered as being a surprisingly environmental friendly type of material. The degradation of silicones leads to small silica particles or hydroxysilanes that are already part of nature, while volatile degradation products are harmless towards the atmosphere.[12]

It is important to note that polysiloxanes are absolutely stable towards UV irradiation. Only the very shortest wavelengths within the sunlight spectrum can cause damage to the silicone. However, the radical stability of silicones can be enhanced if methyl groups are replaced by the more stable phenyl sidechains. Silicones possess a very powerful self-healing process. If OH groups are formed at their surface, silicones do not become wettable and thus vulnerable for a long time, because already shortly after their formation, the silanol groups either migrate to the inside or, which is even more efficient, two silanol groups condense to form a new linkage and finally close the hydrophobic surface.[3]

Polysiloxanes have very low surface tensions and surface energies, which can be deduced to their unique chain structure and conformation that has already been discussed in detail previously. The surface tension of polysiloxanes is actually so low that surfaces of silicone-containing blends or copolymers always consist of nearly 100% silicone, even if the overall silicone ratio of the material is very low.

Because of all the discussed features, silicones show seemingly paradox behavior in different applications. The reasons for this complex behavior are still not fully understood on a molecular level. Nevertheless, there are certainly more important details about these extraordinary polymers that are yet to be discovered.

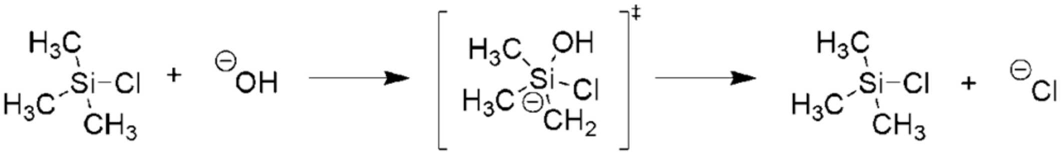
1.2. Synthesis of Silicones

1.2.1. Polycondensation

Synthesis of polysiloxanes via polycondensation of dialkydihydroxysilanes marks the beginning of silicone chemistry in some respects, since it was introduced by Dilthey and Martins virtually by accident. However, polycondensation is not the preferred choice for the controlled synthesis of well-defined polysiloxanes, because as for other monomers, such polymerizations suffer from numerous possible side reactions, high polydispersities, and a lack of control over molecular weights. Nevertheless, it plays an important role in silicone chemistry. It is used in polysiloxane modification reactions and systematic crosslinking, as carried out in the synthesis of silicone elastomers and, even more importantly, for the synthesis of cyclic siloxanes. like hexamethylcyclotrisiloxane (D3) or octamethylcyclotetrasiloxane (D4). Those molecules are applied to the synthesis of polysiloxanes via ring-opening polymerization, a method that will be described later on, and ,therefore, are essential elements in silicone chemistry. Their synthesis involves hydrolysis of dichlorodimethylsilanes, which are synthesized by the "Direktsynthese", that was invented by Mueller and Rochow in the 1940s.[13] The reaction rate of the hydrolysis of chlorosilanes and the condensation between silanols or silanols and chlorsilanes is strongly dependent on the reaction conditions such as temperature, concentration, and pH value. α,ω-dihydroxy- and α,ω-dichloro- as well as α-hydroxy-ω-chlorosilanes are known as intermediate species.[14]

The ratio of products can be influenced by applying the respective conditions. High dilution, for example, leads to a majority of small chains and cycles with a yield of about 40% of octamethylcyclotetrasiloxane.[15] Lower dilution results in a larger amount of products of higher molecular weight, and the formation of chains can almost completely be suppressed by the use of organic solvents.[16]

All reactions described above follow a nucleophilic substitution mechanism, which essentially differs from substitutions at carbon atoms. Two features enable the silicon atom to form a pentavalent transition state that is not possible for carbon. With 117 pm, the radius of the silicon atom is significantly larger than the carbon radius of 77 pm, which provides enough space for the attachment of five substituents. Additionally, as a third period element, silicon can use its free d-orbitals for bond formation. Nucleophilic substitutions on the silicon atom thus pass through a pentavalent transition state. The exact mechanism is described as S_NSi and is depicted in **Scheme 1**.

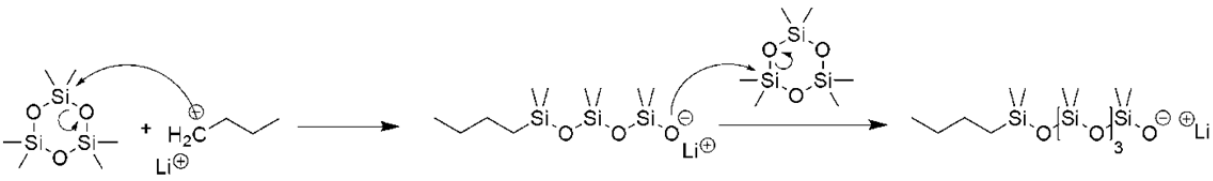


Scheme 1. Mechanism of the nucleophilic substitution (S_NSi) at the silicon atom

On an industrial scale, silicones are usually produced by equilibration polymerization, a method that provides good applicability for large scale production, but does not allow very good control over molecular weights and polydispersities. In this process, a mixture of cyclic and linear oligosiloxanes is polymerized by the use of an acidic or basic catalyst. Commonly used catalysts are sulfuric acid, trifluoromethanesulfonic acid, or bases such as potassium hydroxide or tertaalkylammoniumhydroxide.[17,18] Ring-opening as well as condensation reactions are involved in the polymerization and polydispersities are not influenced by the initiator. The resulting polymers show Schulz-Flory distributions with polydispersity values around 2.[19]

1.2.2. Anionic Ring-Opening Polymerization

If well-defined polysiloxanes with exact molecular weights and narrow polydispersity slighly above 1 are required, cyclic oligosiloxanes like octamethylcycloterasiloxane (D4) or hexamethylcyclotrisiloxane (D3) can be utilized in an ionic ring-opening polymerization. Organic substances of low polarity, such as THF, toluene and sometimes acetone are normally used as solvents. Organolithium bases like *n*-butyllithium function as initiators for this living process in which, as for all living polymerizations, the molecular weight can be adjusted by the monomer to initiator ratio. Besides this, other initiators like alkoholates and silanols have been proven to be capable of initiating siloxane polymerizations.[20,21] Furthermore,, more complex structures have been reported, involving difunctional initiators and initiating groups that are attached to naphthalene molecules.[22,23] Living polymerization allows the synthesis of functional polymers by the use of modified termination agents.[24] Anionic ring-opening polymerizations of cyclosiloxanes are terminated by chlorosilanes. Thus, chlorotrimethylsilane is used for nonfunctional polymers. The exact mechanism is depicted in **Scheme 2**.

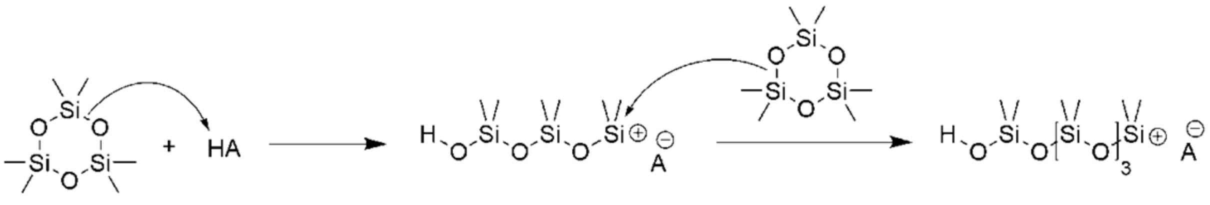


Scheme 2. Mechanism of anionic ring-opening polymerization of D3.

The driving force for this fast polymerization is a gain of entropy, which seems to be paradox at first sight, as a large number of smaller monomers are connected to form one macromolecule. However, the crucial point in this case is the mobility of the silicone atoms within the polymer chain, which is significantly enhanced towards the situation in a six- or eight-membered ring. Unlike in carbon cycles, six membered siloxane rings are more strained than their eight-membered analogues. Therefore, anionic ring-opening polymerization of D3 is much faster than D4,[25] which is due to the fact that silicon-oxygen bond angles are larger than those of carbon-carbon bonds, making eight-membered siloxane rings more stable than their six-membered analoga. Consequently, D3 is the preferred monomer for the controlled synthesis of poly(dimethylsiloxane), as molecular weights of 5000 g/mol and higher can be achieved in less than two hours at ambient temperature. If the cyclic monomers contain larger side chains that are more bulky than the methyl group, the entropical benefit of polymerization is reduced and polymerization proceeds much slower.[26] A further reason for this phenomenon constitutes the fact that the sterical demand of larger side chains decreases the mobility of atoms within the polysiloxane backbone. On the contrary, polymerization rate can be enhanced by using larger counter ions, which increases the ionic character of the growing chain end. Moreover, small amounts of DMSO or DMF can be added as promotors which support separation of the oxyanion at the living chain end and accelerate nucleophilic substitutions by being able to stabilize anionic as well as cationic charges.[27]

1.2.3. Cationic Ring-Opening Polymerization

Alternatively, ring-opening polymerization of cyclosiloxanes can be carried out cationically, using protonic acids like trifluoromethanesulfonic acid as well as Lewis acids, or cationic carbons as initiators.[18,29] The cationic approach is only chosen for special purposes, because it suffers from a high number of possible side reactions and is significantly slower than the anionic process. The exact mechanism is shown in **Scheme 3**.

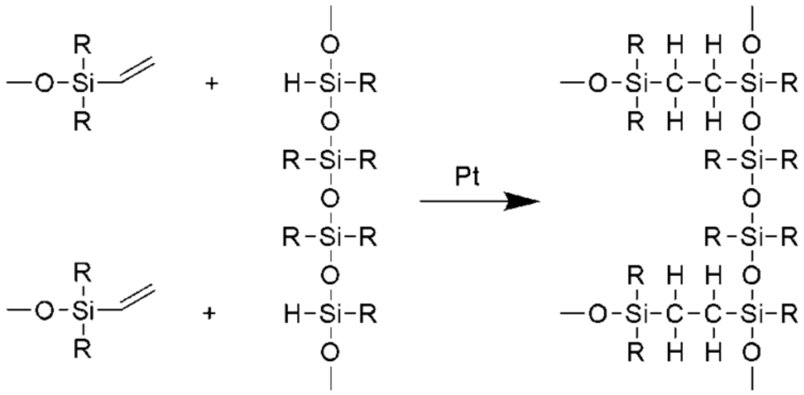


Scheme 3. Mechanism of cationic ring-opening polymerization of D3.

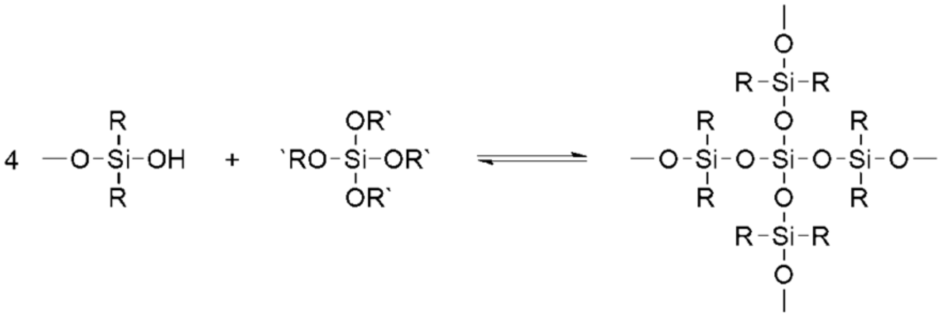
However, there are some advantages of cationic siloxane polymerization, namely that it tolerates some functional groups like carboxylic acid side chains or Si-H bonds.[30] That is why also the cationic ring-opening polymerization, especially of D3, has been studied in detail, partly presenting even newly investigated cationic initiators .[31-33]

1.2.4. Elastomer Synthesis – Crosslinking of Polysiloxanes

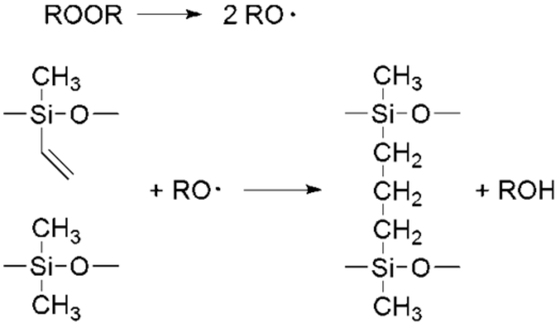
Taking the silicone synthesis into account, the formation of networks to create silicone elastomers can be regarded as one essential aspect. Basically, three different types of reactions are used for the crosslinking of polysiloxane chains. In the so-called "addition crosslinking process", silicone hydride functional polymers are connected to polysiloxane chains that carry vinyl moieties via platinum-catalyzed hydrosilylation. Another frequently employed method is condensation crosslinking, in which alkoxysilanes are attached to each other in condensation reactions. The crosslinking density can be varied by the addition of tri- or tetrafunctional alkoxysilanes that represent junction points in the obtained elastomer. Additionally, one should emphasize that this is the only crosslinking process that is fully reversible and thus does not lead to very high conversions. Thirdly, crosslinking of vinyl-functional polysiloxanes can be achieved via radical reactions, catalyzed by peroxides. All three methods of crosslinking are depicted in **Schemes 4-6.**



Scheme 4. Addition crosslinking via hydrosilylation



Scheme 5. Condensation crosslinking, release of ROH



Scheme 6. Radical crosslinking by peroxides at elevated temperatures

To date, several more sophisticated methods to form crosslinked siloxane networks have been investigated. Novel approaches, for example, include crosslinking polymerizations or take advantage of click reactions. All these aspects will be discussed in the following chapter.

1.3. Silicone Block Copolymers and Their Application

In order to take advantage of the unique properties of polysiloxanes, they have been copolymerized with a large number of different monomers. The essential goal in all these approaches is the effective combination of the silicone-specific features with those of the other polymer to obtain materials with a new set of properties. Inventions that involve rather comprehensive synthetic procedures usually aim towards application in the biomedical field. This also includes a number of structures in which silicones are combined with any kind of biomolecules like sugars, amino acids, or even proteins. More convenient strategies are often used to create amphiphilic siloxane block copolymers that can be used as emulsifiers, foam stabilizers, or the like. However, synthesis of such structures can basically be considered as difficult, because the problem of incompatibility of hydrophilic monomers towards a hydrophobic chain or vice versa is usually a problematic issue. As silicone-based amphiphilic block copolymers are generally very good surfactants, there is a strong need of the development of facile routes to synthesize such structures in a controlled and well-defined fashion.

Synthesizing polysiloxane block copolymers, several different pathways have been applied. Older publications mostly combine two previously synthesized polymers, mostly by hydrosilylation. More recent approaches also deal with the combination of silicones and living radical polymerization techniques or use click reactions to attach functional groups or polymers to polysiloxanes. Another interesting method is the use of silicones as macroinitiators for the ring opening polymerization of cyclic esters or amides. All in all, silicone block copolymers have always been of great interest both academically and industrially up to today because of their intriguing properties and their high application potential. Some of the essential and simultaneously most recent advances of the past years will be described in the following chapters.

1.3.1. Block Copolymers of Silicones with PEG, Polyesters and Polyamides

The largest number of publications about silicone block copolymers certainly deal with the combination of poly(dimethylsiloxane) PDMS and poly(ethylene glycol) (PEG), which can be ascribed to two previously described reasons . Firstly, PEG is a well-established polymer and commercially available in numerous variations. Secondly, it is a hydrophilic polymer, known to be fully biocompatible, being FDA approved, and thus perfectly suitable for biomedical applications. For that purpose, it has been combined with polysiloxanes in many different ways. Initial investigations on the properties of such materials were performed by Haesslin in 1984, who studied PDMS-PEG di- and triblock copolymers with regard to microseparation and their compatibility with water and oils in his first publication. Phase diagrams of the copolymers in water/cyclohexane mixtures and DSC studies have revealed a very strong tendency towards phase separation, even for samples of very low molecular weight.[34] In a following paper in 1985, he was able to show that such polymers form stable aggregates of small size in dilute solution, which was evidenced by viscosimetry, light scattering and small angle neutron scattering.[35] More recently, this was further advanced by the group of Kickelbick in 2003, who used cryogenic transmission electron microscopy to prove the formation of small vesicles from PDMS-*b*-PEG in dilute solution. However, only much larger multilamellar structures were observed at polymer concentrations over 0.12 wt%, which is depicted in **figure 3.**[36]

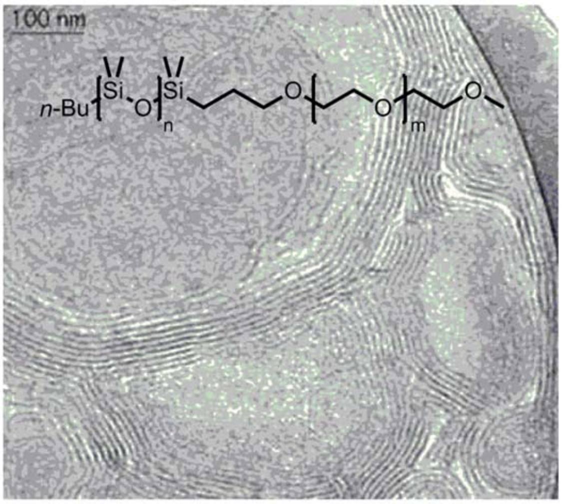
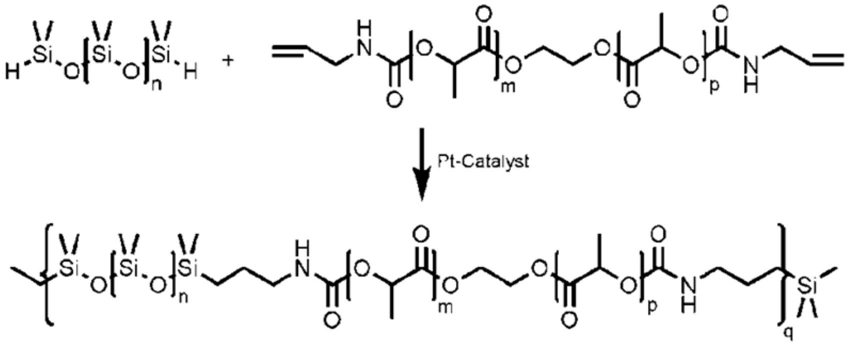


Figure 3. TEM image of multilamellar structures formed by PDMS-*b*-PEG

In the same year, detailed studies on the phase behavior and microstructure of such polymers in the melted state were carried out by Kunieda et al. Depending on the respective chain lengths, cubic, hexagonal and lamellar morphologies could be detected.[37] On the contrary, PDMS-*b*-PEG-*b*-PDMS have been thermodynamically and structurally studied even earlier in 1981 by Galin, who found the same strong tendency for microseparation.[38] In 1992, Wegner et al. took advantage of this microseparation and synthesized photocrosslinkable PDMS-*b*-PEG-*b*-PDMS triblock copolymers and used them for the stabilization of lyotropic mesophases.[39] A more recent example of rather complex structures in this context was published by Webster in 2011. The presented telechelic polysiloxanes carry PEG side chains will shortly be subjected to protein adsorption experiments.[40]

Besides poly(ethylene glycol), different kinds of polyesters have been combined with silicones in the form of block copolymers. Such polymers are readily available by the use of polysiloxane macroinitiators for the ring opening polymerization of lactones. Nevertheless, this was not the path that was followed in the first report of such copolymers in 1995. Sauvet et al. synthesized telechelic Si-H functional PDMS and employed hydrosilylation to connect it with poly(lactic acid) (PLA) that carried double bonds on both chain ends to form a PDMS-PLA multiblock copolymer.[41] The synthesis is shown in **Scheme 7**.



Scheme 7. Multiblock Copolymers of PLA and PDMS

Much later, ABA-type triblock copolymers of PDMS, flanked by two lactide blocks, were reported by Riffle in 2008. These polymers were used to disperse magnetic nanoparticles.[42] In 2010, the group of Hillmyer reported on the same block copolymers, although the synthetic method applied was slightly different from the one that was used by Riffle. Moreover, investigation of the polymers was focused on nanolithographic applications.[43] This work by Hillmyer followed a series of publications of his group that started in 2003, when they reported on the synthesis properties of ABA-type triblock copolymers of poly(lactide) and poly(isoprene).[44] Later on, further works about triblocks with flanking PLA chains have been reported by this group.[45,46] The fact that the combination of PDMS and PLA is also interesting with regard to biomedical applications was pointed out even before in 2001 by Baysal et al.. They synthesized a multiblock copolymer that consists of PDMS and PLA and poly(caprolactone) (PCL) units. Cell growth experiments showed that these polymers allow the attachment and growth of specific cell lines.[47] Although they are in a sense predestined for biomedical use, PCL-*b*-PLA polymers also exhibit potential for application as biodegradable surfactants, which was demonstrated by Lazzaroni et al..[48] Another interesting combination of polysiloxanes and polyesters was published in 2006 by Djonlagic. PDMS was combined with poly(butylentherepthalate) (PBT) and the obtained polymers were examined regarding thermal and rheological properties.[49]

A third essential field of silicone block copolymers are polyurethane (PU)-containing silicones. As silicones are vastly used as stabilizers of PU foams, there are numbers of patents concerning this topic. However, two rather recent examples of interesting synthetic routes towards such copolymers are to be pointed out in this context. In 2002, Schmidt et al. used amino-telechelic poly(dimethylsiloxane)s as a macromonomer and polymerized it with hexamethyldiisocyanate. The resulting polymers were found to effectively gel, when dissolved in silicone fluids.[50] Reverting to this study in 2006, they demonstrated a strong influence of the length of the hard segment on the gelation behavior of the material.[51]

Much more uncommon are the siloxane-ketimine block copolymers that were established in 2008 by Vlad et al.. Their structure is shown in **Figure 4.**

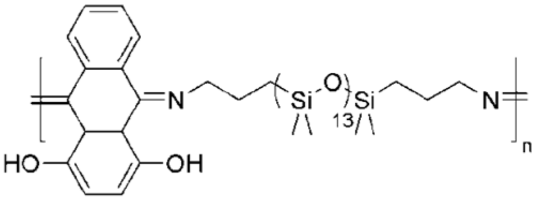


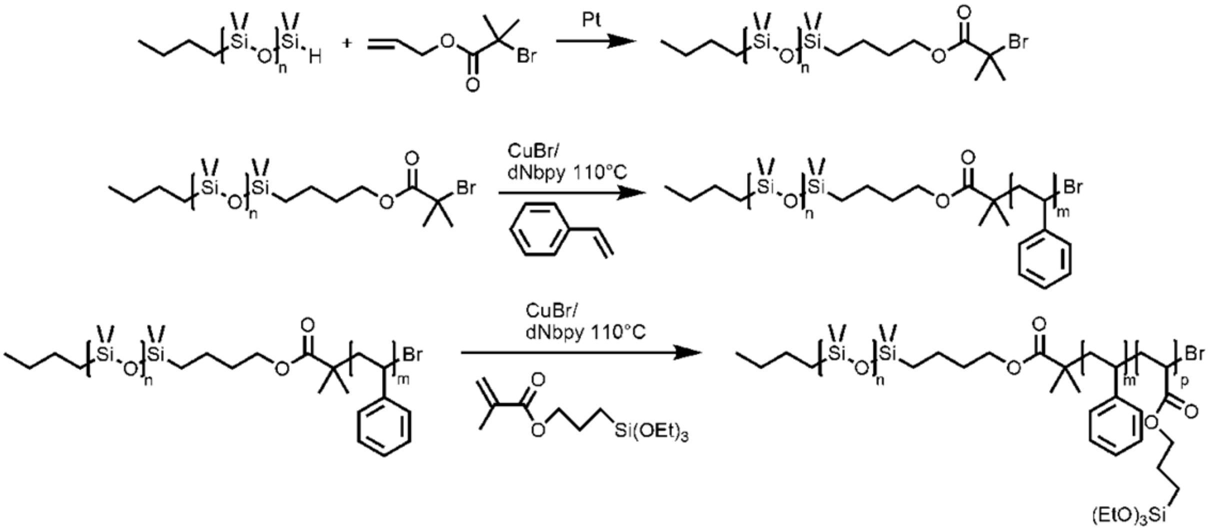
Figure 4. Structure of siloxane-ketimine copolymer

The group was able to depict that these polymers represent a useful tool for the formation of metal complex nanoparticles.[52] However, this is a rather unusual example of silicone-containing block copolymers. However, the combination of silicones and biocompatible polymers like PEG or polyesters or the like is certainly a powerful tool in the development of novel materials, not only for biomedical purposes. Unfortunately, synthetic approaches towards PEG-PDMS Copolymers always include coupling reactions between at least two different macromolecules, which do not lead to fully converted, well-defined products. The performance of for example polymeric surfactants strongly depends on the size of their hydrophilic and hydrophobic segments and is drastically impaired even by small amounts of impurities. Therefore it is an important goal to find options to replace PEG by other hydrophilic polymers that can be synthesized in controlled fashion in the presence of a polysiloxane in order to obtain well-defined silicone-containing amphiphiles. As silicones are stable under the conditions of radical polymerizations, controlled radical polymerization (CRP) techniques like ATRP, RAFT or NMP are especially qualified in this regard.

1.3.2. Silicone Block Copolymers Synthesized by Controlled Radical Polymerization

Within the last years, controlled radical polymerization techniques have increasingly become the most frequently used method for the synthesis of well-defined block copolymers. Such polymerizations are particularly useful in this regard, because they tolerate manifold functional groups and additionally display great applicability for a large number of monomers, especially vinylic compounds, acrylic, and methacrylic acids of almost any kind. Moreover, they are easy to carry out and still provide well-defined polymers in a controlled fashion. The essential principle behind all controlled radical polymerization techniques is basically the reversible deactivation and activation of the radical species at the growing chain end. This process that is characterized by the two decisive reaction constants $k_{(act)}$ and $k_{(deact)}$ leads to an overall decrease in the concentration of radicals and thus effectively prevents side reactions that usually accompany free radical polymerizations.[53,54] Consequently, these polymerizations follow the kinetics of controlled living processes, that is otherwise only obtainable in anionic polymerization. However, in contrast to ionic polymerizations, controlled radical polymerizations are much more tolerant towards slight impurities and can even be carried out in aqueous media.[55] The most popular methods of controlled radical polymerization by far are "atom transfer radical polymerizations" (ATRP) and reversible addition-fragmentation chain transfer-" (RAFT)-polymerization. Applying these polymerizations in the synthesis of polysiloxane-containing block copolymers is especially useful, as silicones are not stable towards basic or acidic conditions and therefore cannot be subjected to the conditions of anionic or cationic polymerizations. Yet, the combination of silicones and controlled radical polymerization is still only rarely found in literature. Nevertheless, there are some reports, in which silicones are applied as building blocks for the synthesis of new block copolymers via ATRP, and only very few examples in which the RAFT process is applied for that purpose. Even smaller is the number of publication in which other controlled radical polymerization techniques like nitroxide-mediated polymerization (NMP) or iodine transfer polymerization (ITP) have been applied in this context.[56-60]

Not surprisingly, it was the group of Matyjaszewski who firstly reported on the synthesis of a telechelic poly(dimethylsiloxane) macroinitiator for ATRP of styrene and several acrylates and methacrylates in 1999.[61] At the same time, they used a silicone surface that was covered with ATRP-initiating groups for the synthesis of functional polymer particles.[62] Another *grafting-from* approach on a silicone surface was published by Huck et al. in 2007. They prepared a silicone elastomer by hydrosilylation between hydrosilane and vinylsilane groups. As the former were used in excess for network formation, an ATRP initiator could be attached to the free hydrosilane groups on the elastomers′ surface. Afterwards, poly(oligoethyleneglycol methacrylate) was synthesized from this surface.[63] Besides this, there are some more papers that pursue more or less the same concept of using a macromolecular PDMS initiator for ATRP to synthesize diblock copolymers. With such macroinitiators, acrylic acid and ethyl methacrylate have been polymerized.[64,65] Not only the usual copper catalysts, but also special nickel complexes can be used in the synthesis of such diblocks, which has been shown in 2006 by Dubois et al..[66] Furthermore, reports describing ABA-type triblock copolymers have been published. Obviously, these can easily be synthesized from difunctional polysiloxane macroinitiators. This approach was followed inter alia for the synthesis of poly(butyl methacrylate)-*b*-poly(dimethylsiloxaane)-*b*-poly(butyl methacrylate), poly(oligoethyleneglycol methacrylate)-*b*-poly(methylphenylsiloxane)-*b*-poly(oligoethyleneglycol methacrylate) and poly(hydroxyethyl methacrylate)-*b*-poly(methylphenylsiloxane)-*b*-poly(hydroxyethyl methacrylate).[67,68] More complex copolymer structures have been developed by the groups of Wang and Matyjaszewski. Wang presented a block copolymer consisting of a PDMS block and a second block that represents a statistical copolymer of poly(methylacryl amide) and poly(vinylstyrene). Under radical polymerization conditions, the vinyl groups at the styrene units create crosslinks to form a branched amphiphilic polymer network, which can be used as gelling agent for silicone oils.[69] On the contrary, the polymer that was reported by Matyjaszewski is a real ABC-type triblock copolymer, namely poly(dimethylsiloxane)-*b*-poly(styrene)-*b*-poly(3-(dimethoxymethylsilyl)propyl acrylate), of which the triethoxysilyl groups of the third block were employed to covalently attach it to a silicon surface.[70] Their synthesis is depicted in **Scheme 8**.

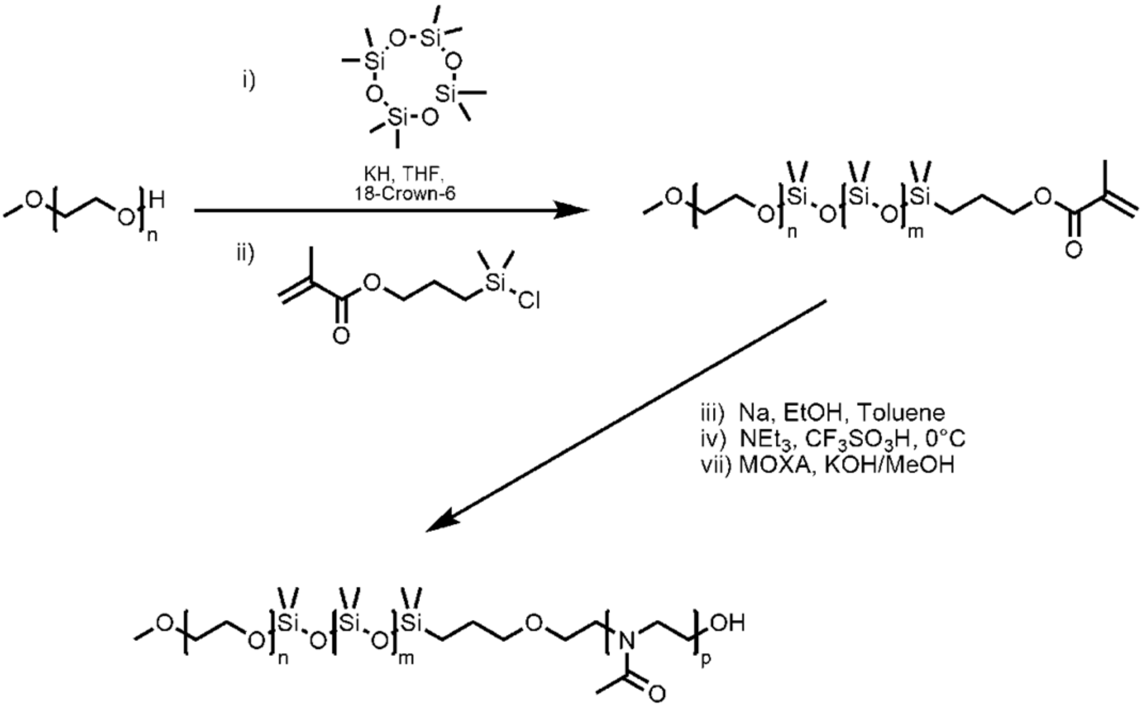


Scheme 8. Synthesis of PDMS-*b*-PS-*b*-PDMSA

While ATRP has already been used at least a couple of times with regard to the synthesis of polysiloxane-containing block copolymers, the application of RAFT is a real rarity in this context. This may be due to the much more complex synthesis of RAFT agents compared to ATRP initiators. For example, RAFT transfer-agents cannot be attached to a polysiloxane by hydrosilylation as in case of ATRP initiators, because the sulfur atoms they contain poisons the platinum catalyst. However, to the best of our knowledge, there are four publications regarding the combination of silicones and RAFT. While three of those have been published just recently, it was the group of Professor Stenzel who firstly introduced a PDMS macro RAFT agent in 2004.[71] This was continued in 2008 by Künzler and Shipp, who used an almost identical approach for the synthesis of poly(N,N-dimethylacrylamide)-*b*-poly(dimethylsiloxane)-*b*-poly(N,N-dimethylacrylamide) triblock copolymers.[72] The last two publications that deal with this topic are from 2009 and 2011 and both report on the synthesis of poly(dimethylsiloxane)-*b*-poly(styrene).[73,74] Yet, it remains arguable if the effort that is required for the synthesis of silicone-containing block copolymers by using RAFT polymerization is justified by the benefit of structures that are accessible from it. Nevertheless, CRP techniques in general and particularly ATRP have been proven to be a powerful tool for the synthesis of silicone-containing block copolymers.

1.3.3. Silicone Block Copolymers for Biomedical Applications

Silicones and silicone-containing block copolymers are particularly suitable for application in the biomedical field. This can be ascribed to their unique set of properties such as physiological inertness, high thermal and oxidative stability, low toxicity, and good blood compatibility. Accordingly, they have been used in a number of medical instruments and implants. These include artificial skin, drainage implants, maxillofacial prostheses, finger joints, medical adhesives, cardiac pacemakers, contact lenses, drug-delivery systems, and others.[75-80] The total amount of silicones that have been used in long-term medical devices until 2002 has been estimated to approximately 90.000 kilograms.[81] However, the hydrophobic and foreign nature of silicones has been proven to cause problems, especially with regard to the interaction with the body on a molecular level. This can lead to the induction of foreign body reactions and the development of infections particularly at the interface between silicone and tissue. [82-84] These problems can at least partly be overcome by the use of silicone containing block copolymers. While mostly retaining the beneficial polysiloxane properties like high gas permeability or elasticity, the more hydrophilic part of these mostly amphiphilic polymers provides improved wettability and thus tissue compatibility. A large number of different silicone block copolymers have been reported to date. These include PDMS-*b*-poly(methyl methacrylate) PDMS-*b*-poly(amide-6), PDMS-*b*-poly(sulfone), PDMS-*b*-poly(bisphenol-A), PDMS-*b*-poly(styrene), PDMS-*b*-poly(ethylene glycol) and PDMS-*b*-poly(urethane).[85-90] In these early publications, such block copolymers were usually characterized with regard to their surface properties, using microscopic technologies like transmission electron microscopy (TEM). The recent research in this field is more focused on specific applications and oftentimes includes cell studies in order to investigate toxicity, cell-uptake, and other biomedically important parameters. The use of silicones in drug delivery devices is certainly the most frequent example for polysiloxanes in medical applications. Their usability concerning drug release devices has been shown in several publications. Drug release from different silicone carriers was investigated in depth by Imanishi et al. in 2003. They showed that controlled release kinetics are possible for water soluble as well as insoluble drugs.[91] Moreover, 3-dimesional silicone matrices were proven to be suitable for the controlled release of progesterone by Imani et al..[92] A group that extensively studied poly(dimethylsiloxane)-containing block copolymers, their ability to form vesicular structures in aqueous media, and the application of these so-called “polymersomes” as “nano-containers” is that of Meier et al. In 2002, they published a first work that describes the synthesis of an ABC-type triblock copolymer of poly(ethylene glycol), poly(dimethylsiloxane) and poly(methyl oxazoline) (PEG-*b*-PDMS-*b*-PMOXA).[93] These polymers form vesicles with asymmetric membranes in water. The two water-soluble blocks of PEG and PMOXA can be situated either on the inner or outer side of the vesicular membrane, depending on the respective block length ratio. The structure of this triblock copolymer, whose tedious synthesis involves three different, subsequently used polymerization techniques is depicted in **Scheme 9.**



Scheme 9. Synthesis of PEG-*b*-PDMS-*b*-PMOXA

However, Meier et al. later focused on a slightly different copolymer for the same type of application, namely ABA-type triblock copolymers, in which a central poly(dimethylsiloxane) block is flanked by two hydrophilic blocks of poly(methyl oxazoline) (PMOXA-*b*-PDMS-*b*-PMOXA). These polymers were shown to form stable vesicles in aqueous solution, which can serve as “nano-containers”, small spherical objects that provide a chemically isolated interior in which various reactions can take place. In following work, those vesicles were loaded with statin to permit receptor-specific targeting.[94] Additionally, single proteins were encapsulated into the vesicles to carry out enzymatic reactions selectively inside the polymersome.[95,96] In 2007, the group even reported on the incorporation of membrane proteins into the membrane of those vesicles, allowing selective transport of respective molecules to the interior.[97]

In order to develop silicones suitable for biomedical applications, polysiloxanes were combined with all kinds of biomolecules. Attaching sugars, proteins, or other biomolecules to silicones provides two major benefits. Firstly, it leads to an enhanced biocompatibility of the material and can significantly improve interaction between the silicone and surrounding tissue, which is a crucial aspect especially with regard to temporary or permanent implants. Secondly, such biomolecules are, apart from fats, hydrophilic and thus enhance the wettability of the material, which also leads to better body compatibility. Besides, even functional molecules can be attached to the silicone in order to enable selective targeting of the material via ligand-receptor interactions. Stadler et al. were the first ones to use this concept, which was presented in "Macromolecular Chemistry and Physics" in 2001. They applied hydrosilylation chemistry to attach protected, mono vinyl-functionalized mono-, di- and oligosaccharides to statistic copolymers that consist of dimethylsiloxane and hydromethylsiloxane units. The solution properties of the resulting polymers were investigated, proving that deprotection of the attached saccharides significantly influences solubility and conformation.[98] The structure of one of this glycosylated polysiloxanes is illustrated in **Figure 5.**

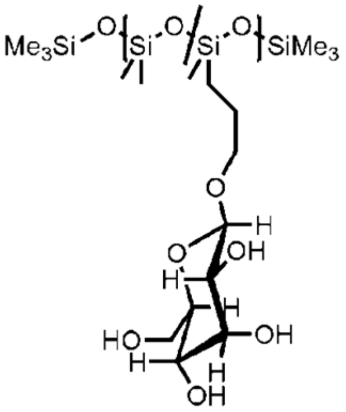


Figure 5. Glycosylated Polysiloxane

This work followed a publication from 1997, in which different sugars were covalently connected to silica particles. However, enzymatic reactions were used instead of hydrosilylation in this special case.[99] The very same approach was followed by Hamaide et al. in 2008. Silicon-hydride-containing silicone oils were reacted with protected cellobiose that carried one terminal double bond.[100] After deprotection, the resulting glycopolysiloxanes were used as nanoparticle stabilizers for miniemulsion polymerization.

However, one can also apply the reverse way of using hydrosilylation chemistry to equip polysiloxanes with sugars, which was done by Brook et al.. They synthesized Si-H-functional sugars, which were then attached to poly(dimethylsiloxane)s that are terminated by two vinyl groups.[101] Surprisingly, the obtained glycopolysiloxanes showed higher hydrolytic stability than normal PDMS. The group of Hamaide additionally reported on a second synthetic route for the synthesis of glycopolysiloxanes in the same year. Acetylene-functionalized sugars were reacted in an azid-in click reaction with polysiloxanes that are equipped with azide groups. The click reaction provides significantly improved conversion for the attachment of sugars, yielding polysiloxanes with high degrees of glycosilylation. Yet, synthesis of the starting compounds involves more reaction steps and is much more tedious than in case of the hydrosilylation approach.[102]

Sugars are not the only type of biologically active molecules that can be attached to a silicone. A more specialized example is the attachment of ion selective receptors, which are used e.g. in ion-selective electrodes. Such receptors, namely calix[4]arene and benzo-15-crown-5, have covalently been bound to poly(dimethylsiloxane)s in order to decrease their mobility. This was achieved via hydrosilylation by Moeller et al.[103]

Silicones cannot be only functionalized with biomolecules. Biomolecules, more precisely proteins, can also be used as enzymes for reactions that involve silicone polymers. The fact that enzymes are capable of converting polysiloxanes is quite surprising, because silicones are known to be fully inert towards living organisms. Nevertheless, it seems as if the high flexibility of the polymer backbone allows polysiloxanes to enter the active site of certain enzymes and can thus readily be converted. The enzyme that was used in this context was lipase B from candida antarctica (CALB). Clarson et al. used CALB for the esterification between double-carboxylic acid-terminated PDMS and dihydroxyl-functional poly(ethylene glycol), which leads to multiblock copolymers of PDMS and PEG.[104] The same reaction was applied for the reaction between hydroxyl- or amino-terminated PDMS and dimethylterephthalate in order to synthesize silicone aromatic polyesters or polyamides.[105]

In summary, the biomedical sector is definitely the most and fastest growing field of novel silicone applications. Inventions that involve polysiloxane-containing block copolymers usually aim towards high tech applications for drug delivery or selective membranes. While older publications almost exclusively use hydrosilylation chemistry to connect two polymer blocks, several routes that combine polysiloxanes or siloxane polymerization with any other kind of polymerization technique have been reported in the last 10 years. Furthermore, there are an increasing number of publications dealing with the use of click reactions in silicone chemistry.

1.3.4. Silicone Block and Graft Copolymers as Surfactants

Due to their specific properties, silicone surfactants can provide advantages in the performance of several different materials. The most important silicone-feature in this context is their high surface activity. Because of their outstanding properties, silicone surfactants are used inter alia in a large number of personal care products, as spreading and wetting agents and in the manufacture of plastic foams.[106] Moreover, they have been proven to be able to significantly increase the stability of microemulsions as well as emulsions in critical CO_2. Silicone surfactants also possess the ability to facilitate the wetting of extremely hydrophobic surfaces, an effect that is known as "superwetting".[107]

The phase behavior of silicone surfactants has been studied extensively. The vast majority of these studies deal with the investigation of AB-type block copolymers of poly(dimethylsiloxane) and poly(ethylene glycol). Kunieda et al. found liquid crystal phases for such block copolymers in water. The demanded space for a single monomer chain increases with increasing chain lengths of both the hydrophilic and the hydrophobic block.[108] In a further publication, the same group demonstrated that the unique features of PDMS chains are advantageous with respect to their use as surfactants. Unlike long-chain organic surfactants, silicon copolymers do not become insoluble with increasing chain length.[109] The same type of block copolymer has also been used to effectively stabilize W/O emulsions. Those can be highly concentrated and are highly thermally stable if silicone surfactants are employed as emulsifiers.[110] Besides linear block copolymers, polysiloxanes that are grafted with hydrophilic side chains of poly(ethylene glycol) have also been proven to stabilize oil-water interfaces.[111] The micellization of such polymers has extensively been studied by Lin and Alexandridis. Their work revealed that the addition of cosolvents like ethylene glycol or formamide causes an increase of the CMC. Furthermore, they have illustrated that the size of the micelles is additionally influenced in most cases.[112]

The most popular silicone surfactant is known by its product name "dimethicone". It also consists of a polysiloxane chain which is grafted either with poly(ethylene glycol) or random copolymers consisting of ethylene- and propylene-oxide units. Their general structure is shown in **Figure 6**.

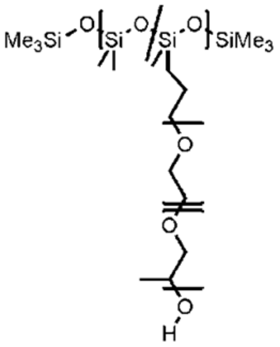


Figure 6. General structure of dimethicone, graft polysiloxane used for pharmaceutical application

The solubility of dimethicones of course depends on the ratio of grafted and non-grafted units. More surprisingly, it is the molecular weight that determines the functional properties of such dimethicones. Polymers of low molecular weight are very good wetting agents. Their strong wettability enables them to penetrate tissue and cause skin irritation. The higher the molecular weight, the less wettable are dimethicones. On the contrary, larger molecules are usually used as emulsifiers.[113]

Poly(ethylene glycol)-grafted silicones are still subject of research and their properties as surfactants are still not fully understood. In 2000, Gallardo et al. used the rather unusual ”hanging drop” method to measure dynamic surface tensions in order to investigate the critical micelle concentration (CMC) of these polymers.[114] Again, the unique character of silicones is revealed, as the results cannot fully be explained by the existing definitions that are based on hydrocarbon surfactants. For example, the surface tension at which micelles start to form is not consistent to the value at which turbidity appeared. Solutions become turbid at concentrations that are significantly lower than the CMC, and the point at which micelle formation begins, therefore, cannot clearly be established for silicone surfactants. The release of markers like halide salts, KNO_3, and ephedrine hydrochloride from W/O/W double emulsions stabilized by the same type of polymers was examined in 1994 by Sela et al.[115] They concluded that such emulsions can be used as slow release systems. The release mechanism seems to comply with a transport process that involves reverse micelles and additionally tends to be dependent on the hydrophobicity of the respective marker.

There are certainly other hydrophilic side groups that can be attached to linear polysiloxanes. The synthesis of such structures is always based on random copolymers that consist of dimethylsiloxane and hydromethylsiloxane units. The latter can be functionalized by hydrosilylation reactions. The overall hydrophilicity is consequently not only influenced by the polarity of the attached side chain, but also by the amount of functional monomer units within the starting material. The group of Somasundaran recently reported on the synthesis of such silicones that are equipped with varying polar side groups. These include primary and secondary amines as well as carboxylic acids and again, polyethers. Langmuir isotherms and phase diagrams have been generated and rheological investigations were carried out. Results show that the silicone part forms a film at the oil surface, while the hydrophilic groups submerge into the aqueous phase.[116] In addition, a strong dependence of the emulsion stability on the method of emulsification was observed in a following paper in 2009. The applied shear rates play an important role in this regard.[117] The same synthetic approach was also pursued by Kuo and Lee, who prepared silicones with tertiary amine side groups. The polymers were investigated by several microscopic methods and, more interestingly, their defoaming properties were examined in detail, showing that performance decreases with an increasing amount of hydrophilic side groupsand increases when raising the defoamer concentration.[118] In 2008, Amdouni and Chevalier reported on the synthesis of polysiloxanes that are grafted with cyclodextrines. These polymers are also capable of forming stable emulsions, but additionally the cyclodextrine groups can at the same time be used to encapsulate drugs, which was exemplarily demonstrated with griseofulvin, an antifungal substance.[119] The exact structure of the polymer is shown in **Figure 7**.

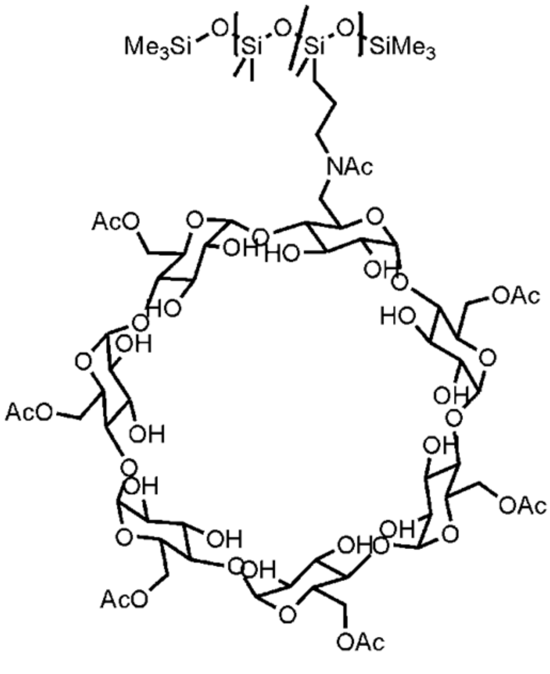


Figure 7. Cyclodextrine-grafted Polysiloxane

Another two interesting and unusual types of silicone-stabilized emulsions were published by Brook et al. in 2008 and 2012.[120,121] The first paper deals with a two component system consisting of triethoxysilyl-terminated poly(dimethylsiloxane) and albumin. Extremely stable O/W emulsions are formed, which is due to an interaction between the hydrophilic Albumin and silicone, which takes place at the oil-water interface. In the second paper, the emulsifying properties of poly(ethylene glycol)s that carry a short hyperbranched siloxane unit at both of their chain ends are presented.

Silicone surfactants are not only of an immense industrial importance because of the widespread possibilities for their application, but remain subject of current research. Again, the unique features of silicones are the reason for a behavior that is significantly different from common hydrocarbon surfactants. The exact mechanisms and interactions at the interfaces in such emulsions are therefore still not fully understood.

In order to utilize the silicone-specific properties and the great performance of polymeric surfactants that consist of a polysiloxane as their hydrophobic segment, new routes towards the controlled synthesis of such macromolecules are still to be developed. The high surface activity of silicones makes them perfectly suitable for these purposes, but the synthesis of amphiphilic structures derived from silicones remains difficult from several points of view. The instability of the polysiloxane backbone towards acidic and basic conditions, the incompatibility of hydrophilic monomers, the hydrophobic polysiloxane, and the limited number of reactions that can be used to functionalize silicones are crucial aspects in this regard. The investigation of new strategies for silicone modification and the controlled synthesis of silicone-containing block copolymers with precisely adjustable block lengths and narrow polydispersities are thus a decisive point towards the establishment of novel silicone-based materials, particularly with regard to high tech applications, whose demand is constantly rising. Some of the synthetic methods that have been established during the last years like click chemistry or CRP techniques provide solutions for these challenges. Despite the enormous progress of this field, the respective polymeric structures and the synthetic pathways that make them available are yet to be developed.

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2. Development of Novel Silicone-Based Polymers

Hydrophilic and Functional Silicones and Silicone-Containing Block Copolymers

2.1. Hydrophilic Silicones with Glycerol Side Chains

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Abstract

A new type of hydrophilic silicone polymer was synthesized by a convenient synthetic protocol, applying a "grafting-to"-approach. Using different Si-H functionalized poly(dimethylsiloxane)s, silicones with hydrophilic grafts or amphiphilic ABA triblock copolymers were obtained, using hydrosilylation to connect the hydrophilic structures to the silicone. The hydrophilic side chains consist of either glycerol side chains or hyperbranched polyglycerol units. These side chains contain at least two and up to about 13 hydroxyl groups. The materials were characterized by ^{1}H and ^{29}Si NMR- as well as IR spectroscopy. Glass transition temperatures and solubility of the polymers were analyzed and found to be in linear correlation with their amount of hydrophilic groups. These parameters can thus be readily tailored by variation of either the number of Si-H bonds in the poly(dimethylsiloxane)-*co*-poly(methylhydrosiloxane) precursor or the polarity of the hydrophilic side chain. The synthesized polymers were incorporated into standard LSR formulations and mechanical properties of the resulting rubbers were investigated, showing no impairing effect on the material.

Introduction:

Silicone polymers offer a variety of unique properties that distinguish them from other materials. For instance they exhibit constant viscosity over a broad temperature range as well as an extremely high gas permeability. In addition, they are absolutely bio-inert, which makes them interesting in the field of medical applications. Nevertheless, one of the most important silicone features, namely their hydrophobicity, poses a drawback for a number of applications. Several synthetic routes to silicone polymers and elastomers with increased hydrophilic properties have been reported during the last 15 years. Despite limited attention in scientific literature, hydrophilic silicones offer high potential for various applications, inter alia in the field of medical and care products as well as automobile and machine technology. The fact that most of the new innovations in this field are rather to be found in patent literature than in scientific journals demonstrates the industrial relevance of such materials. Hydrophilic silicones are currently used in shampoos, perfumes and as paint additive. The vast majority of known concepts for the synthesis of hydrophilic silicones include the combination of poly(dimethylsiloxane)s (PDMS) and linear, hydrophilic poly(ether)s, usually poly(ethylene)- or poly(propylene oxide)s, attached to the silicone either as linear copolymers or by grafting the polyether chains onto a PDMS backbone, as described in a number of patents.[1-5] Silicones containing hydrophilic side groups with hydroxyl functions have been reported, but only very few publications concerning such polymers are available.[6-8] Another interesting approach, especially with regard to biomedical applications, is grafting of silicones with carbohydrates. Initial work on these structures was done by Wagner et al. in the 1990s.[9] Different kinds of carbohydrates carrying an olefinic function were attached to random copolymers of dimethyl and hydromethylsiloxane units using hydrosilylation reactions[9-15]. Contemporaneously, Stadler et al. followed the same concept, focussing on the attachment of different kinds of oligo- and polysaccharides.[16-18] **Figure 1** shows some examples of hydrophilic poly(siloxane)s established to date.

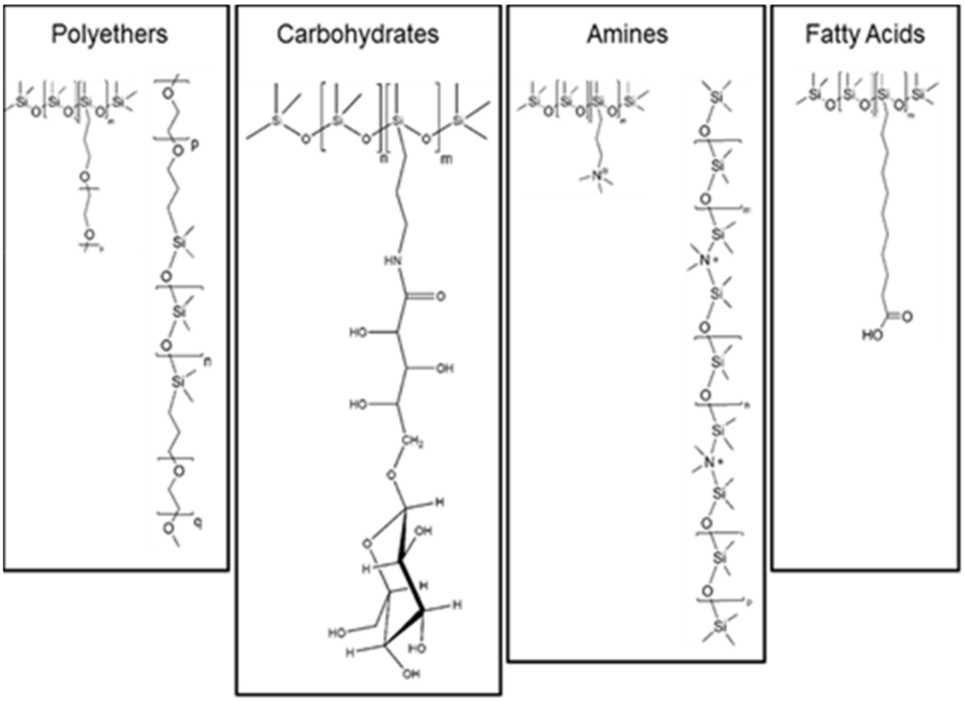


Figure 1. Established types of hydrophilic poly(siloxane)s.

However, preparation of such polymers still necessitates complex synthetic routes and several reaction steps. Thus, the development of a facile route including only few synthetic steps to produce hydrophilic poly(siloxane)s is an important step. Of special interest in this regard is the fabrication of silicone elastomers with polar surface. The addition of hydrophilic polysiloxanes to silicone rubber formulations in order to achieve hydrophilic surfaces is a promising concept in this context. As the generation of a hydrophilic surface by methods that are available nowadays is always linked to tedious post-modification steps like plasma- or laser treatment of the elastomer surface, it is desirable to be able to produce wettable silicone elastomers directly from the crosslinking process.

Here we report on the development of one- or two-step synthetic approaches to novel hydrophilic silicones. Starting from Si-H functionalized poly(siloxane)s, silicones with hydrophilic grafts were obtained, using hydrosilylation chemistry to connect a protected hydrophilic molecule to the silicone, followed by subsequent deprotection of the resulting polymer (Scheme 1). The preparation of the protected side chain was carried out by means of a Williamson ether coupling of 1-2-isopropylidene-glycerol and allyl-bromide to obtain 1,2-isopropylidene-3-allyloxy-glycerol. Furthermore, another similarly simple route that results in poly(siloxane)s substituted with hyperbranched poly(glycerol) was investigated by introducing n-aminopropyl side chains to the previously mentioned poly(siloxane)s using hydrosilylation chemistry. Following a procedure for bisglycidolization of primary amines introduced by our group, these amine functions can be used to initiate glycidol polymerization (Scheme 2).[19] Since hyperbranched poly(glycerol) provides a high number of hydroxyl groups,[20] these side chains generate a significant increase in hydrophilicity of the modified poly(siloxane). Solubility and hydrophilicity can be readily tuned by the use of poly(dimethylsiloxane)-*co*-poly(methylhydrosiloxane) copolymers with different amounts of Si-H units. It is an intriguing issue, in which manner properties like solubility and glass transition temperature depend on the number of hydroxyl groups within the polymer chains. The synthesized poly(siloxane)s were added to standard LSR formulations and the influence on mechanical properties, wettability and crosslinking dynamics have been investigated.

Experimental Section:

Instrumentation.

^{1}H NMR spectra were recorded at 300 MHz on a Bruker AC and are referred internally to residual proton signals of the deuterated solvents. ^{29}Si NMR spectra were recorded at 79.49 MHz on a Bruker AMX 400 and referenced externally to the TMS-signal. FT-IR spectra were recorded on a Nicolet SDXC FT-IR spectrometer equipped with a diamond ATR unit. DSC measurements were carried out with a Perkin Elmer 7 series thermal analysis system and a Perkin Elmer TAC 7/DX thermal analysis controller in the temperature range from -100 to 100 °C at heating rates of 20 K min^{-1} under nitrogen. Sample rubber sheets for testing the mechanical properties e.g. hardness, tear strength, yield strain and tear propagation strength were prepared as following: the two component LSR was mixed with a Krups 3Mix 7000 kitchen mixer for 5 min and press-cured at 175°C for 10 min with a pressure of 200 kN (A-step). The rubber sheets were post-cured in a Fontijne press at 200°C for 4 hours in a Binder FED240 oven with fresh air ventilation (B-step). The Shore A hardness was tested with a Zwick 3150 equipment according DIN 53505, calculating the mean from 3 single measurements. Tear strength and yield strain were tested with a Zwick Z010 equipment according to DIN 53504 / 3, calculating the mean from 5 single measurements. Tear propagation strength was tested according to ASTM-D 624 B using the Zwick Z010 equipment, calculating the mean from 5 single measurements. To obtain a curing curve (strain – torque diagram) according to DIN 53529 part 1+2 5,0g of the mixed LSR was placed into the Alpha Technologies (Dynisco) Rubber Process Analyzer RPA2000 and cured for 10 min at 175°C. The RPA2000 workbench enterprise software determined the torque maximum (S' max) and the torque minimum (S' min). The T_{60} time is the time, where 60% of the S' max is achieved. The contact angles of destilled water were tested with a KRÜSS DSA100 equipment. The water drop was placed on the rubber sheet and the contact angles were measured immediately.

Nomenclature.

Random dimethylsiloxane-hydromethylsiloxane copolymers are designated according to their amount of methylhydrosiloxane units, e.g. $PDMS\text{-co-}PMHS_{30}$. The hydrophilized copolymer products are designated according to the kind of side chain that is attached (either Gly for the n-propyl-glyceryl or hbPG for the hyperbranched polyglycerol side chain) and the amount of grafted monomer units, e.g. $PDMS(Gly)_{30}$.

Reagents.

Random dimethylsiloxane-hydromethylsiloxane copolymers PDMS-*co*-$PMHS_{10}$, PDMS-*co*-$PMHS_{30}$, PDMS-*co*-$PMHS_{80}$, the hydromethylsiloxane homopolymer PMHS and Karstedt`s catalyst were kindly provided by Momentive Performance Materials. PDMS-*co*-$PMHS_{7}$ and PDMS-*co*-$PMHS_{25}$ were purchased from ABCR. Allylamine, 1,2-isopropylidene-glycerol, allyl bromide and DOWEX 50 WX8 cation exchange resin were purchased from Acros and used as received. Glycidol was purchased from Acros and freshly distilled from CaH_2 before use. THF was purchased from Acros and distilled from sodium before use. Extra dry dioxane and all other solvents were purchased from Acros and used as received, if not mentioned otherwise. Deuterated chloroform-d_1 and DMSO-d_6 were purchased from Deutero GmbH and dried and stored over molecular sieves.

Synthetic Procedures.

1,2-isopropylidene-3-allyloxy-1,2-propanediol. In a 1 l round bottom flask equipped with a dropping funnel was put 1,2-isopropylidene-glycerol (26.4 g, 0.20 mol) and 400 ml of a 20:80 mixture of DMSO and toluene. To this solution, freshly ground KOH (28.0 g, 0.50 mol) was added under vigorous stirring. After dissolving of the added base is completed, allyl bromide (29.0 g, 0.24 mol) was added dropwise. The resulting mixture was stirred overnight at room temperature and then filtered and neutralized with ammonium chloride solution. The aqueous phase was extracted with toluene three times, the combined toluene phases dried over Na_2SO_4 and solvent was removed under reduced pressure. Yield: 31.7 g (92.0%) of a yellow, slightly viscous liquid. ^{1}H-NMR (300 MHz, $CDCl_3$) δ[ppm] = 1.35 (s, 3H, -C*H*$_3$), 1.43 (s, 3H, -C*H*$_3$), 3.45 (dd, 1H, Allyl-O-C*H*$_2$), 3.52 (dd, 1H, allyl-O-C*H*$_2$), 3.73 (dd, 1H, -CHOR-C*H*$_2$-OR), 4.01-4.10 (br, 3H, -CHOR-C*H*$_2$-OR, CH_2=CH-C*H*$_2$), 4.28 (quin, 1H, R_2C*H*-OR), 5.24 (m, 2H, R-CH=C*H*$_2$), 5.89 (m, 1H, R-C*H*=CH_2)

Dimethylsiloxane – methyl-n-propyl-isopropylideneglycerylethersiloxane copolymer. In a 100 ml round bottom Schlenk flask, 3 g polymer together with a 1.2 -fold excess of 1,2-isopropylidene-3-allyloxy-1,2-propanediol (referring to the amount of Si-H-groups) were dissolved in dry dioxane. The flask was set under argon atmosphere and sealed with a rubber septum. The mixture was heated to 80°C and the reaction was started by adding one drop of Karstedt`s catalyst via syringe. After 8-12 hours IR spectra showed complete disappearance of the Si-H bond. The solvent was removed under reduced pressure, the residual olefinic compound was removed by dialysis in chloroform and the resulting product was further dried under high vacuum for approx. 12 hours. ^{1}H-NMR (300 MHz, $CDCl_3$) δ[ppm] = -0.06-0.15 (s, Si-C*H*$_3$), 0.42-0.55 (br, Si-C*H*$_2$), 1.36 (s, R2C(C*H*$_3$)$_2$), 1.42 (s, R_2C(C*H*$_3$)$_2$), 1.55-1.67 (br, Si-CH_2-C*H*$_2$), 3.37-3.45 (br, CH_2-C*H*$_2$-O), 3.48-3.56 (m, RO-C*H*$_2$-CHR-OR), 3.70-3.77 (m, O-C*H*$_2$-CHOR-CH_2-OR), 4.02-4.10 (m, O-C*H*$_2$-CHOR-CH_2OR), 4.22-4.30 (m, R_2C*H*-OR)

Dimethylsiloxane – methyl-n-propyl-glycerylethersiloxane copolymer. To remove the acetalic protective-groups, 1 g polymer and 1 g cation-exchange resin were dissolved in 10 ml chloroform and stirred for two hours. The solvent and the formed acetone were removed under reduced pressure and the product was dried under high vacuum for 12 hours. ^{1}H-NMR (300 MHz, DMSO-d^6) δ[ppm] = -0.29-0.18 (s, Si-C*H*$_3$), 0.34-0.53 (br, Si-C*H*$_2$), 1.39-1.57 (br, Si-CH_2-C*H*$_2$), 3.11-3.44 (br, C*H*$_2$OR, C*H*$_2$OH), 3.48-3.59 (br, C*H*-OH), 4.25-4.55 (br, R-O*H*)

Dimethylsiloxane – methyl-aminopropylsiloxane copolymer. In a 100 ml round-bottom SSchlenk flask, 3 g polymer together with a 1.2 -fold excess of allylamine (referring to the amount of Si-H-groups) were dissolved in dry dioxane. The flask was filled with argon atmosphere and sealed with a rubber septum. The mixture was heated to 60°C and the reaction was started by adding one drop of Karstedt`s catalyst via syringe. After 5-12 hours IR spectra showed complete disappearance of the Si-H bond. The solvent and residual allylamine were removed under reduced pressure and the product was dried under high vacuum for approx. 12 hours. ^{1}H-NMR (300 MHz, $CDCl_3$) δ[ppm] = -0.11-0.20 (s, Si-C*H*$_3$), 0.42-0.58 (br, Si-C*H*$_2$), 0.91-1.02 (br, R-N*H*$_2$), 1.39-1.54 (br, Si-CH_2-C*H*$_2$), 2.60-2.71 (br, R-C*H*$_2$-NH_2)

Dimethylsiloxane – methyl-polyglycerolsiloxane copolymer. In a 100 ml Schlenk flask, 3 g of amine-functionalized polymer together with 15 equivalents (referring to the amount of amine funtionalities) of glycidol were dissolved in a suitable amount of dry THF. The flask was set under argon atmosphere and sealed with a rubber septum. The resulting mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and residual glycidol was evaporated by heating the mixture to 80°C for 12 hours under high vacuum. ^{1}H-NMR (300 MHz, DMSO-d^6) δ[ppm] = -0.22-0.15 (s, Si-C*H*$_3$), 0.33-0.50 (br, Si-C*H*$_2$), 1.31-1.46 (br, Si-CH_2-C*H*$_2$), 2.24-2.58 (br, N(C*H*$_2$-)$_3$), 3.19-3.79 (br, C*H*$_2$-OR, C*H*$_2$-OH, C*H*-OR, C*H*-OH), 4.47-4.88 (br, R-O*H*)

Results and Discussion

Synthesis of glycerol-functionalized poly(siloxane)s.

To significantly increase hydrophilicity of the poly(siloxane) backbone via a route as simple as possible, glycerol-1-allylether has been directly attached by platinum catalyzed hydrosilylation. It is important to note that due to the charge distribution of the Si-H bond, in which in contrast to carbon-bound hydrogen, the hydrogen atom is partially negatively charged, nucleophilic substitution of the silicon-bound hydrogen by attack of alcohol functions is a prevalent side reaction. Therefore, hydrosilylation of glyceryl-1-allyl ether always occurs together with the formation of alkoxy-subsituted siloxane units. As addition of the polymer chain to the olefinic ether thus can occur at two sides of the molecule, this reaction leads to crosslinked poly(siloxane)s as the major product. Thus, hydrosilylation reactions at hydroxyl functional olefins cannot be carried out without the occurence of a significant amount of side products As a proof of principle, hydosilylation of PDMS-co-PMHS with glycerol-1-allyether has been carried out in various solvents. All reactions led to crosslinked products within less than one hour of reaction time, and IR spectra showed complete disappearance of the Si-H bond (see Supporting Information). However, carrying out the reaction in isopropyl alcohol did not lead to crosslinked products. In this case, all copolymers could reproducibly be converted with glycerol-1-allylether without any crosslinking. ^{1}H NMR and IR spectroscopic data of the samples evidences successful transformation. Due to the high excess of alcohol groups of the solvent, the formation of isopropoxy-substituted siloxane units becomes dominant over the nucleophilic substitution reaction between the Si-bound hydrogen and the hydroxyl functions of the glycerol ether. In this manner, crosslinking of the polymer chains can be avoided. Nevertheless, even in the presence of a high excess of isopropyl alcohol, the desired hydrosilylation remains the overall dominant reaction. However, the resulting poly(siloxane)s contain a significant amount of alkoxy-substituted units and this synthetic route can thus be concerned as unsuitable if well defined products are desired. To get rid of this problem, a synthetic way was developed in which the two hydroxyl groups of the glycerol ether side chain are protected by an acetalic function. The protected molecule can be linked to the silicone copolymer via hydrosilylation, followed by mild deprotection to yield a hydrophilized polysiloxane. The acetal-protected glyceryl-1-allylylether (1,2-isopropylidene-3-allyloxy-1,2-propanediol) was synthesized by means of a Williamson coupling of allyl bromide with solketal. (see **Figure 2**)

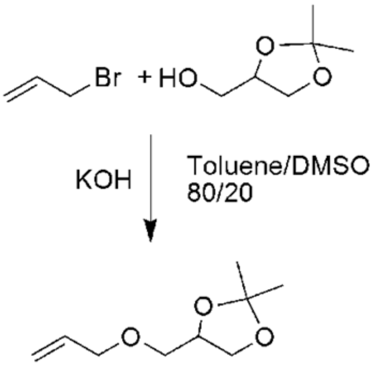


Figure 2. Synthesis of 1,2-isoropylidene-3-allyloxy-1,2-propanediol

Dioxane was found to be a suitable solvent for all hydrosilylation reactions. All ^{1}H NMR spectra showed complete disappearance of the Si-H proton as well as the double bond signals of the allyl ether, and a peak at about 0.5 ppm arises from the Si-bound methylene group of the side chain, confirming full conversion of the hydrosilylation reaction (see **Figure 3**). Deprotection was carried out in slightly acidic medium by use of a cationic exchange resin within 120 minutes. The complete synthetic pathway is shown in **Figure 4**.

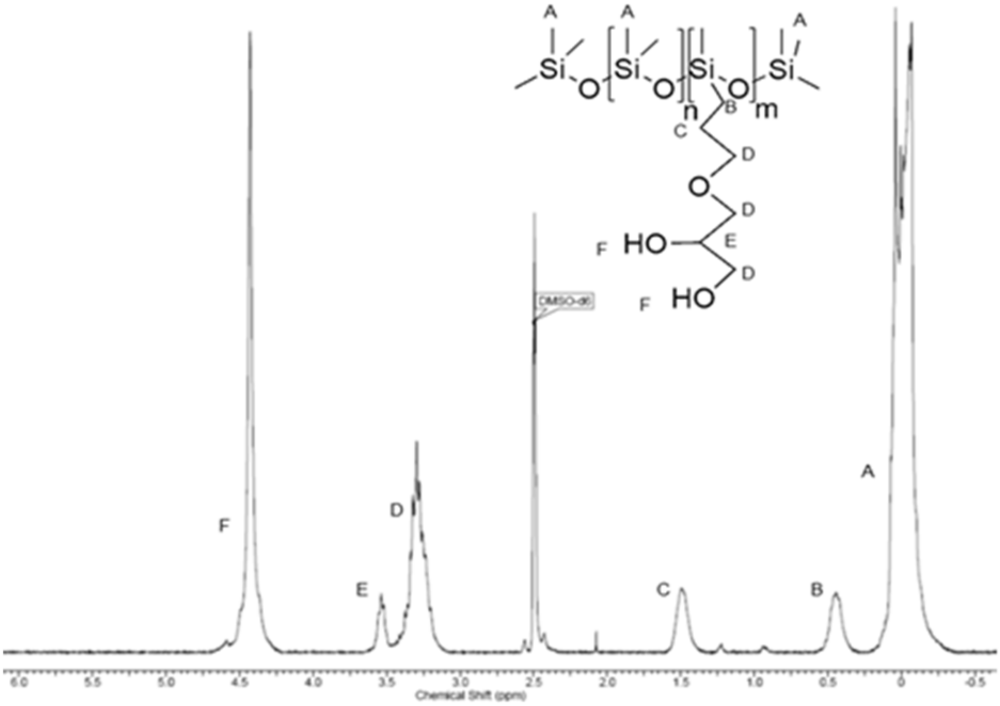


Figure 3. ^{1}H NMR spectrum (300MHz, DMSO-d_6) of PDMS(Gly)$_{30}$.

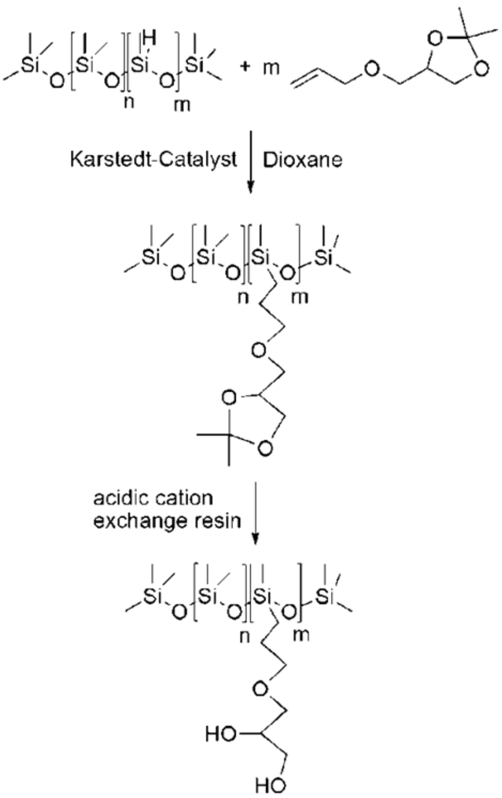


Figure 4. Synthesis of poly(siloxane) with hydrophilic glycerol side chains

During the deprotection step, the pH value needs to be adjusted carefully, because the poly(siloxane) backbone is not stable under extremely acidic or basic conditions. The use of a cation exchange resin thus is the method of choice, because deprotection can be achieved under mild reaction conditions. **Figure 3** shows the ^{1}H NMR-spectrum of the polymer obtained. We used several dimethylsiloxane-methylhydrosiloxane copolymers with a content of methylhydrosiloxane units between 7 and 80 % as well as a methylhydrosiloxane homopolymer to obtain poly(siloxane)s with different levels of hydrophilicity. **Table 1** shows the polymers that have been used for hydrosilylation reactions.

Table 1. Poly(siloxane) precursors

sample	M_n[a]	PDI[a]	% of SiMeH
PDMS-*co*-PMHS$_{10}$	10000	2.3	10
PDMS-*co*-PMHS$_{30}$	4000	1.7	30
PDMS-*co*-PMHS$_{80}$	850	1.2	80
PMHS	1700	1.4	100

[a] Molecular weights and PDIs were determined by gel permeation chromatography

All polymers were successfully hydrophilized by the described method. The exact dimension of the increase of hydrophilicity obviously depends on the density of glycerol side chains, which depends on the amount of Si-H groups within the starting copolymers. The related changes in solubility and other properties are discussed below.

Synthesis of poly(siloxane)s containing hyperbranched poly(glycerol) side chains.

In order to further increase hydrophilicity, we planned to introduce side chains that contain a significantly higher number of polar groups, such as polyglycerol.[19]However, to attach a polymeric graft like a poly(alcohol), several problems had to be solved. Since the unmodified PDMS-*co*-PMHS is extremely hydrophobic, dissolving it together with a very hydrophilic poly(alcohol) is difficult. When following this pathway, the alcohol groups need to be protected in an extensive polymer modification reaction. Besides, the “grafting to” process suffers from severe drawbacks concerning quantitative conversion and purification. Grafting polymeric side chains from the poly(siloxane) is crucial as well, as the conditions of an anionic polymerization would destroy the base-labile Si-O backbone of the silicone. Taking these problems into account, an alternative route for grafting a poly(alcohol) to a poly(siloxane) chain was developed, taking advantage of a synthesis developed by our group, in which bisglycidolized amines were prepared by nucleophilic addition of a primary amine to two glycidol molecules.[20,21] If an excess of glycidol is used under the same conditions reported for the bisglycidolization, hyperbranched poly(glycerol)s of low molecular weight can be synthesized. To apply this procedure to the modification of PDMS-*co*-PMHS, the starting copolymers were functionalized by hydrosilylation of allyl amine, producing poly(dimethylsiloxane)-*co*-poly(methyl-aminopropylsiloxane).(**Figure 5**)

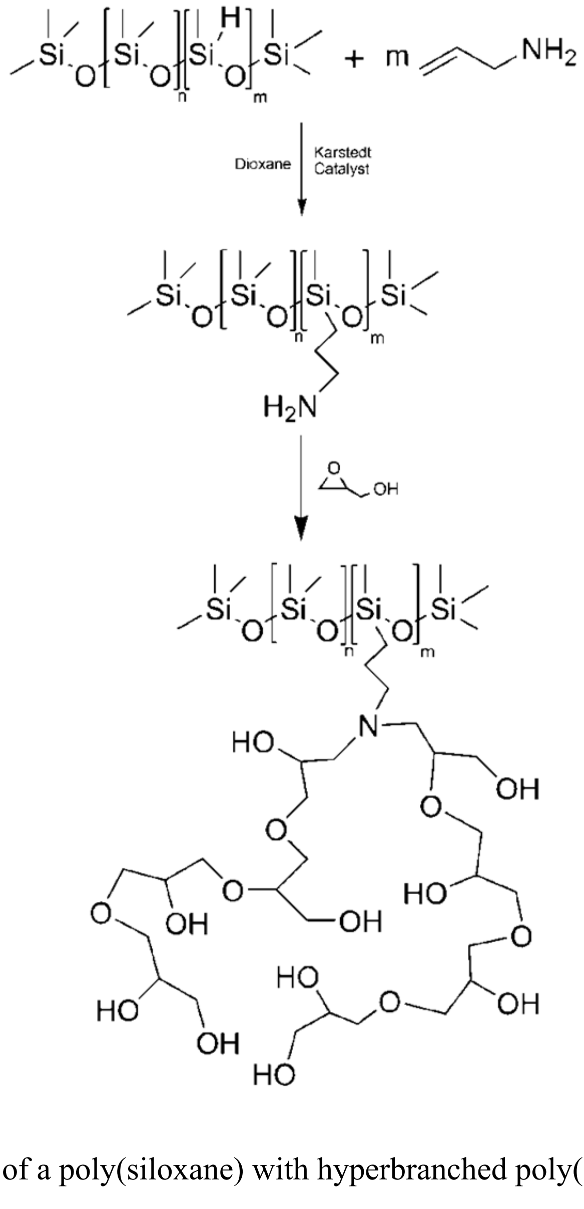


Figure 5. Synthesis of a poly(siloxane) with hyperbranched poly(glycerol) side chains

Hydrosilylation of allyl amine is a delicate synthetic step, because the free amine inactivates a certain amount of the hydrosilylation catalyst. Therefore, reactions were carried out using twice the amount of Karstedt catalyst as in common hydrosilylation reactions. After significantly longer reaction times, the Si-H bonds could quantitatively be converted into n-propyl amine side chains. Subsequently, the amine-functionalized polymers were converted with a 5-20fold excess of glycidol with respect to the amine-groups. This resulted in siloxane copolymers, grafted with small chains of hyperbranched poly(glycerol). The average degree of polymerization of the hyperbranched poly(glycerol) side chains was determined by ^{1}H NMR spectroscopy, using the integrals of the poly(glycerol) backbone. The average value that was calculated from the NMR spectra refers to eleven glycidol monomers per side chain. **Figure 6** shows the ^{1}H NMR spectrum of a siloxane copolymer grafted with hyperbranched poly(glycerol) side chains.

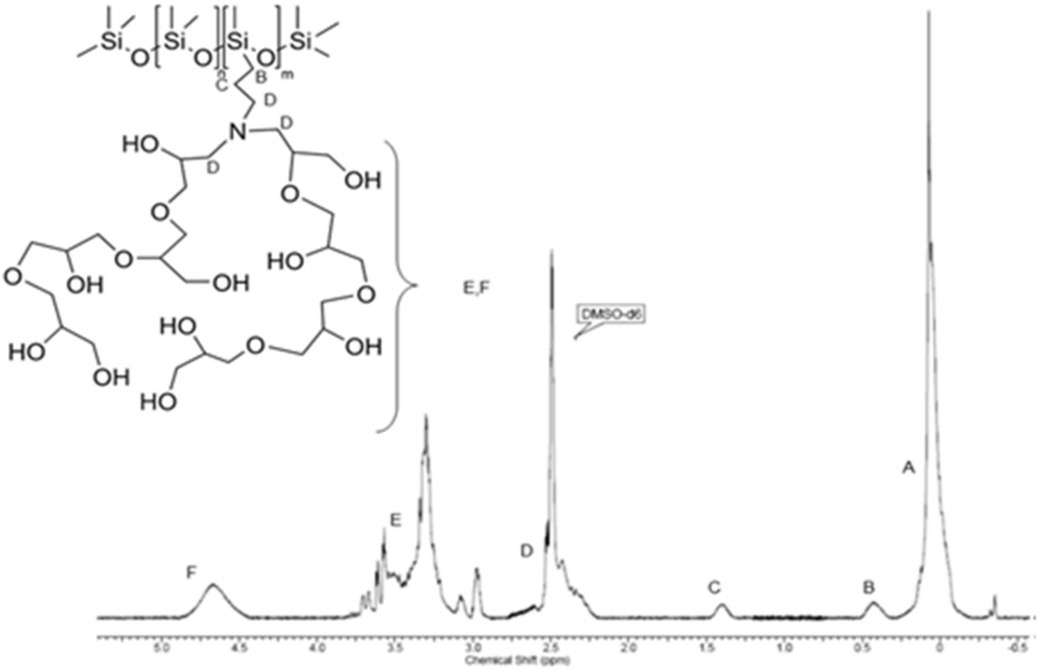


Figure 6. ^{1}H NMR spectrum (300MHz, DMSO-d_6) of PDMS(Gly)$_{30}$.

While it is possible to initiate the polymerization of glycidol by a primary amine, control over the molecular weight could not be achieved. Using a 15fold excess of glycidol, hyperbranched poly(glycerol) containing an average amount of about eleven monomer units could reproducibly be obtained, whereas higher degrees of polymerization were not realized.

Nevertheless, the described synthesis demonstrates a suitable procedure that provides easy access to silicones that are grafted with highly hydrophilic poly(alcohol)s.

The polymers prepared consist of a hydrophobic backbone and hydrophilic side chains and can therefore be seen as extremely amphiphilic structures. The materials show completely different viscosity and solubility in comparison to PDMS. The Si-H content of the starting copolymer is the main parameter influencing the extent of these effects.

Solubility of hydrophilic poly(siloxane)s.

An important feature of silicone polymers based on PDMS is their hydrophobicity. Despite the polar character of the Si-O bond, the organic moieties connected to silicon provide a shielding effect that causes insolubility in water or polar organic solvents. By the attachment of polar side chains, polarity and thus solubility can be tailored. Hydrophilic groups are found to have an influence both on the viscosity and the glass transition temperature of the polymer. The impact of all these properties is dependent on the degree of functionalization of the precursor polymer. To quantify their hydrophilicity, the modified poly(siloxane)s were dissolved in various solvents of different polarity. The weight fraction of the hydrophilic side chains was calculated from the percentage of methylhydrosiloxane units of the different polymers and the molecular weight of the side chain. These values were used as a measure for the hydrophilicity of the modified silicones. A second value that can be used is the number of hydroxyl groups per gram polymer (**Figure 7**).

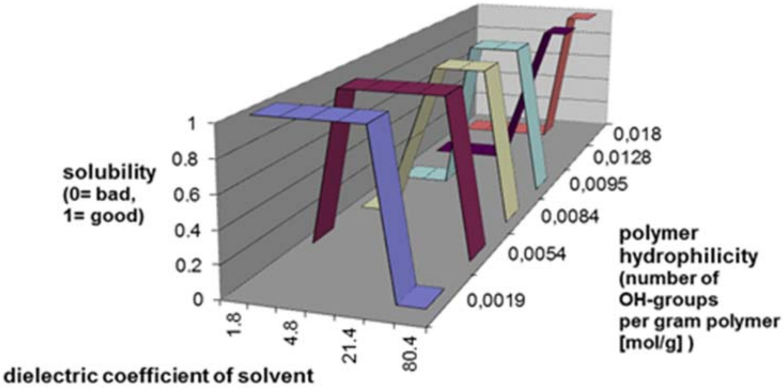
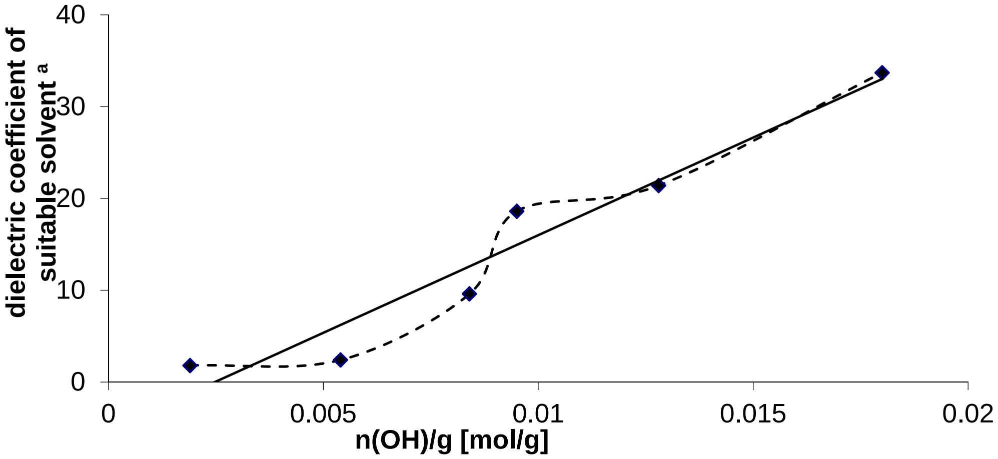


Figure 7. The solubility of the hydrophilic poly(siloxane)s was tested in various solvents of different polarity. Experiments were carried out at a concentration of 1 mg/ml at room temperature.

Although the analyzed structures exhibit a hydrophobic backbone and hydrophilic grafts, solubility is defined mainly by the side chains. The structure can be described as brush-like, with the side chains of the polymer forming the hydrophilic bristles of the brush. These bristles are capable of shielding the nonpolar polymer backbone, forming a hydrophilic surface of the polymer. The density of this hydrophilic surface depends on the percentage of methylhydrosiloxane units in the starting polymer. A higher hydrophilicity of the polymers thus leads to an increasing solubility in nonpolar solvents. To quantify this effect, solubility of the poly(siloxane)s was tested in 7 solvents of different polarity. **Figure 8** shows the results of the solubility experiments.



[a] Values show the dielectric coefficient of the most nonpolar suitable solvent

Figure 8. Correlation of hydrophilicity of the polymer, quantified by the value of OH groups per gram, and the polarity of the most apolar suitable solvent leads to a linear relationship between hydrophilicity and solubility

In contrast to the starting polymers, the hydrophilized poly(siloxane)s are not only soluble in nonpolar solvents. It can be seen that with increasing number of hydroxyl groups and thus hydrophilicity the solubility of the polymer switches to more hydrophilic solvents. A modified poly(siloxane) carrying about two mmol OH groups per gram is still very well soluble in nonpolar solvents like pentane, whereas for the silicone with 18 mmol/g, only methanol and water are suitable solvents. Polymers with a number of OH groups between these two are neither soluble in solvents like acetone or isopropanol with intermediate polarity. Figure 3 demonstrates that there is an almost linear relationship between hydrophilicity of the polymer and the minimum polarity of a suitable solvent. The results show that, concerning their solubility, the synthesized polymers exhibit an enormous versatility over a broad range. The solubility in polar solvents increases, depending on the type and number of side chains that are grafted onto the poly(siloxane) backbone. Water soluble silicones can be designed by grafting methylhydrosiloxane homopolymers with glycerol or hyperbranched poly(glycerol). Therefore, starting from different dimethylsiloxane-methylhydrosiloxane copolymers, poly(siloxane)s of any solubility can specifically be designed.

Thermal properties of hydrophilic poly(siloxane)s.

The glass transition temperatures of the synthesized poly(siloxane)s have been measured by DSC analysis to examine the effect of increasing hydrophilicity on the thermal properties of the materials. Molecular weights of the samples analyzed ranged between 2.000 and 17.000 g/mol. Polymers with side chains consisting either of glycerol or hyperbranched poly(glycerol) and varying in grafting density over a broad range have been studied. **Table 2** shows the precise data of the polymers.

Table 2. Hydrophilic poly(siloxane)s

sample	M [g/mol][a]	weight% of graft	n(OH)/g [mol/g]
PDMS(Gly)$_{13}$	11500	13	0.002
PDMS(Gly)$_{35}$	6100	35	0.005
PDMS(Gly)$_{57}$	1900	57	0.008
PDMS(Gly)$_{67}$	4600	67	0.010
PDMS(hbPG)$_{78}$	16800	78	0.013
PDMS(hbPG)$_{90}$	7200	90	0.018

[a] calculated from the amount of methylhydrosiloxane units in the starting copolymer

The hydrophilic character of the samples is again quantified by calculating the number of hydroxyl groups per gram polymer. According to expectation, the glass transition temperature of the sample rises with increasing hydrophilicity. This effect is very pronounced and is ascribed to the increasing effect of hydrogen bonding in the materials. Whereas the glass transition of the least hydrophilic polymer is still very low at about -110°C, the one with the highest content of hydrophilic side chains shows a glass transition at -10 °C. This demonstrates that by varying the hydrophilicity between 2 and 18 mmol of hydroxyl groups per gram polymer, an increase of the glass transition temperature of more than 100K occurs. **Figure 9** shows the increase of the glass transition temperature as a function of polymer hydrophilicity. Again, there is an almost linear dependence between these two parameters. This linear correlation allows to predict the glass transition temperature of such a poly(siloxane) via its calculable value of hydrophilicty. (For DSC curves see supporting information.)

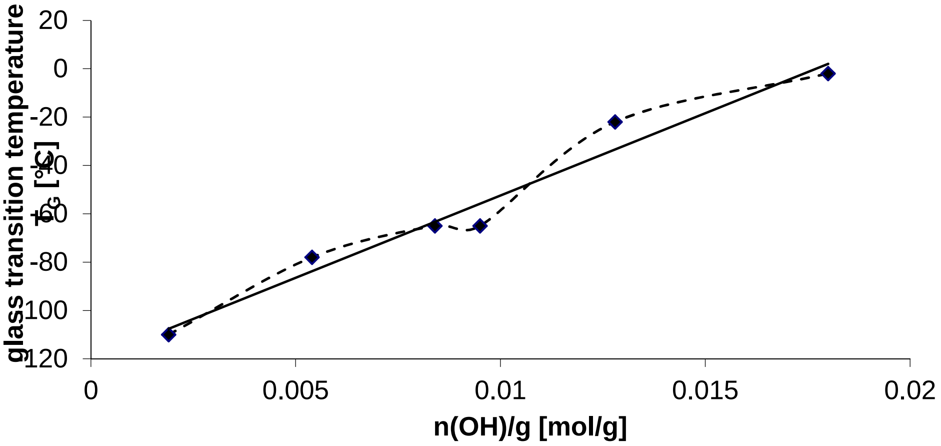


Figure 9. Correlation of hydrophilicity of the polymer, quantified by the value of OH groups per gram, and their glass transition temperature. Again, an almost linear relationship is observed.

Incorporation of hydrophilic silicones into liquid silicone rubber (LSR) formulations

The synthesized hydrophilic silicones were incorporated into standard LSR formulations in order to investigate their influence on the properties of the silicone rubbers. This was done particularly to check if an impairment of the mechanical properties of the resulting rubbers occurs and if an enhanced wettability of the rubber surface can be achieved. Furthermore, possible effects on the crosslinking kinetics that derive from the added silicones have been examined. The standard LSR formulation, consisting of vinyl terminated PDMS and PDMS chains that contain several hydride groups was modified in such a way that a specific amount of the distributing agent that assures efficient and homogeneous dispensation of the silica fillers within the polymer network was replaced by the hydrophilic poly(siloxane)s.

Mechanical Properties.

Hardness, tear strength, yield strain and tear propagation strength were tested. As the rubbers were subjected to two hardening steps, results are divided into A-step and B-step values. **Figure 10** summarizes the results from mechanical tests that were carried out on the rubber materials.

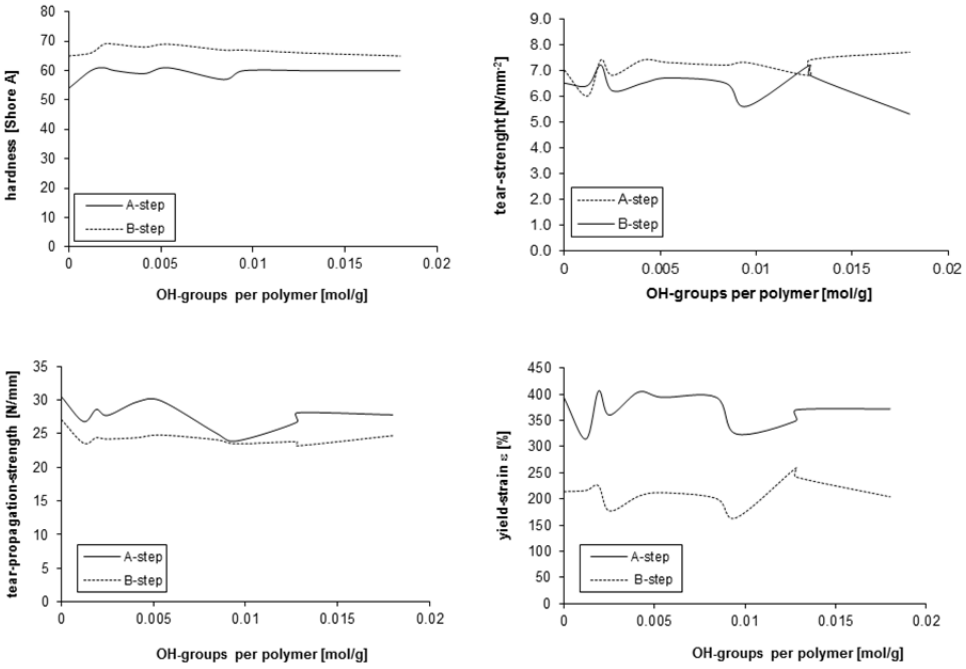


Figure 10. Results of mechanical tests in dependence of the hydrophilicity of the added polymer.

The second hardening step leads to an increased hardness of the material as well as lower tear strength, tear-propagation strength and yield strain values. Much more crucial is the fact that in all cases, only marginal changes of the mechanical properties of the rubbers are observed. Consequently, no trend concerning mechanical changes in dependence on the hydrophilicity of the added poly(siloxane) is visible. The results thus prove that the addition of the new modified polymers does not lead to an impairment of the silicone-specific properties of the resulting rubbers, which is an advantageous feature with respect to applicability of the material.

Contact Angle.

In order to investigate the wettability of the elastomer surface, contact angle measurements were carried out. Unfortunately, no enhanced wettability could be observed for any of the produced rubbers. Independently of the nature of the added hydrophilic poly(siloxane), contact angle values were more or less constant in a range between 90 and 100° (see supporting information). We assume that the reason for this missing effect on the surface properties is due to insufficient mobility of the hydrophilic poly(siloxane)s within the elastomer network. As they replace a certain amount of the distributor, the hydroxyl functional polymers can be suggested to bind to filler particles. As one polymer chain carries a large number of hydroxyl groups, several filler particles can be bound to one hydrophilic poly(siloxane), so that the mobility of these chains is significantly limited, inhibiting their migration to the elastomer surface.

Crosslinking Kinetics.

The process of crosslinking of the novel silicone rubber formulations was investigated by the use of a rubber process analyzing unit (RPA). Strain – torque diagrams were recorded, revealing that crosslinking is significantly accelerated by the addition of the hydrophilic silicones. T_{60} values decreased with an increased hydrophilicity of the added polymer (see. **Figure 11**). The assumption that this accelaration is just due to remains of platinum catalyst within the hydrophilic polymers was refuted by the fact that no curing occured without addition of platinum catalyst to the formulation. However, the reasons for this effect are not clear to us yet.

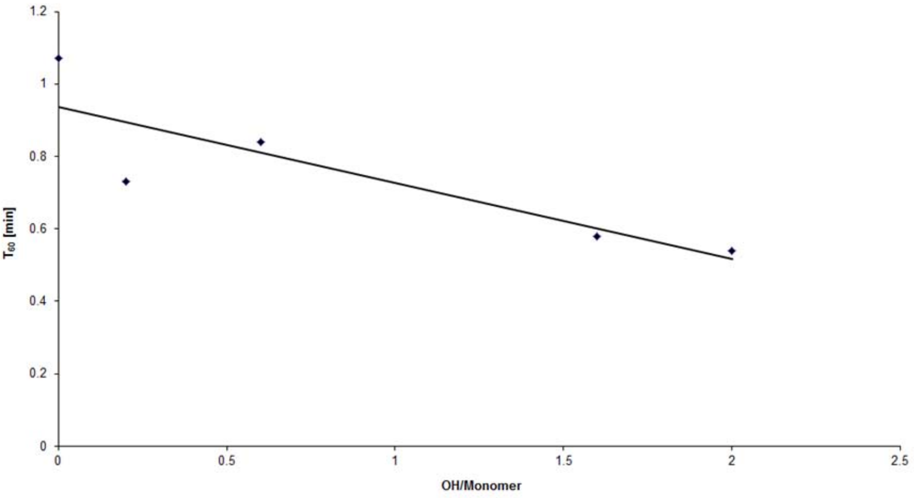


Figure 11. crosslinking speed as a function of hydrophilicity of the added polymer

Furthermore, the relationship between the hydrophilicity of the added polymer and S` $_{\text{min}}$, the elastic torque at the beginning of the RPA measurement, which characterizes the shear thinning and therefor the viscosity of the material was analyzed. Surprisingly, no systematic correlation between these two values could be observed. The polar nature of the added silicone seems to have no influence on the viscosity of the resulting elastomer. Nevertheless, we found a correlation between the S`$_{\text{min}}$ values and the chain length of the added polymer (see **figure 12**).

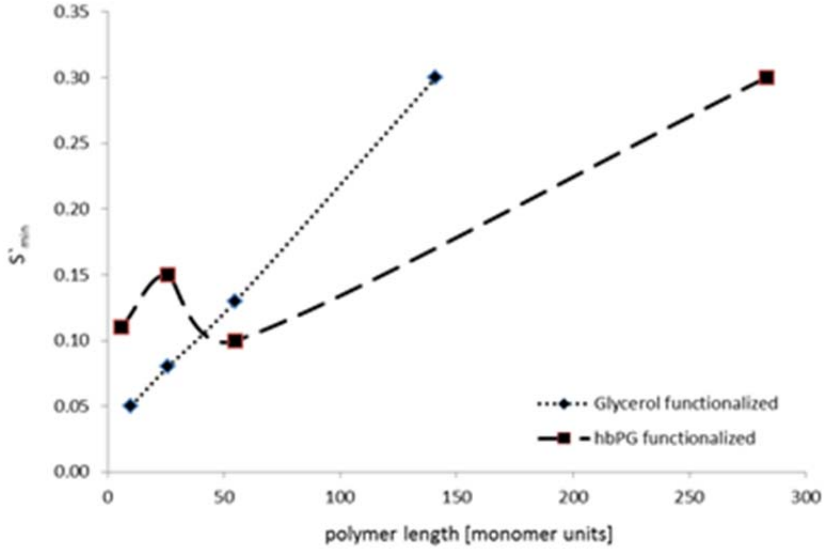


Figure 12. S`$_{\text{min}}$ as a function of the chain length of the added polymer

We assume that the reason for this effect is an enhanced number of silica particles that can be bound to a longer polymer chain. With an increased number of filler particles that are attached to one polymer, the mobility of the elastomer network decreases, which leads to an enhanced viscosity of the material. It is important to note that as the same LSR formulation was used for all produced elastomers, it can be assumed that the network density is equivalent for all samples.

Conclusion:

A new type of poly(siloxane)s carrying side chains of high hydrophilicity was synthesized via a facile two- or three step protocol. Poly(dimethylsiloxanes)s containing different amounts of methylhydrosiloxane units and thus providing different degrees of functionalization served as starting materials. In the first of two synthetic routes, a protected diol was connected to the polymer via hydrosilylation, followed by deprotection of the alcohol functions to obtain glycerol-like moieties at the PDMS backbone. In a different approach, a propylamine side chain was attached to the silicone backbone and was previously used to initiate the ring opening polymerization of glycidol to yield poly(siloxane)s with grafts of hyperbranched poly(glycerol). Solubility of the polymers was tested in various solvents of different polarity, revealing a linear relationship between the amount of polar groups in the polymer and its solubility in polar solvents. Furthermore, the hydrophilic moieties also turned out to significantly influence glass transition temperature of the silicone. In analogy to the solubility, a linear correlation between the T_G and the hydrophilicity of the modified silicones could be observed. Moreover, the hydrophilic silicones were incorporated into standard liquid silicone rubber formulations in order to investigate their influence on the properties of the resulting elastomer. No deteriorating effect on the mechanical features was observed, but unfortunately also no change in the surface wettability could be achieved. However, addition of the hydrophilic silicones accelerates crosslinking and leads to a higher viscosity of the material. In summary, the described polymers represent a yet unknown class of hydrophilic silicones which could be synthesized by a remarkably easy route within few reaction steps. This pathay allows easy synthesis of silicones that exhibit a desired solubility and glass transition temperature simply by varying the nature and amount of hydrophilic side chains. They thus offer high potential in a large field of different applications including medical devices, automobile parts and cosmetics.

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2.2 Polysiloxane-Backbone Block Copolymers in a One-Pot Synthesis: A Silicone Platform for Facile Functionalization

Paul Boehm, Mihail Mondeshki, Holger Frey*

Abstract

Block Copolymers consisting exclusively of a silicon-oxygen backbone are synthesized by anionic ring-opening polymerization of cyclic siloxanes. After formation of a poly(dimethylsiloxane) (PDMS) block by butyllithium-initiated polymerization of D3, a functional second block is generated by subsequent addition of tetramethyl tetravinyl cyclotetrasiloxane ($D4^V$), resulting in diblock copolymers comprised of a simple PDMS block and a functional poly(methylvinylsiloxane) (PMVS) block. Polymers of varying block length ratios were obtained and characterized by ^1H and ^{29}Si NMR spectroscopy as well as SEC. The vinyl groups of the second block can easily be modified with a variety of side chains using hydrosilylation chemistry to attach compounds with Si-H bond. Conversion of the hydrosilylation use for polymer modification was investigated by DOSY NMR spectroscopy.

Introduction

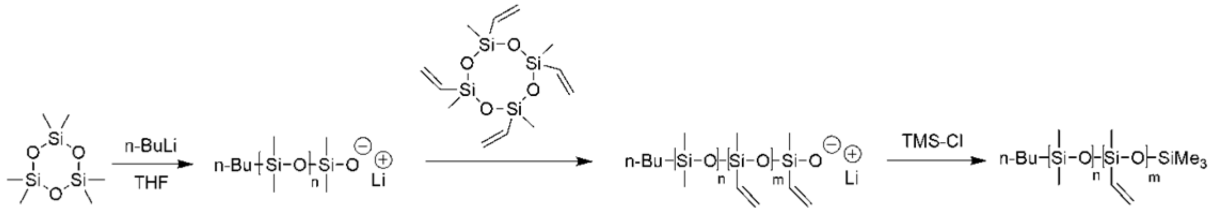
Polysiloxanes or silicones have been known for many years and are industrially produced on a remarkably large scale. They feature a set of unique properties, which has led to a high demand for silicones in different fields of applications like electronics, textile chemistry, cosmetics and many others. Because of the extraordinary flexibility of the polysiloxane chain, they possess the lowest glass transition temperatures of all known polymers and remain flexible even at very low temperatures. Besides, silicones are highly temperature resistant, show extremely low surface tension and high gas permeability. Concerning clinical applications and their use in cosmetics, silicones are especially qualified because of their absolute inertness towards biological systems.

There are numerous reports, in which silicones were used as a segment of block copolymer structures with carbon-based organic polymers in order to utilize their special features in combination with other materials properties. The best known example are polysiloxanes grafted with hydrophilic polyether chains, such as poly(ethylene glycol) (PEG). Such materials are also the subject of several patents and are often used in cosmetic products. Their specific properties have also been discussed in a number of publications.[1,2,3] Further information on polymer structures combining silicones with almost a variety of other polymers, either in the form of random or block copolymers or with grafted[4,5], branched[6,7,8] or star-shaped[,9,10,11] morphology and crosslinked polymer networks[12,13,14] can be found in literature. These approaches rely on the combination of polysiloxanes with organic polymer chains. The organic part of the molecule can either be attached by means of a grafting-through approach, or else the polysiloxanes are equipped with initating groups to be employed as a macroinitiator for the polymerization of a second monomer. Although most of these macromolecules exhibit properties that are strongly influenced by their siloxane content, there is always a "non-silicone" part present that leads to a decisive attenuation of the silicone-specific properties of the material.

In contrast, there are hardly any reports on block copolymer structures that solely consist of a flexible silicon-oxygen backbone.[15,16] Despite the fact that the controlled synthesis of polysiloxanes via anionic ring-opening polymerization is a well-known and established procedure, block-like structures derived from different cyclic siloxane monomers have hardly been explored. However, such macromolecules are promising for a whole set of possible applications related to the phase segregation present in common block copolymers, while fully retaining the silicone-specific features like thermal stability and gas permeability. Possible applications include emulsifiers, silicone compatible additives or low temperature devices.

Kickelbick et al. synthesized siloxane block copolymers with a functional block bearing epoxide moieties.[17] In a follow-up publication in 2004, they added several functional groups by ring-opening the epoxide through nucleophilic attack with amines or alcohols.[18] However, this method suffers from side reactions due to the oxy-anion formed after ring-opening. According to the authors these side reactions include inter- and intramolecular crosslinking, manifest in gelation and thus insolubility of most of the obtained products.

In the current work a new route for the synthesis of functional polysiloxane block copolymers was developed. Copolymers consisting of a nonfunctional poly(dimethylsiloxane) (PDMS) block and a functional block of poly(methylvinylsiloxane) (PMVS) have been synthesized via anionic ring-opening polymerization. Butyllithium was used to initiate polymerization of hexamethyltrisiloxane (D3). Subsequent to the polymerization of D3, the second block was synthesized by addition of tetramethyltetravinylcyclotetrasiloxane to generate well defined block copolymers. Subsequently, modification via hydrosilylation with different Si-H containing molecules has been carried out (**Scheme 1**).



Scheme 1. Synthesis of PDMS-*b*-PMVS block copolymers in a two-step, one-pot reaction

Experimental Part

Materials.

All reagents and solvents were purchased from Acros Organics or Sigma-Aldrich and used without further purification unless otherwise stated. Octadecyldimethylsilane, triethoxysilane and (1,2)-epoxypropoxypropyl dimethylsilane were purchased from Gelest and used as received. Tetramethyl-tetravinylcyclotetrasiloxane was purchased from Gelest and purified by distillation prior to use. THF was dried over sodium and freshly distilled prior to use.

Instrumentation.

^{1}H NMR spectra (300 MHz) were recorded using a Bruker AC 300 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. All DOSY NMR spectra were recorded at ambient temperature on a digital Bruker Avanche DRX 400 MHz spectrometer with B_0 field corresponding to ^{1}H resonance frequency of 400.31 MHz. The spectrometer was equipped with a commercial Bruker 5 mm inverse probehead. ^{29}Si NMR spectra were recorded on a digital Bruker Avanche DRX 400 MHz spectrometer at a frequency of 79.53MHz.For SEC measurements in trichloromethane, a setup consisting of a Waters 717 plus Autosampler, a TSP Spectra Series P 100 pump, three PSS-SDV-5 µl-columns with 100, 1 000, and 10 000 Å pore diameter, respectively, a UV (275 nm) and an RI detector was used. Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service (PSS).

Polymerization.

8 g of hexamethylcyclotrisiloxane were cryotransferred into a 100 ml schlenk flask. The flask was set under argon atmosphere and 30 ml of dry THF were added via syringe. Then the polymerization was started by injecting the respective amount of a 1.6 M solution of *n*-butyllithium in hexane. After the appropriate time to complete D3 polymerization, freshly distilled tetramethyltetravinylcyclotetrasiloxane (8 g) was added to the living polymer. The polymerization was quenched by injection of a 1.5 fold excess of trimethylchlorosilane with respect to the initiator concentration employed. After 30 minutes, the flask was opened and water and *n*-pentane were added to the polymer solution. The organic phase was isolated, the aqueous phase extracted with pentane again and the organic phase washed twice with water. After that, the organic phase was dried with $MgCl_2$, the solvent removed under reduced pressure, and the polymer dialyzed in THF for at least one night. After solvent evaporation the isolated polymer was dried under high vacuum at 140°C to obtain a yield of 14.6 g (91%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.18\text{-}5.71$ (m, $C\mathit{H}{=}C\mathit{H}_2$), 1.32, (br, $C\mathit{H}_2C\mathit{H}_2CH_3$), 0.90 (t, $C\mathit{H}_3$), 0.55 (t, $SiC\mathit{H}_2$), 0.30- -0.19 (br, $SiC\mathit{H}_3$) ^{29}SI NMR (xxxMHz, $CDCl_3$): $\delta = 8.08$ (s, $Si(CH_3)_3$), -22.05 (br, $Si(CH_3)_2$), -35.00 (s, $SiCH{=}CH_2$)

Polymer modification via Hydrosilylation.

In a 100 ml Schlenk flask, 0.5 g of PDMS-*b*-PMVS were dissolved in dry chloroform. The flask was set under argon and the respective amount of hydrosilylation agent was injected through a rubber septum via syringe. The reaction mixture was heated to 60 °C and one drop of Karstedt´s catalyst was added. The reaction was stirred at 60 °C overnight. Then the solvent was removed under reduced pressure and the polymer was purified by dialysis in THF. Yield: 95-99%.

Poly(dimethylsiloxane-*b*-2-(dimethyloctadecylsilyl)ethyl-methylsiloxane)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.18-5.73 (m, $CH{=}CH_2$), 1.42-1.19 (br, CH_2), 0.90 (t, $CH_2CH_2CH_3$), 0.55 (t, $SiCH_2$), 0.28 - -0.12 (br, $SiCH_3$)

Poly(dimethylsiloxane-*b*-2-(1.2-epoxypropoxypropyldimethylsilyl)ethyl-methylsiloxane)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81-3.67 (br, OCH_2CH), 3.61-3.35 (br, OCH_2CH and CH_2CH_2O), 3.22-3.11 (br, $CH_2CH(O)CH_2$), 2.86-2.77 (br, $CH(O)CH_2$), 2.68-258 (br, $CH(O)CH_2$), 1.71-1.52 (br, CH_2CH_2O), 1.44-1.17 (br, $CH_2CH_2CH_3$), 1.01-0.80 (br, CH_2CH_3), 0.63-0.44 (br, $SiCH_2$) , 0.37 - -0.25 (br, $SiCH_3$)

Poly(dimethylsiloxane-*b*-2-(triethoxysilyl)ethyl-methylsiloxane)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.96-3.71 (br, OCH_2CH_3), 1.37-1.04 (br, OCH_2CH_3 and $CH_2CH_2CH_3$), 0.94-0.83 (t, $CH_2CH_2CH_3$), 0.66-0.42 (br, $SiCH_2$), 0.31- -0.17 (br, $SiCH_3$)

Results and Discussion

Block Copolymer Synthesis

The polymer modification of silicones is a frequently used method for the synthesis of functional or hydrophilic silicones.[19,20,21] In most cases, the polymers that are used in these approaches are polysiloxanes with varying amounts of Si-H functional monomer units that are randomly distributed at the poly(dimethylsiloxane) chain. Such polymers can easily be synthesized by equilibration polymerization, using the respective mixture of Si-H functional and non-functional cyclic monomers. However, this method cannot be applied for the synthesis of well-defined block copolymers. Since an in situ synthesis of block copolymers requires living polymerization techniques, anionic ring-opening polymerization is the method of choice with regard to controlled siloxane polymerization. However, the Si-H bond is reactive towards nucleophiles and reacts via nucleophilic substitiution of the silicon-bound hydrogen. Therefore it is not possible to apply anionic polymerization techniques when using Si-H containing monomers, because the anionic growing chain ends are likely to attack the hydrogen-carrying silicon atom, leading to undesired crosslinking and other side reactions. Thus it is inevitable to use another kind of monomer equipped with a stable functional group that is not affected by the conditions of an anionic polymerization and at the same time offers the possibility for further polymer modification reactions. Hence, the cyclic monomer tetramethyltetravinylcyclotetrasiloxane ($D4^V$) was used to form the functional segment of the block copolymer. The vinyl groups of the resulting macromolecule were modified subsequent to the polymer synthesis to attach different functional units at the polysiloxane backbone. The dimethylsiloxane-*b*-methylvinylsiloxane block copolymers were synthesized by subsequent addition of the two monomers without intermediate work-up. As, with regard to anionic ring-opening, cyclotrisiloxanes are known to polymerize much faster than cyclotetrasiloxanes due to the difference in ring strain, the polymerization was started by initiating D3 ring-opening with n-butyl lithium. After full conversion of the first monomer, the second block was started by adding $D4^V$ to the living polymer chains. The reaction was quenched by addition of trimethylchlorosilane as a terminating agent to create trimethylsilyl endgroups. The polymerization procedure is depicted in **Scheme 1** (vide supra). During the polymerization, samples were taken in specific time intervals to monitor the progress of the reaction. The results obtained from SEC measurements showed that D3 polymerization is fast, and molecular weights of 2000 to 3000 g/mol can be achieved within less than one hour at ambient temperature. In contrast, synthesis of the second functional block, deriving from $D4^V$ polymerization was found to be almost an order of magnitude slower, and it was not possible to achieve full conversion of the D4 monomer. However, as $D4^V$ polymerization provided satisfying results, there was no need to use its six-membered analog trimethytrivinyl-cyclotrisiloxane, which is known to polymerize faster.[22] (For kinetic data see the Supporting Information section). The reason for this large difference in the polymerization rates is the different ring strain of the two monomers. As bond angles in siloxanes are significantly larger than those of carbon-carbon bonds, 6 membered siloxane rings are much more strained than their 8 membered analogs, leading to faster polymerization of cyclotrisiloxanes than for cyclotetrasiloxanes.[22] Nevertheless, for block copolymers that are synthesized by subsequent monomer addition, it is essential to ascertain the absence of statistically distributed monomers between the distinct blocks, which would be obtained, if the second monomer is added before reaching full conversion of the first. In order to support this, ^{29}Si NMR spectra of the block copolymers have been recorded (see Supporting Information). These spectra show sharp and distinct signals at the respective shift values for the silicon atoms within the PDMS chain at -22 ppm and the PMVS block at -35 ppm, respectively. The trimethylsilyl end groups can be discerned at 7 ppm. The fact that none of the signals split into triplets, which would occur if there was a part of the polymer in which the monomers are randomly distributed, proves that both blocks are fully separated, i.e. that growth of the second block commences only after full conversion of D3 and formation of the first block.

PDMS-*b*-PMVS block copolymers of several different block length ratios were synthesized. The size of the PDMS block was varied between 1000 and 7000 g/mol and that of the PMVS blocks from 1000 to 5000 g/mol. **Table 1** gives the molecular weight data and block length ratios of some of the synthesized polymers.

Table 1. Block Length Ratios and Molecular Weight Data of PDMS-*b*-PMVS Block Copolymers

M_n PDMS-PMVS (targeted)	**M_n PDMS-PMVS (NMR)**	**Block length ratio (NMR)**	**M_n (SEC)**	**M_w (SEC)**	**PDI (SEC)**
3000-3000	4000-1800	69:31	4200	4800	1.13
3000-3000	2600-2100	55:45	1900	2400	1.29
2000-4000	2400-1600	60:40	2700	3200	1.2
4000-2000	5200-1600	77:23	6700	8600	1.29
6000-2000	6600-2100	76:24	8200	10000	1.27
2000-4000	3300-4300	43:57	3800	5800	1.53
1000-5000	1600-4500	26:74	3700	5000	1.37
3000-3000	3800-2200	63:37	5900	7100	1.20
5000-1000	6000-1000	86:14	6300	10000	1.61
1000-5000	1300-2500	34:66	3100	4300	1.39

With regard to the PDMS block, the degrees of polymerization calculated from ^{1}H NMR spectra always were in very good agreement with theoretical values, and block lengths could be precisely adjusted. Due to incomplete monomer conversion, the molecular weights obtained for the PMVS block were always smaller than estimated from the amount of D4 monomer used. **Figure 1** shows a representative ^{1}H NMR spectrum of one of the synthesized polymers.

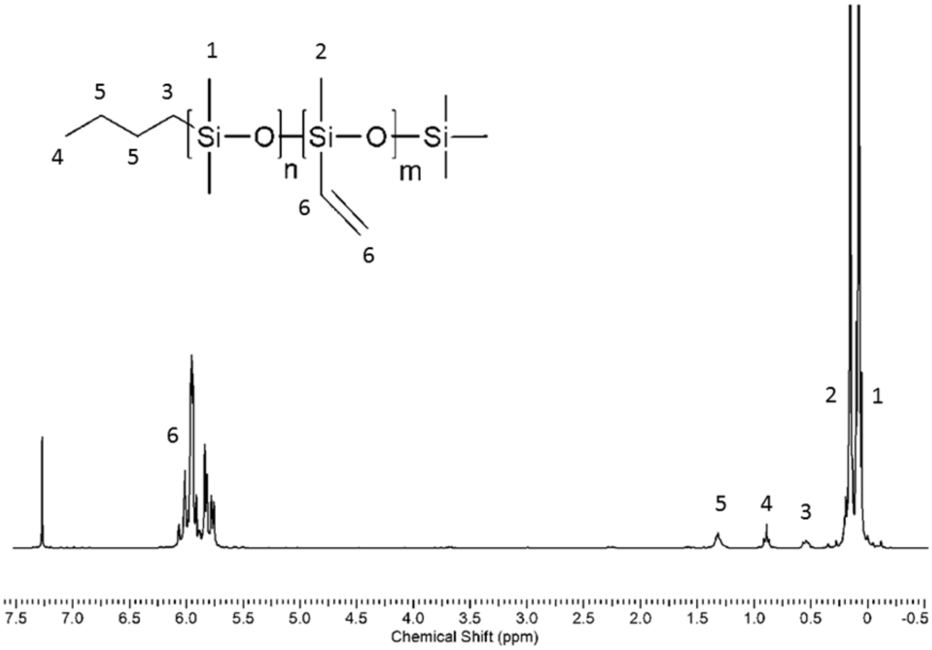
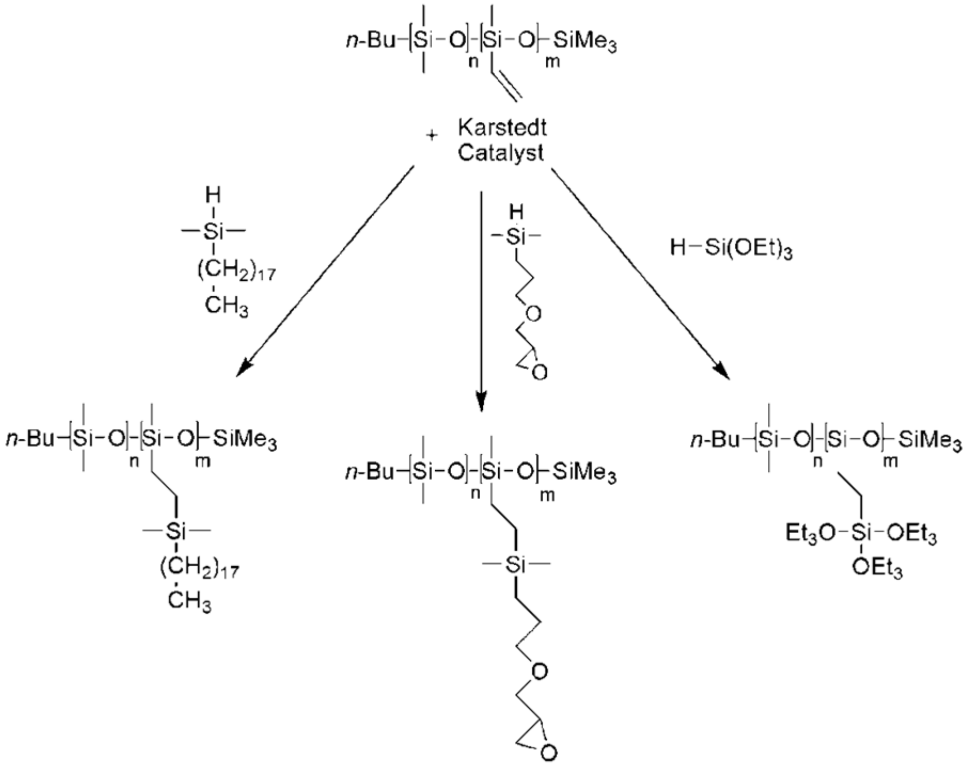


Figure 1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of PDMS-*b*-PMVS

The signals of the initating *n*-butyl group are observed at 0.5, 0.8 and 1.3 ppm, respectively. Their integrals were used to calculate the degree of polymerization of both polymer blocks, taking into account the vinyl signals of the PMVS block at approximately 5.9 ppm and the methyl protons of the silicone backbone at 0.0 ppm.

Polymer Modification by Hydrosilylation

Different side chains have been attached to the vinyl groups of the functional polymer block using hydrosilylation chemistry. This pathway offers the opportunity to synthesize block copolymers that possess a mere silicon-oxygen backbone and consist of a nonfunctional PDMS block and a second block that can bear a variety of functional groups as side chains. Nevertheless, in order to be attached to the polymer, the functional molecules must possess a Si-H group that is reactive towards platinum-catalyzed hydrosilylation. In the present work, we chose three readily available Si-H containing molecules of different polarity and functionality. These are (glycidoxypropyl)tetramethyldisiloxane, dimethyloctadecylsilane and triethoxysilane. The reaction between these compounds and the PDMS-*b*-PMVS polymers is shown in **Scheme 2**.



Scheme 2. Functionalization of PDMS-*b*-PMVS via hydrosilylation

It has to be noted that full conversion of all vinyl groups could only be achieved in the reaction with triethoxysilane, which is in accordance with the fact that electron withdrawing substituents at the silicon atom increase the reactivity of the Si-H bond.[23] All other hydrosilylations showed a small amount of residual vinyl groups (less than 10%). We assume this also to be due to the high steric demand of the two larger Si-H-functional molecules that inhibits full conversion of the vinyl groups that are attached to every second atom of the polymer backbone. As a detailed investigation of the resulting polymers was not achieved by conventional NMR spectroscopy, diffusion-ordered spectroscopy ((DOSY)-NMR spectroscopy) was carried out on the modified block copolymers. This 2D-method correlates the chemical shift of the protons with the translation diffusion coefficient of the respective molecule they belong to. In the spectrum shown in **Figure 2**, all proton signals appear on one horizontal line, meaning that they do not differ in their diffusion coefficient.

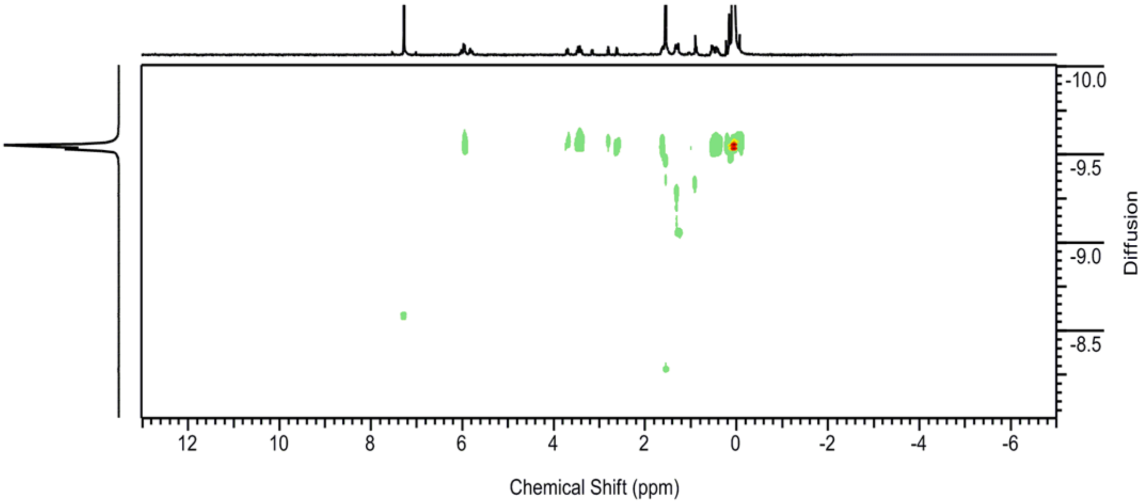


Figure 2. DOSY NMR spectrum (400.31 MHz, $CDCl_3$) of Poly(dimethylsiloxane-*b*-2-(1.2-epoxypropoxypropyldimethylsilyl)ethyl-methylsiloxane)

The fact that the signals of all protons deriving from the attached side chains show the same diffusion coefficient as the protons belonging to the polymer backbone proves that all measured side chains are connected to the polymer structure. This is important, because for all hydrosilylations, an excess of the Si-H compound was used in order to attain maximum conversion. The small residual signals of higher diffusion coefficients at 0.9 ppm and 1.3 ppm derive from solvent traces that were present in the analyzed solution. The absence of excess Si-H compound, proven by DOSY NMR spectroscopy, shows that it could adequately be removed by subsequently dialyzing the polymer in THF. Moreover, SEC diagrams of the hydrosilylation products show a clear shift of the molecular weight distribution maximum, compared to the PDMS-*b*-PMVS precursor without any change in the polydispersity of the resulting modified polymer (see Supporting Information for SEC traces).

Conclusion

A new pathway for the controlled two-step, one-pot synthesis of well-defined polysiloxane block copolymers that consist of a mere silicon-oxygen backbone has been developed. Applying anionic living polymerization techniques followed by hydrosilylation for polymer modification, this new type of functional silicones can be obtained in two reaction steps in a one-pot reaction. Block length sizes and ratios as well as the number of functional groups can be precisely adjusted and functionalization via hydrosilylation provides good conversions without notable side reactions. In the present work, substituents bearing ethoxysilanes or epoxides as well as long aliphatic chains have been successfully attached to the precursor polymer. As a large variety of molecules equipped with Si-H function is available via reaction with dimethylchlorosilane by means of a nucleophilic substitution of the chlorine, this route offers great versatility as a platform for the synthesis of functional polysiloxane copolymers for surface attachment via a reactive blocks and for complex fluids.

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Supporting Information:
“Polysiloxane-Backbone Block Copolymers: A Platform for Facile Functionalization”

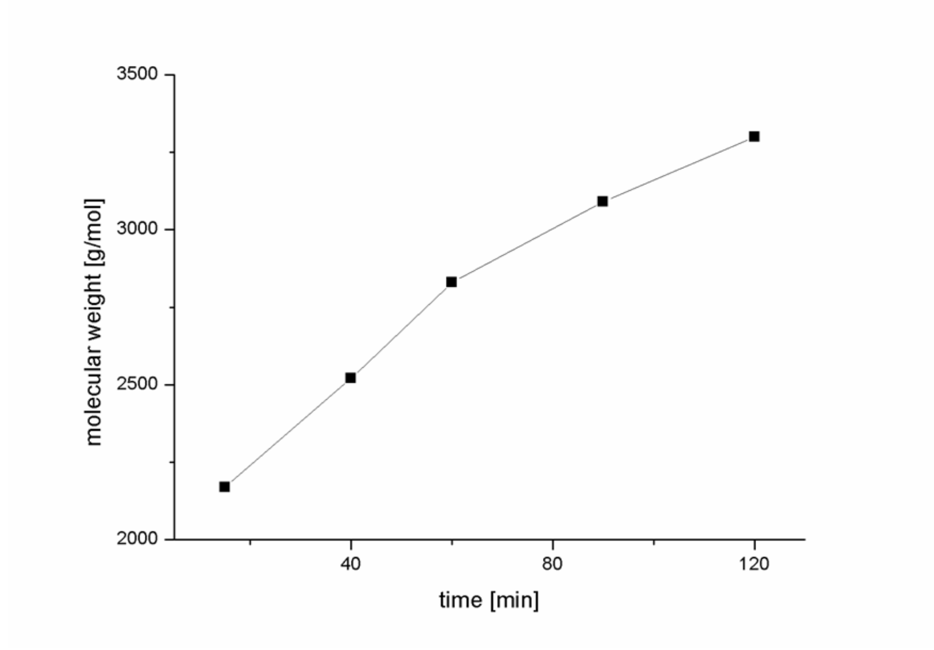

Figure S1. Increase of molecular weight in D3 polymerization initiated by *n*-BuLi

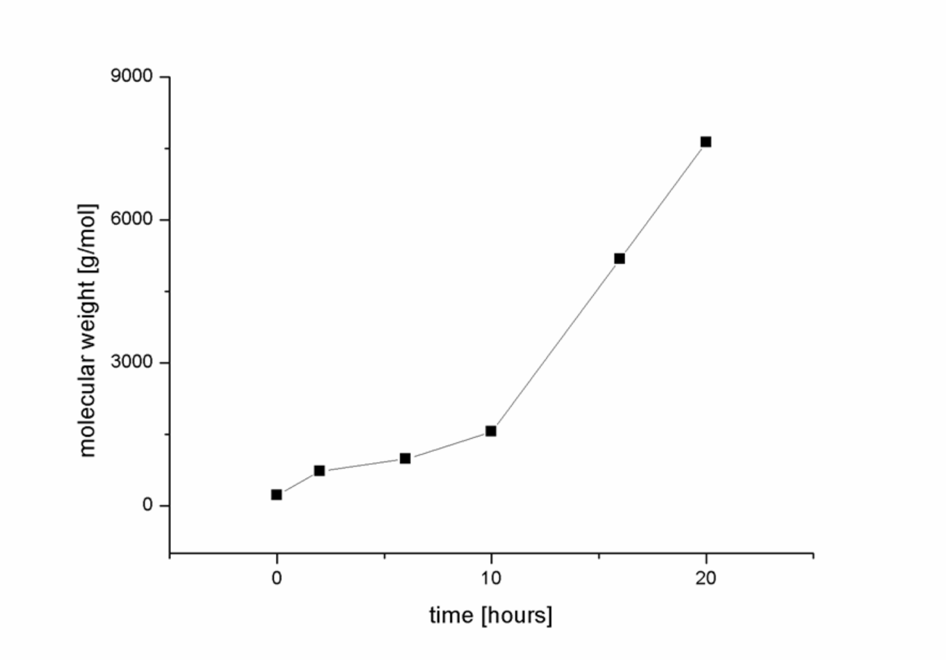

Figure S2. Increase of molecular weight in $D4^V$ polymerization initiated by living PDMS chains

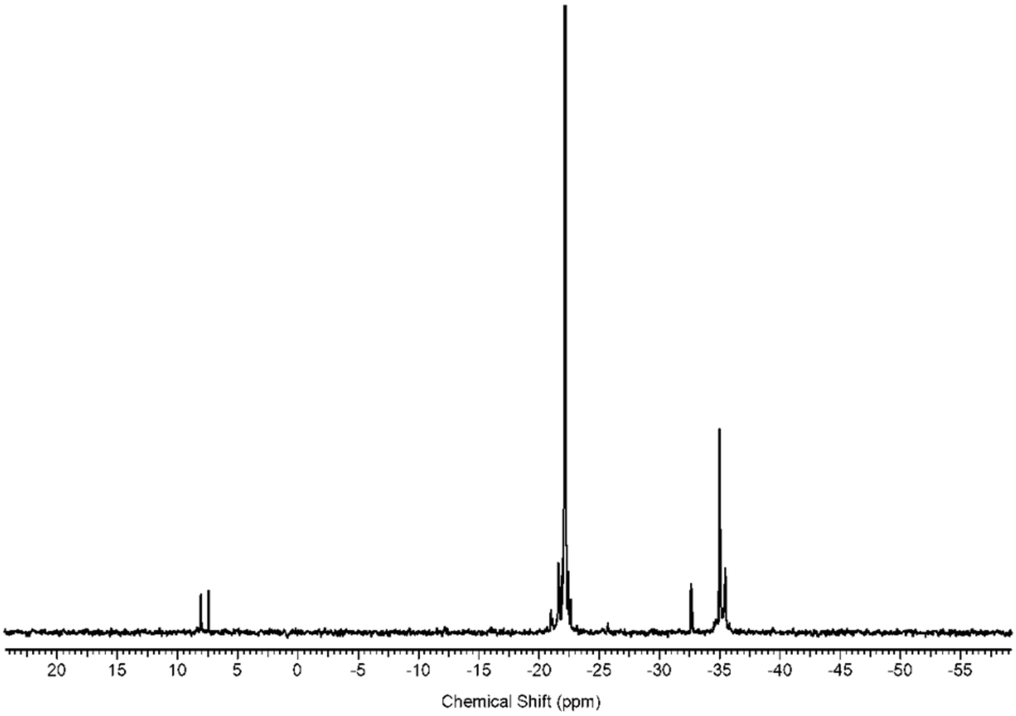

Figure S3. ^{29}Si NMR spectrum (79.53 MHz, $CDCl_3$) of PDMS-*b*-PMVS

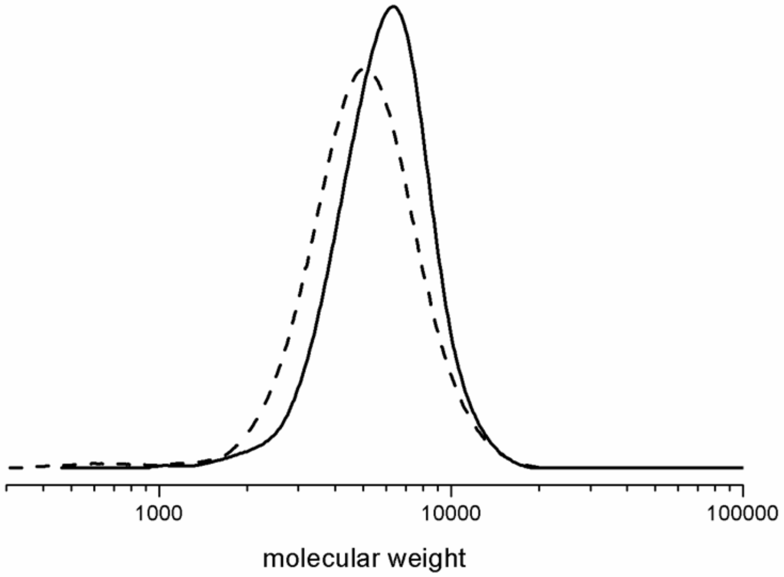

Figure S4. SEC traces (PS standard, eluent: chloroform) of PDMS-*b*-PMVS (dashed line) and the product of its hydrosilylation with (glycidoxypropyl)-tetramethyldisiloxane (straight line)

2.3. Block Copolymers Based on Poly(lactide) and Poly(dimethylsiloxane) – Strongly Segregated Systems

Paul Böhm, Anna M. Fischer, Jochen S. Gutmann, Marcin Makowski, Michael Kappl, Holger Frey

ABSTRACT

AB- and ABA-type block copolymers consisting of poly(dimethylsiloxane) and poly(lactide) segments have been developed. The synthesis was carried out using hydroxyl end-functionalized poly(dimethylsiloxane)s, prepared via anionic or cationic ring-opening polymerization (ROP), as a macroinitiator for the ring-opening polymerization of the dilactide. Block-length ratios were calculated from ^{1}H NMR and were in the range of 1:9 to 9:1 (PDMS:PLLA) and molecular weights between 1.000 and 36.000 g/mol were synthesized, obtaining PDIs of 1.2 to 1.3. Thermal properties were analyzed by DSC measurements and the bulk structure and surface morphology of the different polymers was investigated by use of AFM and TEM analysis. Both PLLA- and PDLA-based block copolymers have been prepared and were demonstrated to form stereocomplexes. Materials derived from stereocomplexation of the poly(lactide) blocks offer potential for application in the field of thermoplastic silicone elastomers.

Introduction

During the last decade, there is an extensively growing interest in poly(lactide)s (PLA), especially for packaging purposes. Compared to common commodity plastics they owe some important advantages, as they are based on renewable resources and thus environmentally friendly while providing the same performance as commonly used polymers like for example poly(ethylene). Poly(lactide) is biodegradable, possesses good barrier properties and adapts well in the biological environment.[1-3] However, there are still some PLA features that need to be improved with respect to their application, especially its thermal stability and mechanical properties. Also with regard to processing steps like extrusion, a reduction of the high brittleness of poly(lactide) would be beneficial. An enhancement of the thermal stability of PLA can be achieved by stereocomplexation between poly(L-lactide) and poly(D-lactide), which leads to a significant increase of its melting point.[4-8] Moreover, the stereocomplexation of PLA can be used to form or stabilize molecular assemblies, which is of special importance with regard to PLA-containing block copolymers. The use of PLA stereocomplexation to stabilize certain morphologies has been demonstrated in several examples.[9-12] Moreover, block copolymerization can also be used to enhance the properties of poly(lactide).[13-18]

In the current work we aim at a facile synthetic route towards block copolymers combining poly(lactide) and poly(dimethylsiloxane). The properties of silicones, especially poly(dimethylsiloxane)s are strikingly different from those of poly(lactide). This is particularly true with regard to the thermal behavior. Because of the high flexibility of the silicon-oxygen backbone, the glass transition temperature of poly(siloxane)s is lower than -100°C, which represents the lowest value of all known polymers. Therefore, the high flexibility and low viscosity of silicones is retained even at very low temperatures.[19-22] Besides, silicones exhibit a set of unique properties that distinguishes them from almost any other polymer with organic backbone.[23-26] They show extraordinarily high gas permeability, they are stable against atmospheric oxygen and UV-light and bioinert. This is the reason why silicones are of great importance and have gained an enormous market share in polymer industry. Consequently, silicones are especially qualified to soften polylactides, while additionally providing a set of beneficial properties that complement the features of the resulting material.

The different properties of poly(dimethylsiloxane)s (PDMS) and poly(L-lactide)s (PLLA) motivated us to generate a series of AB- and ABA-type block copolymers comprising these polymers. Very recently, Hillmyer et al. reported on the photolithographic application of

PLLA-*b*-PDMS-*b*-PLLA ABA-type block copolymers synthesized by using a commercially available, bifunctional PDMS macroinitiator for the ring-opening polymerization of lactide.[27] Admittedly, the combination of these two polymers is extraordinarily interesting from several points of view, at which a precise investigation of the influence of different block length ratios on the properties of the resulting copolymers is required. Therefore we synthesized mono- and difunctional PDMS chains of several block lengths, investigating AB- as well as ABA-type block copolymer structures. The synthetic routes are shown in Figures 1 and 2. Polymers were characterized by ^{1}H NMR spectroscopy, and the molecular weights distributions were determined via size exclusion chromatography (SEC). The thermal properties of the di- and triblock copolymers were characterized by differential scanning calorimetry (DSC) measurements. Small-angle X-ray scattering (SAXS) as well as atomic force microscopy (AFM) were used to examine the bulk- and surface morphology of the material. Furthermore, the stereocomplexation between PDLA-*block*-PDMS-*block*-PDLA and PLLA-*block*-PDMS-*block*-PLLA was studied by DSC analysis.

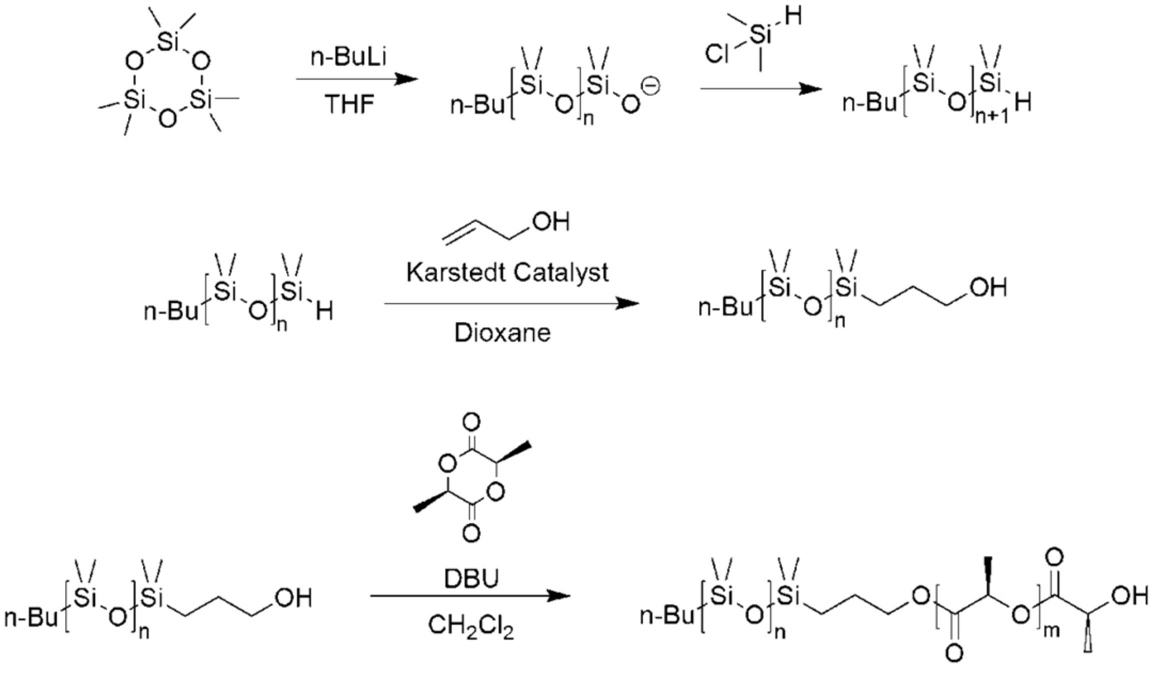

Figure 1. Synthesis of PDMS-*b*-PLLA diblock copolymers.

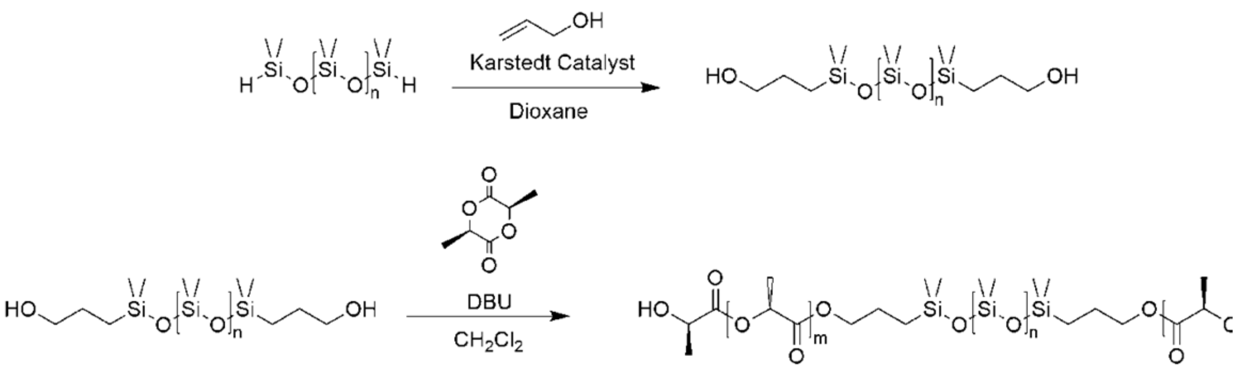

Figure 2. Synthesis of PLLA-*b*-PDMS-*b*-PLLA triblock copolymers.

Experimental Section

Reagents. All reagents and solvents were purchased from Acros Organics or Sigma-Aldrich and used without further purification unless otherwise stated. 1,8-Diaza-bicyclo[5.4.0]undec-7-ene (DBU) was purified by stirring with CaH_2 and subsequent distillation under Argon atmosphere and was stored at low temperatures for a maximum of one week prior to use. L-Lactide was purchased from Purac (Groningen, Netherlands), recrystallized twice from toluene and stored under vacuum prior to use. Hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) were purified by stirring with CaH_2 and freshly distilled before use. Dimethylsilylchloride and tetramethyldisiloxane were freshly distilled before use. Amberlite IRA 743 ion exchange resin was dried under reduced pressure at 60°C. Acid treated bentonite "Tonsil Optimum 210 FF" was purchased from Sued-Chemie and used as received.

Instrumentation. ^{1}H NMR spectra (300 MHz) were recorded using a Bruker AC 300. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in chloroform, a setup consisting of a Waters 717 plus autosampler, a TSP Spectra Series P 100 pump, three PSS-SDV-5 µl-columns with 100, 1 000, and 10 000 Å pore diameter, respectively, a UV (275 nm), and an RI detector was used. Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service (PSS). DSC curves were recorded on a Perkin Elmer DSC 7 and a Perkin Elmer Thermal Analysis Controller TAC 7/DX. Samples were measured in the range of -100 to 200°C with a heating and cooling rate of 20 or 10 K/min, respectively.

AFM images were taken in dynamic mode, using a Dimension 3100 from Veeco Instruments, CA, equipped with Olympus OMCL-AC240TS cantilevers suitable for soft materials imaging. Polymers were dissolved in methylene chloride and spin coated on a silicon wafer. Before spin coating, the silicon wafers were cleaned in an ultrasonic bath using ethanol and acetone and dried with nitrogen. After spin coating some of the samples where heated to 160°C for at least one hour to allow rearrangement of the polymer chains. Images were taken from droplets that formed during the dewetting process caused by heating the sample. Transmission Electron Micrographs were taken on a Philips EM-420, equipped with a slow-scan CCD camera and a LaB_6 cathode, operating at an acceleration voltage of 120 kV.

Synthetic Procedures. *Mono hydride-terminated PDMS by anionic ring-opening polymerization of D3.* Hexamethylcyclotrisiloxane (D3) was cryo-transferred into a 100 ml Schlenk flask equipped with a stirring bar. The flask was purged with argon and sealed with a rubber septum. D3 was dissolved in anhydrous THF, which was added via syringe. Polymerization was started by adding the respective amount of *n*-butyllithium (1.6M solution in hexane). After 2 hours of stirring at ambient temperature, the reaction was quenched by a 1.5 fold excess (with respect to the amount of initiator) of chlorodimethylsilane, and the solution was stirred for another 30 minutes. Subsequently, water was added and the polymer was extracted by threefold extraction with pentane. The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. After drying under high vacuum the polymer was obtained in 95% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.71 (s, 1H, Si*H*), 1.33 (br, 4H, $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$), 0.89 (t, 3H, $C\mathit{H}_3CH_2CH_2$), 0.53 ($SiC\mathit{H}_2$), 0.07 (br, $SiC\mathit{H}_3$, backbone).

Double hydride-terminated PDMS by cationic ring-opening polymerization of D4. D4 was distilled into a Schlenk flask equipped with a stirring bar. While the flask was purged with argon, 0.02 weight% of acid-treated bentonite was added and the flask sealed with a rubber septum. A respective amount of tetramethyldisiloxane was then added via syringe and the mixture was heated to 60°C. After an appropriate amount of time, the reaction was cooled to room-temperature. The polymer was dissolved in chloroform and filtered to remove the bentonite catalyst. The polymer was obtained by removing the solvent under reduced pressure and drying the polymer under high vacuum to yield double hydride-terminated PDMS in 85% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.71 (s, 2H, Si*H*), 0.07 (br, $SiC\mathit{H}_3$, backbone).

Hydrosilylation with hydride-terminated poly(dimethylsiloxane)s. A 100 ml Schlenk flask, equipped with a stirring bar and sealed with a rubber septum was put under argon atmosphere and the polymer together with a 1.3 fold excess of allyl alcohol were added and dissolved in anhydrous dioxane. The mixture was heated to 70°C and two drops of Karstedt`s catalyst were added via syringe. After 8 hours, the reaction was cooled to room-temperature, the solvent removed under reduced pressure and residual allyl alcohol was disposed by distillation. To remove platinum, the obtained polymer was again dissolved in dioxane, Amberlite ion exchange resin was added and the stirring mixture was heated under reflux for two days. Subsequently, the ion exchange resin together with the adsorbed platinum was filtered off and the pure polymer was obtained by removing the solvent under reduced pressure. Yield: 98%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.58 (br, 4H, CH_2OH), 1.58 (br, 4H, CH_2CH_2OH), 0.52 (br, 4H, $SiCH_2$), 0.07 (br, SiC_{H3}, backbone).

Ring-opening polymerization of lactide. In a 100 ml Schlenk flask equipped with a stirring bar, the homo- or bishydroxy-functionalized PDMS macroinitiator together with the respective amount of lactide were dissolved in anhydrous methylene chloride (5 ml CH_2Cl_2/g lactide). The polymerization was started by adding 1 mol% of DBU (with respect to the amount of lactide) via syringe. After 20 minutes of stirring at ambient temperature, the reaction was quenched by addition of 1.3 mol% of benzoic acid (with respect to the amount of DBU), dissolved in methylene chloride. The reaction mixture was washed with water three times, the combined layers dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield the block copolymer in 90 % yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 5.16 (q, $CH(CH_3)$, poly(lactide) chain) 4.36 (q, 2H, $HOCH(CH_3)$), 4.09 (br, 4H, CH_2CH_2O), 1.59 (d, $CH(CH_3)$, poly(lactide) chain), 1.32 (br, 4H, $SiCH_2CH_2$), 0.89 (br, 3H, $CH_2CH_2CH_3$), 0.54 (br, 4H, $SiCH_2$), 0.07 (br, $SiCH_3$, poly(dimethylsiloxane) chain)

Stereocomplexation of PLLA and PDLA chains. Stereocomplexation between PLLA and PDLA blocks of two block copolymers was induced following the method of Ikada et al.[27] Both polymers were dissolved in methylene chloride to obtain a concentration of 1 g/ml. The two solutions were mixed dropwise under vigorous stirring at a 1:1 volume ratio. The mixed solution was cast on a flat glass slide, allowing the solvent to slowly evaporate for about 5 days. The resulting films were then dried in vacuo for 24 hours.

Results and Discussion

Anionic ring-opening polymerization of hexamethylcyclotrisiloxane. In order to synthesize PDMS with a silicon-bound hydrogen atom at only one end of the polymer chain, termination of the anionic ring-opening polymerization of hexamethylcyclotrisiloxane was carried out with chlorodimethylsilane. A 1.6 molar solution of *n*-butyllithium in hexane was used to initiate the polymerization. Due to its high ring strain, polymerization of the D3 monomer proceeds fast even at ambient temperature. Although polymerization time depends on the designated chain length, full conversion was achieved after 2 hours at most. The molecular weight of the obtained polymers was analyzed by SEC and additionally calculated from ^{1}H NMR spectroscopic data, correlating the integral values of the initiator and the methyl groups of the PDMS backbone. The values obtained by both methods are in good agreement at least for smaller chains. Nevertheless, the discrepancy between these two values becomes larger with growing size of the PDMS chain. (See Supporting Information for a table of the SEC and ^{1}H NMR data of some of the PDMS macroinitiators). Molecular weight distributions of the polymers obtained are in the range of 1.1 – 1.3. The SEC curve of a PDMS macroinitiator is shown in figure 3.

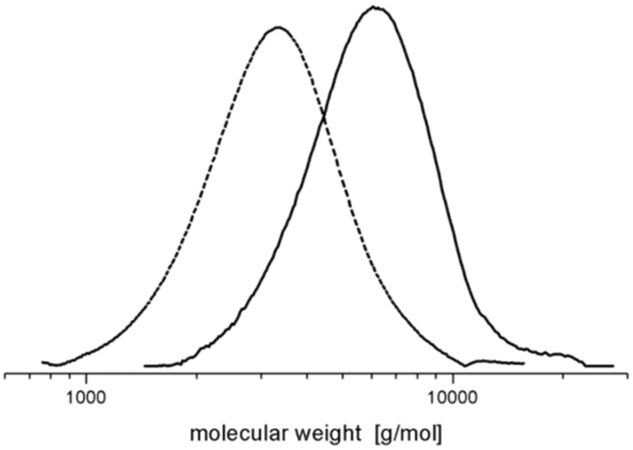

Figure 3. SEC (PS standard, eluent: chloroform) diagrams of hydroxyalkyl-terminated PDMS macroinitiator (---) and PDMS-*b*-PLLA (—)

Cationic ring-opening polymerization of octamethylcyclotetrasiloxane. Cationic ring-opening polymerization of the D4 monomer was carried out to obtain bifunctional poly(dimethylsiloxane)s. For this purpose we took advantage of a method developed in 2007 by Chen et al. in which acid treated bentonite is used as a catalyst.[29] Bentonite is a special kind of bleaching earth that is actually used for decoloration of oils or textiles. It is made of montmorillonite, an aluminumhydrosilicate in which some of the silicon atoms are replaced by iron(III) and some of the aluminum atoms are replaced by magnesium. This leads to negatively charged metal layers between the oxygen atoms that stabilize the montmorillonite structure. This charge can be neutralized by any kind of cation located between the anionic layers. The fact, that these neutralized cations can be replaced easily, makes bentonite something like a natural cation exchange resin. Although the mechanism of this kind of polymerization is not definitively cleared to date, it is proposed that initiation takes place by adsorption of the cyclic monomer on the surface of the heterogenous catalyst followed by ring-opening through a free proton located inside the montmorillonite. Subsequently, polymerization proceeds by electrophilic attack of the silicon cation on another cyclic monomer. Termination occurs when the growing chain attacks a molecule of the terminating agent tetramethydisiloxane, leading to silicon-bounded hydrogen at each end of the polymer chain. The use of acid treated bentonite thus provides a facile route to obtain bifunctional poly(siloxane)s of narrow molecular weight distribution over a broad size range.

The synthesized polymers were characterized by ^{1}H NMR spectroscopy and SEC and show molecular weight distributions around 1.3 to 1.4. However, full conversion could not be accomplished and a certain amount of residual monomer had to be removed under vacuum at high temperature even after a polymerization time of several days. Due to the fact that back- and end biting processes become more and more dominant with longer reaction times, leading to broader molecular weight distributions and a higher amount of low-molecular weight species, we optimized polymerization times between 8 and 20 hours, depending on the chain length of the desired polymer. ^{1}H NMR spectroscopic data of the obtained polymer can be found in the supporting information.

Hydrosilylation of allyl alcohol with mono- and bifunctional poly(dimethylsiloxane)s. Hydrosilylation reaction with allyl alcohol was carried out in order to accomplish hydroxyalkyl-functionalities at one or accordingly both ends of the poly(siloxane). Dioxane was chosen as solvent to properly dissolve the hydrophobic PDMS macroinitiator as well as the more hydrophilic allyl alcohol. A platinum-divinyltetramethyldisiloxane complex (Karstedt catalyst) was used to catalyze the hydrosilylation reaction. The reaction process was followed by IR spectroscopy, observing the gradual disappearance of the stretching vibration of the Si-H bond at about 2150 cm^{-1}. According to these results, hydrosilylations were carried out for 3 hours to ensure full conversion. Complete conversion could easily be proven by ^{1}H NMR spectroscopy, showing that neither a peak of silicon-bounded hydrogen of the PDMS chain nor olefinic protons of the allyl alcohol are left in the spectrum. A 1.3

fold excess of the olefinic compound was used in all hydrosilylation reactions. This point is crucial because unreacted PDMS chains would retain as macromolecular impurities which can hardly be removed after polymerization of the lactide block. It is important to note that despite the fact that nucleophilic substitution of the silicon-bounded hydrogen by hydroxyl groups is a well-known side reaction in hydrosilylation of alcohols, no alkoxy-substituted silicon could be found in the ^{29}Si NMR spectra of the product.[30]

Ring-opening polymerization of lactide from PDMS macroinitiators. The hydroxyalkyl-functionalized poly(dimethylsiloxane)s were used as macroinitiators for the ring-opening polymerization of the cyclic lactide monomer to obtain the desired poly(lactide)-poly(dimethylsiloxane) copolymers. A base-catalyzed mechanism was conducted for the lactide polymerization, using the well-known catalyst DBU, which works superb for ring-opening lactide polymerization on a laboratory scale. DBU-catalyzed lactide polymerization features an optimal balance of fast polymerization kinetics and well-controlled polymerization. Although all polymerizations were carried out at room temperature, the reaction time did not exceed 20 minutes. The degree of polymerization could be controlled by adjusting a suitable monomer/initiator ratio. Due to the size distribution of the PDMS macroinitiator it was difficult to target a precise chain-length of the PLLA block. For initiators of smaller molecular weight (< 4000 g/mol), the exact value was calculated from the signal integrals in the ^{1}H NMR spectrum, but because of growing impreciseness in the proportion of the different peak integrals, the M_n determined by SEC was used as a measure for the molecular weight of the hydroxyalkyl-terminated PDMS. Nevertheless, molecular weight distributions of the resulting block copolymers appeared considerably narrow after addition of the poly(lactide) block. In some cases, especially regarding the polymers composed of initiators of higher molecular weight, PDIs of the block copolymers were even smaller than that of the initiating PDMS. Certainly, it has to be taken into account that in case of the ABA-type triblocks, no information about the homogeneity of the size of the two PDMS-flanking PLLA blocks was available. Molecular weight of the AB- and ABA-type block copolymers was determined by SEC, but could also be calculated by ^{1}H NMR spectroscopy. For this purpose, signal integral of the methin proton of the PLLA end group was compared to the integral of the methin protons within the PLLA chain to calculate the length of the PLLA block, whereas the ratio between the integrals of the butyl-initiator and the methyl groups of the PDMS chain was used to determine the PDMS block length. **Figure 4** shows the ^{1}H NMR spectrum of a PDMS-*b*-PLLA copolymer.

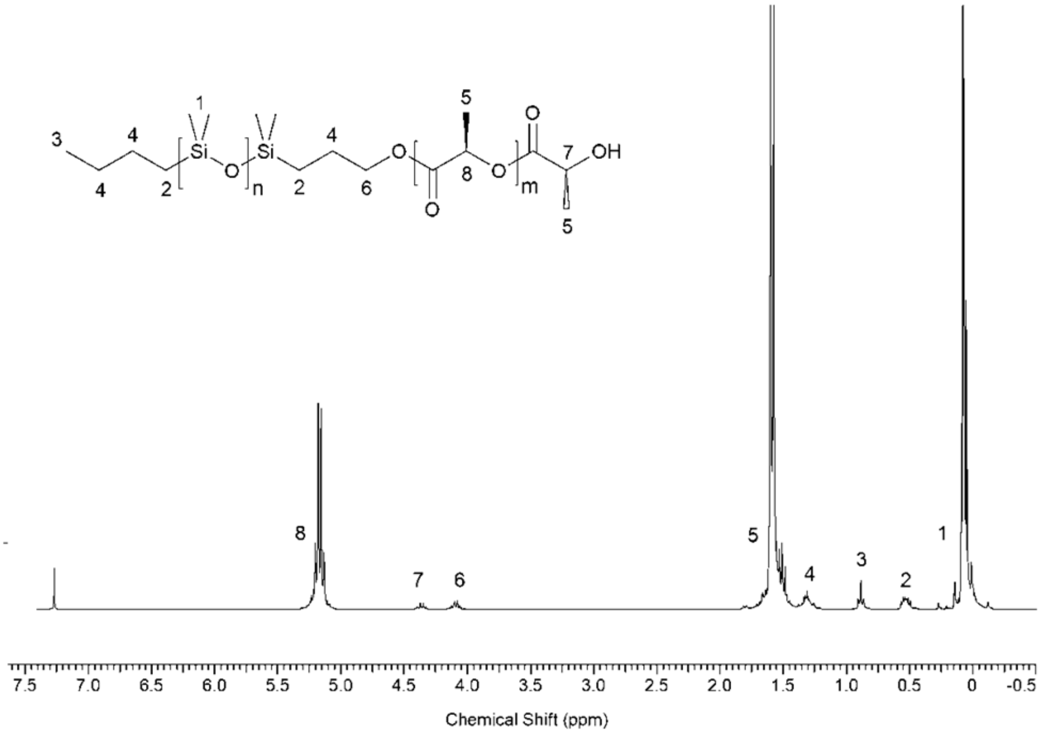

Figure 4. ^{1}H NMR spectrum (300MHz, $CDCl_3$) of PDMS-*b*-PLLA.

An overview of the block copolymers that were synthesized during this work is shown in **Table 1 and 2**.

PDMS block (g/mol)*	PLLA block (g/mol)*	M_n (g/mol)$^+$	M_w (g/mol)$^+$	PDI
1400	4600	8600	11600	1.15
1300	2500	7900	10400	1.31
3000	3200	5000	6000	1.19
4100	5100	6500	8200	1.27
1000	8700	7100	9100	1.28
3800	1400	3900	4900	1.28
8400	2800	6200	8000	1.29
10900	1700	6000	7900	1.30
700	600	1800	2400	1.30

*calculated from ^{1}H NMR spectrum ($CDCl_3$, 300 MHz)
$^+$SEC data, polystyrene standard, eluent: chloroform

Table 1. Molecular weights of PDMS-*b*-PLLA diblock copolymers

PDMS block (g/mol)*	PLA block (g/mol)* (per side)	M_n (g/mol)$^+$	M_w (g/mol)$^+$	PDI
9000	8300	20200	25000	1.24
2800	3200	9600	12900	1.34
3500	3300	9100	12000	1.30
6800	1500	10900	15200	1.40
26400	4900	36400	55300	1.64

*calculated from ^{1}H NMR spectrum ($CDCl_3$, 300 MHz)
$^+$SEC data, polystyrene standard, eluent: chloroform

Table 2. Molecular weights of PLLA-*b*-PDMS-*b*-PLLA triblock copolymers

The size of the PDMS block was varied between 1.000 and 20.000 g/mol and the molecular weight of the PLLA chains is in the range between 1.000 and 9.000 g/mol. However, determining the exact size of the polymer becomes more difficult with increasing chain lengths. This is due to the fact that, as already mentioned above, calculations based on the correlation of the different peak integrals is only reliable up to a certain polymer size. Additionally, poly(styrene) standards were used to calibrate the SEC instrument, which somehow led to a systematic underestimation of the molecular weights of the samples. Nevertheless, the values of the molecular weight determined by SEC and ^{1}H NMR spectroscopy are in good agreement at least for the smaller polymers.

Thermal properties of the block copolymers. Differential scanning calorimetry (DSC) was used to investigate the thermal properties of the synthesized block copolymers and the extent to which the phase transitions of the several blocks depend on the polymers` composition. Poly(dimethylsiloxane) homopolymers usually exhibit a very low glass transition temperature of about -125°C and a melting point of approximately -40°C. Depending on their chain-length, poly(L-lactide) homopolymers show a glass transition at 38 – 56 °C and a melting point between 135 and 170 °C. The respective values of the analyzed poly(dimethylsiloxane)-poly(lactide) block copolymers show only a slight dependency on the presence of the other block. Admittedly, the fact that these values are visible in the DSC experiment indicates that within the bulk structure of these polymers, the distinct blocks are arranged in separate domains, which explains the fact that they only slightly influence each other with regard to glass transition, crystallization and melting temperature. Nevertheless, a certain dependence of the polymer composition on the crystallization temperature of the PDMS block was observed. Table 3 depicts the results of the DSC measurements of some of the synthesized polymers. In case of the AB-like PDMS-*b*-PLLA block copolymers, crystallization of the PDMS block seems to be facilitated by an increasing length of the PLLA block. This is most probably due to a “fixation” of the actually very flexible PDMS chains by crystalline PLLA segments that ease crystallization of the PDMS block. The contrary effect occurred regarding the glass transition of the PLLA block of the diblock copolymers. The highly flexible PDMS chains seem to impede the transition of the PLLA chain into the glassy state, leading to a decrease of the PLLA glass transition temperature with an increasing length of the PDMS block. However, there was no effect of the block length ratios on the melting point of the PLLA block which varied between 135 and 145 °C without showing any kind of systematic dependence. It should also be noted that some block copolymers showed neither a crystallization- nor a melting point of the PDMS block, an effect that is well-known for PDMS-containing block copolymers.[31] Basically the same tendencies are visible in case of the ABA triblock copolymers, whereas the PDMS block tends to be much less affected by the PLLA block than vice versa. There are rather small differences in the crystallization temperature of the PDMS block, while the PLLA glass transition temperature is perceptibly decreasing with an increasing PDMS block length. This indicates an effect that becomes arbitrative in the process of stereocomplexation of the PLLA blocks of these copolymers which will be discussed further down, namely that the high flexibility of the PDMS chain significantly disturbs an accurate high order orientation of the system at least in some cases.

PDMS content *	T_C (PDMS) $^+$	T_G (PLLA) $^+$	T_M (PLLA) $^+$	ΔH_M [J/g]
AB diblock copolymers				
23	-59.1	73.4	143.4	40.97
26	-60.9	66.3	141.3	34.35
33	-73.7	59.5	140.1	35.49
44	-74.4	33.4	150.8	21.50
50	-75.4	23.7	141.5	15.47
ABA triblock copolymers				
50	-76.6	67.1	135.5	16.72
52	-73.4	53.8	134.8	23.70
82	-54.3	46.4	110.14	22.83

* given in weight%
$^+$ (°C)

Table 3. DSC data of AB- and ABA-type block copolymers

Stereocomplexation. Hetero stereocomplexation of poly(lactide) was used to non-covalently crosslink the triblock copolymers. In order to achieve this, the same PDMS macroinitiator was used to carry out ring-opening polymerization of the L-lactide monomer to yield PLLA-*b*-PDMS-*b*-PLLA and for polymerization of D-lactide, which leads to PDLA-*b*-PDMS-*b*-PDLA. Fortunately, we managed to obtain two block copolymers of almost the same length of PLLA/PDLA blocks, so that stereochemistry of the lactide units is the only difference between them. It is well-known that poly(lactide)s of different contrary stereochemistry have the ability to form complexes that exhibit high thermal stability and are stable even under harsh conditions. Nevertheless, formation of such stereocomplexes can be crucial if the poly(lactide) chain is part of a di-, tri-, or multiblock copolymer because specific orientation and aggregation usually deriving from incompatibility of the different blocks often hinders free accessibility of the poly(lactide). In order to induce stereocomplexation, solutions of both polymers are rapidly mixed and the solvent is slowly evaporated at room temperature to assure a slow and thorough aggregation process. Differential scanning calorimetry was used to trace stereocomplexation. The complexes formed between PDLA and PLLA chains exhibit a melting point of about 210°C, whereas poly(lactide) melts at about 140°C. Successful stereocomplexation can thus be proven by an increase of the poly(lactide) melting point. Figure 5 shows the DSC curves of a PLLA containing triblock copolymer before and after stereocomplexation with its respective D-lactide analogon.

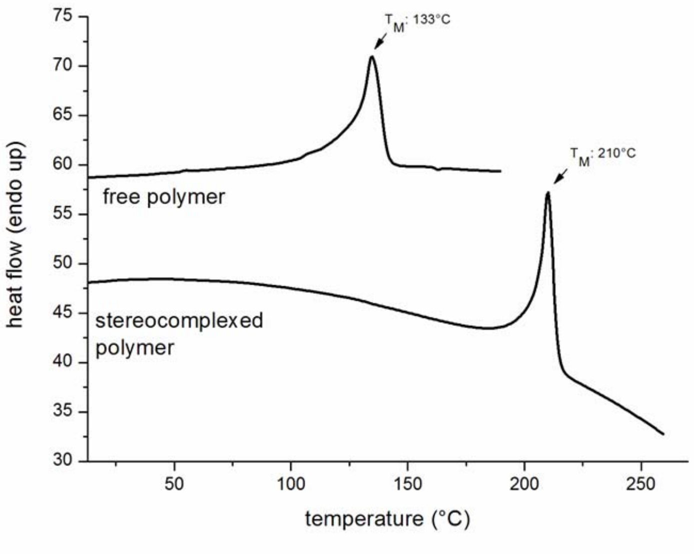

Figure 5. Melting points of PLLA45-b-PDMS47-b-PLLA45 before and after stereocomplexation, determined by DSC (heating rate: 20K/min)

Although we suspected flexible, elastomeric features because of the high PDMS content of the material, mechanical properties of the samples were poor with regard to softness and plasticity. In fact, the obtained materials were hard and brittle instead of showing elastomeric properties. We assume that the reason for this is the high entanglement of the central PDMS chain, which significantly lowers the mobility within the flexible PDMS domains of the network and thus impedes a softening effect of the poly(siloxane) block on the material. Nevertheless, it could be shown that sterecomplexation works with the triblock copolymers, leading to an extensive increase in the melting point of the poly(lactide) domain.

Atomic Force Microscopy (AFM). To further analyze the structural orientation of the block copolymer, AFM images were taken from samples spin coated on silicon wafers. Without further treatment, none of the polymers showed any significant structural organization either on topography or on the phase image. Thus, samples were then heated to 160°C for at least one hour in order to allow reorganization of the material on the silicon surface. According to the results of the SAXS measurements, this treatment led to formation of organized morphologies. Lamellar patterns were observed for ABA- as well as AB-type block copolymers on topography and phase image, again proving that annealing the material above the PLLA melting point is essential for the formation of structural organization of those polymers. Phase and topography images of one diblock and one triblock copolymer are shown in **Figure 7** and **8**. We analyzed the images of one diblock and one triblock copolymer, namely $PDMS_{51}$-*b*-$PLLA_{19}$ and $PLLA_{44}$-*b*-$PDMS_{38}$-*b*-$PLLA_{44}$ by power spectral density function to determine the average distance between the distinct lamella. For the diblock copolymer shown in **Figure 7** the distance was estimated to 18.90 nm, in case of the triblock, the same processing afforded a value of 22.07 nm. The correlations between molecular weight and lamellar thickness are in good agreement with the theories of microphase separated structures developed by Meier, Helfand, Semenov and Kawasaki, stating that $D \sim M^a$, with an exponent of 0.66 or close to 0.66.[18] These calculated distances are reasonable compared to the block lengths that were calculated from the degree of polymerization and an estimated monomer length of 0.29 nm for PDMS and 0.37 nm for PLLA, taking into account that there has to be a certain overlap of the adjacent chains of the same block. Therefore, the calculated values of chain length of 21.76 nm for $PDMS_{51}$-*b*-$PLLA_{19}$ and 44.32 nm for $PLLA_{44}$-*b*-$PDMS_{38}$-*b*-$PLLA_{44}$ are higher than those determined by the spectral density function. Figure 9 depicts the model that is suggested for the lamellar orientation of the polymer chains. For the ABA-type triblock copolymer, comparison of the theoretical and the calculated values of chain length suggests that the region of overlapping chain ends is 11.12 nm on each side, which corresponds to 30 lactide units. However, for the diblock copolymer, the overall overlap is only 2.86 nm in length. In that case, the existing data does not give information about the ratio of the overlapping lengths on the PDMS and the PLLA end of the chain.

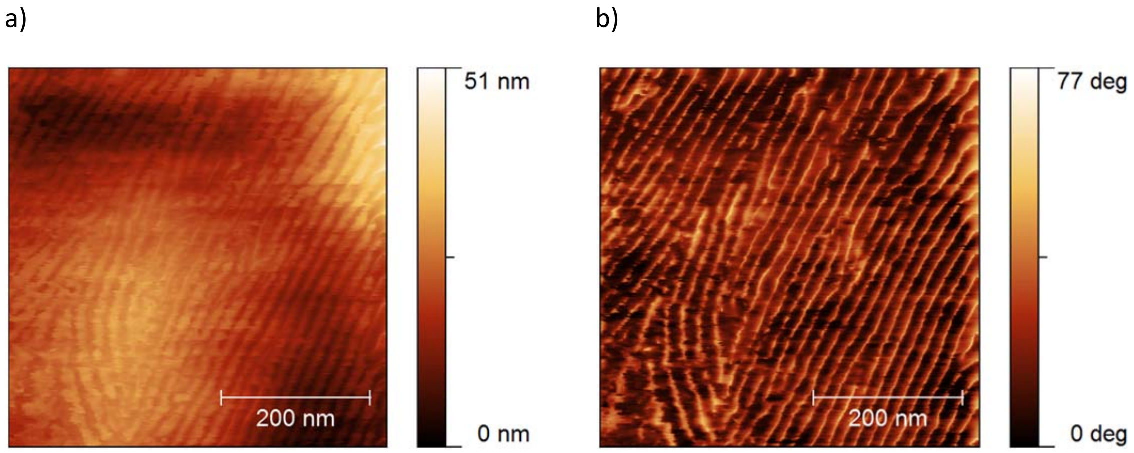

Figure. 7. Topography (a) and phase images (b) of PDMS$_{51}$-*b*-PLLA$_{19}$ with periodicity of lamellar structure with an interval of 18.90 nm. The bright area on the phase image corresponds to softer parts of the polymer structure.

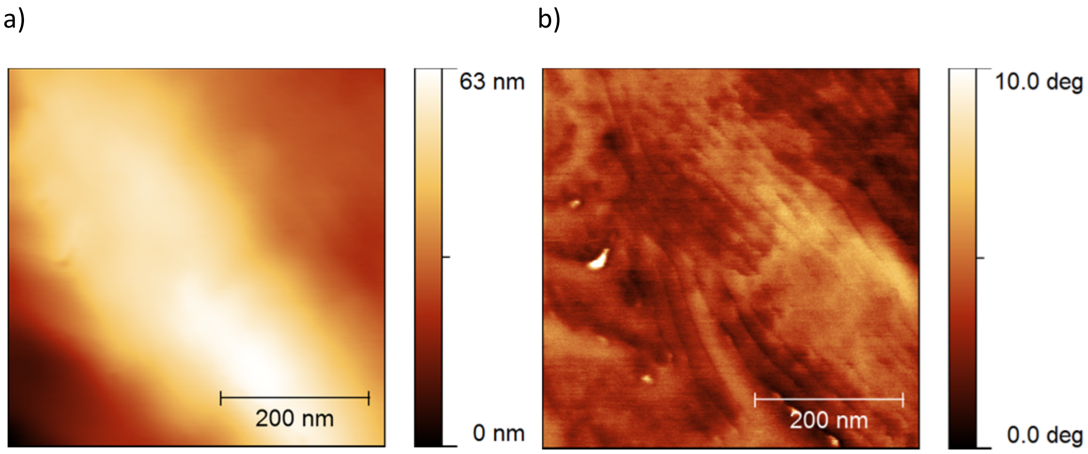

Figure. 8. Topography (a) and phase images (b) of PLLA$_{44}$-*b*-PDMS$_{38}$-*b*-PLLA$_{44}$ with periodicity of lamellar structure with an interval of 22.07 nm. The bright area on the phase image corresponds to softer parts of the polymer structure

Conclusion:

We developed a novel kind of AB- and ABA-type block copolymer consisting of poly(dimethylsiloxane) and poly(lactide) segments. The synthetic pathway contained the controlled cationic or anionic ring-opening polymerization of cyclosiloxanes to obtain previously mono- and difunctional PDMS precursors. These were used as macroinitiators for the ring-opening polymerization of lactide, yielding diblock or triblock copolymers with narrow molecular weight distributions. AFM images revealed strong phase separation of the poly(siloxane) and poly(lactide) domains, resulting in a lamellar patterned structure of the material. We took advantage of the lamellar ordering by inducing stereocomplexation of the poly(lactide) blocks in order to stabilize the patterned structure. The material thus consists of alternating soft PDMS segments and hard segments of stereocomplexed poly(lactide). As the PDMS segments are extremely flexible and the hard domains can be deformed when heated over their melting point of about 210°C, this material represents a structure that can be suitable for applications in the field of thermoplastic elastomers. The addition of the flexible PDMS segments leads to significant softening compared to pure PLA, which is a significant advantage with regard to the processing of the material.

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Supporting Information
“Block Copolymers Based on Poly(lactide) and Poly(dimethylsiloxane) – Strongly Segregated Systems”

M_n (g/mol)	M_w (g/mol)	PDI	M_n (g/mol)	M_w (g/mol)	PDI
monofunctional			difunctional		
800	1000	1.16	2900	4300	1.49
1000	1200	1.25	3900	5400	1.39
3100	4400	1.40	7100	11200	1.57
4000	5400	1.36	9400	13300	1.41
4300	5800	1.36	24000	39000	1.63
10000	13400	1.33			

Table S1. Size and molecular weight distributions of mono- and difunctional PDMS macroinitiators SEC data, PS standard, eluent: chloroform

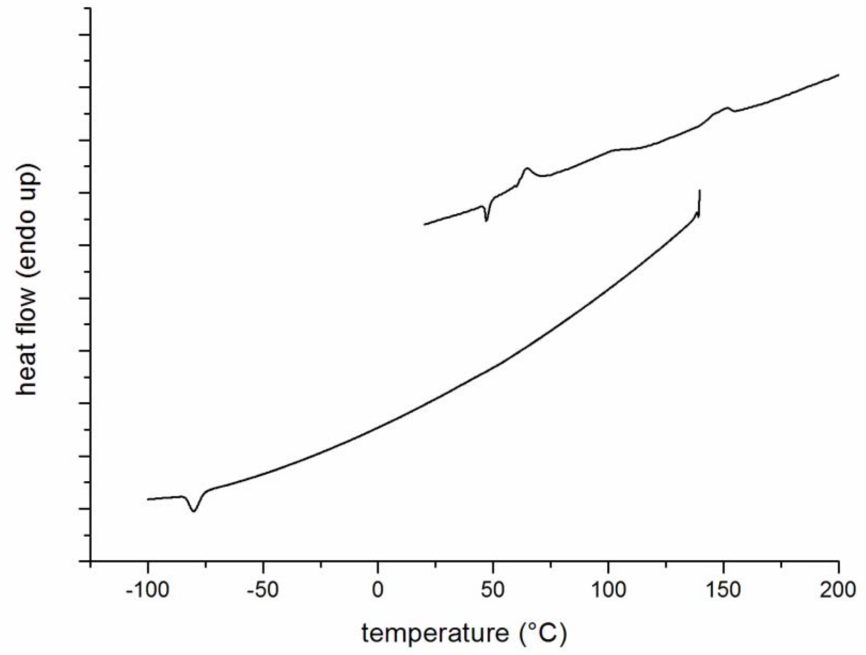


Figure S1. DSC diagram of PLA_{xx}-*b*-$PDMS_{378}$-*b*-PLA_{xx}, showing PDMS crystallization at -80°C, PLA glass transition at 62°C and PLA melting point at 151°C. heating/cooling rate: 20K/min

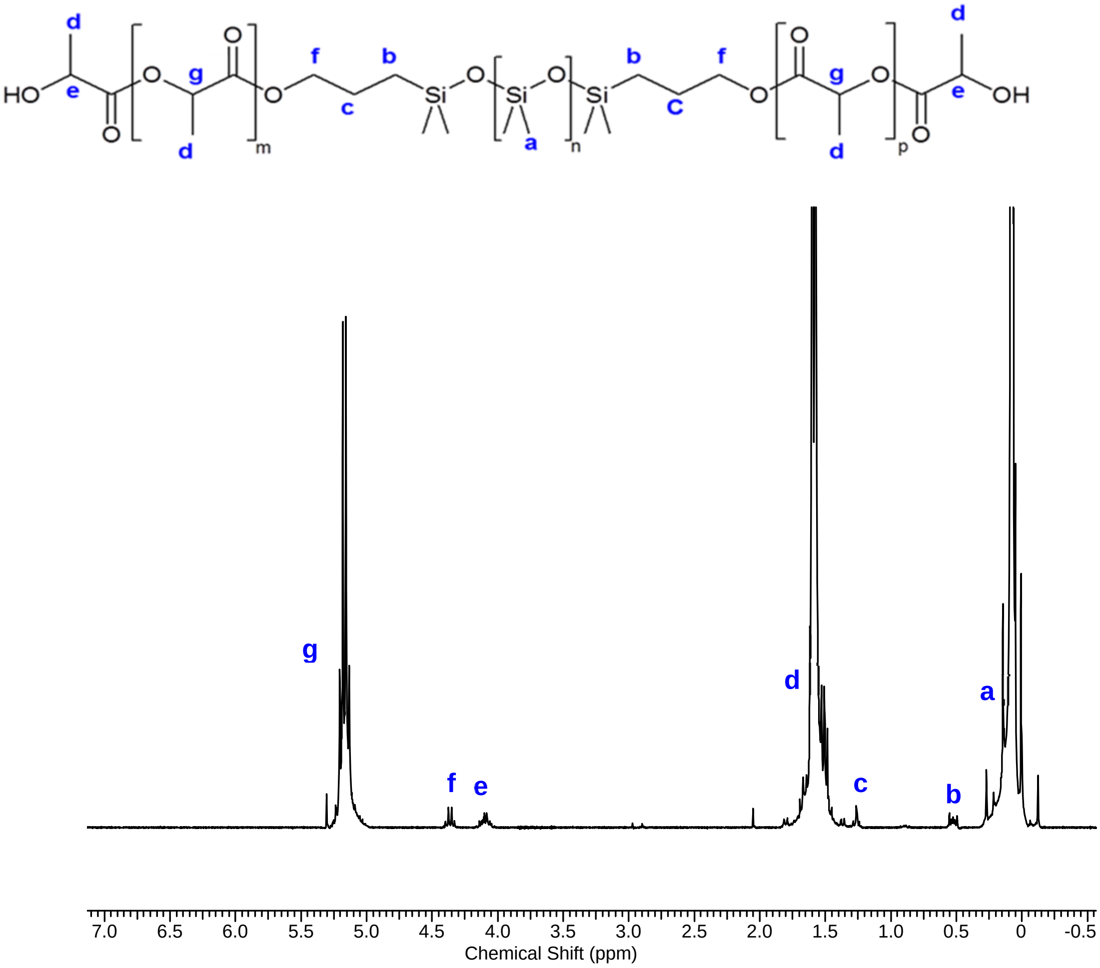


Figure S2. Structure and ^{1}H NMR spectrum (300MHz, $CDCl_3$) of PLA-*b*-PDMS-*b*-PLA Triblock copolymer. Peaks are assigned by letters a-g.

2.4. Thermoresponsive Silicone Block Copolymers

Paul Böhm, Clemens K. Weiß and Holger Frey

ABSTRACT

Silicone-containing amphiphilic block copolymers with thermoresponsive, polar POEGMA block have been synthesized by combination of anionic ring-opening polymerization of hexamethyltrisiloxane (D3) and atom transfer radical polymerization (ATRP) of oligo(ethyleneglycol) methacrylate. The firstly synthesized poly(dimethylsiloxane) was converted into an ATRP macroinitiator, using hydrosilylation chemistry. The resulting block copolymers show molecular weights in the range of 8000-15000 g/mol and narrow polydispersities M_w/M_n of 1.3 to 1.4 and were analyzed by ^{1}H NMR spectroscopy, confirming the targeted block lengths. Interfacial properties were investigated using spinning drop tensiometry, showing that the block copolymers are powerful surfactants. Measurements at different temperatures revealed interesting effects of the LCST of the POEGMA-block on surface properties, which tend to be significant only at concentrations below the polymers´ critical micelle concentration.

Introduction

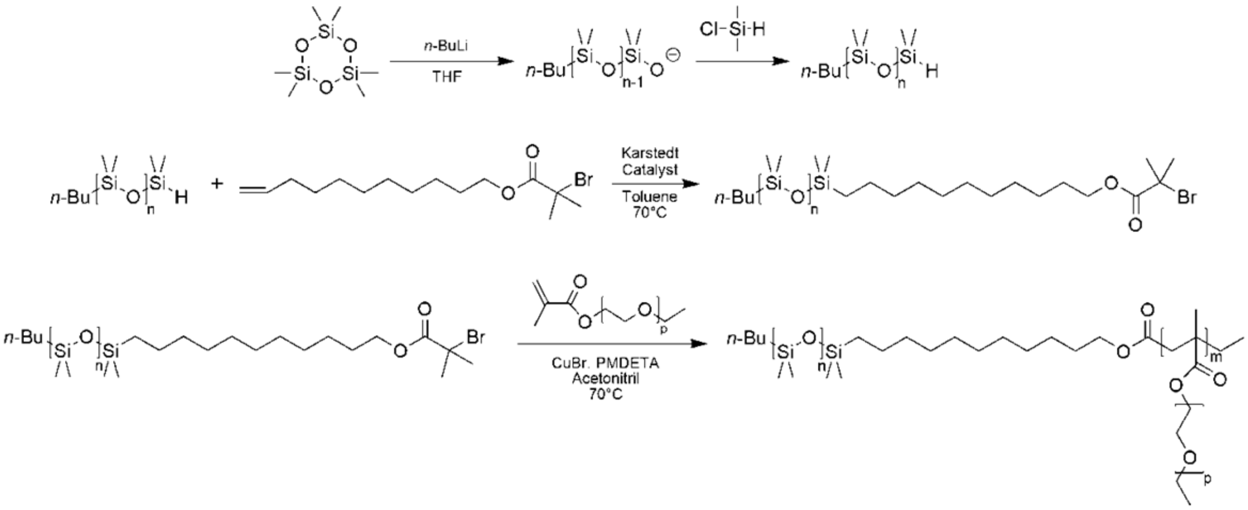
Polymer based surfactants are well-established and widely used in different kinds of products such as paints, washing agents and for personal care.[1] Such surfactants usually consist of either a hydrophobic chain that carries a hydrophilic group (usually ionic) at one chain end or an amphiphilic block copolymer with one hydrophilic and one hydrophobic block, as it is the case for nonionic surfactants.[1] Compared to small molecules, polymeric surfactants are advantageous concerning functionality, flexibility and diversity. However, as polymers are of course not as well defined as low molecular weight surfactant molecules, there is a high demand for synthetic routes towards very precisely-defined polymer structures. Especially the method of controlled radical polymerization, offers great new possibilities in this regard. Atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT) polymerization are valuable tools for the synthesis of well-defined, amphiphilic block copolymers.[2-5] Recently, increasing efforts have been made towards polymeric surfactants that respond to a certain stimulus like pH, temperature or salt concentration. In most cases, copolymers with two hydrophilic blocks of which one of them becomes hydrophobic upon a respective stimulus are used for this purpose.[6-8]

One important class of macromolecular surfactants are polysiloxane-containg diblock copolymers, which are often designated "superspreaders".[9] Ususally, the hydrophobic block of these copolymers is formed by poly(dimethylsiloxane) (PDMS). Silicones exhibit high flexibility even at very low temperatures, show low surface tensions and they are biocompatible and transparent.[10-13] The extraordinary high surface activity of PDMS leads to significant reduction of interfacial tensions and thus a high performance as surfactants and emulsifiers for their respective copolymers. Moreover, they have been shown to stabilize of microemulsions as well as emulsions in critical CO_2.[14] Silicone surfactants also possess the ability to facilitate the wetting of extremely hydrophobic surfaces, an effect that is known as "superwetting" or "superspreading".[15]

In recent years, the phase behavior of silicone surfactants has been studied extensively. The vast majority of these studies deals with the investigation of AB-type block copolymers of poly(dimethylsiloxane) and poly(ethylene glycol). Liquid crystalline structures were found for such copolymers, and they are particularly qualified as surfactants because of the very good solubility especially of large PDMS blocks.[16-18] Block Copolymers of PDMS and poly(2-(dimethylamino)ethyl methyacrylate) (DMA) have also been proven to show surfactant properties. The polymers were synthesized via two different synthetic approaches by Armes et al..[19,20] Moreover, a large number of publications report on the synthesis of silicone-based surfactants in which the polysiloxane is grafted with hydrophilic sidechains. In most cases, these side chains consist of poly(ethylene glycol), but also other hydrophilic groups like for example cyclodextrins are reported.[21-25]

In order to generate amphiphilic, silicone-containing surfactants that respond to a temperature stimulus, our aim was to combine the hydrophobic poly(dimethylsiloxane) with a hydrophilic, temperature-responsive block of poly(oligoethyleneglycol methacrylate) (POEGMA). This material shows a cloud point in the range of 25 to 75°C, depending on the length and end group of its oligo(ethylene glycol) side chain.[26-28] One more important advantage of POEGMA is that it is, like PDMS, absolutely biocompatible and thus especially qualified for biomedical application.[27] To date, numerous POEGMA-containing block polymers have been developed for use in the biomedical field.[30-33]

In the current work monofunctional PDMS samples modified with an isobutyryl bromide end group were synthesized via hydrosilylation. These macroinitiators have been used for the ATRP of oligo(ethyleneglycol) methacrylate (OEGMA). The controlled radical polymerization was carried out in acetonitrile at 70°C, using N,N,N´,N´´,N´´-pentamethyldiethyltriamine (PMDETA) as a ligand for the catalyzing Cu-complex. The synthetic strategy is shown in **scheme 1**.



Scheme 1. Synthesis of PDMS-*b*-POEGMA

A somewhat analogous approach has been followed by Matyjaszewski et al. to generate block copolymers of PDMS and poly(2-(hydroxymethyl) methacrylate) (PHEMA). However, different polymerization conditions and another type of linker were used in this publication.[34] PDMS-b-POEGMA copolymers of different molecular weight and block-length ratios were obtained with low to moderate polydispersities between 1.3 and 1.4. The products were analyzed by ^{1}H NMR spectroscopy and size exclusion chromatography (SEC). The surface tension at the interface between silicone oil and water was measured by the spinning drop method, recorded at different temperatures between 5 and 25°C.

Experimental Section

Materials. All reagents and solvents were purchased from Acros Organics or Sigma-Aldrich and used without further purification unless otherwise stated.

Instrumentation. ^{1}H NMR spectra (300 MHz) were recorded using a Bruker AC 300 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in trichloromethane, a setup consisting of a Waters 717 plus Autosampler, a TSP Spectra Series P 100 pump, three PSS-SDV-5 µl-columns with 100, 1 000, and 10 000 Å pore diameter, respectively, a UV (275 nm), and an RI detector was used. Calibration was carried out using poly(styrene) standards provided by Polymer Standards Spinning drop tensiometry was performed using an SVT20 spinning drop tensiometer (Dataphysics, Filderstadt, Germany). All measurements were performed using water of ultrahigh purity (pure or as solvent). Typically, a droplet of approx. 40 µl of a silicone oil of low viscosity was added to a cooled aqueous solution (5°C) of the block copolymer. Interfacial tensions were determined at 5°C and 25°C, whilst spinning at 8000 rpm, by video analysis of one side of the cylindrical droplet.

Mono hydride-terminated PDMS. A certain amount of D3 was cryo-transferred into a 100 ml Schlenk flask equipped with a stirring bar. The flask was purged with argon and sealed with a rubber septum. The D3 was dissolved in anhydrous THF which was added added via syringe. Polymerization was started by adding the respective amount of *n*-butyllithium (1.6m solution in hexane). After 2 hours the reaction was quenched by a 1.5 fold excess (with respect to the amount of initiator) of chlorodimethylsilane and the solution was stirred for another 30 minutes. Subsequently, water was added and the polymer was extracted by threefold extraction with pentane. The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. After drying under high vacuum pure polymer was obtained in 95% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.71 (s, 1H, Si*H*), 1.33 (br, 4H, $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$), 0.89 (t, 3H, $C\mathit{H}_3CH_2CH_2$), 0.53 ($SiC\mathit{H}_2$), 0.07 (br, $SiC\mathit{H}_3$, backbone).

10-undecylenyl-2-bromo-isobutyrate. 11 g (0,065 mol) 10-undecylenyl alcohol and 8,7 g (0,085 mol) triethylamine were put in a one-necked round bottom flask. The flask was set under argon atmosphere and the solution cooled with an ice bath. Then 20 g (0,085 mol) of 2-bromo-isobutyryl bromide in 50 mL THF were added dropwise. After the addition was completed, the reaction mixture was allowed to reach room temperature and stirred overnight. Diethylether was added and the organic phase washed with a 2M hydrochloric acid solution and twice with water, then dried over $MgSO_4$ and the diethylether removed under reduced pressure. The resulting dark-orange liquid was purified by column chromatography (hexane/ethyl acetate 25:1 to afford 14.74 g (0.046 mol, 71%)of 10-undecylenyl-2-bromo-isobutyrate as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.20-1.45 (b, 12H, CH_2), 1.55-1.75 (m, 2H, OCH_2CH_2), 1.90 (s, 6H, CH_3), 2.00-2.10 (m, 2H, $CH_2CH{=}CH_2$), 4.20 (t, 2H, OCH_2CH_2), 4.80-5.00 (m, 2H, $CH{=}CH_2$), 5.75-5.90 (m, 1H, $CH{=}CH_2$)

PDMS Macroinitiator. A solution of 1 g of mono hydride-termninated PDMS and a 1.3 fold excess of 10-undecylenyl-2-bromo-isobutyrate in 20 ml of dry toluene was put in a 50 ml schlenk flask and set under argon atmosphere. Under stirring, the solution was heated to 70°C. Then one drop of Karstedt catalyst was added via syringe and the reaction mixture stirred at 70°C for approximately 16 hours. Then the amine-functional ion exchange resin Amberlite IRA 743 was added to adsorb the platinum catalyst and the mixture was again stirred overnight. Afterwards, the ion exchange resin together with the adsorbed catalyst were removed by filtration and the reaction solution concentrated under reduced pressure. The polymer was then precipitated by dropwise addition to a large excess of methanol and taken up in chloroform. Evaporation of the solvent and drying under high vacuum afforded the PDMS macroinitiator as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.10 (s, $SiCH_3$), 0.55 (t, 4H, $SiCH_2$), 0.90 (t, 3H, CH_3CH_2), 1.20-1.40 (br, 20H, CH_2CH_2), 1.65 (m, 2H, OCH_2CH_2), 1.95 (s, 6H, CCH_3), 4.20 (t, 2H, OCH_2)

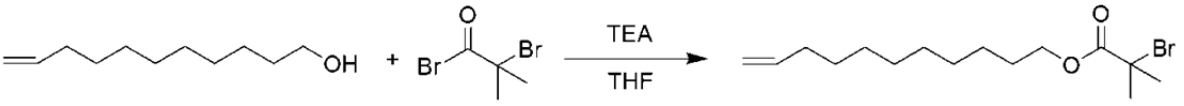
PDMS-*b*-POEGMA. In all polymerizations, the initiator/copper/ligand ratio was [1]:[1]:[1]. Monomer/initiator ratios were calculated according to the targeted molecular weight of the POEGMA block. Acetonitrile was predegassed by three freeze-pump-thaw cycles. . In a typical procedure, the PDMS macroinitiator and the respective amount of oligoethylenglycol methacrylate were charged into an argon-flushed Schlenk-tube, dissolved in predegassed acetonitrile (volume ratio monomer:solvent 3:7) and degassed in three freeze-pump-thaw cycles. The ligand, N,N,N′,N′′,N′′-pentamethyldiethyltriamine (PMDETA), was charged in a separate Schlenk-tube, dissolved in predegassed acetonitrile and degassed in three freeze-pump-thaw cycles. Subsequently, the ligand solution was injected into a pre-evacuated Schlenk-tube, containing the respective amount of copper-(I)-chloride. The tube was flushed with argon and stirred until the green copper-complex formed. The polymerization was initiated by injecting the copper/PMDETA complex to the monomer/initiator solution and carried out over night at 70°C. The reaction was quenched by exposure to air. Chloroform was added to the reaction mixture, which was subsequently filtered over a short column filled with neutral aluminum oxide to remove the copper catalyst. Then solvent was removed from the colorless solution in vacuum and residual monomer and macroinitator were removed by precipitating the polymer in cold pentane and subsequent dialysis in THF. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.10 (s, $SiCH_3$), 0.50 (br, 4H, $SiCH_2$), 0.85 (br, CCH_3 (POEGMA backbone)), 1.05 (s, 6H, CCH_3), 1.15-1.30 (br, 20H, CH_2CH_2), 1.75-2.00 (br, CCH_2 (POEGMA backbone) and OCH_2CH_2), 3.45-3.75 (br, OCH_2), 4.1 (br, $COOCH_2$)

Results and Discussion

Macroinitiator Synthesis.

The synthetic strategy that was applied for the synthesis of the presented block copolymers involved the use of a PDMS macroinitiator for the atom transfer radical polymerization of oligoethyleneglycol methacrylate. Anionic ring-opening polymerization and platinum catalysed hydrosilylation were combined in a 3-step procedure to afford a polysiloxane that is capable of initiating the ATRP process.

In a first step, hexamethylcyclotrisiloxane (D3) was polymerized by means of an anionic ring-opening polymerization, initiated with *n*-butyllithium. Even at room temperature, chain growth is fast, and molecular weights of 1000 to 4000 g/mol can be achieved within less than two hours. The process was terminated by addition of chlorodimethylsilane, which leads to a PDMS that carries one terminal Si-H function that can be reacted with any double bond, applying hydrosilylation chemistry. Using this method, well defined monofunctional poly(dimethylsiloxane)s with molecular weights between 1000 and 4000 g/mol and narrow polydispersities have been synthesized. As the SEC results are based on the calibration with polystyrene standards, the molecular weights obtained from this method have to be considered as apparent values. Therefore, the exact molecular weight of the polysiloxanes was calculated via ^{1}H NMR spectroscopy, comparing the resonances of the initiating butyl group to those of the PDMS backbone (see Supporting Information for ^{1}H NMR spectrum). However, molecular weights calculated from NMR turned out to be in good agreement with the values obtained by SEC. Subsequently, the PDMS chains were transformed into macroinitiators by attaching an ATRP-initiating group. The most obvious structure for this purpose derives from the esterification of 2-bromoisobutyrylbromide with allyl alcohol. The synthesis was carried out by deprotonating the alcohol by triethylamine and then adding the acyl bromide dropwise to the alcoxide solution. However, the platinum catalysed hydrosilylation between this molecule and the polysiloxane chain was always incomplete, with a maximum amount of 60% of functionalized PDMS. According to the results reported by Matyjaszewski et al. in 1999, we assume this to be caused by the short distance between the reacting double bond and the ester group of the 3-propenyl-2-bromoisobutyrate. The carbonyl bond is likely to interfere with the addition-elimination process of platinum-catalyzed hydrosilylation and can thus impede full conversion. To overcome this problem, it was decided to use undecenyl alcohol, instead of allyl alcohol in order to obtain an effective spacer that prevents impeding hydrosilylation due to the carbonyl group of the ester. The reaction between 10-undecenyl alcohol and 2-bromo-isobutyrylbromide was carried out in analogy to the procedure applied with allyl alcohol (see **scheme 2**).



Scheme 2. Synthesis of 10-undecenyl-2-bromo-isobutyrate

However, the product had to be isolated by column chromatography as its boiling point was too high for distillation. Nevertheless, the resulting 10-undecenyl-2-bromo-isobutyrate was obtained in good yields exceeding 80%. According to expectation, hydrosilylation of the compound by the Si-H-functional PDMS was considerably more efficient, leading to nearly 100% conversion of the PDMS chains. The ATRP initiator was then successfully attached to poly(dimethylsiloxane)s of molecular weights between 1000 and 4000 g/mol to create polysiloxane-based ATRP macroinitiators of various chain lengths.

ATRP of Oligo(ethylenglycol) methacrylate.

The POEGMA block of the targeted amphiphilic block copolymer was added via ATRP of oligo(ethylenglycol) methacrylate (OEGMA), using the previously synthesized PDMS macroinitiator. As the polarity of the OEGMA monomers differs strongly from the hydrophobic PDMS macroinitiator, the most significant issue with regard to suitable polymerization conditions was to find a suitable solvent for all reaction components. As acetonitrile is capable of sufficiently dissolving the hydrophobic macroinitiator as well as the hydrophilic OEGMA monomers, it was chosen as solvent for the atom transfer radical polymerization process. However, the macroinitiators with molecular weights exceeding 3000 g/mol sometimes were not fully dissolved throughout the whole polymerization. In the process of discovering the suitable polymerization conditions, the ligands of the copper complex as well as the reaction temperature and polymerization time were varied, leading to the conclusion that the process is very slow and it is difficult to fully consume the hydrophilic oligo(ethyleneglycol) methacrylate monomer. We assume that this is also caused by the strong difference in polarity between the OEGMA monomers and the macroinitiator. Even in a good solvent, the monomers are rarely in close contact with the initiating site. However, with an increasing number of monomers adding to the growing second block, this problem should become more negligible. The polymerizations were finally carried out using pentamethyldiethylenetriamine (PMDETA) as a ligand for the catalyzing copper complex at a reaction temperature of 70°C. All polymerization reactions were carried out overnight to ensure maximum monomer conversion. The ^{1}H NMR spectrum of a typical PDMS-*b*-POEGMA copolymer is shown in **Figure 1**.

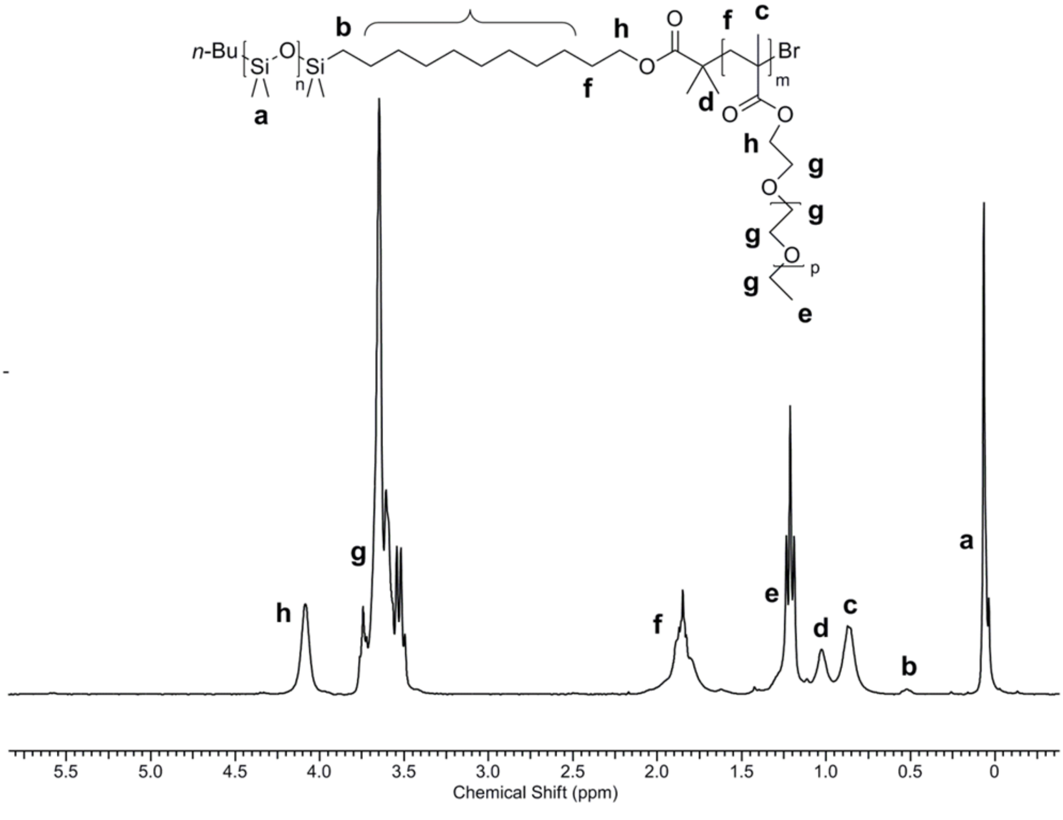


Figure 1. 1H NMR (300 MHz, CDCl$_3$) of PDMS-*b*-POEGMA

Concerning polymer purification, sdifficulties occurred if the molecular weight of the macroinitiator exceeded 3000 g/mol. As full conversion of the initiator could not be achieved, the residual PDMS homopolymer needed to be removed after the polymerization. This was achieved by selective precipitation of the block copolymer in cold pentane, which was only possible for PDMS chains that possessed molecular weights lower than 3000 g/mol. If the macroinitiator was too large, it could not be fully removed from the copolymer, which was evidenced by a small low molecular weight shoulder in the final SEC traces. However, a number of block copolymers with different block ratios and low molecular weight distributions were finally obtained by the use of smaller polysiloxane macroinitiators. **Table 1** summarizes SEC data and block-length ratios of some of the block copolymers prepared.

molecular weight PDMS block (monomer units)	molecular weight POEGMA block (monomer units)	Block length ratio (% of monomer units, PDMS:POEGMA)	polydispersity
1700 (23)	10200 (41)	36:64	1.37
1200 (16)	13500 (55)	23:77	1.38
1200 (16)	7200 (29)	36:64	1.34
2300 (31)	9100 (37)	46:54	1.32

Table 1. GPC data of PDMS macroinitiators and PDMS-*b*-POEGMA block copolymers

Interfacial Properties

With their hydrophobic poly(dimethylsiloxane) segment and the hydrophilic block of poly(oligoethyleneglycol methacrylate), the synthesized polymers should provide intriguing properties as surfactants in silicone-oil- water systems. Since solubility of the POEGMA block is temperature-dependent, the performance as a surfactant can be assumed to change with temperature. The lower critical solubility temperature of the POEGMA homopolymer amounts to 27°C. However, the PDMS block tends to decrease this value, as the block copolymers are not water soluble at ambient temperature. In order to dissolve the polymers, they were cooled to 5°C. In order to investigate the behavior of the synthesized amphiphilic block copolymers at the surface between silicone-oil and water, spinning drop tensiometry was applied. The spinning drop technique (SDT) represents a versatile method for the detailed investigation of liquid-liquid interfaces. Here, the interfacial tension □ is determined by the shape of a droplet of an organic phase in a water-filled capillary.[33] When the capillary is spun at a certain speed, the balance between centrifugal and interfacial forces governs the exact shape of the droplet.[34] The use of a closed system and the possibility to vary the centrifugal forces by changing the spinning rate render SDT a more reliable method to determine interfacial tension than, for example, the use of the Du-Nouy ring method with a two-layer system. We have studied the interfacial activity of the synthesized poly(dimethylsiloxane)-*block*-poly(oligoethyleneglycol methacrylate) copolymers at the interface between silicone-oil and water. In the examined system, the amphiphilic polymer surfactant should migrate to the surface of the silicone droplets, with its hydrophobic PDMS block immerging into the silicone, while the hydrophilic block stays dissolved in the aqueous phase.

The interfacial tension of two block copolymers differing in the length of their hydrophobic and hydrophilic segments has been analyzed. Interfacial tension values were recorded for aqueous solutions of different concentrations between 0.002 and 0.1 g/l at temperatures of 5°C and 25°C. For measurements at 25°C, solutions that were kept at 5°C to ensure solubility of the polymer were injected into the capillary, a droplet of silicone-oil was added and the resulting emulsion was heated after placing it in the measurement-cell. Droplets were found to be stable at a rotation speed of 8000 rpm. Critical micelle concentrations (CMC) were determined by plotting against the polymer concentration. The plots for one of the copolymers at 5°C and 25°C are shown in **Figures 2 and 3**.

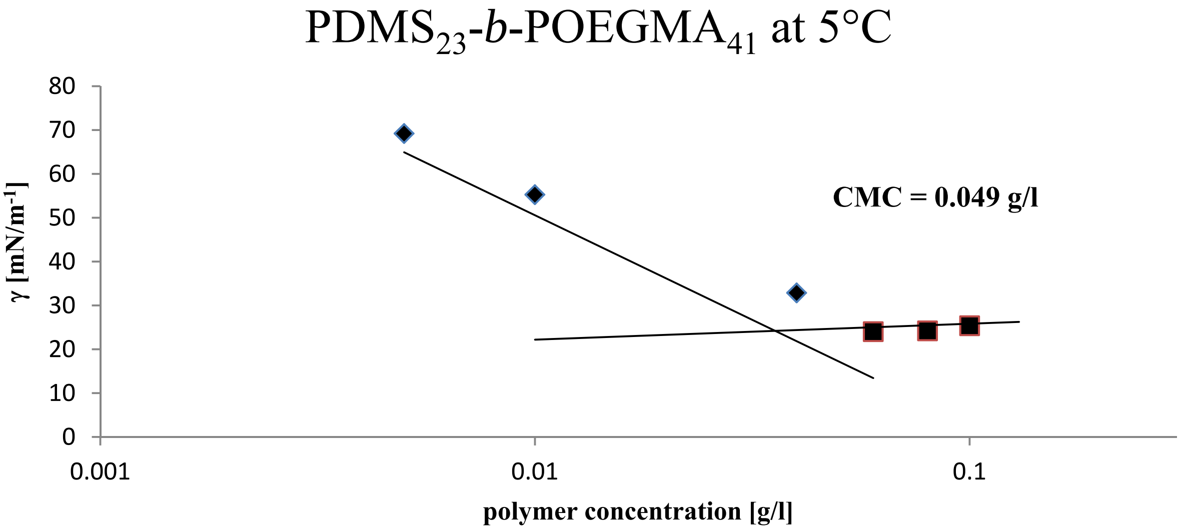


Figure 2. CMC plot of $PDMS_{23}$-*b*-$POEGMA_{44}$ at 5°C

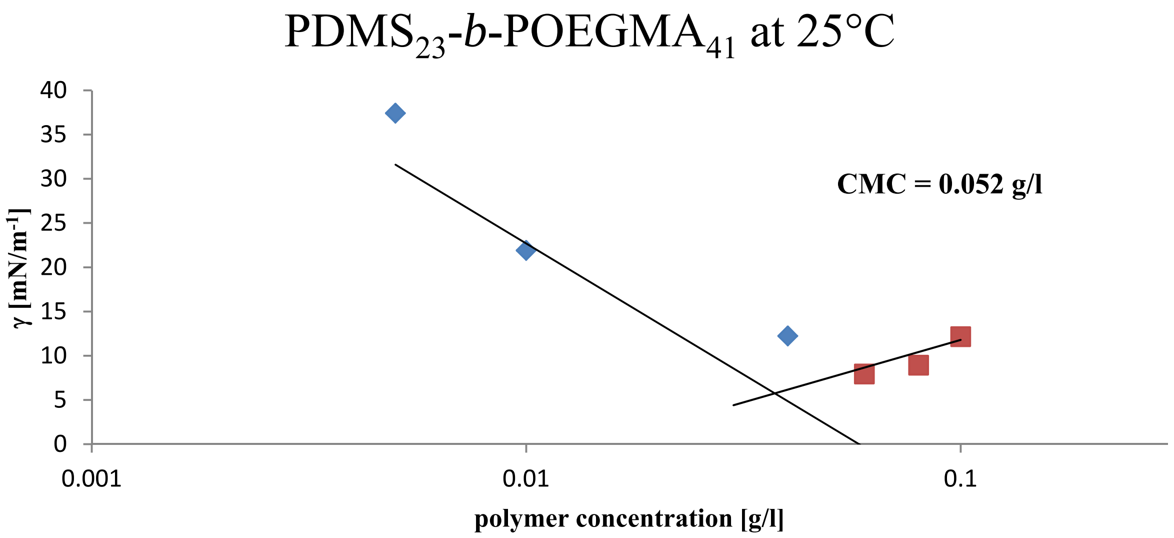

PDMS$_{23}$-*b*-POEGMA$_{41}$ at 25°C

Figure 3. CMC plot of PDMS$_{23}$-*b*-POEGMA$_{44}$ at 25°C

Results show that temperature does not significantly influence the critical micelle concentration. However, the surface tension values drastically change with an increase in temperature. **Table 2** summarizes the surface tension for the presented block copolymer and the value of their temperature-induced change.

concentration	γ at 5°C [g/l]	γ at 25°C [g/l]	Δ
0	55.30	37.39	17.91
0.005	69.21	37.42	31.79
0.010	55.27	21.90	33.37
0.040	32.89	12.23	20.66
0.060	24.05	7.95	16.11
0.080	24.22	8.93	15.29
0.100	25.40	12.16	13.23

Table 2. γ values for PDMS$_{23}$-*b*-POEGMA$_{44}$

Results reveal that increasing the temperature leads to a dramatic change of the surface tension values when exceeding the lower critical solution temperature (LCST) of the POEGMA block. In order establish, whether this effect is solely caused by the amphiphilic polymer surfactant, silicone drops were added to pure water and the surface tension values was measured via spinning drop tensiometry at 5°C and 25°C respectively. The surface tension accounted for 55.30 mN/m^{-1} at 5°C and 37.39 mN/m^{-1} for 25°C, which makes a difference of 17.91 mN/m^{-1}. This difference is caused by the temperature-dependent change of densities of both the aqueous and the silicone phase. it can be concluded that at least □-values at concentrations of 0.06 g/l and higher are not influenced by the surfactant at all. However, the high □-values that were observed at concentrations below 0.06 mN/m^{-1} cannot fully be ascribed to density changes. In this context, that fact that significant changes are only observable at polymer concentrations below the critical micelle concentration is particularly interesting. We assume that the crucial factor in this regard is the packing density of the surfactant at the interface. The collapse of the hydrophilic block of POEGMA that occurs at temperatures above its LCST should go together with an increased demand for space at the aqueous side of the interface. The high molecular density at concentrations around and above the CMC may inhibit this chain collapse, forcing the hydrophilic block to remain in the fully dissolved conformation, which it usually favors only at temperatures below its LCST. This interesting effect will be investigated in more detail in following work. However, the comparison between the surface tension of the pure silicone-in-water system and the values at different polymer concentrations evidence that the PDMS-*b*-POEGMA block copolymers can serve as powerful surfactants at concentrations below their CMC. This effect is pronounced both at 5°C as well as 25°C. Their temperature-sensitivity and the influence of concentration on the same are very interesting effects that will be further analyzed in future work.

Conclusion

Hydrophobic PDMS macroinitiators for atom transfer polymerization (ATRP) can be synthesized by attaching a newly developed ATRP initiator that carries an undecenyl linker and is equipped with a double bond to Si-H-terminated poly(dimethylsiloxane) via platinum-catalyzed hydrosilylation. The use of such macroinitiators for the ATRP of the hydrophilic monomer oligo(ethylenglycol) methacrylate is a facile approach to the controlled synthesis of novel, well-defined silicone surfactants with thermo-responsive hydrophilic block. The obtained block copolymers can be used to significantly decrease the surface tension between silicone-oils and water, which was shown by applying the spinning drop tensiometry technique. At concentrations below the critical micelle concentration of the respective polymer, surface activity is strongly temperature-dependent. The superspreading properties of the synthesized structures are currently under investigation.

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Supporting Information
“Thermoresponsive Silicone Block Copolymers”

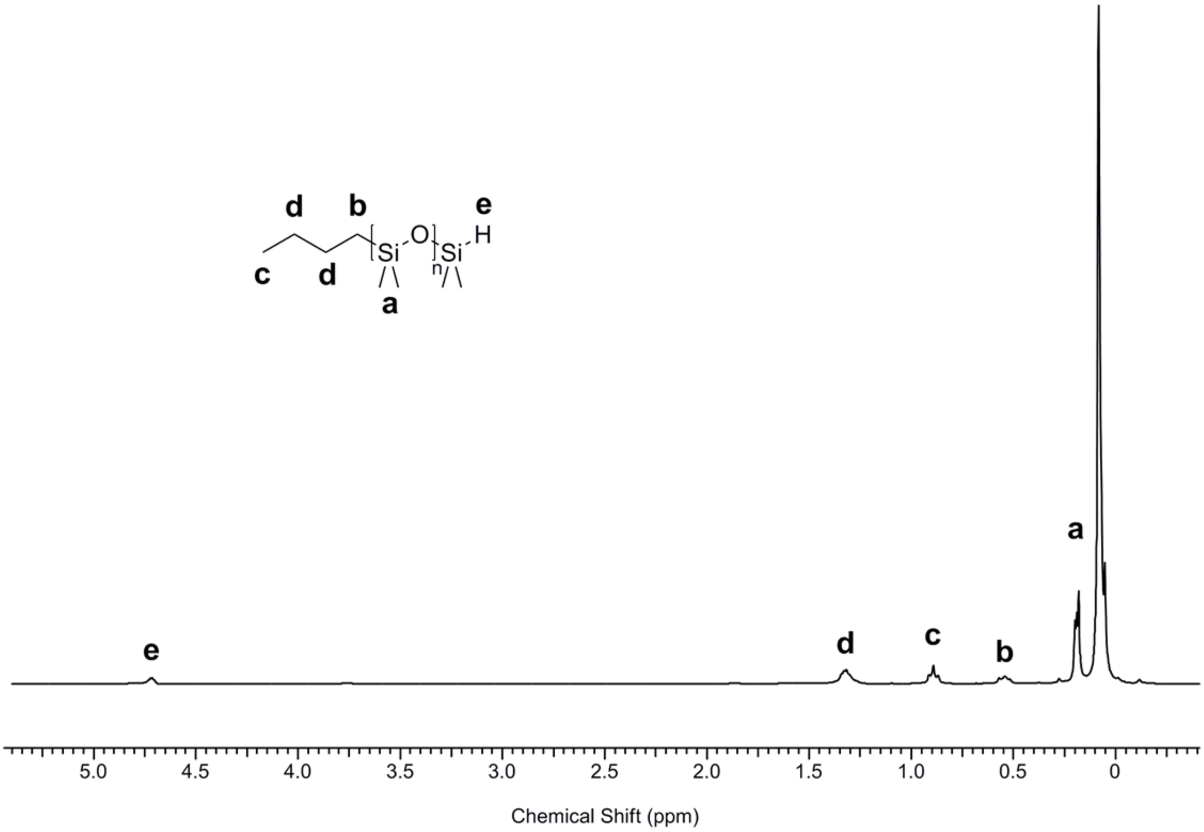

Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) of PDMS precursor

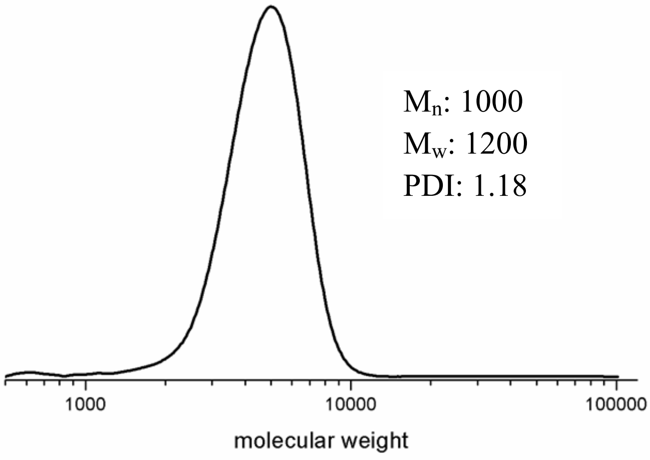

Figure S2. GPC diagram (PS standard, eluent: chloroform) of PDMS precursor

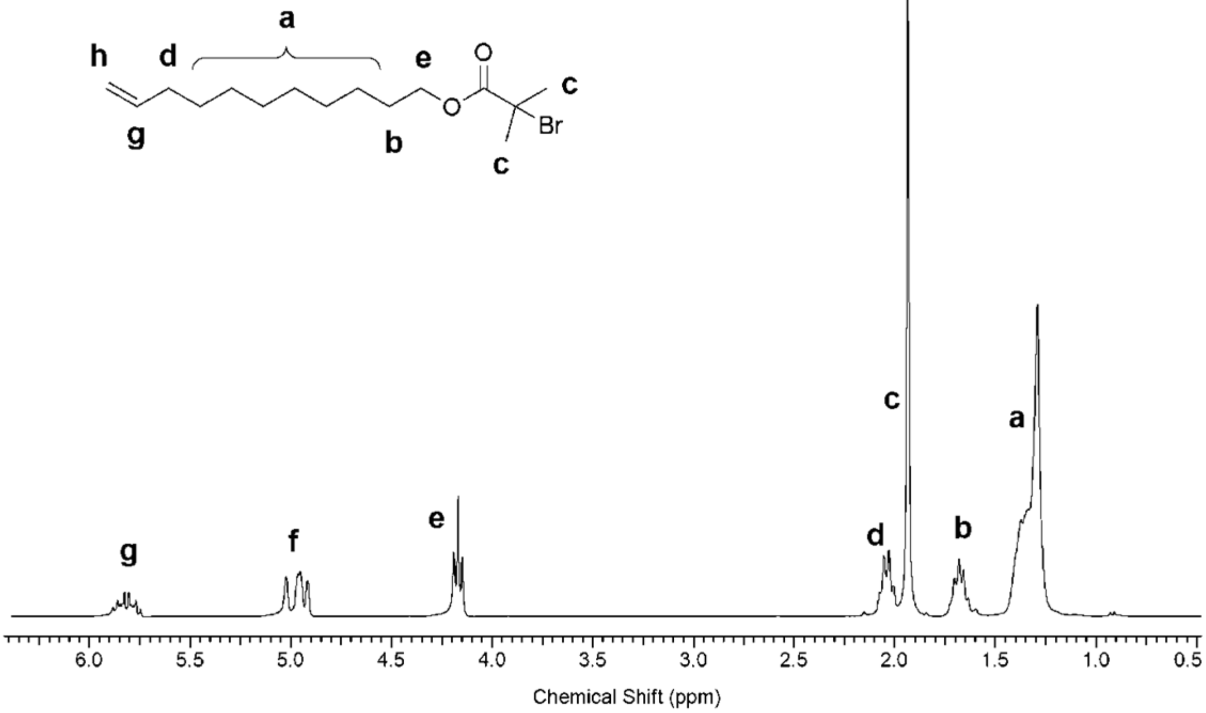

Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$) of Linker

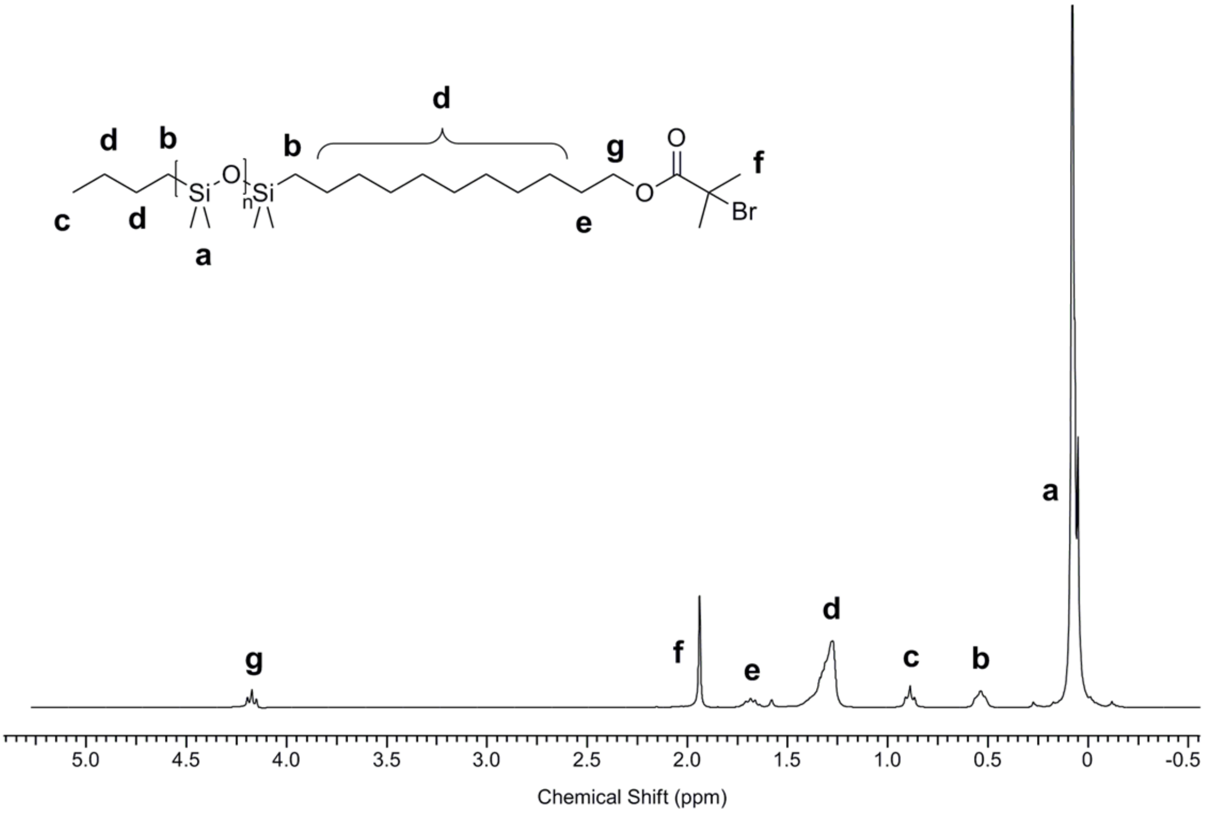

Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$) of PDMS macroinitator

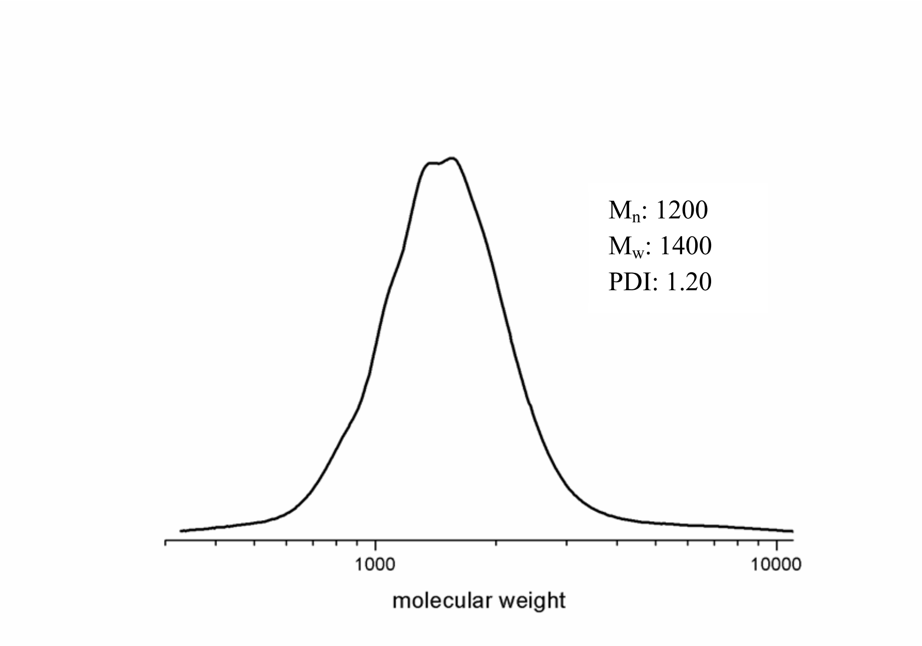

Figure S5. GPC diagram (PS standard, eluent: chloroform) of PDMS macroinitiator

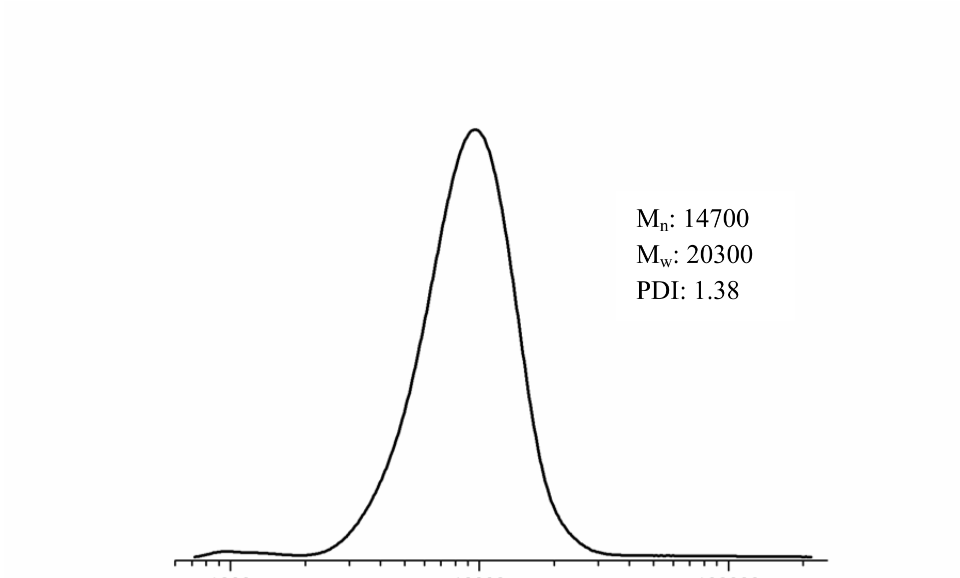

Figure S6. GPC diagram (PS standard, eluent: chloroform) of PDMS-*b*-POEGMA

2.5. Amphiphilic Poly(OEGMA) Block Copolymers with Tunable Thermoresponsiveness

Paul Böhm, Anja Kröger and Holger Frey

ABSTRACT

We report on a new class of thermoresponsive block copolymers of poly(oligoethylene glycol methacrylate) (POEGMA) and poly(L-lactide) (PLLA). The synthesis is based on a bifunctional initiator, from which the POEGMA block is synthesized via ATRP and the second block is subsequently generated by ring-opening polymerization of dilactide. The LCST of the POEGMA block was tailored by random copolymerization of two different OEGMA monomers and thereby adjusted to approximately 40°C. Successful synthesis was proven by NMR analysis and SEC measurements that demonstrate narrow molecular weight distributions over a range of molecular weights and compositions. Aggregation of the block copolymers in aqueous media was investigated by dynamic light scattering and transmission electron microscopy, revealing temperature dependent aggregation of single micelles or larger structures of spherical shape. In addition, a trifunctional initator was synthesized and applied in order to provide the block copolymers with a propargyl moiety located at the junction of both blocks. This group was subsequently used to attach rhodamine B to the polymer by click reaction. These materials were employed to follow the thermally triggered release of a model dye.

Introduction

The interest in amphiphilic block copolymers has been increasing at a constant pace. By combination of two or more polymer chains that are highly incompatible and show strongly differing properties, materials that are notably interesting for a broad range of applications are accessible. For instance, immiscibility of the blocks leads to the formation of separate domains within the material, and etching of one of these domains can be used in lithography.[1] In the case of ABA block copolymers, if the flanking blocks are able to crystallize such structures can also be used as thermoplastic elastomers.[2] The ability of amphiphilic block copolymers to form aggregates like vesicles or micelles in aqueous solution can be used to encapsulate functional molecules like drugs, using them as nano-containers to carry out chemical reactions selectively inside such a vesicle.[3] Depending on its polarity, the functional molecule can be incorporated either in the interior of the vesicle or in its membrane. In this area, structures that respond to certain stimuli, such as a change of the pH value or temperature are of special interest. In this regard, thermoresponsive polymers like poly(N-isopropyl acrylamide) (PNIPAM) or poly(oligoethylene glycol methacrylate) (POEGMA), are particularly valuable.[4,5] Especially PNIPAM is widely used as a component of block copolymers with thermoresponsive features. In 1989, Ando et al. firstly reported on poly(N-isopropyl acrylamide) being soluble in water only beyond a temperature of 32°C, induced by a thermally induced change in its hydration shell.[6,7] However, meanwhile several other polymers are known to be thermoresponsive. In the present work, we took advantage of the thermoresponsive properties of the rather hydrophilic POEGMA, which in analogy to PNIPAM precipitates in aqueous solution when heated above its lower critical solubility temperature (LCST). An important advantage of POEGMA is that it is fully biocompatible and thus especially qualified for biomedical application.[8] Besides, the value of its LCST depends on the length and the end group of the oligo(ethylene glycol) side chain.[9] In 2003, Ishizone et al. showed that the LCST of POEGMA can be adjusted by copolymerization of methacrylates with oligoethylene glycol sidechains of varying length.[10] Lutz et al. found that the LCST of copolymers from oligoethylene glycol methacrylate and 2-(2-methoxyethoxy) ethyl methacrylate can be tailored by varying the monomer composition.[11] Meanwhile POEGMA and POEGMA-containing block copolymers have been used in several ways to design biomedically applicable polymeric structures.[12-15] The thermoresponsive behavior of POEGMA has even been applied to design a new type of thermogels.[16] Moreover, POEGMAs connected to functional biomolecules like chitosan, galactose, porphyrine and even to fullerenes have been reported.[17,18,19,20] Accordingly, POEGMA copolymers comprised of monomers that are different with regard to the length and the end group of their ethylene glycol chain show different LCSTs. This effect has been used to create thermoresponsive polymer aggregates, especially for biomedical applications.[21,22,23] In the present work we combined the thermoresponsive, hydrophilic POEGMA with poly(L-lactide) (PLLA), a hydrophobic polymer that is incompatible with POEGMA. PLLA is a fully biocompatible and biodegradable material that is widely used for biomedical applications such as bone fixation screws and temporary implants. In addition, The chirality of its monomer units determines the degree of crystallization and stereocomplexation of the PLLA blocks can be used to form and stabilize aggregates formed in solution.[24,25,26] We used a bifunctional initiator introduced by our group in recent work to synthesize a POEGMA block via atom transfer radical polymerization (ATRP).[27] Despite the fact that both polymers are well-known, at present there are only few studies regarding the combination of polyesters and polymethacrylates in the form of functional block copolymers. Nevertheless, the rather rigid and hydrophobic structure of isotactic poly (L-lactide) is particularly appropriate to serve as the hydrophobic inner part of block copolymer membranes of micelles or vesicles that are intended to carry hydrophobic guest molecules. Moreover, its high biocompatibility makes it especially suitable for biomedical applications. In previous work carried out in our group, a novel acrylate monomer, namely 1,3-benzylidene glycerol methacrylate (BGMA) was introduced and polymerized by means of ATRP, followed by the preparation of a poly(L-lactide) block by ring opening polymerization. After deprotection of the poly(methacrylate) block in aqueous solution, the obtained polymers formed vesicular structures which were capable of carrying the hydrophobic dye pyrene.[28] As our objective was the creation of aggregates that disassemble via a temperature stimulus close to human body temperature, the LCST of the POEGMA block was adjusted to approximately 40°C. This was achieved by random copolymerization of two different kinds of OEGMA monomers, namely oligo(ethylene glycol) methylether methacrylate with an average molecular weight of 300 g/mol and oligo(ethylene glycol) ethylether methacrylate (246 g/mol molecular weight). The PLLA block was subsequently generated by ring-opening polymerization of the lactide monomer, providing the hydrophobic domain of the amphiphilic macromolecule The resultinglinear POEGMA-*block*-PLLA block copolymers that have been characterized by ^{1}H and ^{13}C NMR spectroscopy, as well as size exclusion chromatography (SEC). Extending this concept, we took advantage of a trifunctional initiator that was synthesized in five synthetic steps.[29,30,31,32] This was used to create a single in-chain functionality, namely a triple bond, between the two polymeric blocks at the junction point. This was then applied as an anchor point for the attachment of the dye rhodamine B by click reaction.

Experimental Section:

Materials. All reagents and solvents were purchased from Acros Organics or Sigma-Aldrich and used without further purification unless otherwise stated. 1,8-diaza-bicyclo[5.4.0]undec-7-en (DBU) was purified by stirring with CaH_2 and subsequent distillation under Argon atmosphere and was stored at low temperatures for a maximum of one week prior to use. L-Lactide was purchased from Purac (Groningen, Netherlands), recrystallized twice from toluene and stored under vacuum prior to use.

Instrumentation. ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC 300 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in trichloromethane, a setup consisting of a Waters 717 plus Autosampler, a TSP Spectra Series P 100 pump, three PSS-SDV-5 µl-columns with 100, 1 000, and 10 000 Å pore diameter, respectively, a UV (275 nm), and an RI detector was used. Calibration was carried out using poly(styrene) standards provided by Polymer Standards Service (PSS). Transmission Electron Micrographs were taken on a Philips EM-420, equipped with a slow-scan CCD camera and a LaB_6 cathode, operating at an acceleration voltage of 120 kV.

Encapsulation and release of Nile Red. Nile Red and the block copolymer were dissolved in a minimal amount of THF. Water was added dropwise to induce micelle formation and nile red encapsulation. Then THF was removed by slow evaporation and undissolved nile red was removed by filtration.. The resulting pink solution was heated slowly in a water bath until precipitation of nile red indicated decomposition of the micelles.

2-Bromo-2-methyl propionic acid 2-hydroxyethyl ester. Anhydrous ethylene glycol (35 g, 0.56 mol) was added to a 250 ml three-necked round bottom flask equipped with a magnetic stir bar, a dropping funnel, a thermometer and a rubber septum, which was degassed and purged with argon 3 times prior to the reaction. The flask was cooled to 0°C in an ice bath and □-bromo-isobutyryl-bromide (6.48, 0.03 mol) was added slowly through the dropping funnel. After the addition was completed, the reaction was stirred at 0°C for another 3 hours before quenching with 50 ml of water. The product was extracted with chloroform (3x50 ml), the combined organic extracts were dried with anhydrous $MgSO_4$, filtered and chloroform was removed by rotary evaporation. The product was further purified by distillation, yielding a clear, colorless liquid (5.38 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 4.30 (t, 2 H, CH_2OH), 3.86 (t, 2 H, O-CH_2-), 1.94 (s, 6 H, -CH_3).

Isopropylidene-2,2-bis(methoxy)propionic Acid. Bis-methoxypropionic acid, 10.00 g (74.55 mmol), and 13.8 mL (111.83 mmol) of 2,2-dimethoxypropane and 0.71 g (3.73 mmol) of *p*-toluenesulfonic acid monohydrate were dissolved in 50 mL of acetone. The reaction mixture was stirred for 2 h at room temperature. After the catalyst was neutralized by adding approximately 1 mL of a NH_3/EtOH (50:50) solution, the solvent was evaporated at room temperature. The residue was then dissolved in (250 mL) CH_2Cl_2 and extracted with two portions of (20 mL) water. The organic phase was dried with $MgSO_4$ and evaporated to give isopropylidene-2,2-bis(methoxy)propionic acid as white crystals: 12.0 g (92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.20 (s, 3H, -CH_3), 1.39 (s, 3H, -CH_3), 1.42 (s, 3H, -CH_3), 3.65 (d, 2H, -CH_2O), 4.18 (d, 2H, -CH_2O).

Acetonide-2,2-bis(methoxy)propionic Anhydride. Acetonide-2,2-bis(methoxy)propionic acid (8.2 g, 0.047 mol) was stirred in CH_2Cl_2 (30 mL). *N,N`*- Dicyclohexylcarbodiimide (DCC) (4.85 g, 0.024 mol) was added to the mixture and stirring was continued for 48 h at room temperature. The DCC-urea was filtered off and the solvent evaporated. The viscous residue was diluted in 1 L of hexane and stirred until a white solid formed. Thereafter, the solution was cooled to -78 °C for 1 h, filtered through a glass filter, and dried under vacuum to afford acetonide-2,2-bis(methoxy)propionic anhydride as white crystals (4.0 g, 0.012 mol, 51%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 1.21 (s, 6H, -CH_3), 1.36 (s, 6H, -CH_3), 1.41 (s, 6H, -CH_3), 3.66 (d, 4H, -CH_2O), 4.18 (d, 4H, -CH_2O). ^{13}C NMR (75.5 MHz, $CDCl_3$) □(ppm): 17.83, 21.75, 25.72, 43.83, 65.85, 98.56, 169.68.

Propargyl Acetonide-2,2-bis(methoxy)propionate. Propargyl alcohol (0.52 g, 0.009 mol) and DMAP (0.17 g, 0.001 mol) were dissolved in pyridine (2.22 g, 0.028 mol) in a 250 mL round bottom flask, followed by the addition of 5 mL CH_2Cl_2. Isopropylidene-2,2-bis(methoxy)propionic anhydride (4.0 g, 0.012 mol) was added slowly. The solution was stirred at room temperature overnight. The reaction was quenched with 2 mL of water under vigorous stirring, followed by dilution with CH_2Cl_2 and the solution was washed with 10% of $NaHSO_4$ (3×30 mL), and 10% of Na_2CO_3 (3×30 mL) and brine (30 mL). The organic phase was dried with $MgSO_4$, filtered and concentrated. The crude product was purified by flash chromatography on silica, eluting with hexane (100 mL) and gradually increasing the polarity to ethyl acetate:hexane (10:90, 700 mL), followed by EA:hexane (15:85) to give acetonide-2,2-bis(methoxy)propionic acid propargyl ester as a colorless oil. Yield: 35.9 g (95 %). ^{1}H

NMR (300 MHz, $CDCl_3$) δ(ppm): 1.08 (s, 3H, CH_3CCOO), 1.25 (s, 3H, CCH_3), 1.29 (s, 3H, CCH_3), 2.43 (t, 1H, C≡C*H*), 3.20 (d, 2H, CCH_2OCCH_3), 4.06 (d, 2H, CCH_2OCCH_3), 4.61 (d, 2H, CH_2C≡CH). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ(ppm): 18.67, 22.92, 24.83, 42.11, 52.59, 65.87, 75.00, 77.83, 98.32, 173.60.

Propargyl 2,2-Bis(hydroxymethyl)propionate. 1.5 g DOWEX 50W-X2-200 resin were added to a solution of propargyl acetonide-2,2-bis(methoxy)propionate (1.0 g, 0.005 mol) in 30 mL of methanol in a 100 mL round bottom flask. The mixture was stirred at 40 °C for 12 hours. The resin was filtered off and the filtrate was concentrated and dried under high vacuum to give 2,2-bismethoxypropionic acid propargyl ester as a colorless oil. Yield: 0.81 g (0.005 mol, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 1.06 (s, 3H, CH_3CCOO), 2.50 (t, 1H, C≡C*H*), 3.54 (s (br), 2H, CCH_2OH), 3.63 (d, 2H, CCH_2OH), 3.78 (d, 2H, CCH_2OH), 4.67 (s, 2H, CH_2C≡CH); ^{13}C NMR (75.5. MHz, $CDCl_3$) δ(ppm): 18.86, 49.36, 52.24, 65.87**,** 75.21, 77.35, 174.77.

Propargyl-2-hydroxymethyl-2-(□-bromoisobutyraloxymethyl)-propionate. Propargyl 2,2-Bis(hydroxymethyl)propionate (1.5 g, 0.009 mol and triethylamine (1.2 ml, 0.009 mol) were dissolved in 30 ml of THF. 2-bromo-isobutyryl bromide (1.1 ml, 0.009 mol) was dissolved in 5 ml THF and added dropwise to the solution at 0°C under argon atmosphere. After the addition was completed, the reaction mixture was stirred for another 24 h, the formed precipitate separated by filtration and the solvent removed under reduced pressure. The product was further purified by column chromatography (EA/petroleum ether 1/4), yielding 2.1 g (0.006 mol, 74%) of the desired product. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 1.27 (s, 3H, C-CH_3), 1.91 (s, 6H, CBr-CH_3), 2.49 (t, 1H, C≡C*H*), 3.75 (s, 2H, CH_2OH), 4.28-4.45 (m, 2H, C-CH_2-OCO), 4.73 (d, 2H, CH_2-C≡CH).

ATRP of Oligo(ethylene glycol methacrylate). In all polymerizations, the initiator/copper/ligand ratio was [1]:[1]:[1]. Monomer/initiator ratios were calculated according to the targeted molecular weight of the POEGMA block. Acetonitrile was predegassed by three freeze-pump-thaw cycles. In a typical procedure, 13.3 mmol of a monomer mixture of 30% oligo(ethylene glycol) methylether methacrylate (M_n = 300 g/mol) (1.2 g, 4.0 mmol) and 70% oligo(ethylene glycol) ethylether methacrylate (M_n= 246 g/mol) (2.3 g, 9.3 mmol) and initiator (141 mg, 0.7 mmol) were charged into an argon-flushed Schlenk-tube, dissolved in 1.6 ml of predegassed acetonitrile and degassed in three freeze-pump-thaw cycles. The ligand, 2,2-bipyridine (bipy) (210 mg, 0.7 mmol), was charged in a separate Schlenk-tube, dissolved in 1 ml of predegassed acetonitrile and degassed in three freeze-pump-thaw cycles. Subsequently, the ligand solution was injected into a pre-evacuated Schlenk-tube, containing 96 mg (0.7 mmol) of copper-(I)-chloride. The tube was flushed with argon and stirred until the dark red copper-complex formed. The polymerization was initiated by injecting the copper/bipy complex to the monomer/initiator solution and carried out over night at room temperature. The reaction was quenched by exposure to air. Trichloromethane was added to the reaction mixture, which was subsequently filtered over a short column filled with neutral aluminum oxide to remove the copper catalyst. Then solvent was removed from the colorless solution in vacuum and residual monomer was removed by dialysis in methanol. The polymer was obtained as a colorless material, depending on the molecular weight more or less viscous liquid. ^{1}H NMR (D$_2$O, 300 MHz) δ (ppm): 4.08 (s, COO-CH_2), 3.78-3.46 (m, O-CH_2-CH_2-O, O-CH_3), 2.14-1.70 (br, CR$_2$-CH_2-CR$_2$), 1.21 (t, O-CH$_2$-CH_3), 1.12-0.74 (br, CR$_2$-CH_3).

Ring-opening polymerization of lactide. The □-hydroxyl-POEGMA macroinitiator and L-Lactide were charged into a Schlenk-flask. The flask was sealed with a rubber septum and repeatedly flushed with argon after evacuation. Freshly distilled dichloromethane (5 ml/g lactide) was added via a syringe. Polymerization was initated after 2 min by injecting DBU (corresponding to 1 mol% of the monomer). Polymerization was quenched after 20 min by injecting benzoic acid (corresponding to 1.2 mol% of the monomer) dissolved in a small amount of dichloromethane. Subsequently, DBU, benzoic acid and residual monomer were removed by extraction with water. The organic phase was dried with MgSO$_4$ and the solvent removed under reduced pressure to yield a white solid. ^{1}H NMR (D$_2$O, 300 MHz) δ (ppm): 5.29-5.20 (br, H8), 4.44-4.26 (m, H7), 4.16-3.98 (br, H6), 3.77-3.30 (br, H5), 2.10-1.71 (br,H4), 1.68-1.41 (br, H3), 1.21 (t, H2), 1.09-0.73 (b, H1).

11-Azido-1-undecanol. 11-bromo-1-undecanol (5 g, 0.02 mol) and sodium azide (1.94 g, 0.03 mol) were dissolved in a 2:1 mixture of ethanol and water. The solution was heated to reflux and stirred for 24 h. Then ethanol was removed under reduced pressure and the residual solution extracted with ethyl acetate (3x20 ml) The organic phase was dried over MgSO4, filtrated and the solvent evaporated to yield 3.83 g (0,018 mol, 90%) 11-azido-1-undecanol. ^{1}H NMR (DMSO, 300 MHz) δ (ppm): 3.62-3.57 (t, 2H, CH_2-OH), 3.20 (t, 2H, CH_2-N$_3$), 1.58-1.50 (br, 4H, CH_2-CH$_2$-OH and CH_2-CH$_2$-N$_3$), 1.25 (br, 15H, C$_7H_{14}$ and CH$_2$-OH)

Rhodamine B-11-azidoundecanyl ester. Under argon atmosphere, Rhodamine B (2 g, 0.004 mol was dissolved in a minimum amount of dimethylformamide (DMF). The solution was cooled in an ice bath and vigorously stirred, while oxalylchloride (9 g, 0.07 mol) was added dropwise. After the addition was completed, stirring was continued and the progress of the reaction was monitored via thin film chromatography. In most cases, full conversion was achieved after about 30 min. The acid chloride of Rhodamine B was isolated under reduced pressure over night and immediately used for the esterification step. Therefore it was again dissolved in dry DMF and cooled to 0°C. Then 5 ml of pyridine were added and 11-azido-1-undecanol (1 g, 0.005 mol, dissolved in approx. 10 ml of DMF) was added dropwise under stirring. After stirring for 24 h the solvent was removed under reduced pressure and the product purified by column chromatography (MeOH/AcOEt 1/2) ESI MS: 638 (MH^+)

Attachment of Rhodamine B to POEGMA-*b*-PLLA. In a typical reaction, 50-300 mg of the block copolymer were dissolved in 10 ml of DMF. Sodium ascorbate, $CuSO_4$ and a solution of the respective amount of azide-functional Rhodamin B dissolved in another 10 ml of DMF were added and the resulting solution stirred at 100°C for 12 h. The dye-functionalized polymer was isolated by dialysis against THF and subsequent removal of the solvent on a rotary evaporator.

Results and Discussion

A. Block Copolymer Synthesis

The bifunctional initiator 2-bromo-2-methyl propionic acid 2-hydroxyethyl ester was successfully synthesized by esterification of α-bromo-isobutyryl bromide with ethylene glycol, using a procedure described by Turro et al.[33] In recent work by our group this molecule was employed as a double sided initiator, bearing an isobutyryl bromide function to initiate ATRP on one side of the molecule as well as an OH group that is capable of starting ring opening lactide polymerization on the other side. A large excess of the alcohol component is necessary to prevent formation of the diester compound. The synthesized structure was verified by ^1H NMR spectroscopy. NMR spectra of the synthesized initiator are available in the Supporting Information.

Atom transfer radical polymerization was used for the synthesis of the POEGMA block. Studies on the conditions of ATRP homopolymerization of OEGMA have been conducted in 2009 by Malmström et al..[34] In order to carry out the polymerization slowly and in a well controlled fashion, the rather nonpolar solvent acetonitrile was chosen. In acetonitrile, polymerization proceeds slowly, and all reactions were thus performed over night to achieve complete conversion of the monomer. 2,2-bipyridyl was used as a ligand of the copper(I) ions, the complex formed was of dark red color. The described conditions allow to obtain maximum control over the polymerization and complete monomer conversion. The polymers obtained showed monomodal, narrow molecular weight distributions and the polydispersities measured by SEC with chloroform as an eluent are in the range of 1.1 to 1.3. We targeted molecular weights between 1000 to 8000 g/mol. Successful synthesis was also confirmed by ^{1}H NMR-spectra recorded in in D_2O.

The lower critical solubility temperature of POEGMA strongly depends on the length and the end group of the oligo(ethylene glycol) side chain of the monomer. The LCST can be varied in the range of 20°C to 70°C. To create a copolymer that is suitable for biomedical applications, we decided to adjust the LCST of the POEGMA block at around 40°C, which is only slightly higher human body temperature. To this end, we randomly copolymerized two different OEGMA-monomers. The first comonomer possessed a molecular weight of about 300 g/mol and a methyl-terminated oligoethylene glycol chain, the other comonomer had a molecular weight of about 246 g/mol and an ethyl ether end group. Homopolymers of the former show an LCST of about 65°C, the latter of about 20°C at neutral pH values.[4] A series of copolymers of different composition was synthesized and their LCST was determined by turbidimetry. According to Lutz et al., results show that there is a strong correlation between the monomer composition and the cloud point of the copolymer obtained. The LCST of these polymers linearly increases with decreasing content of the methyl ether end capped oligo(ethylene methacrylate) monomer. Polymers consisting of 35% of the methyl- and 65% of the ethyl-terminated monomers showed cloud points of approximately 39-41°C. Therefore all polymerizations were carried out using this monomer composition.

Synthesis of POEGMA-*b*-PLLA by ring-opening polymerization of dilactide using a POEGMA macroinitiator. The final block copolymers were obtained by using the hydroxy-functional POEGMA as an initiator for the ring-opening polymerization of dilactide. A standard protocol for the ring opening lactide polymerization was applied for all polymerizations. A base catalyst, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), was used to catalyze the reaction, providing sufficient monomer conversion together with good control to lead narrow molecular weight distributions. Methylene chloride, which is a common solvent for lactide polymerization, was used because it is well suitable to dissolve the POEGMA macroinitiator. After a reaction time of 20 minutes, the polymerization was stopped by addition of benzoic acid, which is convenient to realize full conversion of the lactide monomer. The solid state properties of the obtained POEGMA-*b*-PLLA are strongly dependent on the ratio of the block lengths. If the POEGMA block is dominant, the polymers are obtained as a soft, white and rubber like solids, whereas the materials became increasingly brittle with growing PLLA content. All copolymers were characterized by ^{1}H and ^{13}C NMR (see Supporting Information) spectroscopy. Molecular weights and molecular weight distributions were analyzed via SEC measurements, showing values of 1.2 to 1.5 for molecular weights between 6000 and 20000 g/mol. Alle samples prepared are listed in Table 1. Figure 2 displays the complete synthetic route for the preparation of POEGMA-*b*-PLLA, Figure 3 depicts the ^{1}H NMR spectrum of a typical block copolymer and Figure 4 shows GPC data of a POEGMA macroinitiator and the POEGMA-*b*-PLLA that was synthesized from it.

Sample Number	$M_{(calc.)}$ POEGMA [g/mol]	$M_{(calc.)}$ PLLA [g/mol]	M_n (SEC) [g/mol]	M_w (SEC) [g/mol]	PDI
1	4200	6000	9700	12000	1.24
2	9000	2000	10000	13500	1.35
3	5100	1000	5800	7800	1.35
4	3700	7000	9600	12200	1.27
5	6000	1000	7600	10700	1.41
6	4000	1000	11500	17300	1.50
7	8000	4000	8600	10300	1.20
8	10000	6000	14700	20700	1.41

Table 2. POEGMA-*b*-PLLA block copolymers

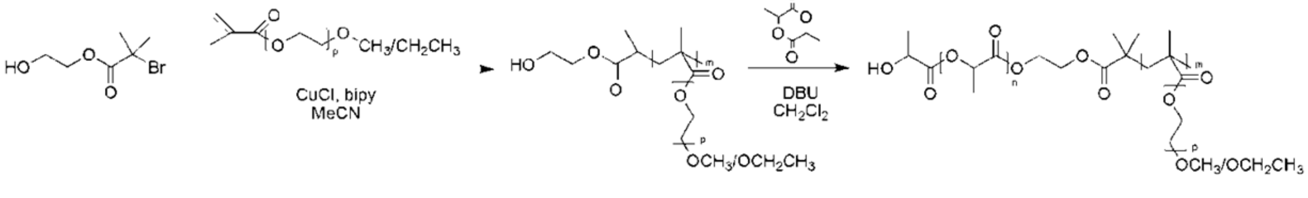

Figure 2. Synthesis of POEGMA-*b*-PLLA

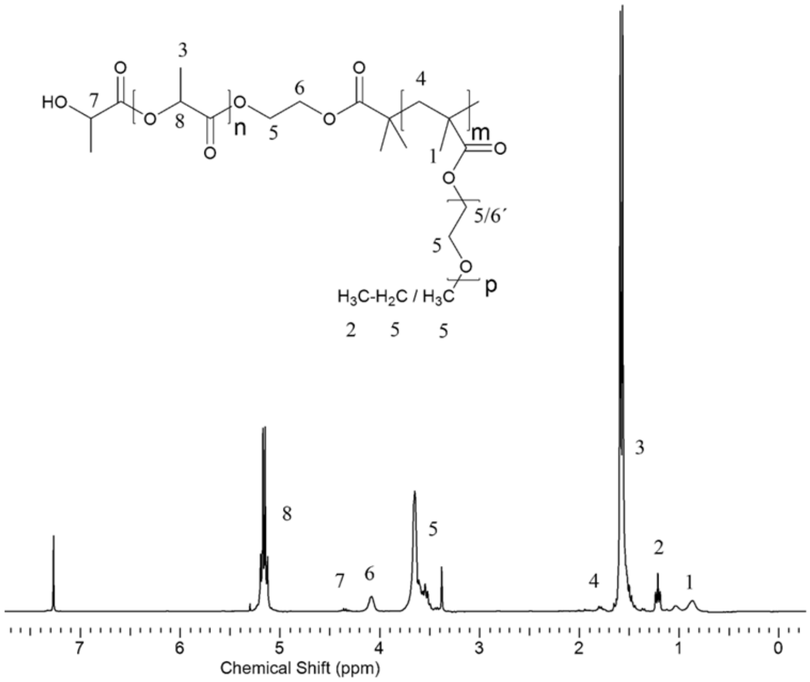

Figure 3. ^{1}H NMR spectrum (300MHz, $CDCl_3$) of POEGMA-*b*-PLLA

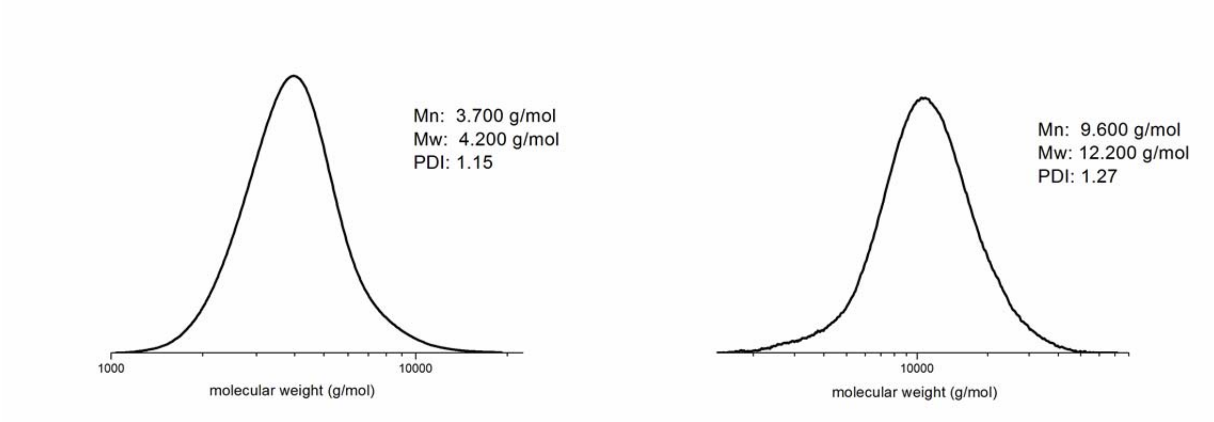

Figure 4. SEC data of a typical POEGMA macroinitiator (left, PEG standard, eluent: DMF) and the POEGMA-b-PLLA block copolymer that was synthesized from it (sample 4, right, eluent: chloroform).

Dynamic Light Scattering (DLS). Due to the amphiphilic nature of the block copolymers, we expected them to form spherical micelles in aqueous environment. To investigate their aggregation behavior, the polymers were transferred into water by the following procedure: A large excess of water was added dropwise to a solution of the polymer in a minimum amount of THF, followed by 2 days of dialysis against water. The resulting solution that was subjected to DLS measurements had a concentration of about 0.1 mg/ml. The sizes of the observed aggregates are in good agreement with the results from the TEM images discussed below. Diameters of 70 to 110 nm were obtained, and the size distribution was narrow for all measured samples. However, as the influence of the block length ratio on the size of the particles is fairly marginal, we were not able to establish a clear correlation between these two values. This becomes clear when comparing the diameter of micelles formed from POEGMA$_{14}$-*b*-PLLA$_{14}$and POEGMA$_{22}$-*b*-PLLA$_{14}$, showing values of 110 nm and 75 nm, respectively. (See Supporting Information for DLS plots).

Transmission Electron Microscopy (TEM). In order to further investigate the aggregation behavior of the synthesized macromolecules, transmission electron micrographs were taken from aqueous solution. Samples were prepared as follows: Aqueous solutions of the block copolymer were prepared as described before, this time at a concentration of approximately 10 mg/ml and subsequently drop-cast on copper grids. The obtained images show aggregates of spherical shape. According to the solubility of the polymer blocks, the observed aggregates form in such a way that only the hydrophilic POEGMA block stays in contact with water, while the PLLA block is represents the inner part of the micelles. Figure 5 shows TEM images of one of the synthesized polymers. When the polymer was kept at room temperature, drop casting revealed polymer micelles of approximately 80 nm in diameter and narrow size distribution. Of course these values vary with the chain length and the block length ratios of the investigated polymer. Interestingly, if the aqueous polymer solutions are heated above the LCST of the POEGMA precursor previous to the drop casting procedure, the obtained TEM images depict much larger aggregates. The observed structures are also spherical, but exhibit a broader size distribution, resulting in diameters of 100 to 400 nm. It is not yet clear to us how this structural change occurs and how it goes together with the release of incorporated dye that is described below. Besides this, we are not sure about what the driving forces for this process are, but heating the samples tends to induce a conformational change in the structure of the polymer chains which we ascribe to the thermoresponsive POEGMA block. As a result, the favored form of aggregation changes from micelles to spherical aggregates of significantly larger size.

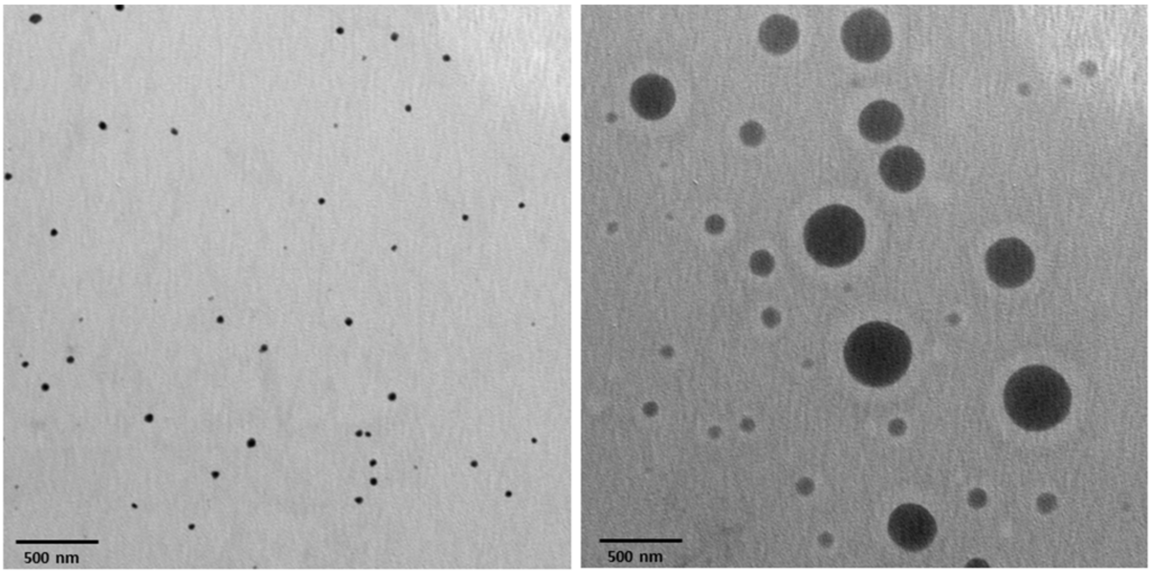

Figure 5. TEM micrographs of POEGMA-*b*-PLLA, drop-cast at room temperature (left) and after heating to 50°C for 30 sec (right).

Inclusion and Temperature-Triggered Release of Nile Red. In order to investigate the temperature dependent decomposition of the block copolymer micelles, they were loaded with a model hydrophobic guest. For this purpose, the hydrophobic dye nile red was chosen. This dye appears pink only when it is dissolved in hydrophobic media. To load the polymer vesicles with nile red, both polymer and the dye were dissolved in a minimum amount of THF. Then a large excess of water was added dropwise in order to induce micelle formation and concomitant nile red encapsulation. Afterwards, the residual THF was removed under reduced pressure and the solution filtered through a 0.2 μm syringe filter to remove small amounts of undissolved nile red. The resulting aqueous solution is of pink color, confirming that nile red must be incorporated in the hydrophobic interior of the block copolymer micelles. In order to demonstrate the temperature triggered decomposition of the micelles and the accompanied release of the dye, the solution was heated to 50°C for 2 minutes. As a result, nile red was exposed to the aqueous environment, which resulted in immediate precipitation, and the solution turned colorless (See Supporting Information). **Figure 6** shows an aqueous solution of polymer micelles loaded with nile red on the left, in the center a sample of the same solution after heating and on the right the result of the same experimental procedure, carried out without the addition of the block copolymer. In this case the dye precipitated after evaporation of THF and was thus completely removed during filtration, It has to be taken into account that the temperature that is needed to induce the release of the guest molecule significantly exceeds the LCST of 40°C that was measured for the POEGMA precursor. We suggest this to be due to a change of the LCST caused by the influence of the subsequently added poly(L-lactide) block. As the block copolymers are insoluble in water, it was not possible to measure the LCST of the POEGMA block after addition of the PLLA chain. We therefor assume that the LCST of the POEGMA as a part of the copolymer is higher than that of the respective homopolymer which would explain the fact that the micelles do not decompose below 50°C.

POEGMA-*b*-PLLA with in-chain propargyl functionality.

Synthesis of the trifunctional initiator Propargyl-2-hydroxymethyl-2-(α-bromoisobutyraloxymethyl)-propionate.

To broaden the spectrum of possible applications for the novel block copolymers of POEGMA and PLLA that are capable in terms of micelle formation and temperature triggered response, we wanted to add functionality to the so far unfunctional polymer. We therefore took advantage of a trifunctional molecule synthesized in five step procedure. Besides the free hydroxy group that is needed to start the ring-opening lactide polymerization and the isobutyrylbromide function that is used to initiate the ATRP, this structure carries a triple bond that allows to easily attach molecules to the block copolymer via click reaction with an azide. The resulting block copolymer therefor consists of exactly one functional group at the junction point between the two blocks. **Figure 7** depicts the 5-step reaction pathway that was applied to synthesize this molecule.

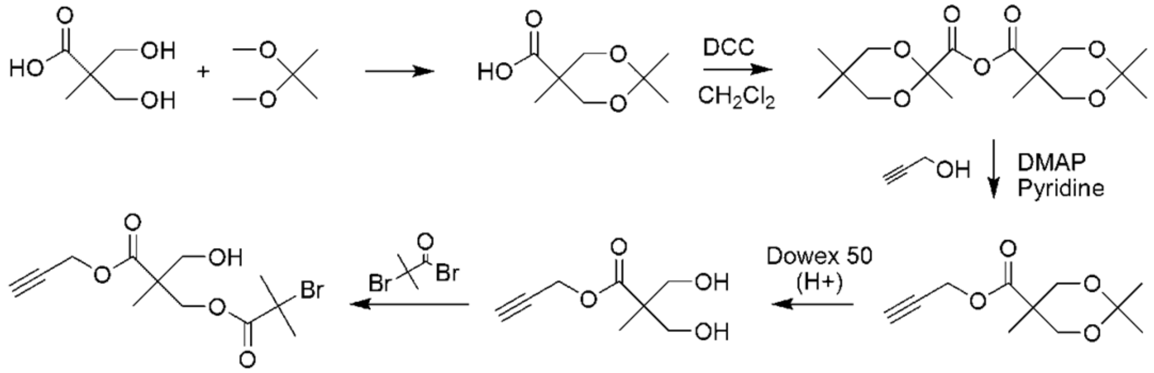

Figure 7. Synthetic pathway to propargyl-2-hydroxymethyl-2-(□-bromoisobutyraloxymethyl)-propionate

Synthesis of the block copolymer was carried out in exact analogy to the ones in which the difunctional initiator was used. A set of block copolymers with narrow PDIs and different block length ratios was synthesized. However, the slightly higher steric demand of the new initiator compared to the difunctional one seems to impede the access of lactide monomers to the free hydroxyl group. We suggest this to be due to interaction with the carbonyl group of the propargyl ester moiety. This results in an incomplete lactide conversion and forced us to use a large excess of lactide. Therefore, only rather long PLLA chains of 3000 g/mol and longer were accessible. The terminal acetylenic proton of the initiator is clearly visible in the NMR spectrum of the obtained block copolymers, proving that both ATRP and ROP of lactide do not harm the triple bond at the intersection which can thus be addressed by any kind of azide-functional molecule (see supporting information for ^{1}H NMR and SEC diagrams).

Attachment of rhodamine B

To confirm accessibility of the triple bond the block copolymer carries at its junction point, the goal was to attach rhodamin B. For this purpose, this dye needs to be equipped with an azide function. This was done using the acid group of the rhodamine, which was firstly converted to the acid chloride, followed by esterification with a long chain primary aliphatic alcohol that carries an azide group. Moreover, we assumed that a linker of effectual length is needed between the rhodamine and the azide group, as it would be difficult for a large molecule like rhodamine B to get in close contact with the propargyl moiety at the junction point of the block copolymer. The linking molecule we chose was 11-azido-1-undecanol, which was synthesized from 11-bromo-1-undecanol by a simple nucleophilic substitution reaction using sodium azide. This molecule was connected to the rhodamine B chloride via esterification (see supporting information for ESI MS of the azide modified rhodamine B). **Figure 8** shows the synthetic strategy that was applied.

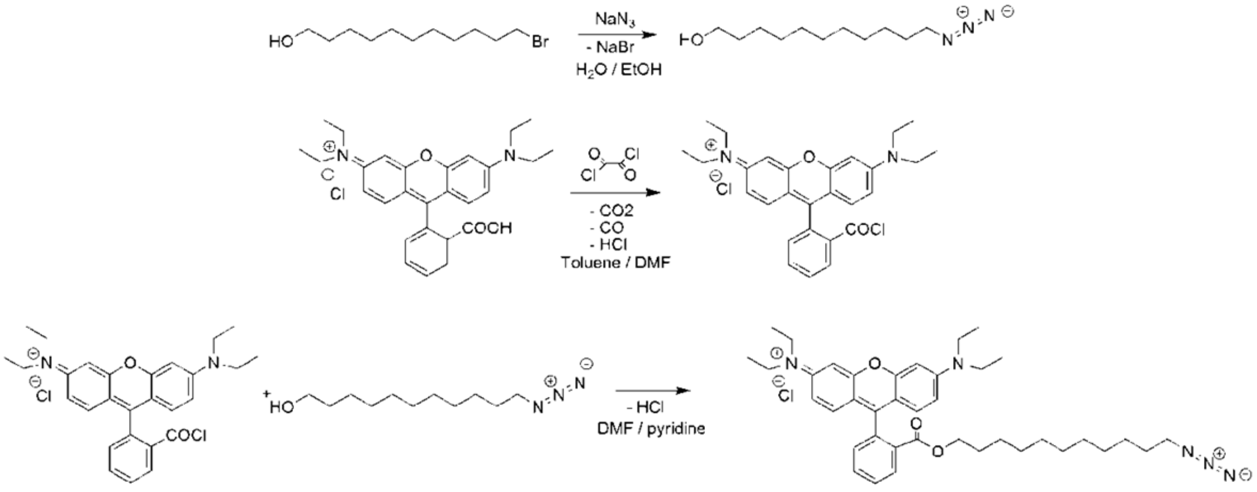

Figure 8: Synthesis of azide functional rhodamine B

The Huisgen click reaction between the acetylene at the intersection between the two polymer blocks and the azide group of the modified rhodamine B was carried out by the use of a catalytic system of $CuSO_4$ and sodium ascorbate at a temperature of 100°C. DMF was found to be suitable to properly dissolve both the amphiphilic polymer and the dye. In order to remove the excess of dye, the reaction mixture needed to be dialyzed for several days. The results of the coupling reaction were analyzed by SEC. As the unmodified block copolymer could not be detected by the UV detector of our SEC device, it showed a strong signal for the polymers that had previously been coupled to rhodamine B. Interestingly, the attachment of the dye seems to have an influence on the bulk structure of the polymer, leading to a decrease of the detected molar mass. It appears that the polymer chains wrap around the rhodamine molecule, which is located at the approximate center of the polymer. This leads to a closer packing and thus to an increased retention time within the polystyrene stationary phase. Nevertheless, the results show that linkage of a functional molecule like a dye to the propargyl unit of the polymer is possible by click reaction. **Figure 9** shows the SEC trace of the rhodamin B functionalized block copolymer.

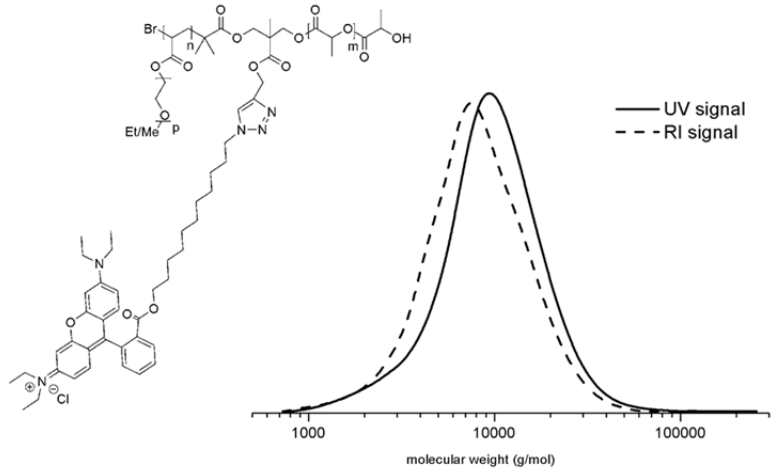

Figure 9. SEC diagram of rhodamine functionalized polymer

Conclusion.

A series of block copolymers of poly(oligoethylene glycol methacrylate) and poly(L-lactide) have been synthesized by means of atomic transfer radical polymerization of oligoethylene glycol methacrylates and ring opening polymerization of lactide. The resulting polymers show molecular weights between 8000 and 20000 g/mol and narrow polydispersities around 1.2. To adjust the LCST of the POEGMA block, two different OEGMA monomers were randomly copolymerized in the adequate ratio to obtain an LCST of approximately 40°C. The amphiphilic copolymers form spherical aggregates in aqueous solution, which was shown by dynamic light scattering and transmission electron microscopy. Furthermore, a trifunctional initiator was employed to create exactly one functional group, namely a triple bond, at the intersection between the two polymer blocks. This group was utilized to attach rhodamine B to the center of the block copolymer via click reaction. With its amphiphilic structure that leads to spherical aggregation in aqueous environment, the full biocompatibility of both blocks and the ability to attach further functional molecules to its junction point by simple click reaction, the synthesized polymers represent an advantageous new material with high application potential especially in the field of biomedicine and drug delivery.

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Supporting Information
“Amphiphilic Poly(OEGMA) Block Copolymers with Tunable Thermoresponsiveness”

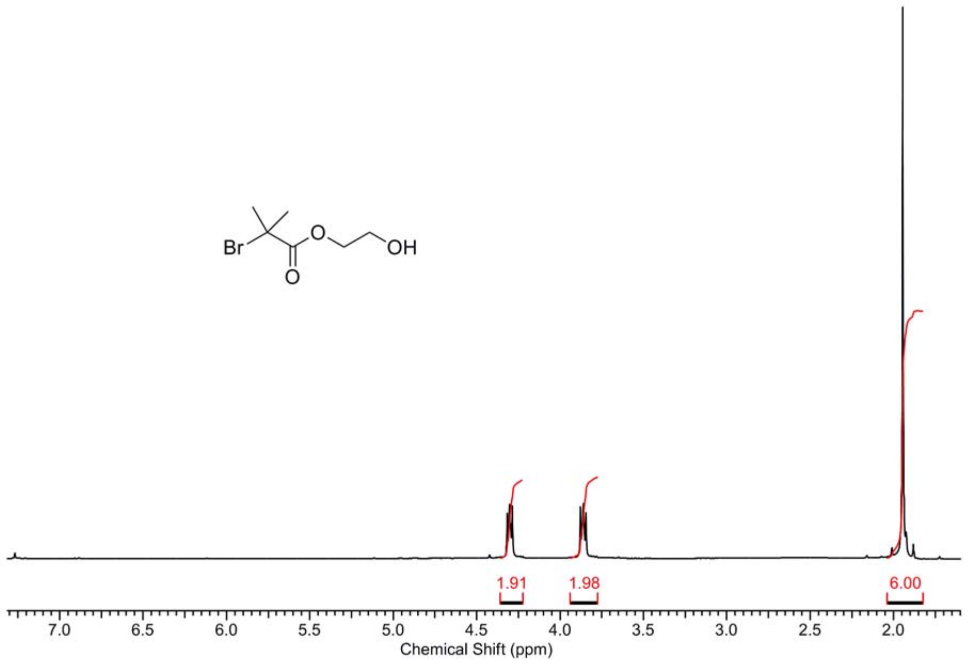

Figure S1. ^{1}H NMR spectrum (300 MHz, CDCl3) of the difunctional initiator 2- Bromo-2-methyl-propionic acid 2-hydroxyethyl-ester

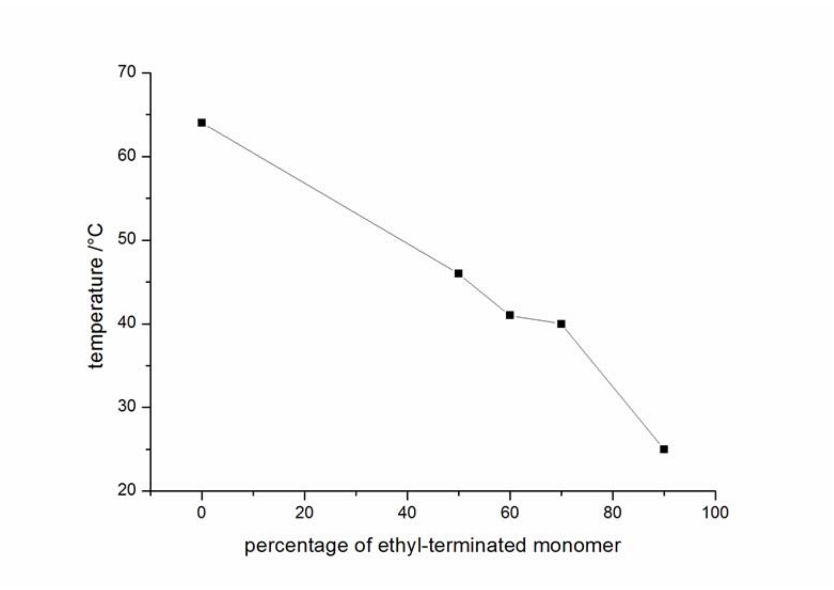

Figure S2. Results of the turbidimetric analysis of the cloud points of POEGMA copolymers depending on the monomer composition (heating rate: 1K/min).

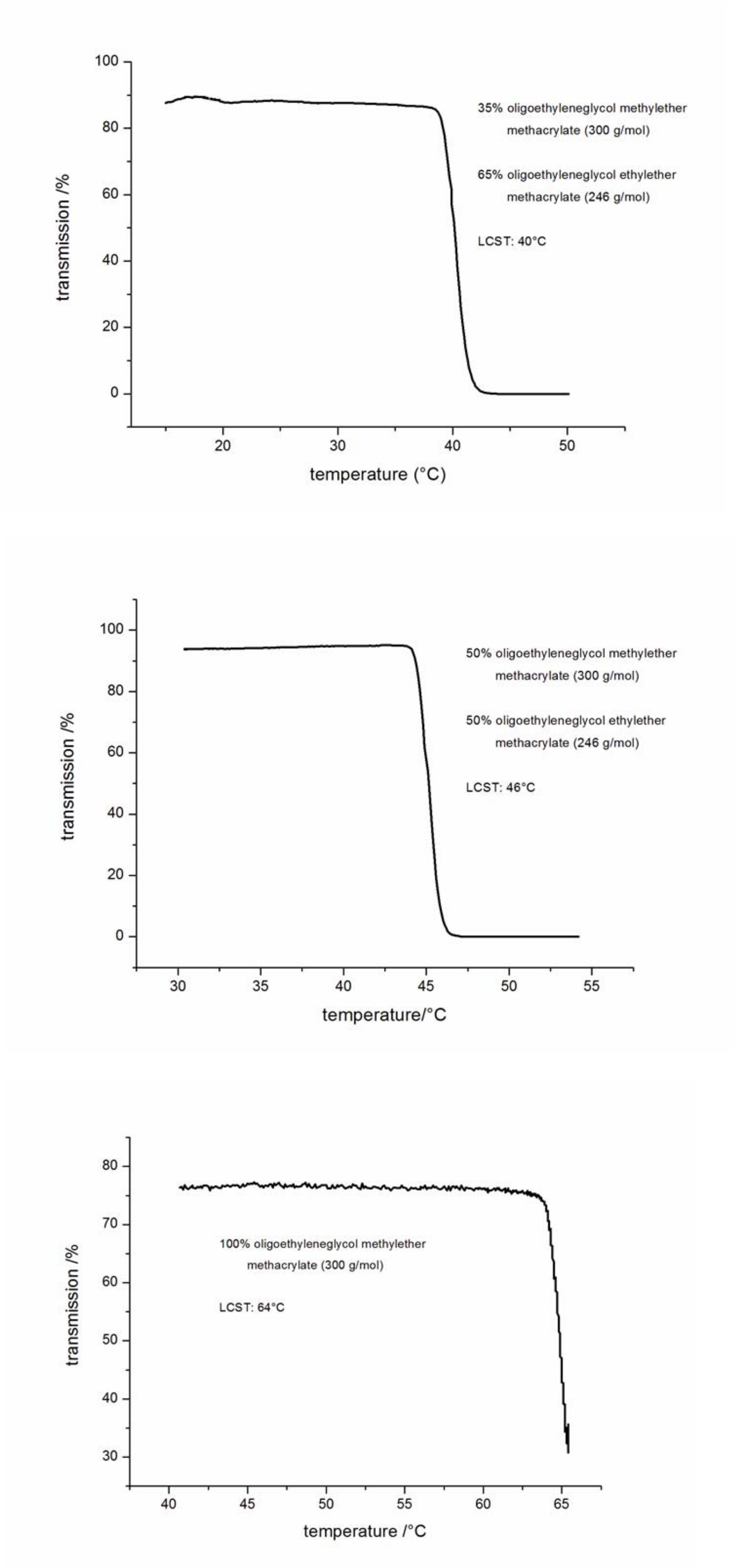

Figure S3. Turbidimetric LCST analysis of three different POEGMA macroinitiators containing 35, 50 and 100% of the methylether terminated OEGMA monomer

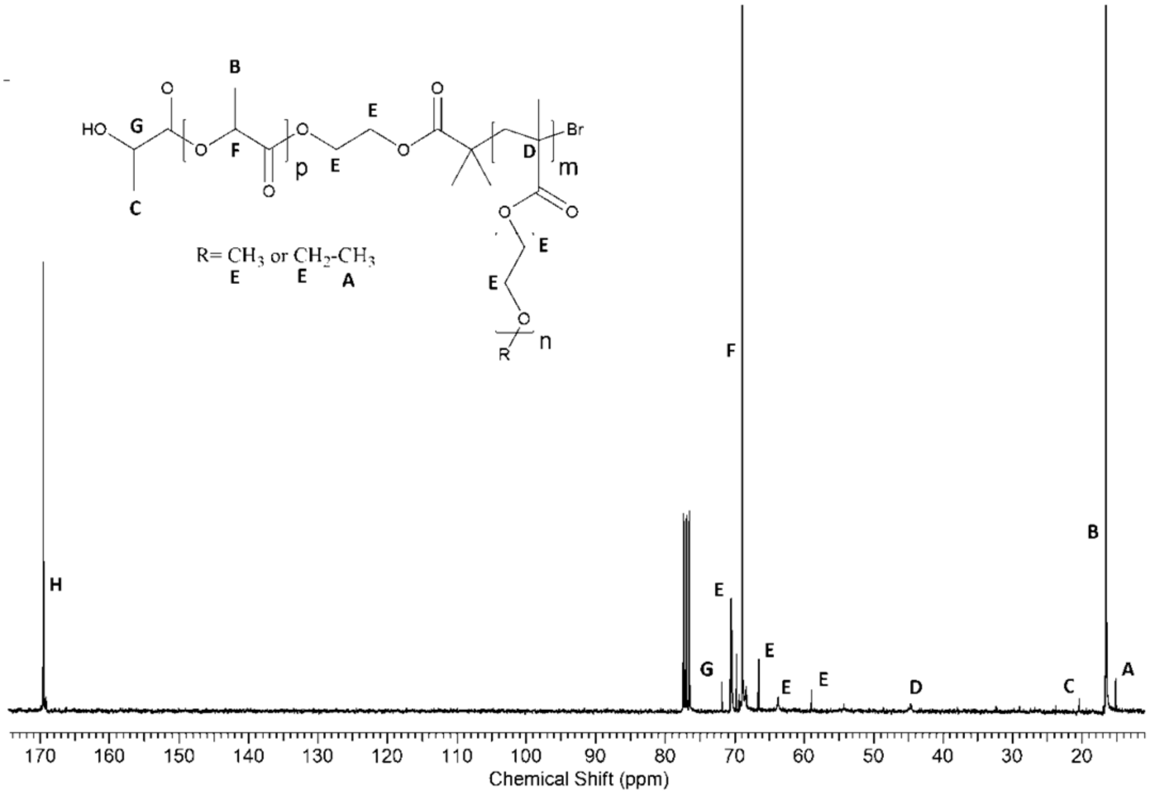

Figure S4. ^{13}C NMR (75,5 MHz, $CDCl_3$) of POEGMA-b-PLLA

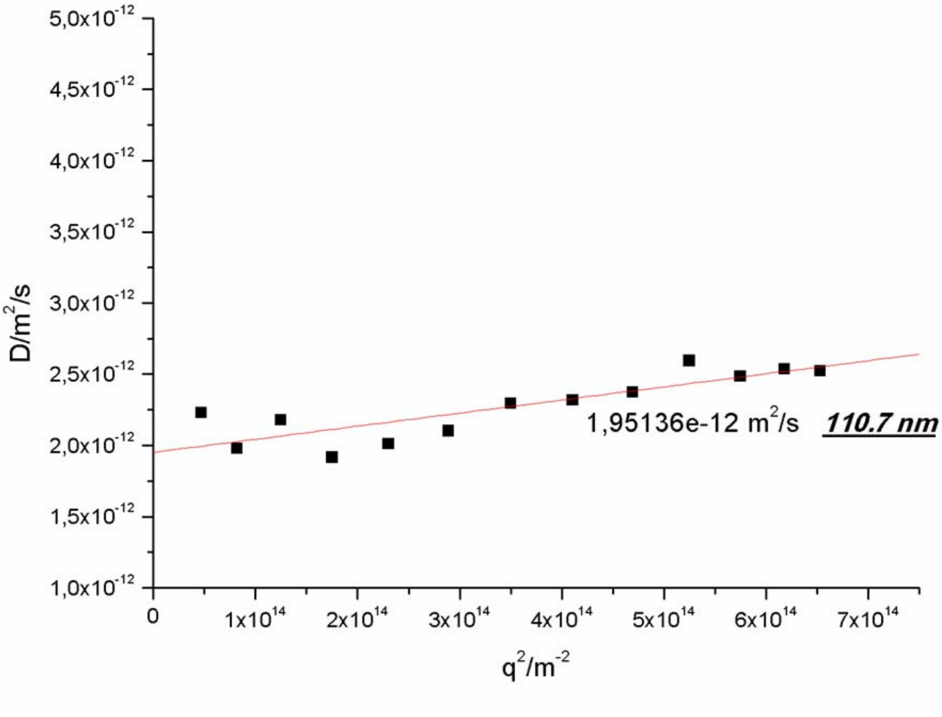

Figure S5. DLS measurement of $POEGMA_{14}$-*b*-$PLLA_{14}$

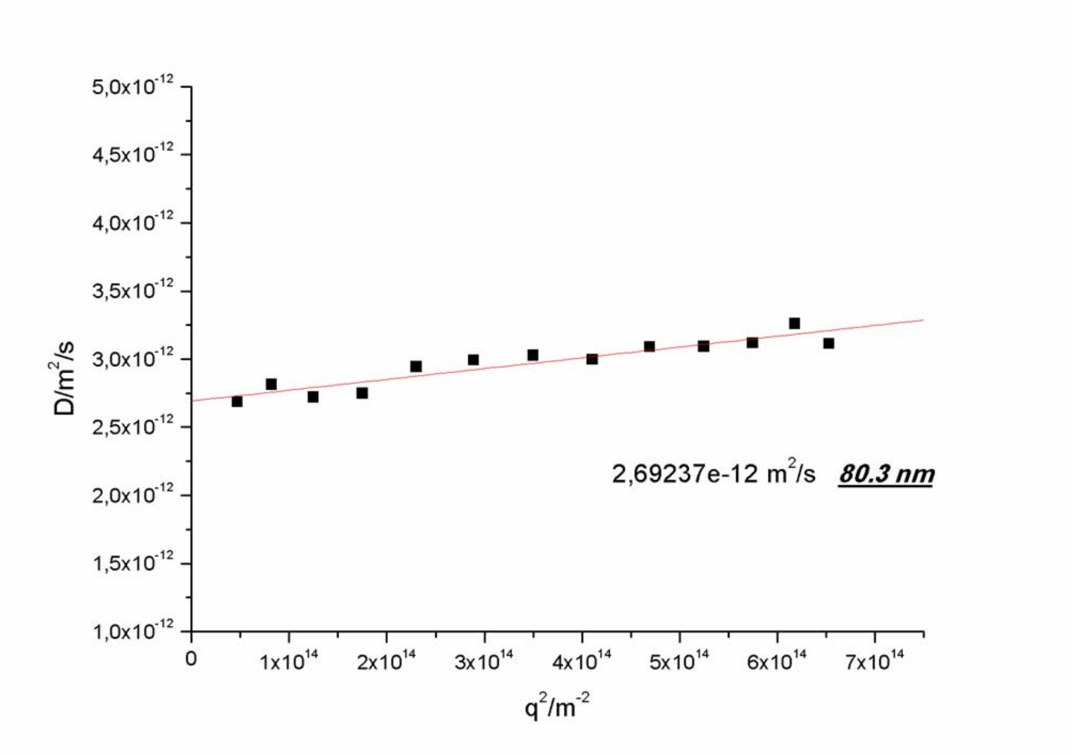

Figure S6. DLS measurement of POEGMA$_{17}$-*b*-PLLA$_{70}$

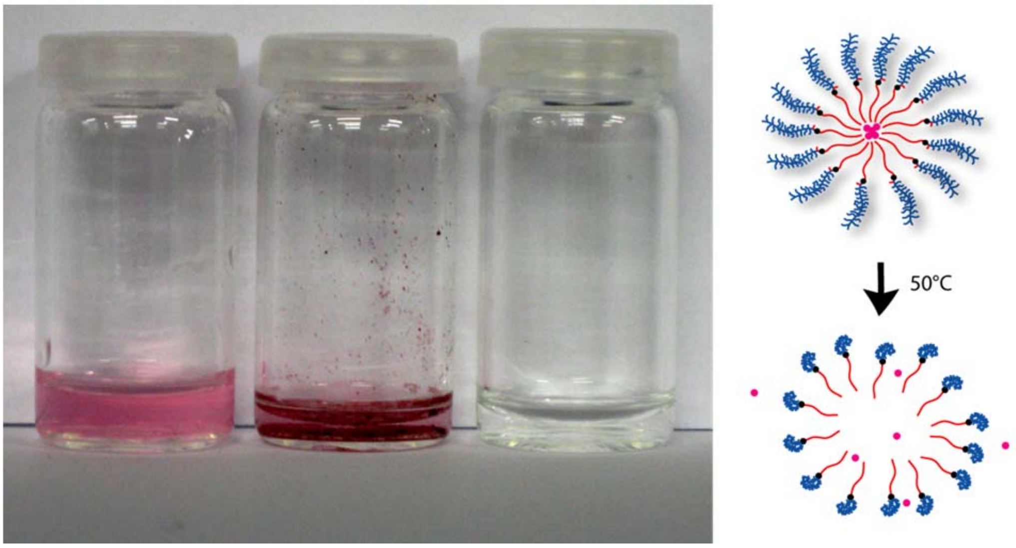

Figure S7. Aqueous solution of block copolymer micelles loaded with nile red (left), the same solution after heating to 50 °C (middle) and a blank, prepared without addition of the block copolymer.

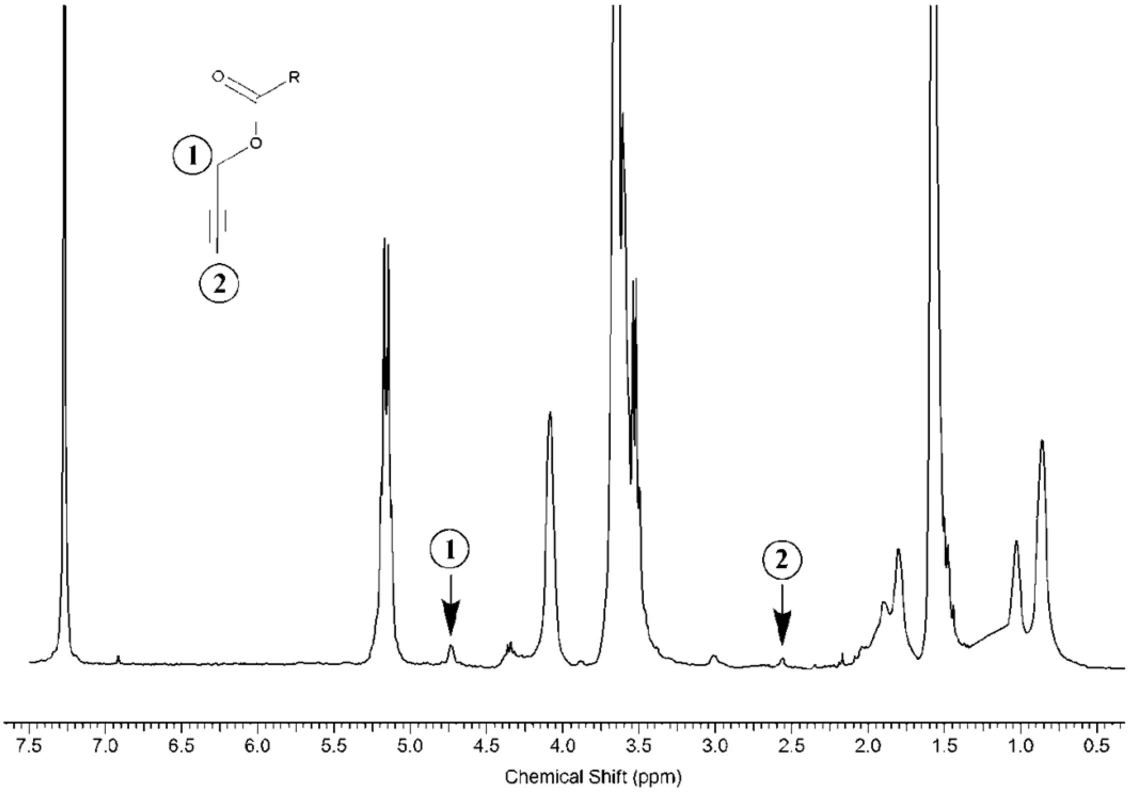

Figure S8. ^{1}H NMR (300 MHz, CDCl$_3$) of POEGMA-*b*-PLLA carrying one internal triple bond

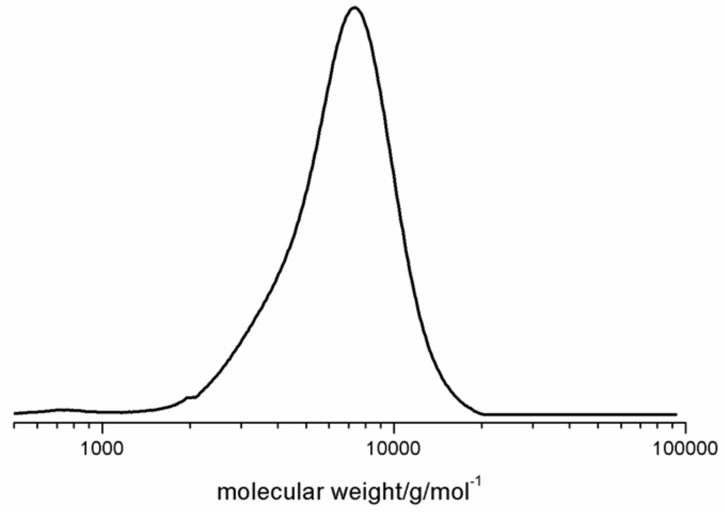

Figure S9. SEC diagram (PS standard, eluent: CHCl$_3$) of POEGMA-*b*-PLLA carrying one internal triple bond

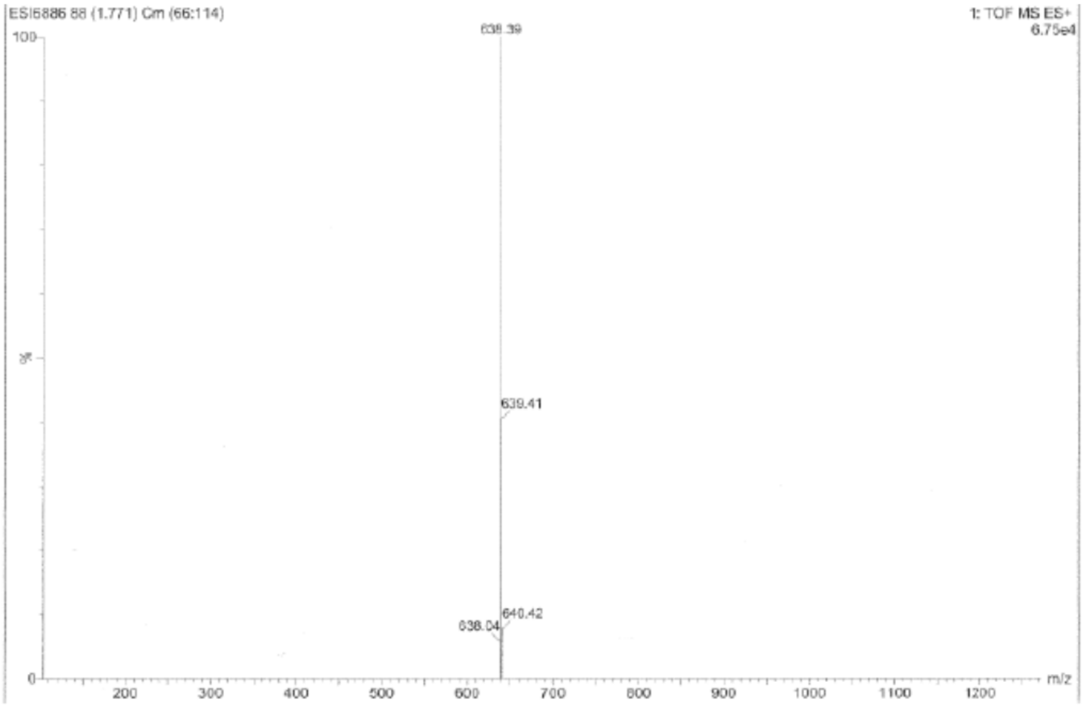

Figure S10. ESI-MS of azide-functionalized rhodamine B

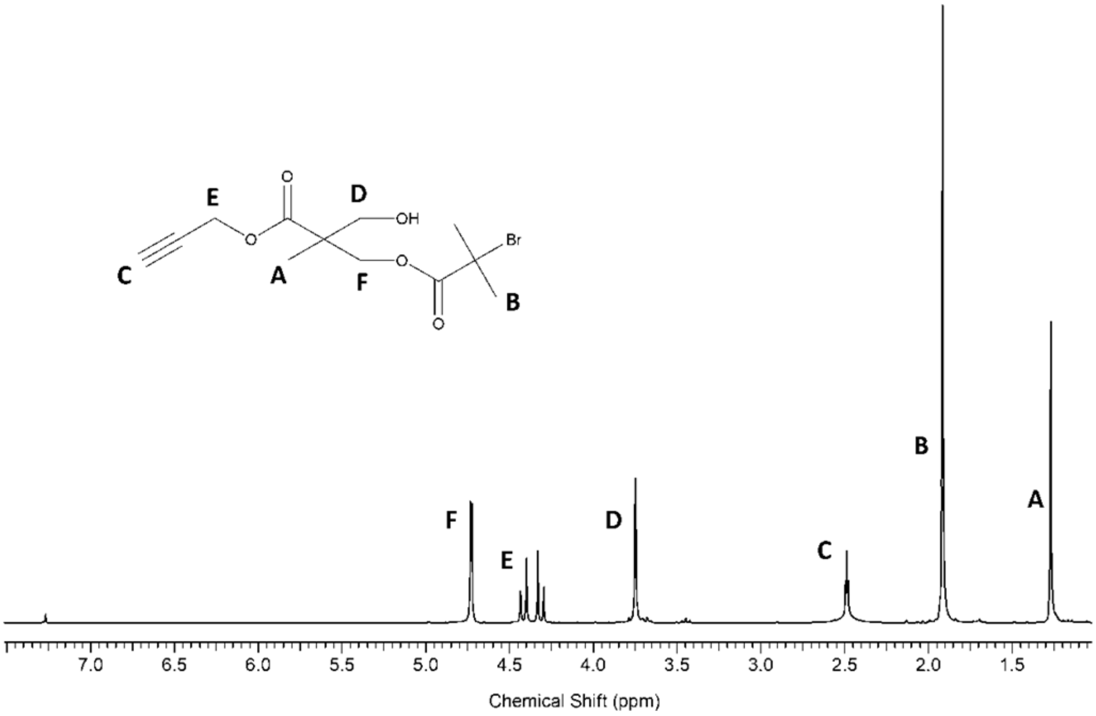

Figure S11. ^{1}H NMR of propargyl-2-hydroxymethyl-2-(a-bromoisobutyraloxymethyl)-propionate