Communication

Light-triggered radical silane-ene chemistry using a monoalkyl substituted bis(trimethylsilyl)silane[a]

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Chain transfer agents (e.g. thiols) enrich radical photopolymerization for use in advanced applications such as stereolithography, optical materials and biomedicine. Resulting thiol-ene-based photopolymers exhibit numerous benefits such as tunable thermomechanical properties, and give access to spatially resolved functional materials. Silane-ene chemistry could serve as alternative to this popular thiol-ene approach. A monoalkyl substituted bis(trimethylsilyl)silane (MSiH) was synthesized by a simple one pot procedure. Photoinitiated radical silane-ene chemistry has been performed with multiple alkenes and the conversions were assessed by ^{1}H NMR spectroscopy. Compared to the most reactive silane from literature, tris(trimethylsilyl)silane (TTMSSiH), the radical reactivity of MSiH is reduced in all tested formulations, but the possibility for further functionalization and accessibility of multifunctional MSiH-derivatives is upheld. A silane-acrylate formulation was found to be

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most promising. In comparison to a thiol-acrylate system, a more uniform conversion of the chain transfer agent and alkene is shown for the silane-acrylate formulation with MSiH. The promising results for the silane-acrylate system were confirmed by further tests (i.e. NMR spectroscopy, GPC and MALDI MS), giving additional information on molecular weight regulation and radical mechanism. First MSiH-based photopolymer networks have been fabricated and analyzed via DMTA, thus paving the way for future silane-acrylate networks.
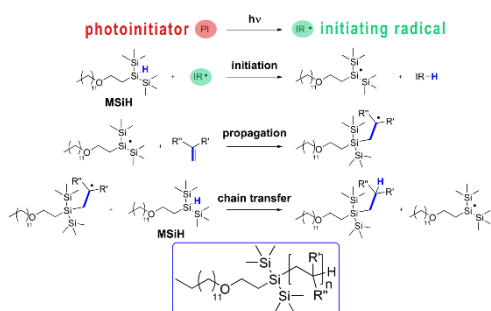
1. Introduction

Radical photopolymerization is setting foot in many advanced applications such as 3D-structuring,[1, 2] biomedicine[3, 4] and electronics.[5] Contrary to the vast expansion into different fields of application, the availability of curable materials is still mostly limited to multifunctional acrylates, which results in photopolymers with brittle behavior. The induced polymer network formation proceeds via an uncontrolled, fast radical chain growth mechanism that yields inhomogeneous network architectures and causes shrinkage stress due to gelation at low conversions.[6] By implementing chain transfer agents into the resin formulations the radical chain growth mechanism can be altered, thus enabling the regulation of the radical photocuring by concentration, composition and functionality of the respective chain transfer agents. Resulting regulated photopolymer networks exhibit tunable thermomechanical properties and give access to a great manifold of functional materials. Thiol-ene chemistry[7] has emerged as the most popular tool for the regulation of radical photocuring by implementing a mixed chain growth / step growth-like mechanism (depending on the alkene used) resulting

in more homogeneous polymer network architectures and tunable material properties. In thiol-ene systems with homopolymerizable alkenes such as (meth)acrylates competing radical-mediated homopolymerization is expected, whereas for thiol-ene chemistry with electron-rich alkenes (e.g. vinyl ether) a nearly ideal one-to-one reactivity between alkene and the thiol can be expected. Issues with the use of thiol-ene chemistry can be malodor[8] and poor storage stability,[9] which have been topics of research to broaden the commercial use of thiol-ene chemistry.

Powerful alternatives to the thiol-ene approach have been developed with the implementation of phototriggered copper catalysed alkyne-azide cycloaddition (CuAAC)[10] or addition fragmentation chain transfer (AFCT) reagents (e.g. β-allyl sulfides,[11] β-allyl sulfones[12] and vinyl sulfonate esters[13]) yielding a rapid formation of bulk photopolymers without the aforementioned drawbacks. Additionally, phosphane-ene[14] and iodo-ene[15] chemistry have been investigated as powerful concepts for new crosslinked photopolymer networks. All of these approaches show great potential for the formation of new spatially resolved functional materials.

Silane-ene[16] chemistry has been proposed as a further potential candidate by implementing silanes with abstractable hydrogens. Additionally, such silanes are also of significant interest for photografting applications on silicon surfaces[17] and in silicon polymer science.[18] With the establishment of a working silane-ene system, radical oxygen inhibition could possibly be prevented.[19] New reactive silanes could also be used as radical reducing agents[20] or type II coinitiators.[21, 22] Multifunctional silanes (e.g. polysilanes) have also been reported as macrophotointiators for free radical polymerization.[23, 24] By studying the chemical bond dissociation energy of Si-H bonds for various silanes[25] and the reactivity of silyl radicals towards the addition to alkenes,[26] tris(trimethylsilyl)silane (TTMSSiH) has been identified as the most suitable component.[25] However, aside from its great ability to undergo radical silane-ene reactions, multifunctional components based on TTMSSiH are not easily accessible. By

changing one of the three trimethylsilyl (TMS) groups on TTMSSiH with a carbon-based substituent, a potential precursor for future silane-ene networks could be generated.

Overall, the target of this study was the synthesis and evaluation of a silane with two trimethylsilyl groups, one alkyl substituent and an abstractable hydrogen on the Si-atom. This would give a similar derivative to TTMSSiH with potentially comparable radical reactivity but the possibility of modification on the alkyl substitutent.[25] This alkyl substituted bis(trimethylsilyl)silane (monofunctional silane, MSiH) should then be tested towards its reactivity with different alkenes which have the ability to homopolymerize (e.g. acrylate) or result in a pure radical step-growth reaction (e.g. vinyl ether). The most promising silane-ene formulations should then be further investigated using GPC (for determining molecular weight regulation), MALDI MS (investigating the radical mechanism) and DMTA (analyzing thermomechanical properties of regulated photopolymer networks).

2.   Experimental Section

2.1. Chemicals and general methods for synthesis

The chemicals tris(trimethylsilyl)silane (TTMSSiH; abcr), lauryl vinyl ether (LVE; Sigma Aldrich), methyl 3-mercaptopropanoate (MSH; Sigma Aldrich), lauryl mercaptan (LSH; Sigma Aldrich), benzyl acrylate (BnA; abcr), benzyl methacrylate (BnMA; Sigma Aldrich), vinyl benzoate (VB; Sigma Aldrich), N-acryloylmorpholine (NAM; Sigma Aldrich), allyl benzoate (AB, Lancaster), 2-norbornene-5,6-dicarboxylic anhydride (NDA; Merck), lauryl acrylate (LA; Condea), 1,10-decanediol diacrylate (D3A; TCI) and the photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173; Ciba) were purchased from the respective companies and used without further purification.

A Bruker Avance DRX-400 was used for NMR measurements at 400 MHz for ^{1}H (100 MHz for ^{13}C, 79.5 MHz for ^{29}Si), and chemical shifts were reported in ppm. They were referenced to the solvent residual peak for ^{1}H and ^{13}C nuclei (CDCl$_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm).

Chemical shifts of ^{29}Si nuclei are reported to $SiMe_4$ as external standard and further an INEPT pulse sequence was used for enhancement of the ^{29}Si signals. Multiplicities are referred to as s (singlet), d (doublet), and m (multiplet) and coupling constants (J values) are given in Hz. Silica gel chromatography was performed with a Büchi MPLC-system equipped with the control unit C-620, fraction collector C-660, and RI-detector Refractom. Commercial grade reagents and solvents were used without further purification. An Ocean Optics USB 2000+ spectrometer was used to measure the total irradiation intensities at the position of the samples.

2.2. Synthesis of a monosubstituted bis(trimethylsilyl)silane MSiH

A mixture of photoinitiator Darocur 1173 (7.6 mg, 0.045 mmol), silane TTMSSiH (1120.4 mg, 4.5 mmol) and dodecyl vinyl ether DVE (960.0 mg, 4.5 mmol) was degassed with argon. Afterwards, the solution was magnetically stirred and exposed to filtered UV light (40 min, 320-500 nm, ~ 10 mW cm^{-2} on the surface of the reaction solution) from an Exfo OmniCure S2000 broadband Hg-lamp. Then potassium tert-butoxide (KO^{t}Bu, 526.0 mg, 4.68 mmol) and dry THF (9 ml) were added and the reaction was stirred 2 h at room temperature. Afterwards the solution was drained slowly onto 20 ml ice-cold 2 N HCl. The aqueous phase was extracted 4 times with petrol ether (PE, 15 ml each) and the combined organic phases were dried over Na_2SO_4. After removal of the solvent under vacuum the crude product was purified with MPLC (R_f = 0.22 in PE) to give 2-(2-(dodecyloxy)ethyl)-1,1,1,3,3,3-hexamethyltrisilane MSiH (1454.0 mg, 83%) as a colorless liquid.

^{1}H NMR (400 MHz, CDCl$_3$, δ): 3.48-3.44 (m, 2H, CH$_2$), 3.39 (t, J = 6.8 Hz, 2H; CH$_2$), 2.95 (t, J = 4.7 Hz, 1H; SiH), 1.60-1.53 (m, 2H; CH$_2$), 1.34-1.13 (m, 20H; CH$_2$), 0.88 (t, J = 6.8 Hz, 3H; CH$_3$), 0.16 (s, 18H; CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 70.5 (C2), 70.4 (C2), 31.9 (C2), 29.9 (C2), 29.8 (C2), 29.7 (C2), 29.6 (C2), 29.6 (C2), 29.5 (C2), 29.3 (C2), 26.2 (C2), 22.7 (C2), 14.1 (C1), 8.9 (C2), 0.1 (C1); ^{29}Si NMR (79.5 MHz, CDCl$_3$, δ): -12.6, -15.0.

2.3. Photoinitiated silane-ene reactions in bulk

Photointiated radical reactions with various alkenes were performed. Mixtures (~ 100 mg) of alkene (1 eq.), chain transfer agent (CTA, i.e. MSiH, TTMSSiH or MSH, 1 eq.) and Darocur 1173 (0.5 mol%) were prepared (1/1 molar ratio of double bond DB / silane SiH) and the respective formulations were divided into 2 NMR tubes. One of the tubes was exposed to filtered UV light (5 min, 320-500 nm, ~ 26 mW cm^{-2} on the surface of the NMR tube) from an Exfo OmniCure S2000 broadband Hg-lamp. Then CDCl$_3$ (0.5 ml) was added to the samples (non-irradiated reference samples were diluted immediately) to quench the reaction. The obtained conversions for alkene (double bon conversion, DBC) and CTA (silane SiHC and thiol conversion SHC) were evaluated via ^{1}H NMR spectroscopy. Conversion data assessed with NMR is reliable with an error of < 1%. Moreover, the accuracy of the adapted NMR method can be assumed with ± 3%.

For GPC and MALDI MS measurements samples (~ 100 mg) containing chain transfer agent (MSiH or MSH, 0.25 eq.), benzyl acrylate (1 eq.) and Darocur 1173 (0.5 mol%) were prepared (4/1 ratio of DB/SiH). The samples were irradiated for 5 min in an Intelli-Ray 600 UV-oven with a broadband Hg-lamp (600 W; UV-A: 125 mW cm^{-2}; Vis: 125 mW cm^{-2}) and conversion measurements were performed as described above.

For DMTA measurements D3A was used as reference resin. Formulations with a 2/1 molar ratio of difunctional D3A and additive (LA, MSiH or LSH) were prepared yielding a 4/1 ratio of DB/SiH. The formulations were mixed with Darocur 1173 (0.5 mol%), poured into a silicone mold (~ 5 × 2 × 40 mm^3) and photocured analogously to the GPC samples. Here, the monothiol LSH with lauryl substituent was used as reference instead of MSH. This ensures comparable influence of the flexible side chain on the thermomechanical properties of the final photopolymer. The irradiation time was changed to 2 x 5 min and the samples flipped in between irradiation periods to ensure uniform curing.

Detailed experimental parameters for GPC, MALDI MS and DMTA can be found in the supporting information.

3. Results and Discussion

3.1. Synthesis of MSiH

The first goal was the synthesis of a silane with two trimethylsilyl groups, one alkyl substituent and an abstractable hydrogen on the Si-atom. This gives a similar derivative to reference TTMSSiH with potentially comparable radical reactivity but the possibility of modification on the alkyl substitutent. Therefore, we have developed a one-pot procedure to form the desired monofunctional silane MSiH mimicked from TTMSSiH (Figure 1a). Starting from TTMSSiH and a non-hompolymerizable alkene (e.g. dodecyl vinyl ether) an intermediate product with three TMS groups is formed. Darocur 1173 was used as radical photoinitiator and UV irradiation was applied to initiate the radical addition step. The reactive silane functionality Si-H is then formed in a second reaction step by selective, basic cleavage of one TMS group using KO^{t}Bu.[27] The monofunctional silane MSiH was synthesized in a simple one-pot procedure giving high yields (> 80%). Contrary to state-of-the-art hydrosilylation reactions[28] we have performed a metal catalyst-free technique,[26, 29] using photoinitiator, where a wide variety of different alkenes could be functionalized with the respective silane unit.
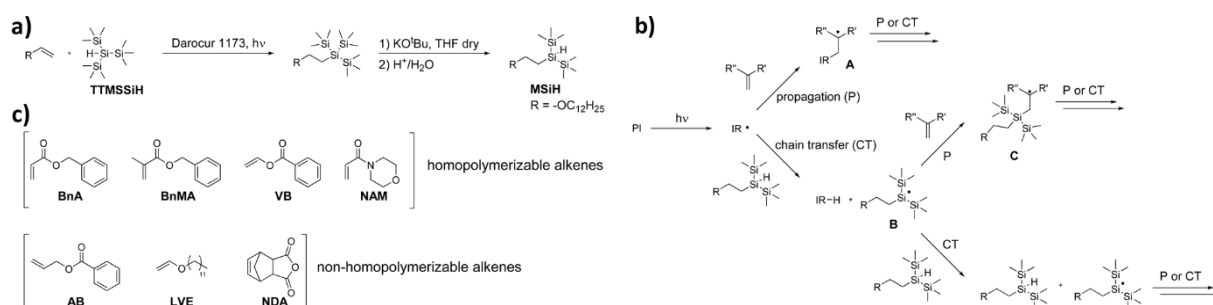

Figure 1. (a) General synthetic scheme for monofunctional silane (e.g. MSiH); (b) silane-ene mechanism; (c) alkenes tested for reactivity with MSiH.

3.2. Mechanism and reactivity of MSiH with various alkenes

Analogously to thiols, the synthesized silane MSiH should be introduced as a potential chain transfer agent for radical photopolymerization. The expected radical silane-ene mechanism should proceed similarly to thiol-ene chemistry (Figure 1b) and has previously been reported.[16] After formation of an initiating radical (IR•), via photoexcitation of a radical type I photoinitiator (PI) in this case, the radical fragment either initiates polymerization through propagation (P) into the C=C double bond of the vinyl derivative or abstracts a hydrogen from a monofunctional silane (chain transfer CT step). In case of P, the formed radical (A) can undergo further radical chain growth propagation or perform a CT step by abstracting a hydrogen from a silane compound. The CT step terminates a growing radical chain and forms a silyl radical (B) that has to be reactive enough to reinitiate radical polymerization by attacking an alkene (P). Favored hydrogen abstraction over propagation by the silyl radical will result in reduced kinetic chain-lengths, as described by the Mayo Equation. Furthermore, if the resulting silyl radical is unfavorable towards propagation over termination by radical combination, inhibition of the polymerization would be observed until the chain-transfer agent is consumed. A good measure for the probability of P or CT step can be derived from the chain transfer constant (C_{tr}), which is defined as the ratio of rate constant for chain transfer to rate constant for propagation (k_{tr}/k_p).

The C_{tr}s for various silanes in styrene and methyl methacrylate have already been evaluated in a thermal polymerization at 60 °C using AIBN as radical source.[30] However, the C_{tr} is not only influenced by the chemical structure of the silane, but also by reaction temperature[31], thus making the prediction towards bulk photopolymerizations at ambient conditions difficult. The C_{tr} is different for each potential silane-ene formulation. Therefore, various alkenes need to be tested towards their ability to undergo radical step growth reactions with the respective silane MSiH.

The photoinitiated reaction between MSiH and a series of vinyl functionalites (i.e. derivatives with reactive double bonds; Figure 1c) was evaluated in order to determine which vinyl functionalities coreact best with the new silane. Benzyl acrylate BnA, benzyl methacrylate BnMA, vinyl benzoate VB and N-acryloylmorpholine NAM as monomers that have the ability to undergo homopolymerization and three alkenes that do not undergo radical propagation (i.e. allyl benzoate AB, lauryl vinyl ether LVE and 2-norbornene-5,6-dicarboxylic anhydride NDA) were selected as potential derivatives with reactive double bonds. The conversion of the performed reactions should be assessed using ^{1}H NMR spectroscopy and the ratio between silane conversion (SiHC) and conversion of the vinyl functionality (i.e. double bond conversion, DBC) should enable a first prediction on which silane-ene combination shows the highest potential. In order to verify the significance of the presented data, the most promising silane from literature TTMSSiH and a monofunctional thiol (MSH, methyl 3-mercaptopropanoate) were additionally studied as reference compounds. The general reactivity of the different silane-ene combinations (equimolar, in bulk) was investigated using UV irradiation (320-500 nm) from a mercury lamp and Darocur 1173 (0.5 mol%) as the photoinitiator. All samples were irradiated for 5 min and ^{1}H NMR spectra were recorded before and after irradiation. By integrating the silane and double bond signals and referencing it to a proton signal from a non-reactive hydrogen in the mixture (e.g. benzylic protons for BnA) the double bond conversion (DBC) and the conversion of SiH (SiHC) were calculated. For example, the decrease of the SiH peak at 2.95 ppm (for MSiH) and of the three double bond signals between 5.7 and 6.7 ppm (for BnA) were analyzed and referenced to the benzylic area at 4.7 to 5.2 ppm (Figure 2, for other alkenes see respective Figures S4-8).
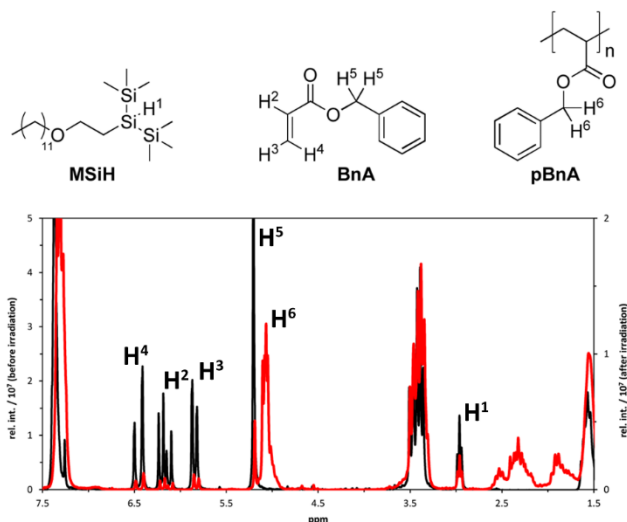
Figure 2. ^{1}H NMR of an equimolar BnA/MSiH formulation before (black) and after irradiation (red).

The accumulated results for the silane-ene reactions with MSiH show the great potential of MSiH especially for acrylates and vinyl esters (Table 1). In both cases, silane conversions SiHC are with 69% (for acrylate) and 65% (for vinyl ester) quite high, as are the values for DBC (92% for acrylate BnA and 72% for vinyl ester VB). Compared to the silane reference TTMSSiH, the reactivity is reduced for MSiH with all alkenes which could be expected from previous literature.[25] However, the ratio for conversion of silane compared to alkene (SiHC/DBC) remains similar for MSiH (except for acrylamide NAM). Overall, MSiH shows reactivity in the photoinitiated radical reactions with all tested homopolymerizable alkenes. When compared to the reactivity of the thiol reference MSH, the silane MSiH shows better results with acrylate BnA, but reduced reactivity with methacrylate BnMA, vinyl ester VB and acrylamide NAM. Both the silane- and thiol-ene reaction are not expected to follow an ideal alternating chain transfer / propagation reaction mechanism with acrylates, which explains the poor results for thiol-ene. However, in acrylate-based systems with MSiH a more homogeneous consumption of double bond and SiH (SiHC/DBC = 0.75) is shown, yielding a reduction of homopolymerization compared to the thiol-based formulation (SHC/DBC = 0.56). With acrylates representing the industrially most relevant substance group, a powerful silane derivative for silane-acrylate chemistry has been found.

Unfortunately, with non-homopolymerizable allyl and vinyl ethers (AB/MSiH and LVE/MSiH) the silane-ene reactions did not yield high conversion and performed poorly compared to reference TTMSSiH and the thiol-ene reactions. This shows that the presented silane-ene reaction does not coreact well with electron-rich vinyl functionalities. Here, the radical reactions should proceed in an ideal alternating mechanism of Si• radical addition to the alkene and H-abstraction of Si-H by the subsequently formed radical. As a consequence, equal conversions for SiH and double bond are expected. The slightly higher silane conversion (SiHC/DBC > 1) for AB/MSiH and LVE/MSiH reactions can be explained by a higher amount of recombination reactions of two silyl radicals due to the lower reactivity with the respective alkenes. Moreover, the slightly lower conversions for SiHC (derived from SiH peak at 2.15 ppm) in the case of AB/TTMSiH and SHC (derived from SH peak at 1.63 ppm) for AB/MSH and NDA/MSH can be explained by the uncertainty of the NMR method (~ 3%) and slight overlapping of the relevant peaks with the formed polymers.

No reactivity was observed for norbornene formulations, NDA/TTMSSiH and NDA/MSiH, which can be attributed to the sterically demanding TMS substituents that possibly hinder the radical attack of the silyl radical onto the norbornene derivative. Another explanation might be the sterically hindered abstraction of the hydrogen (from Si-H), which is also observed in the silane-methacrylate system (conversions < 45%).

Table 1. Conversion data for photoinitiated reactions of MSiH with different alkenes, TTMSSiH and MSH as reference.

alkene	DBC [%]	TTMSSiH			MSiH			MSH		
		DBC [%]	SiHC [%]	SiHC/ DBC	DBC [%]	SiHC [%]	SiHC/ DBC	DBC [%]	SHC [%]	SHC/ DBC
acrylate (BnA)	95	96	80	**0.83**	**92**	**69**	**0.75**	**86**	**48**	**0.56**
methacrylate (BnMA)	92	50	35	0.70	41	26	0.63	63	49	0.78
vinyl ester (VB)	60	> 99	90	**0.90**	**72**	**64**	**0.89**	**95**	**94**	**0.99**
acrylamide (NAM)	> 99	> 99	74	0.74	98	38	0.39	> 99	78	0.78
allyl (AB)	-	83	78	0.94	33	37	1.12	98	94	0.96
vinyl ether (LVE)	-	> 99	> 99	1.00	20	25	1.25	93	*	*
norbornene (NDA)	-	-	-	-	-	-	-	94	86	0.91

-no reactivity; *could not be determined due to peak overlapping

3.4. Investigating the chain transfer potential for MSiH with a monofunctional acrylate

The silane-acrylate system, using acrylate BnA and MSiH, was further examined towards its ability to regulate radical chain growth propagation. Resins with a 4/1 molar ratio of double bond DB to SiH, or SH respectively, were formulated and then UV-cured in the presence of Darocur 1173. GPC measurements were conducted with the cured photopolymers in order to analyze the final number average molecular weight (M_n, calibration with polystyrene standards) and dispersity (Đ) of the linear polymers (Figure 3a, Table S1). A molecular weight reduction for the MSiH-based photopolymer could be confirmed with an M_n of ~ 0.7 kDa compared to the high molecular weight of BnA homopolymer (pBnA) with M_n ~ 59.1 kDa. As expected from the conversion data, MSiH also more homogeneously regulates the photopolymerization of acrylate BnA with a Đ of ~ 2.5 compared to ~ 3.3 for the thiol-based reference. The conversion for both, silane and acrylate, were determined to be well above 90% (Table S1).

A MALDI MS measurement of the silane-acrylate polymer was conducted to identify the respective polymer fragments with an MSi end group (m/z = 387.29) and confirm the silane-ene mechanism (Figure 1b). The found m/z values for the BnA oligomers (m/z = 162.08 per monomer unit) correspond to the respective masses calculated with MSi• as the chain starter

and H as terminating group (e.g. n=2 gives a calculated mass of 712.44; m/z found for $[M+Na]^+$: 735.64; Figure 3b, Table S2). With the most intensive peaks for n = 2, 3, 4 and detected n up to 20 the result is conclusive with the GPC result ($M_n \sim 0.7$ kDa, $M_w \sim 1.8$ kDa).
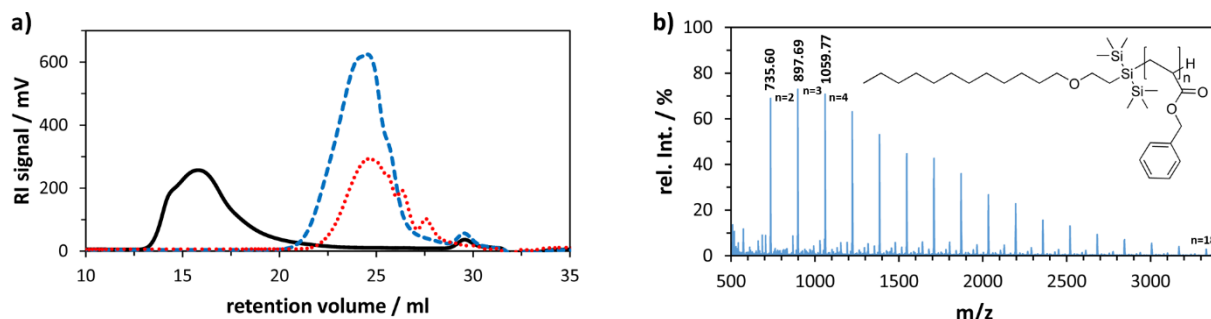

Figure 3. (a) GPC results of pBnA without CTA (—), with MSiH (- - -) and with MSH (•••); (b) MALDI MS of BnA with MSiH.

3.5. First regulated photopolymer networks using MSiH

A first proof of concept for regulated silane-acrylate networks could also be shown by photopolymerization of 1,10-decanendiol diacrylate (D3A) together with MSiH (4/1 ratio of DB/SiH) and Darocur 1173. The homopolymer network of D3A (pD3A) exhibits a rather broad thermal polymer phase transition indicated by the storage modulus G' and tanδ plot (Figure 4). By adding the reactive diluent lauryl acrylate (LA, similar substituent to MSiH) to the photopolymerization, the crosslinking density is reduced and the lauryl substituent softens the network. Nevertheless, the radical chain growth mechanism also yields a rather inhomogeneous network architecture. By adding MSiH as the chain transfer agent to the formulation, the curing mechanism is altered towards a more regulated chain growth / step growth-like mechanism leading to a more uniform polymer network that is comparable to thiol-based acrylate networks (pD3A with lauryl mercaptan, LSH). The rather sharp glass transition (fwhm ~ 30 °C) confirms this assumption and the storage modulus at the rubbery state (G'$_r$ ... G' at T_g + 20 °C) is significantly decreased (9 MPa) compared to the pure acrylate-based networks (114 MPa for pD3A, 34 MPa for pD3A/LA; Figure 4, Table S3). Hence, the crosslinking density is also reduced. The MSiH-based DMTA sample loses its mechanical strength quite early (T_g = -27 °C) and breaks. Therefore, the DMTA signal at higher temperatures was not acquired. TGA analysis

was performed to confirm a thermostability of the new photopolymers up until > 250 °C (Figure S9).
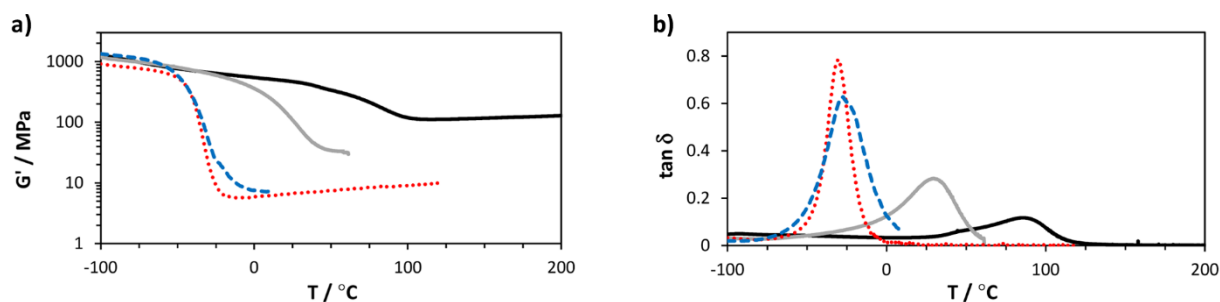

Figure 4. (a) Storage modulus G' and (b) tanδ plots of pD3A without CTA (━), with LA (━), with MSiH (---) and with LSH (•••).

4. Conclusions

In conclusion we have successfully synthesized and characterized a monoalkyl substituted bis(trimethylsilyl)silane MSiH as new monofunctional silane for silane-ene chemistry. In photoinitiated radical reactions MSiH showed reactivity towards all tested alkenes, except norbornene. Acrylates have been identified as most promising alkenes for the silane-ene reaction with MSiH. Moreover, the regulation of radical chain growth for MSiH-acrylate systems was confirmed via GPC measurements and subsequent MALDI MS. The regulation of acrylate-based photopolymer networks was shown by DMTA. For acrylates, the regulation of the radical photopolymerization with MSiH seems promising when compared to the thiol-ene approach. Consequently, multifunctional bis(trimethylsilyl)silanes could pave the way for future silane-acrylate networks serving as an alternative to thiol-ene chemistry for the fabrication of photopolymer networks with tailored architecture.

Supporting Information

Supporting Information is available from the Wiley Online Library

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With the possibility of almost freely designed network architectures, thiol-ene chemistry has gained great significance in the field of photopolymerization. Light-triggered silane-ene chemistry could serve as a powerful alternative to the state-of-the-art thiol-ene approach. A monoalkyl substituted bis(trimethylsilyl)silane has been investigated as a model compound. After screening various ene-compounds silane-acrylate chemistry was identified as the most promising, thus opening the way towards future silane-acrylate networks.

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Light-triggered radical silane-ene chemistry using a monoalkyl substituted bis(trimethylsilyl)silane
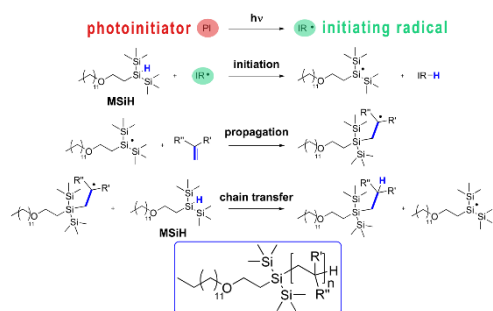
Supporting Information

Light-triggered radical silane-ene chemistry using a monoalkyl substituted bis(trimethylsilyl)silane

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1. **^{1}H, ^{13}C and ^{29}Si NMR spectra of 2-(2-(dodecyloxy)ethyl)-1,1,1,3,3,3-hexamethyl-trisilane MSiH**
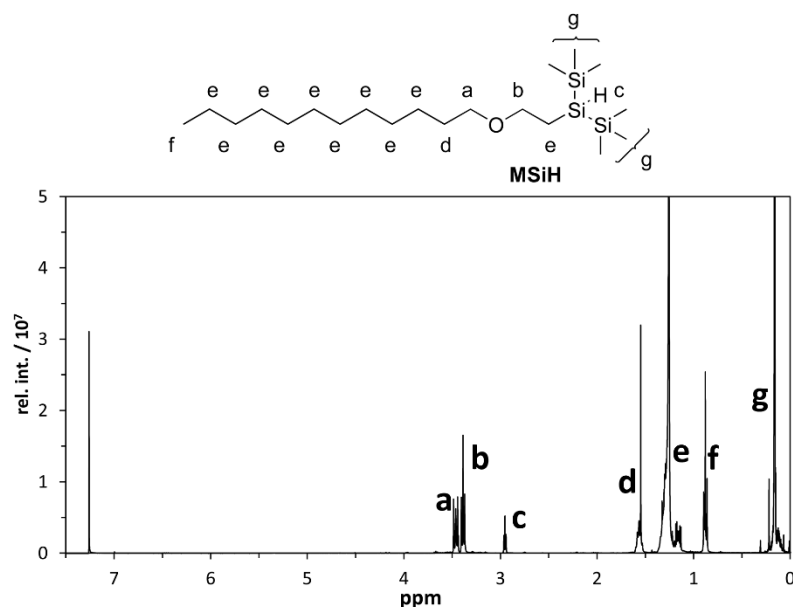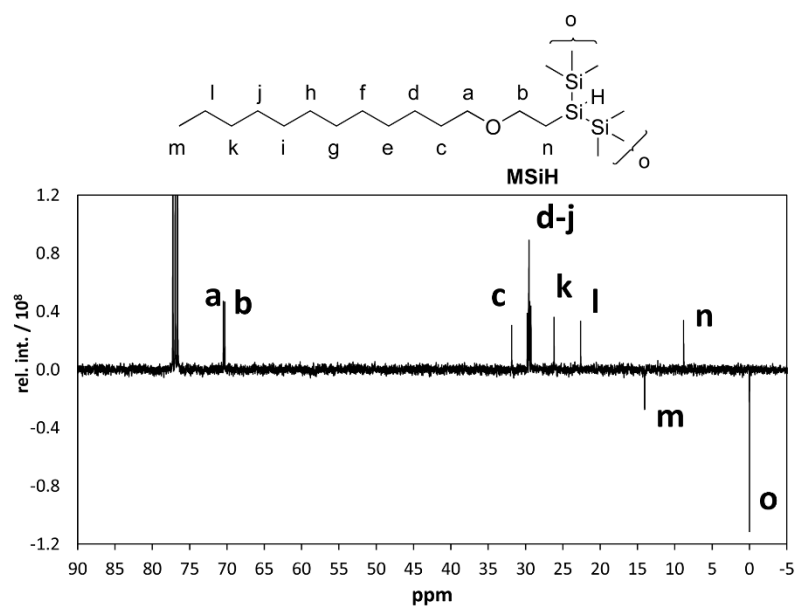

Figure S1. ^{1}H NMR of MSiH.
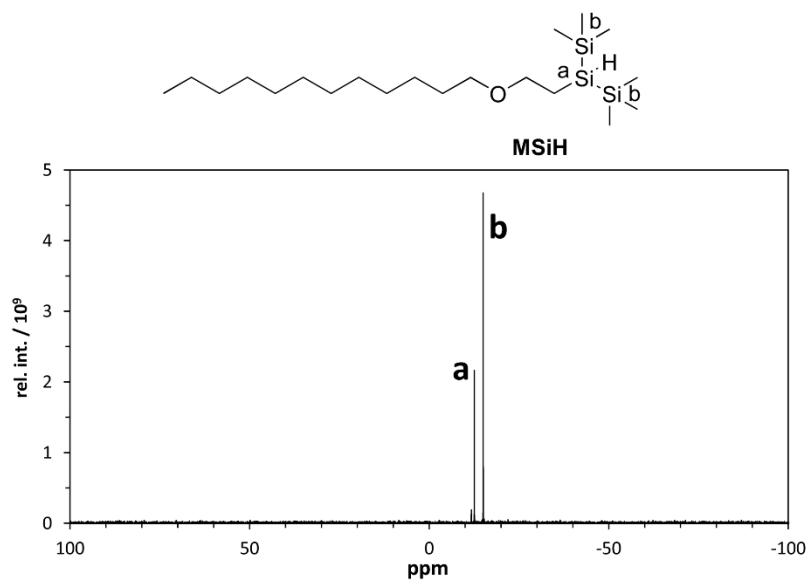
Figure S2. ^{13}C NMR of MSiH.

Figure S3. ^{29}Si NMR of MSiH.

2. Conversion analysis via ¹H NMR spectroscopy

The conversion of the silane-ene reactions were determined by ^{1}H NMR spectroscopic analysis. For the BnMA/MSiH formulation internal calibration was performed with the benzylic CH_2 signal of benzyl methacrylate (Figure S4).
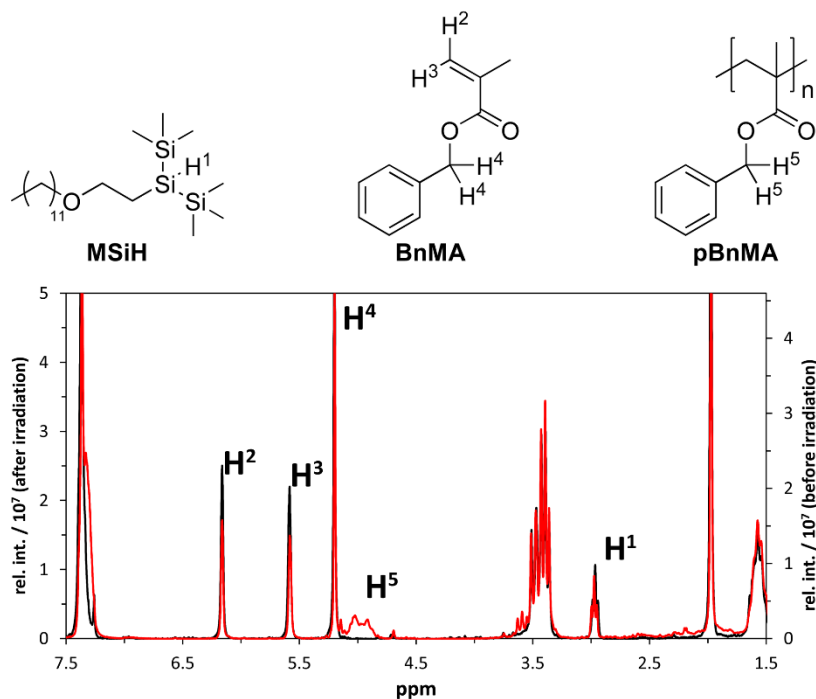

Figure S4. ^{1}H NMR of an equimolar BnMA/MSiH formulation before (black) and after irradiation (red).

For the VB/MSiH formulation internal calibration was performed with the ortho-H signal from the aromatic ring of vinyl benzoate (Figure S5).
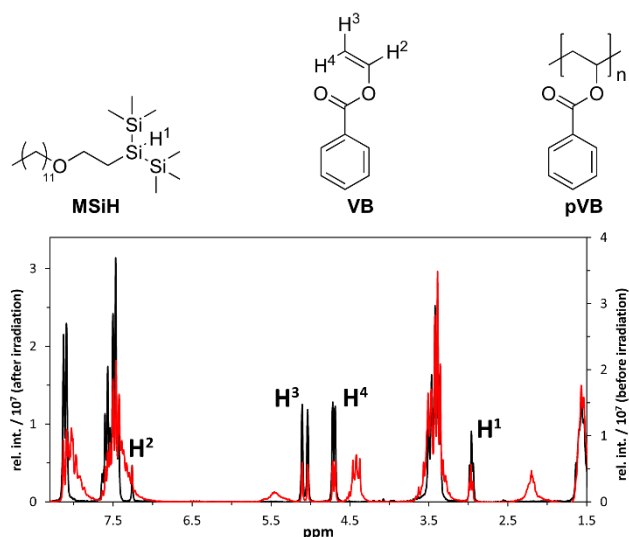

Figure S5. ^{1}H NMR of an equimolar VB/MSiH formulation before (black) and after irradiation (red).

For the NAM/MSiH formulation internal calibration was performed with the CH$_2$ signals of N-acryloyl morpholine (Figure S6).
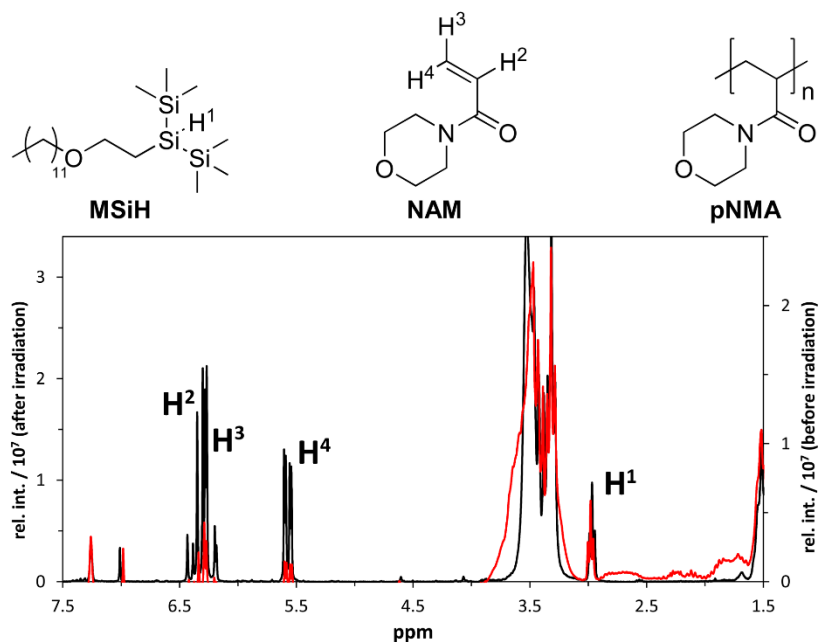

Figure S6. ^{1}H NMR of an equimolar NAM/MSiH formulation before (black) and after irradiation (red).

For the AB/MSiH formulation internal calibration was performed with the ortho-H signal from the aromatic ring of allyl benzoate (Figure S7).
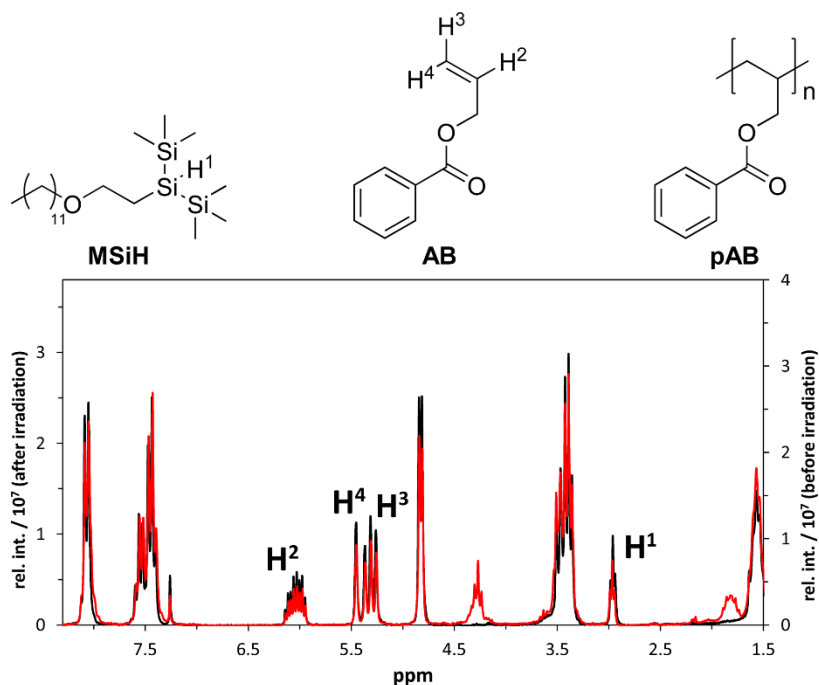

Figure S7. ^{1}H NMR of an equimolar AB/MSiH formulation before (black) and after irradiation (red).

For the LVE/MSiH formulation internal calibration was performed with the cumulated CH_3-signals from silane MSiH and vinyl ether LVE (Figure S8).
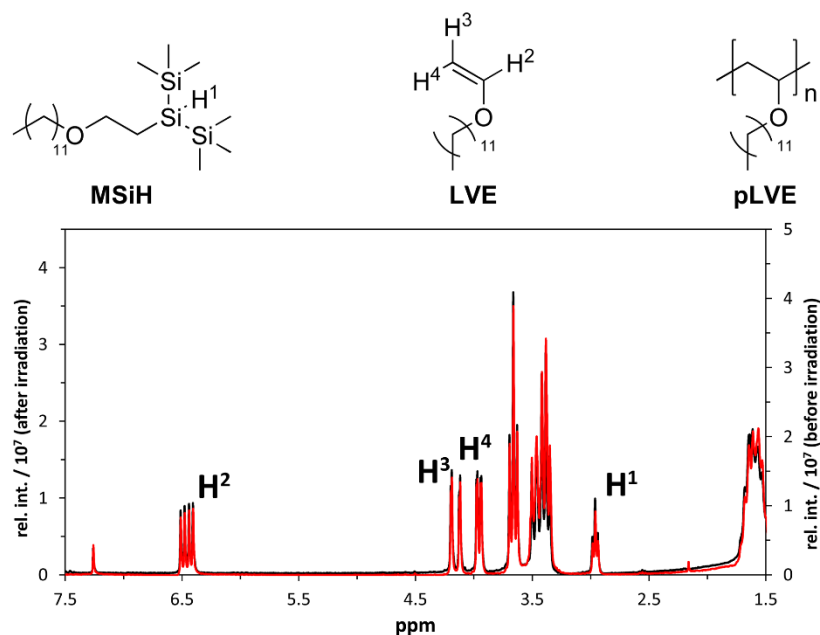

Figure S8. ^{1}H NMR of an equimolar LVE/MSiH formulation before (black) and after irradiation (red).

3. GPC

A Waters GPC system was used for GPC measurements. Three columns connected in series (Styragel HR 0.5, Styragel HR 3, and a Styragel HR 4), a Waters 515 HPLC pump and a Waters 2410 RI detector were used. The columns were maintained at 40 °C and a flow rate of 1.0 ml min^{-1} was used. For molecular weight calibration polystyrene standards were used and THF was used as solvent. Before GPC measurements the polymers were not precipitated.

Table S1. GPC results for pBnA (reference) and formulations with chain transfer agent (i.e. MSiH and MSH) in a 4/1 ratio of DB/SiH or SH.

alkene	CTA	M_n / kDa	Đ	DBC / %	SiHC/SHC / %
	-	59.1	5.8	91	-
acrylate (BnA)	MSiH	[a]0.7	2.5	94	93
	MSH	[a]0.3	3.3	96	*

[a]outside of calibration range; *could not be determined
M_n .. number average molecular weight
Đ … dispersity
DBC, SiHC, SHC ... double bond , silane and thiol conversion

4. MALDI MS

A Synapt G2 HDMS (Waters, UK) operated in positive ion mode was used for MALDI MS experiments. Matrix solutions of 20 mg dithranol /ml prepared in methanol:chloroform (1:1) were used. 2 mg/ml sodium trifluoroacetate (NaTFA) was used as cationizing agent and the analyte (BnA/MSiH, 4/1 ratio of DB/SiH) was prepared at 20 mg/ml. Given solutions were mixed in ratio 15:2:5 (matrix:analyte:cationizer) and 1 µl of this mixture was applied on a stainless steel target and dried at room temperature. The instrument was calibrated with a peptide mixture and α-cyano-4-hydroxycinnamic acid as matrix in the mass range 150 – 5000 Da.

Table S2. Peak list of MALDI MS experiment for pBnA with MSiH (4/1 ratio of DB/SiH).

n	m/z [M+Na]$^+$	rel. Int. / %
1	573.51	16
2	735.60	91
3	897.69	100
4	1059.77	95
5	1221.85	84
6	1383.92	70
7	1547.00	61
8	1709.07	60
9	1871.15	50
10	2033.22	36
11	2195.29	30
12	2358.37	22
13	2519.44	18
14	2681.53	13
15	2844.61	10
16	3006.69	7
17	3168.80	5
18	3330.88	4
19	3493.03	3
20	3655.13	2
21	3817.25	1
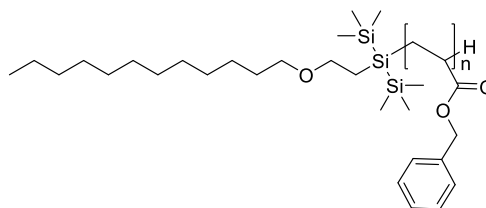
5. DMTA

An Anton Paar MCR 301 equipped with a CTD 450 oven and an SRF 12 measuring system was used for DMTA. The prepared polymer specimens were analyzed in torsion mode (frequency 1 Hz; strain 0.1%) from -100 – 200 °C with a heating rate of 2 °C min^{-1}. The software Rheoplus/32 V3.40 from Anton Paar was used for data recording.

Table S3. DMTA results for D3A, D3A/LA (references) and photopolymers with CTA (i.e. MSiH and LSH; 4/1 ratio of DB/SiH or SH).

alkene	CTA	T_g / °C	fwhm / °C	G'_r / MPa
	-	86	59	114
acrylate (D3A)	MSiH	-27	30	9
	LSH	-31	17	6
acrylate (D3A/LA 2/1)	-	30	43	34

T_g … glass transition temperature
fwhm … full width at half maximum of the loss factor plot
G'_r … storage modulus G' measured at T_g + 20 °C

6. TGA

TGA measurements were performed on a Netzsch F1 Jupiter 449 thermal analysis instrument. Approximately 10 mg of sample (derived from DMTA specimen) were weighed into an aluminum pan. The measurements were conducted at a nitrogen flow rate of 40 ml min^{-1} and a heating rate of 10 °C min^{-1}.
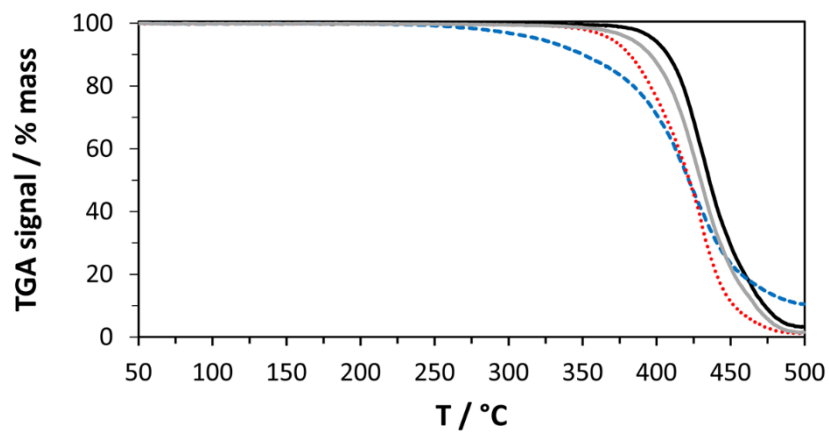
Figure S9. TGA plots of pD3A without CTA (━), with LA (━), with MSiH (---) and with LSH (•••).