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Hydrosilylation as an efficient tool for polymer synthesis and modification with methacrylates

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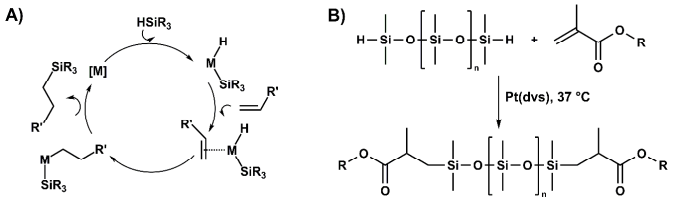
Hydrosilylation is a well-established reaction for the preparation of organo-silicon compounds, in which vinyl groups react with silanes (Si-H) usually catalysed by late transition metal complexes, most often Pt(II) complexes. Hydrosilylation of functional methacrylates provides access to functional poly(dimethylsiloxane)s (PDMS), from appropriate hydride terminated and functional PDMS, in very high yielding reactions without the formation of any side products, odour and without the need for labor-intensive purification. Herein, commercially available telechelic PDMS hydrides (h_2PDMS) have been modified with a range of different methacrylates using very low catalytic amounts of commercial Pt(II) catalysts. The products have been characterized by ^{1}H and ^{13}C NMR, SEC, IR and MALDI-ToF MS demonstrating high selectivity and very high reaction yields. The versatility of hydrosilylation has been exploited for the preparation of ABA triblock copolymers using poly(ethylene glycol) methacrylate and more structural demanding vinyl terminated methacrylic macromonomers as obtained by catalytic chain transfer polymerization (CCTP). ^{1}H NMR revealed the formation of solely anti-Markovnikov products and the high tolerance of the reaction towards other functionalities, such as epoxides present in glycidyl methacrylate. The specific Si-H signals in ^{1}H NMR (4.8 ppm) and IR (2126 cm^{-1}) from the Si-H group allows for facile monitoring the progress of the reaction. SEC and MALDI-ToF MS investigations further highlighted the formation of well-defined polymer systems with near perfectly matching molecular compositions.

Introduction

Highly efficient organic reactions have been used for many years to modify and alter the properties of materials. In particular, the introduction of the "*click chemistry*" concept by Sharpless[1] and coworkers in 2001, has inspired researchers to seek new, and rediscover old, efficient reactions, which are, e.g. high yielding, stereospecific, do not generate side products and hopefully do not require purification by chromatography. Numerous reactions have experienced a renaissance as "click-type" reactions and have been demonstrated to be applicable for the fabrication of diverse materials/polymer architectures for applications in material science, biology and medicine.[2-6] Prominent recent examples include thiol-ene,[7-9] Michael-addition and Diels-Alder reactions.[10]

A highly efficient reaction, which has not received as much attention in this context as we think it merits, is catalytic hydrosilylation,[11, 12] the insertion of an unsaturated vinyl group into a Si-H bond. Poly(organo siloxane)s (POS), silicones,[13] are exploited as building blocks in many industrial products. Poly(dimethyl siloxanes) (PDMS) are probably the most important member of this polymer class exhibiting some excellent material properties, including high flexibility, excellent thermo-oxidative stability, high moisture resistance, low glass transition temperature (T_g) and non-toxicity.[13] Due to these unique properties, POS, and in particular PDMS, are used in diverse applications, for example in semiconductor devices, aerospace, decorative coatings, biomaterials, as mold release agents, anti-foam and foaming agents, personal care products, additive materials, high performance elastomers and deformers and are ubiquitous in our homes and lives.[14-16] The first hydrosilylation reaction of trichlorosilane and 1-octene in the presence of acetyl epoxide was reported by Sommer et al. in 1947.[17] Since then, hydrosilylation has become one of the most powerful reactions in silicone polymer and surface chemistry.[18] The mechanism for the late transition metal catalyzed hydrosilylation (usually using d^8 and d^{10} metals) was proposed by Chalk and Harrod in 1965 (Scheme 1A).[12] The oxidative addition of a silane to the metal complex is followed by migratory insertion of the alkene into the M-H bond. In a reductive elimination step, the Si-C bond is formed and the metal complex is regenerated.



Scheme 1 Chalk-Harrod hydrosilylation mechanism catalyzed by a late transition metal catalyst (A),[12] and general hydrosilylation reaction of hydride terminated PDMS (h_2PDMA) with methacrylates (B).

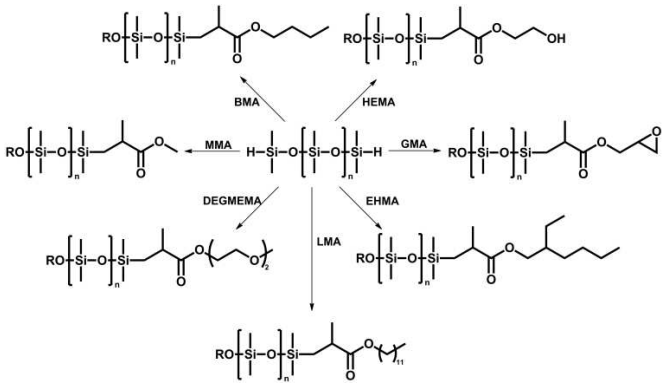
To date, several studies on the modification of end-functional hydride PDMS (h_2PDMS) and copoly(dimethyl)(methyl-hydrogen)siloxane have been reported.[19] The latter approach was used for the preparation of acrylate containing[20] and fluorinated PDMS, respectively.[21] Hydrosilylation of h_2PDMS systems was demonstrated as a technique for the introduction of (meth)acrylic acid,[22, 23] amine and epoxy terminal end groups.[24] The addition of Si-H can be favorably compared with thiol-ene chemistry (addition of S-H) which has been the focus of many publications in recent years.[7, 9] Hydrosilylation has the advantage of having starting materials with little or no odor which are extremely stable other than to react very selectively with vinyl groups in the presence of appropriate catalysts. Thus, we decided to investigate the utility of this reaction seeking in particular a way of functionalising macromonomers as prepared by catalytic chain transfer polymerisation (CCTP) as this sterically hindered vinyl group has proved difficult to functionalise in a high yielding and efficient way.

Herein, hydrosilylation is used as a highly efficient reaction for modification with different methacrylates demonstrating a high tolerance towards a range of functionalities in combination with high yields. In this study, linear telechelic h_2PDMS is transformed with methacrylates bearing different groups including methyl, hydroxyl and glycidyl using platinum-divinyltetra-methyldisiloxane (Pt(dvs)) as catalyst at relatively low temperature (37 °C) (Scheme 1B) whereas this type of reaction is often carried out at elevated temperatures. Characterization of the products has been carried out with ^{1}H NMR and FTIR spectroscopy, size exclusion chromatography (SEC) and matrix-assisted laser desorption/ ionization-time of flight mass spectrometry (MALDI-ToF MS). Based on these results, hydrosilylation of methacrylate-based materials and in particular oligomers derived from CCTP is demonstrated as a tool for the synthesis of block copolymers from CCTP products.

Results and Discussion

Modification of hydride terminated PDMS with methacrylates

Hydrosilylation was employed as a versatile and efficient method for the synthesis of functional telechelic PDMS (Scheme 1B). PDMS with hydride α,ω-end groups (h_2PDMS; average M_n 580 g mol^{-1}) was modified with different methacrylates (Scheme 2), including methyl methacrylate (MMA), 2-hydroxylethyl methacrylate (HEMA), glycidyl methacrylate (GMA), lauryl methacrylate (LMA), 2-ethyl hexyl methacrylate (EHMA), butyl methacrylate (BMA) and diethylene glycol methyl ether methacrylate (DEGMEMA).



Scheme 2 Hydrosilylation of methacrylate monomer and h_2PDMS hydride terminated, R represents a function same as another end.

Firstly, MMA was used in order to optimize the reaction conditions with regard to temperature and reaction time. Surprisingly within 60 min at 37 °C the reaction was found to be complete, as determined by ^{1}H NMR (Fig. S1). The characteristic Si-H signal at 4.8 ppm was used to follow the progress of the reaction (Fig. 1). The insertion of the methacrylic alkene functionality into the Si-H bond results in the formation of a Si-C bond and loss of the Si-H group. After 60 min at 37 °C the Si-H signals disappeared whilst new signals between 0.5 and 1 ppm appeared, which can be assigned to the newly formed CH_2 group. A high-field shift of the methacrylate methyl group is observed, characteristic for the transition from an sp^2 to an sp^3 neighboring group. Further evidence of the success of the reaction was obtained by IR spectroscopy (Fig. 2) with the disappearance of the characteristic Si-H band at 2126 cm^{-1} and the appearance of the ester band at 1750 cm^{-1}.

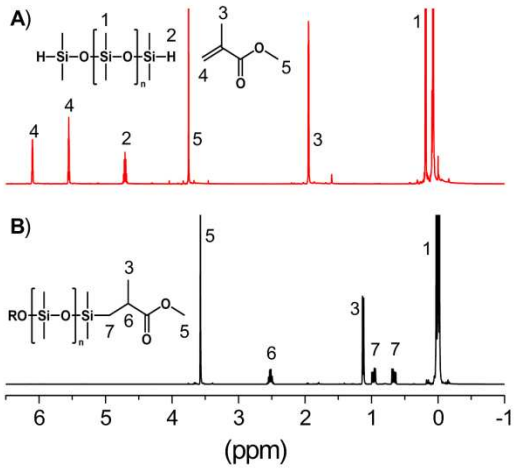


Fig. 1 ^{1}H NMR spectra of the feed mixture of MMA and h_2PDMS (A) and the product MMA-PDMS-MMA (B) in $CDCl_3$.

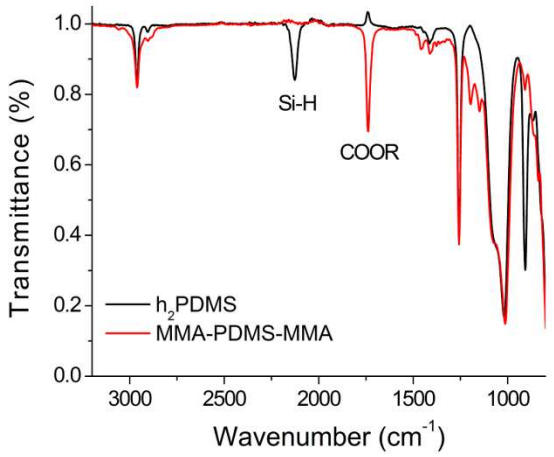


Fig. 2 IR spectroscopy of h_2PDMS and MMA-PDMS-MMA.

Hydrosilylation is a catalytic addition reaction and both the Markovnikov and the anti-Markovnikov products are possible. Previously, it has been reported that hydrosilylation catalysed by rhodium and rhenium complexes follow the anti-Markovnikov rule.[25, 26] Due to the asymmetric substitution of the methacrylates

used in this study, valuable and conclusive information is obtained from the ^{1}H NMR spectrum of the final product (Fig. 1 bottom). A product according to the Markovnikov rule would result in the formation of a quaternary carbon substituted with two methyl groups, whereas an anti-Markovnikov product would contain CH_2 and CH_3 groups (Scheme S1). ^{1}H NMR spectroscopy revealed the formation of the anti-Markovnikov product; the quartet of triplets at 2.5 ppm corresponds to a CH group neighbouring a CH_2 and CH_3 group, and the two signals between 0.5 and 1 ppm originate from the CH_2, which couples to the protons of the vicinal chiral carbon atom. Thus, the conditions applied in this study favour an anti-Markovnikov product, most likely due to the lower steric hindrance of the intermediate state. All modifications in this study were complete after 60 min at 37 °C with quantitative conversions and close to 100% yields after work-up. The formation of anti-Markovnikov products was observed for all methacrylate additions as evidenced by the corresponding NMR spectra (Fig. S2-S14).

In addition, the products were investigated by size exclusion chromatography (SEC) (Fig. 3). Unmodified h_2PDMS showed a monomodal trace with a dispersity ($Đ$) = 1.23. Upon modification a shift to higher molar mass was observed, while retaining narrow molar mass distributions for all hydrosilylation products, except HEMA-PDMS-HEMA. The reaction with HEMA resulted in a rather broad molar mass distribution ($Đ$ = 1.71). Presumably, this could be the result of interactions with the column material and a non-suitable solvent system employed for the amphiphilic product obtained. However, ^{1}H NMR demonstrated quantitative conversion of the Si-H groups without the formation of any side products. To further elucidate this reaction and the products formed, MALDI-ToF MS measurements were conducted.

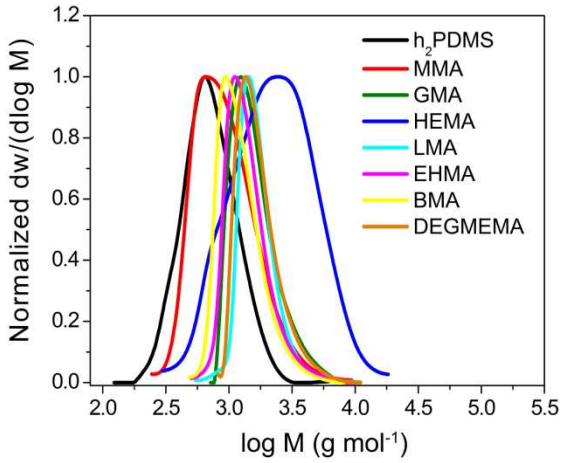


Fig. 3 SEC elution traces of h_2PDMS and methacrylate (x) modified PDMS (x-PDMS-x; SEC eluent: $CHCl_3$ + 2% TEA).

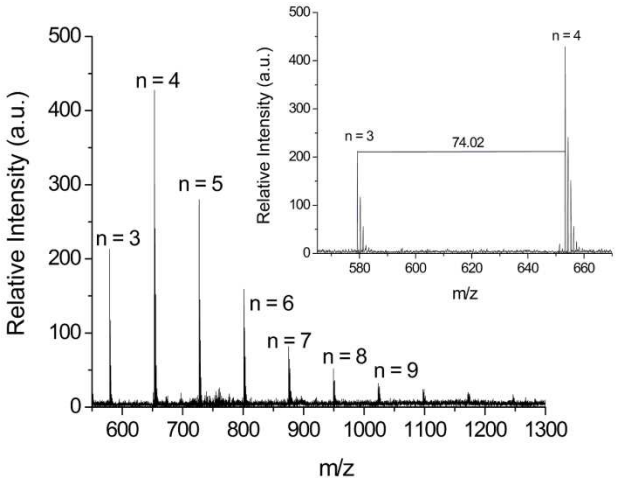
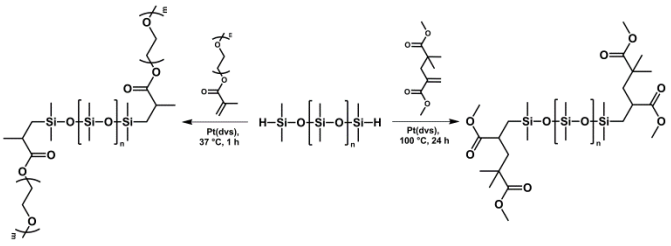


Fig. 4 MALDI-ToF MS spectrum of MMA-PDMS-MMA with the molecular composition $(C_2H_6SiO)_n$ $(C_7H_{15}SiO_2)_2O$ + Na^+), where n represents the repeating unit of PDMS.

Analysis of the MALDI-ToF MS spectra of the MMA and HEMA hydrosilylation products revealed the molecular composition of the two products with distributions, which are in agreement with the expected composition (Fig. 4). The products were analyzed using dithranol as matrix and sodium iodide to improve the ionization. The molar mass increments (74.02 g mol^{-1}) were assigned to the DMS repeating units (Fig. 5 inset). End group analysis proved the successful introduction of MMA and HEMA groups into the polymer, with chemical composition calculated according to $(C_2H_6SiO)_n$ $(C_7H_{15}SiO_2)_2O$ + Na^+ and $(C_2H_6SiO)_n$ $(C_8H_{17}SiO_3)_2O$ + Na^+, respectively. No further distributions and thus side products were observed indicative of the high yields and selectivity of this reaction. The same observations were made for modifications with the other methacrylates (Fig. S15-S21).



Scheme 3 Synthesis of ABA triblock copolymers using PEGMA and CCT oligomer, respectively.

Synthesis of ABA triblock copolymers

Hydrosilylation was further employed for the synthesis of ABA triblock copolymers (Scheme 3). Poly(ethylene glycol)methacrylate (PEGMA; average M_n 300 g mol^{-1}) was selected as a methacrylate terminated polyether. The reaction was conducted according to the protocol established for the small organic methacrylates. Full conversion of h_2PDMS was reached within 90 minute, as indicated by the disappearance of the corresponding Si-H signal (4.80 ppm) in the ^{1}H NMR spectrum (Fig. 5). In addition, even for the reaction with PEGMA exclusively the anti-Markovnikov product was obtained.

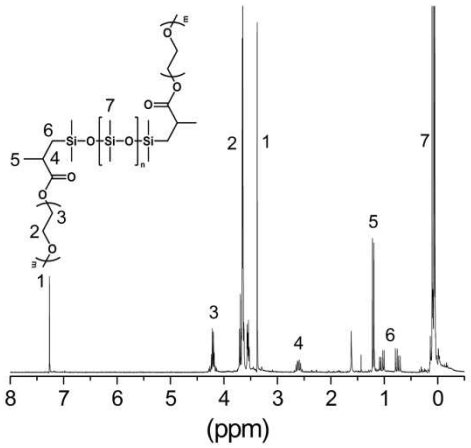


Fig. 5 ^{1}H NMR spectrum of PEG_6-*b*-$PDMS_6$-*b*-PEG_6 triblock copolymer in $CDCl_3$.

SEC analysis further demonstrated the quantitative conversion of the starting materials (Fig. 6). A complete shift of the SEC trace to higher molar mass was observed following the reaction. The absence of the PEG_6MA signal proved the high efficiency of the hydrosilylation modification. A well-defined ABA triblock copolymer was obtained as suggested by the narrow molar mass distribution (M_n = 2200, $Đ$ = 1.19).

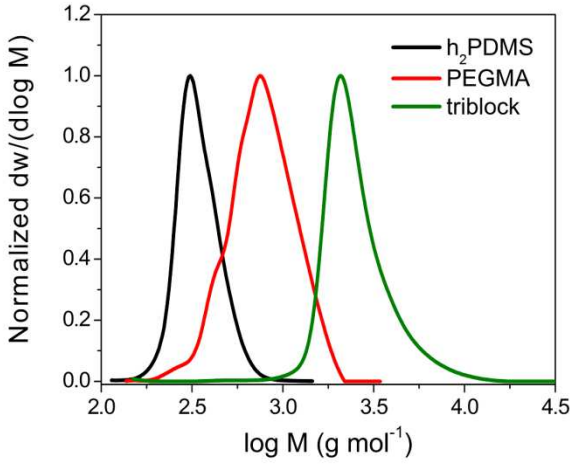


Fig. 6 SEC elution traces of h_2PDMS, PEG_6MA and PEG_6-*b*-$PDMS_6$-*b*-PEG_6 triblock copolymer (SEC eluent: THF + 2% TEA).

MALDI-ToF MS spectrum showed a peak pattern typical for (block) copolymers with molar mass increments corresponding to both the DMS (74.02 g mol^{-1}) and EG (44.03 g mol^{-1}) repeating units (Fig. 7). The chemical composition was confirmed by the isotopic pattern. End group analysis revealed the formation of solely PEG_6MA modified PDMS with the chemical formula $C_7H_{15}SiO_3(C_2H_4O)_m(C_2H_6SiO)_n(C_2H_4O)_oC_7H_{15}SiO_2 + Na^+$, where n, m and o represent the number of repeating units of DMS, EG and EG, respectively. For a detailed analysis, the peak at 931.48 m/z was selected corresponding to the formula $C_7H_{15}SiO_3(C_2H_4O)_4(C_2H_6SiO)_3(C_2H_4O)_4C_7H_{15}SiO_2Na^+$. For a more comprehensive evaluation, the peaks in the inset in Fig. 7 are assigned with the corresponding number of repeating units. Thus, MALDI-ToF confirms that simple hydrosilylation can be used to synthesize amphiphilic copolymers containing silicone hydrophobic middle blocks.

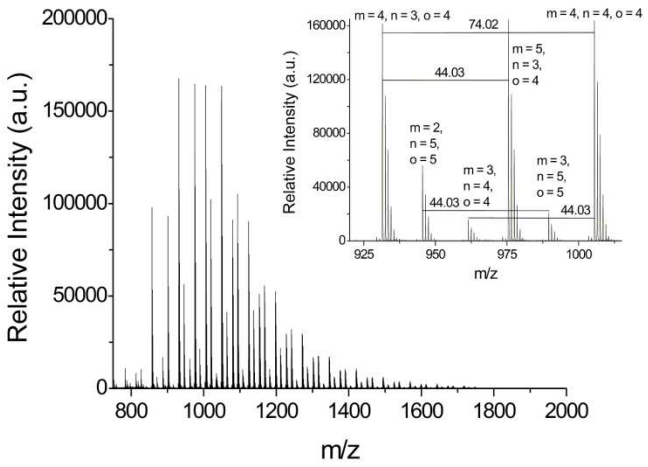


Fig. 7 MALDI-ToF MS spectrum of PEG_6-*b*-$PDMS_6$-*b*-PEG_6 with the molecular composition $C_7H_{15}SiO_3(C_2H_4O)_m$ $(C_2H_6SiO)_n$ $(C_2H_4O)_oC_7H_{15}SiO_2 + Na^+$, where n, m and o represent the number of repeating units of DMS, EG and EG, respectively.

To further demonstrate the versatility of the hydrosilylation reaction for transformation of a relatively unreactive vinyl group, structural demanding vinyl end-functionalized CCT macromonomers[27, 28] were employed for the preparation of ABA triblock copolymers (Scheme 3). In contrast to the hydrosilylation reactions described in this study so far no reaction occurred at 37 °C, which is attributed to the steric hindrance of the substituents of the vinyl groups of CCT macromonomers. Thus, the reaction was conducted at elevated temperatures (100 °C) with a higher h_2PDMS-to-CCTP MMA dimer ratio. After 24 h full conversion of the Si-H groups was observed by ^{1}H NMR (Fig. S29) and IR spectroscopy (Fig. S30) by the disappearance of the Si-H signal at about 4.7 ppm and Si-H band at 2100 cm^{-1}, respectively. In addition, a shift of the SEC trace to higher molar mass was observed (Fig. S31). This opens the way for formation of triblock copolymers from any CCTP product.

Conclusions

Seven different small organic methacrylates have been used to modify terminal hydride substituted PDMS via hydrosilylation in the presence of a commercial platinum(II) catalyst (Pt(dvs)). It was demonstrated that the reactions proceed to very high conversions over 60 min under mild reaction conditions. According to ^{1}H NMR spectroscopy and MALDI-ToF MS investigations, 100% conversions without the formation of side products were obtained for all methacrylates. ^{1}H NMR revealed the synthesis of anti-Markovnikov products. Moreover, hydrosilylation is described as an alternative approach for the synthesis of block copolymers. Well-defined block copolymers were obtained by modification with PEGMA, as proven by ^{1}H NMR spectroscopy, SEC and MALDI-ToF MS. Furthermore, adjustment of the reaction conditions enabled the synthesis of ABA triblock copolymers with sterically demanding vinyl terminated CCT macromonomers.

In summary, hydrosilylation represents a powerful tool for the fabrication of functional PDMS materials, including end-functional PDMS and triblock copolymers. The addition of Si-H can be compared to thiol-ene, S-H, chemistry which has found extensive use in polymer and materials synthesis.[7, 9] The vast variety of commercially available hydride substituted PDMS and functional

methacrylates in combination with the beneficial characteristics of the reaction, such as quantitative conversion at mild conditions, high selectivity and high tolerance towards various functionalities, makes hydrosilylation of methacrylates interesting for a broad range of applications. In particular, the combination of CCTP and hydrosilylation will give access to new exciting polymer systems and functionalization opportunities.

Experimental Materials

Hydride terminated PDMS (h_2PDMS; average M_n 580 g mol^{-1}), 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, toluene, methyl methacrylate (MMA), 2-ethyl hexyl methacrylate (EHMA), glycidyl methacrylate (GMA), lauryl methacrylate (LMA), butyl methacrylate (BMA), diethylene glycol methyl ether methacrylate (DEGMEMA), poly(ethylene glycol methyl ether) methacrylate (PEGMA, average M_n 300 g mol^{-1}), dithranol, sodium iodide and THF were purchased from Sigma-Aldrich and used as received. 2-Hydroxylethyl methacrylate (HEMA) was obtained from Sigma-Aldrich and purified by deionized water/hexane extraction. Platinum-divinyltetramethyldisiloxane (Pt(dvs)) was purchased from Gelest. The MMA macromonomer was synthesized according to literature procedure.[29]

Instruments

IR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. OPUS software was used to analyse absorbance data. Size exclusion chromatography measurements were performed on an Agilent 1260 Infinity Multi-Detector GPC system. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker DPX-300 and Bruker AC-250, with $CDCl_3$ as the solvent. The chemical shifts are given in ppm relative to the signal from residual non-deuterated solvent. For the MALDI measurements an Autoflex TOF/TOF apparatus (Bruker Daltonics, Bremen, Germany) was used.

Kinetic studies of hydrosilylation of methyl methacrylate

Hydrosilylation was performed at 100 °C, 70 °C and 37 °C. In all cases, up to 10 vials with each H_2PDMS (1 g, 1.72 mmol, 1 eq.), methyl methacrylate (0.36 g, 3.59 mmol, 2.1 eq.) and 11 µL of Pt(dvs) were prepared and stirred for a maximum of 120 min. At different time points samples were taken and the conversion of the Si-H bond was determined by ^{1}H NMR spectroscopy.

General procedure for the hydrosilylation of methacrylates

H_2PDMS (1 g, 1.72 mmol, 1 eq.), methacrylate (3.59 mmol, 2.1 eq.) and 11 µL of Pt(dvs) were added into a glass vial and stirred for 60 min at 37 °C. The brownish product was isolated by removal of excess monomer under reduced pressure.

Synthesis of methyl methacrylate functionalized PDMS (MMA-PDMS-MMA)

^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.65 (m, Si-CH_2), 0.93 (m, Si-CH_2), 1.20 (d, CH_3), 2.5 (sex, CH), 3.60 (s, O-CH_3) ppm. ^{13}C NMR ($CHCl_3$): δ = 0.00 (Si-C), 19 (Si-C), 22 (C-C), 30 (C-C), 50 (C-O), 175 (C=O) ppm. IR (cm^{-1}): 2961, 1768, 1257, 1196, 1013, 790, 702 cm^{-1}. GPC ($CHCl_3$): M_n = 690 g mol^{-1}, Đ = 1.42. MALDI-ToF MS (m/z): $C_7H_{15}SiO_3$ $(C_2H_6SiO)_n$ $C_7H_{15}SiO_2.Na^+$, 579.30 (n=3), 653.34 (n=4), 727.38 (n=5), 801.42 (n=6), 875.46 (n=7), 949.50 (n=8), 1023.54 (n=9).

Synthesis of 2-hydroxylethyl methacrylate functionalized PDMS (HEMA-PDMS-HEMA)

^{1}H NMR ($CHCl_3$): δ = 0.00 (s, Si-CH_3), 0.75 (m, Si-CH_2), 1.10 (m, Si-CH_2), 1.25 (m, CH_3), 2.58 (sex, CH), 3.94 (m, CH_2-OH), 4.25 (m, O=C-O-CH_2) ppm. ^{13}C NMR ($CHCl_3$): δ = 0.00 (Si-C), 19 (Si-C), 23 (C-C), 30 (C-C), 55 (C-O), 64(C-O), 175 (C=O) ppm. IR (cm^{-1}): 2962, 1721, 1258, 1161, 1013, 790, 701. GPC ($CHCl_3$): M_n= 1,200, Đ = 2.00. MALDI-ToF MS (m/z): $C_8H_{17}SiO_4$ $(C_2H_6SiO)_n$ $C_8H_{17}SiO_3.Na^+$, 639.24 (n=3), 713.26 (n=4), 787.28 (n=5), 861.30 (n=6), 935.32 (n=7), 1009.33 (n=8).

Synthesis of glycidyl methacrylate functional PDMS (GMA-PDMS-GMA)

^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.70 (m, Si-CH_2), 1.10 (m, Si-CH_2), 1.20 (d, CH_3), 2.55 (sex, CH), 2.80 (m, O-CH_2), 3.20 (sex, O-CH), 3.95 (m, O=C-O-CH_2), 4.45 (m, O=C-O-CH_2) ppm. ^{13}C NMR ($CHCl_3$): δ= 0.00 (Si-C), 19 (Si-C), 22 (C-C), 35 (C-C), 44 (C-O), 49 (C-O), 63 (C-O) 178 (C=O) ppm. IR (cm^{-1}):2961, 1741, 1435, 1258, 1203, 1015, 791, 701. GPC ($CHCl_3$): M_n= 1,400, Đ = 1.18. MALDI-ToF MS (m/z): $C_9H_{17}SiO_4$ $(C_2H_6SiO)_n$ $C_9H_{17}SiO_3.Na^+$, 589.37 (n=2),663.39 (n=3), 737.41 (n=4), 811.43 (n=5), 885.45 (n=6), 959.47 (n=7), 1033.49 (n=8).

Synthesis of lauryl methacrylate functionalized PDMS (LMA-PDMS-LMA)

^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.65 (m, Si-CH_2), 0.93 (m, Si-CH_2), 0.80 (t, CH_3) 1.20 (d, CH_3), 1.30 (m, CH_2) 2.5 (sex, CH), 4.00 (t, O=C-O-CH_2) ppm. ^{13}C NMR ($CHCl_3$): δ= 0.00 (Si-C), 9 (Si-C), 20, 22,25,30,35 (C-C), 60 (C-O) , 175 (C=O) ppm. IR (cm^{-1}): 2959, 2925, 2854, 1736, 1460, 1258, 1197, 1149, 1016, 793. . GPC ($CHCl_3$): M_n= 1,500, Đ = 1.12. MALDI-ToF MS (m/z): $C_{18}H_{37}SiO_3$ $(C_2H_6SiO)_n$ $C_{18}H_{37}SiO_2.Na^+$, 813.58 (n=2) 887.60 (n=3), 961.62 (n=4), 1035.64 (n=5), 1109.60 (n=6), 1183.69 (n=7), 1257.70 (n=8).

Synthesis of 2-ethyl hexyl methacrylate functionalized PDMS (EHMA-PDMS-EHMA)

^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.75 (m, Si-CH_2), 0.90(t, CH_3) 1.00 (m, Si-CH_2), 1.20 (d, CH_3), 1.35 (m, CH_2) 2.55 (sex, CH), 4.00 (d, O=C-O-CH_2) ppm. ^{13}C NMR ($CHCl_3$): δ = 0.00 (Si-C), 9 (Si-C), 12,19,25,35 (C-C), 63 (C-O), 175 (C=O) ppm. IR (cm^{-1}): 2960, 1735, 1461, 1258, 1196, 1148, 1016, 792. GPC ($CHCl_3$) g mol^{-1}: M_n = 1,300, Đ = 1.16, MALDI-ToF MS (m/z) (g mol^{-1}) : $C_{14}H_{29}SiO_3$ $(C_2H_6SiO)_n$ $C_{14}H_{29}SiO_2.Na^+$, 627.41 (n=1) 701.43 (n=2) 775.45 (n=3), 849.48 (n=4), 923.50 (n=5), 997.52 (n=6), 1071.54 (n=7).

Synthesis of butyl methacrylate functionalized PDMS (BMA-PDMS-BMA)

^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.75 (m, Si-CH_2), 0.90(t, CH_3) 1.00 (m, Si-CH_2), 1.20 (d, CH_3), 1.42 (sex, CH_2), 1.55 (quin) 2.55 (sex, CH), 4.00 (t, O=C-O-CH_2) ppm. ^{13}C NMR ($CHCl_3$): δ = 0.00 (Si-C), 11 (Si-C), 20, 23, 28, 30 (C-C), 60 (C-O) , 175 (C=O) ppm. IR (cm^{-1}): 2961, 1736, 1257, 1015, 791. GPC ($CHCl_3$): M_n= 1,100, Đ = 1.17. MALDI-ToF MS (m/z): $C_{10}H_{21}SiO_3$ $(C_2H_6SiO)_n$ $C_{10}H_{21}SiO_2.Na^+$, 589.33 (n=2) 663.36 (n=3), 733.38 (n=4), 811.40 (n=5), 885.43 (n=6), 959.45 (n=7), 1033.48 (n=8).

Synthesis of diethylene glycol methyl ether methacrylate functionalized PDMS (DEGMEMA-PDMS-DEGMEMA)

^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.75 (m, Si-CH_2), 1.00 (m, Si-CH_2), 1.18 (d, CH_3), 2.55 (sex, CH), 3.40 (s, O-CH_3), 3.5 (t, O-CH_3), 3.60 (m, O-CH_3) 4.12 (t, O=C-O-CH_2) ppm. ^{13}C NMR ($CHCl_3$): δ = 0.00 (Si-C), 19 (Si-C), 22, 30 (C-C), 58, 62, 78, 70, 72 (C-O), 175 (C=O) ppm. IR (cm^{-1}): 2961, 1736, 1456, 1258, 1198, 1014, 791. GPC ($CHCl_3$): M_n= 1,500, Đ = 1.15. MALDI-ToF MS (m/z): $C_{11}H_{23}SiO_5$ $(C_2H_6SiO)_n$ $C_{11}H_{23}SiO_4.Na^+$, 681.33 (n=2), 755.31 (n=3), 829.31 (n=4) 903.33 (n=5), 977.35 (n=6), 1051.37 (n=7).

Synthesis of PEG_6-*b*-$PDMS_6$-*b*-PEG_6 triblock copolymer

H_2PDMS (1 g, 1.72 mmol, 1 eq.) and PEGMA (1.04 g, 3.46 mmol, 2.01 eq.) were dissolved in 1.5 mL toluene and 11 µL of Pt(dvs) were added into a glass vial and stirred for 60 min at 37 °C. Subsequently, toluene was evaporated under reduced pressure and 45 mL water were added and the solution was centrifuged for 12 min (7,800 rpm). The supernatant was removed and the precipitate was dissolved in THF, the organic phase was dried over $MgSO_4$, filtered and the volatiles were removed under reduced pressure to give the ABA triblock copolymer. ^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.70 (m, Si-CH_2), 1.05 (m, Si-CH_2), 1.20 (d, CH_3), 2.55 (sex, CH), 3.46 (s, O-CH_3), 3.58 (m, O-CH_2), 4.25 (m, O=C-O-CH_2) ppm. ^{13}C NMR ($CHCl_3$): δ= 0.00 (Si-C), 18(Si-C), 22 (C-C), 30 (C-C), 55, 60, 65, 70 (C-O) 175 (C=O) ppm. IR (cm^{-1}): 2960, 2876, 1734, 1455, 1258, 1199, 1015, 792. GPC (THF): M_n= 2,200, Đ = 1.19. MALDI-ToF MS (m/z) (g mol^{-1}): $C_7H_{15}SiO_3$ $(C_2H_4O)_m$ $(C_2H_6SiO)_n(C_2H_4O)_o$ $C_7H_{15}SiO_2.Na^+$, 857.46 (m=4, n=2, o=4), 901.49 (m=5, n=2, o=4), 931.48 (m=4, n=3, o=4), 945.52 (m=5, n=2, o=5), 975.52 (m=4, n=3, o=5), 1005.51 (m=4, n=4, o=4), 1019.55 (m=5, n=3, o=5), 1049.54 (m=5, n=4, o=4), 1329.67(m=6, n=6, o=6).

Synthesis of $PMMA_2$-*b*-$PDMS_6$-*b*-$PMMA_2$ triblock copolymer

H_2PDMS (5 g, 8.6 mmol, 1 eq.), MMA macromer (4.3 g, 21.5 mmol, 2.5 eq.) and 33 µL of Pt(dvs) were added into a glass vial and stirred for 24 h at 100 °C. The product was isolated by removal of excess monomer under reduced pressure at 137 °C. ^{1}H NMR ($CHCl_3$): δ = 0.00 (m, Si-CH_3), 0.72 (m, Si-CH_2), 0.85 (m, Si-CH_2), 1.44 (d, CH_3), 1.67 (m, CH_2), 2.08 (m, CH_2), 2.51 (m, CH), 3.60 (s, O-CH_3) ppm. ^{13}C NMR ($CHCl_3$): δ = 0.00 (Si-C), 21 (Si-C), 23 (C-C), 33 (C-C), 39(C-C), 50 (C-O), 177 (C=O) ppm. IR (cm^{-1}): 2980, 1700, 1250, 1180, 1003, 790, 70 cm^{-1}. GPC (THF): M_n = 1400 g mol^{-1}, Đ =2.10.

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Notes and references

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