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Synthesis, characterization and thiol-ene polymerization of hydrolyzed/condensed norbornenyl silic acid ester

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Summary

Bicyclo[2.2.1]hept-2-ene-5-yl (norborn-2-ene-5-yl) derivatives of silic acid were synthesized by the Diels-Alder reaction of the corresponding (meth)acryloxypropyl silanes with cyclopentadiene monomer. The norbornenyl silanes were characterized by elemental analyses, IR, ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectroscopy. The hydrolysis and condensation of norbornene-funktionalized silic acid esters yield polysiloxanes which can be crosslinked by the photoinitiated reaction with multifunctional thiols. The shrinking behaviour of the bulk materials which are obtained by this combination of the sol-gel process with the thiol-ene polymerization were investigated.

Introduction

Inorganic-organic composites with numerous variations in structures, properties, and application forms can be prepared by conventional sol-gel techniques [1]. Starting with tetra(alkoxy)silanes undergoing a hydrolysis and condensation reaction only SiO_2-sols and corresponding pure inorganic materials are obtained. The use of unhydrolyzable Si-C-bonded organic groups leads to organic modification of the SiO_2 network. If a polymerizable groups, like vinyl are used as modifying component, their polymerization yield an additional organic network, and the organically modified silicates are called ORMOCERs (organically modified ceramics) [2,3] or also CERAMERs [4], which are sol-gel derived hybrid materials starting from oligomers endcapped with metal alkoxide functionalities.

Many variations of the sol-gel precursors like substituted alkoxy silanes or the various combinations with other alkoxides like $Al(OR)_3$, $Zr(OR)_4$ or $Ti(OR)_4$ were carried out, but examples of variation of organic crosslinking groups are only few and concern essentially epoxy, vinyl and (meth)acryl groups [5,6].

In the present paper the synthesis of norborn-2-ene-5-yl group containing silanes and the photoinitiated crosslinking of corresponding sols with appropriate multifunctional thiols are described.

Experimental

Materials

3-Methacryloxypropyltrimethoxysilane (MTMS), 3-acryloxypropyltrimethoxysilane (ATMS), 3-acryloxypropyldichlormethylsilane (ADCMS), dimethyldiethoxysilane (DMDES) and 3-isocyanatopropyltriethoxysilane (IPTES) were purchased from ABCR and used without further purification. Dicyclopentadiene (DCP), terephthaloyl and isophthaloyl chloride, camphorquinone (CC), N,N-(2-cyanoethyl)methylaniline (CEMA), 2,6-di-tert.-butyl-4-methylphenole (BHT), hydroquinonemonomethylether (MEHQ), 4-dimethylaminopyridine (DMAP), anhydrous ethanol, n-propanol (Fluka), norborn-2-ene-5-methanol (Aldrich) and stannous dioctylcarboxylate (metatin 701, Acima) were used in analytical grade without further purification. The thiols used in the study pentaerythritol tetra(3-mercaptopropionate) (PETMP) and trimethylolpropane tri(3-mercaptopropionate), (TMPTMP) were purchased from Evans Chemetics. The 1,6-hexanediol diacrylate is available from Satomer.

Syntheses

3-Acryloxypropyldimethoxymethyl silane was prepared by methanolysis of ADCMS in the presence of ammonia in 50% yield (b.p. 89-91°C at 300 Pa); ^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.13 (3H,s,Si-CH_3), 0.35-0.65 (2H,m, Si-CH_2), 1.35-1.80 (2H,m,CH_2-CH_2-CH_2), 3.37 (6H,s,O-CH_3), 4.00 (2H,t,O-CH_2) and 5.55-6.45 (3H,m, CH=CH_2).

The norbornenyl silanes can be prepared by Diels-Alder reaction of cyclopentadiene monomer with the corresponding (meth)acrylate silanes:
(Meth)acrylate silane (0.25 mol) and 20 mg MEHQ were stirred under an argon atmosphere at 85-90°C in a three-necked round-bottomed flask equipped with magnetic stirring, an efficient condenser, which is connected with a distillation bridge, a gas introduction tube, and a thermometer. Freshly cracked and distilled cyclopentadiene monomer was continuously condensed in the reaction vessel through the distillation bridge for 7 h (acrylates) or 33 h in case of MTMS. The conversion of the (meth)acrylate silanes were monitored by HPLC. After the addition was complete, excess cyclopentadiene monomer and formed dimer were removed from the reaction mixture by vacuum distillation (0.05 mbar). The crude product was then distilled using a high vacuum pump. NMR analysis of the pure products gave spectra that were consistent with expected structure and indicate that the distillates were a mixture of endo and exo diastereomers of the desired norbornenyl silanes:

3-(Norborn-2-ene-5-methyl-5-carbonyloxy)propyltrimethoxysilane (NMTMS): Colourless liquid in 70% yield, b.p. 98-100°C at 7.0 mPa; $C_{15}H_{26}O_5Si$ (314.45 g/mol): found: C: 57.12 (calculated: 57.30), H: 8.31 (8.33);^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.38-0.83 (2H,m,Si-CH_2), 1.10-2.57 (9H,m,C-CH_3 and 3x -CH_2-), 2.72-3.17 (2H,m,>CH-), 3.57 (9H,s,O-CH_3), 4.07 (2H,t,O-CH_2) and 6.00-6.28 (2H,m,=CH-); ^{29}Si-NMR ($CDCl_3$, δ (ppm)): -42.975 (endo) 42%, -42.992 (exo) 58%; IR (film, cm^{-1}): 1725 (C=O), 725 (H-C=).

3-(Norborn-2-ene-5-carbonyloxy)propyltrimethoxysilane (NTMS): Colourless liquid in 75% yield, b.p. 91-94°C at 5.0 mPa; $C_{14}H_{24}O_5Si$ (300.42 g/mol): C: 55.62 (55.97), H: 7.84 (8.05);^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.38-0.82 (2H,m,Si-CH_2), 1.23-1.97 (6.3H,m,-CH_2-/>CH-CO_{exo}), 2.80-3.30 (2.7H,m, >CH-

/>CH-CO_{endo}), 3.58 (9H,s,O-CH_3), 4.00 (2H,t,O-CH_2) and 5.83-6.31 (2H,m,=CH-); ^{29}Si-NMR ($CDCl_3$, δ (ppm)): -42.890 (endo) 68%, -42,901 (exo) 32%; -42.930 endo 70%, -42.940 (exo) 30%; IR (film, cm^{-1}): 1732 (C=O), 713 (H-C=).

3-(Norborn-2-ene-5-carbonyloxy)propyldimethoxymethylsilane (NDMMS): Colourless liquid in 70% yield, b.p. 94-96°C at 4.0 mPa; $C_{14}H_{24}O_4Si$ (284.42 g/mol): C: 58.58 (59.12), H: 8.23 (8.50); ^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.13 (3H,s,Si-CH_3), 0.55-0.77 (2H,m,Si-CH_2), 1.22-2.07 (6.5H,m,-CH_2-/>CH-CO_{exo}), 2.83-3.30 (2.5H,m,>CH-/>CH-CO_{endo}), 3.55 (6H,s,O-CH_3), 4,00 (2H,t,O-CH_2) and 5.88-6.27 (2H,m,=CH-); ^{29}Si-NMR ($CDCl_3$, δ (ppm)): -42.708 (endo) 69%, -42.835 (exo) 31%; IR (film, cm^{-1}): 1732 (C=O), 712 (H-C=).

3-(Norborn-2-ene-5-methoxycarbamoyl)propyltriethoxysilane (NTES): To a mixture of norborn-2-ene-5-methanol (0.20 mol) and 0,1 g Metatin 701 (catalyst) and 40 mg BHT (inhibitor) IPTES (0.20 mol) was added under stirring and cooling with an icebath within 1 h. After 72 h stirring at room temperature the isocyanate was consumed. The reaction mixture was then distilled at high vacuum (b.p. 136-140 °C at 5.0 mPa) obtaining a colourless liquid in 76% yield. $C_{18}H_{33}O_5Si$ (371.55 g/mol): C: 57.28 (58.19), H: 9.00 (8.95), N: 4.01 (3.77); ^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.33-0.73 (2H,m,Si-CH_2), 1.12-1.92 (13H,m,3x -CH_2-, 3x -CH_3), 2.23-2.37 (1H,m,>C<u>H</u>-CH_2-O), 2.70-2.93 (2H,m,-CH<), 3.17 (2H,q,NH-C<u>H</u>$_2$-), 3.67-3.97 (8H,m,O-CH_2-), 4.90-5.10 (1H,s,-NH-) and 5.85-6.20 (2H,m,=CH-); IR (film, cm^{-1}): 1726 (C=O), 721 (H-C=).

1,6-Hexanediol-di(norborn-2-ene-5-carboxylate) (HDNC) was synthesized according to [7]. Norborn-2-ene-5-methyl terephthalate (NMT) or norborn-2-ene-5-methyl isoterephthalate (NMIT) were prepared by esterification of norborn-2-ene-5-methanol with terephthaloyl or isoterephthaloyl chloride analogous to [8] in the presence of DMAP as catalyst:

NMT: White crystals, 48% yield (mp: 106-107 °C): ^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.55-2.10 (8H,m;-CH_2-), 2.33-3.10 (6H,m,>CH-), 3.80-4.43 (4H,m,-CH_2-O), 5.93-6.32 (4H,m,=CH-), 8.15 (4H,s,$CH_{arom.}$); IR (film, cm^{-1}): 1716 (C=O), 739 (H-C=).

NMIT: High viscous liquid, 65% yield (b.p. 210 °C at 200-205 °C): ^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 1.17-2.10 (8H,m;-CH_2-), 2.38-3.17 (6H,m,>CH-), 3.83-4.53 (4H,m,-CH_2-O), 5.95-6.35 (4H,m,=CH-), 7.58 (1H,t,$CH_{arom.}$); 8.32 (2H,t,$CH_{arom.}$); 8.78 (1H,s,$CH_{arom.}$); IR (film, cm^{-1}): 1723 (C=O), 728 (H-C=).

<u>Sol-Gel-Process</u>

The norbornene group functionalized silane NMTMS were hydrolysed and co-condensed with DMDES by addition of the stoichiometrically necessary amount of water in anhydrous methanol or ethyl acetate in the presence of HCl as catalyst under stirring at room temperature in argon atmosphere. After the water is consumed the photoinitiator and a multifunctional mercaptopropionate or norbornene were added, and the solvent of reaction mixture was evaporated in vacuum. The hydrolysis and condensation of MTMS was carried out analogous.

Poly(NMTMS-co-DMDES): ^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.05-0.20 (6H,s, Si-CH_3) 0.50-0.87 (2H,m,Si-CH_2), 1.07-2.60 (9H,m,C-CH_3 and 3x -CH_2-), 2.73-3.14 (2H,m,>CH-), 3.57 (2,3 mol-% residue Si-O-CH_3), 4.08 (2H,t,-O-CH_2) and 5.98-6.37 (2H,m,=CH-).

Poly(MTMS): ^{1}H NMR ($CDCl_3$, 90 MHz, δ (ppm)): 0.58-0.90 (2H,m,Si-CH_2), 1.63-2.13 (5H,m,C-CH_3 and Si-CH_2-CH_2-), 3.57 (14 mol-% residue Si-O-CH_3), 4.13 (2H,t,O-CH_2); 5.58 and 6.10 (2H,s,=CH-).

Polymerization

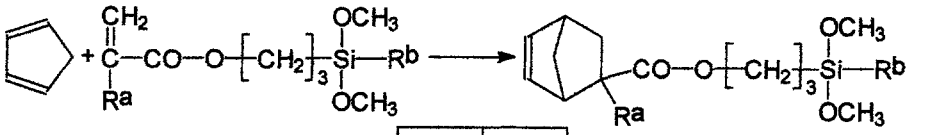
Photopolymerizations were carried out using a Spectramat (Ivoclar) with blue wavelength visible light. A mixture of CC (0.3 weight-%) and CEMA (0.5 weight-%) was used as photoinitiator. The exposure time was 3 minutes. The conversion of thiol-ene addition polymerization was monitored by measuring the ratio of the absorbance of the C-H out of plane bending vibration of the cis-alkene group using the C-H stretching vibration of the hydrocarbon group as an internal standard.

Measurements

^{1}H NMR measurements were recorded on an EM 390 (Perkin-Elmer, 90 MHz) using hexamethyldisilane (HMDS) as the standard. ^{13}C NMR spectroscopic measurements were performed with a AC 300F spectrometer (Bruker, 75 MHz) using $CDCl_3$ or dimethylsulfoxide-d_6 as a solvent and ^{29}Si NMR measurements were performed with a spectrometer AM 200 (Bruker). An FT-IR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra. The purity of norborne silanes, that were distilled with a turbo molecular vacuum pump PD 1.6/50 (Leybold), was determined by HPLC using an apparatus of Methrom, acetonitrile as eluent, a Lambda 1000 UV-spectrometer as detector and a columns Nucleosil 120 5 C18. The polymerization shrinkage was calculated from the density differences of cured and uncured materials. The density of the materials was determined using the water displacement technique.

Results and Discussion

The synthesis of norbornene-functionalized silanes can be achieved by the Diels-Alder reaction of cyclopentadiene monomer with the corresponding (meth)acrylate silanes:



	Ra	Rb
NMTMS	CH_3	OCH_3
NTMS	H	OCH_3
NDMMS	H	CH_3

Starting from commercial available silanes the Diels-Alder reaction with cyclopentadiene monomer gives the desired products in relatively high yields. In result of the stereochemical route of the Diels-Alder reaction mixtures of endo and exo

isomers are obtained and longer the reaction time a higher content exo isomer will be formed [9]. Accordingly, in case of reaction of the lower reactive MTMS, in comparison to acrylate silane ATMS, NMTMS is formed after a reaction time of 33 h with an exo-isomer content of about 58%, in comparison to 32% exo-isomer of NTMS after 7h. In opposite to the starting (meth)acryl silanes the norbornene-functionalized silanes can be purified by distillation in vacuum without that their polymerization occurred. Furthermore, norbornene silanes can be prepared also by other reactions. For example NTES was obtained by addition of norborn-2-ene-5-methanol to the commercial avaiable IPTES.

Characterization of norbornene silanes was carried out by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR and IR spectroscopy and by elemental analysis, respectively. The ^{1}H NMR spectra of prepared silanes show the expected signals of cis-alken protons of the formed norbornene group at 5.85-6.31 ppm. Also results of ^{13}C NMR measurements of norbornene silanes support the proposed structures (Tab. 1). For assignments of the observed signals chemical shift increments compiled by Pretsch et al. [10], the DEPT (distortionless enhancement by polarization transfer) experiment [11] and data of other norbornene derivatives [12] were used. The endo or exo content was calculated on basis of ^{29}Si NMR spectroscopic data. Surprisingly, in case of NTMS the signals of exo and endo isomers are further splitted into two dupletts. On the basis of ^{13}C NMR measurements with a higher resolution (0.170 Hz/point) it was found that the duplett formation is caused by an interaction of the carbonyl group with the (Si-CH_2-)-group, which does not occur in case of NMTMS and NDMMS, respectively.

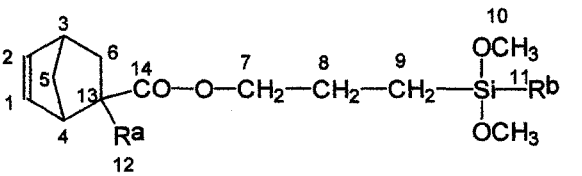
Table 1 ^{13}C NMR spectroscopic data of selected norbornene silanes[1)]

	Chemical shifts[2]									
Silane	1,2[3)]	3,4[3)]	5[3)]	6[3)]	7[3)]	8	9	10	13[3)]	14[3)]
NMTMS[4)]	134.0, 135.8, 138.2, 139.1	43.0, 43.3	47.3, 49.5	38.0, 38.3	66.6, 66.9	22.5	5.8	51.3	50.5, 50.8	177.6, 179.2
NTMS	132.5, 135.8, 137.8, 138.1	41.7, 42.6, 43.3, 43.4	46.4, 49.7	29.3, 30.4	66.2, 66.4	22.2	5.4	50.3	45.8, 46.4	174.8, 176.3
NDMMS	132.1, 135.5, 137.4, 137.7	41.3, 42.2, 42.9, 43.1	46.1, 49.3	28.9, 30.0	66.0, 66.3	21.9	8.9	49.9	45.4, 46.3	174.5, 176.0

1) Shift value in ppm down field from internal HMDS

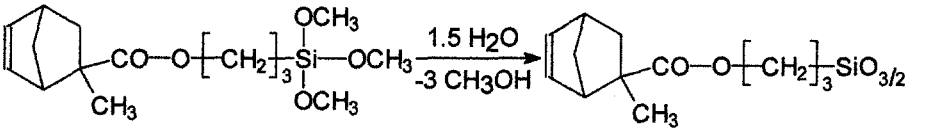
2)

	Ra	Rb
NMTMS	CH_3	OCH_3
NTMS	H	OCH_3
NDMMS	H	CH_3



3) Endo/exo
4) 24.8, 26.9; 12 (endo/exo)

In order to prepare thiol-ene polyadducts with a higher hardness, NMT and NMIT with a more rigid structure were synthesized, but unfortunately only NMIT shows a sufficient solubility in common thiols. The synthesized norbornene silanes were used as sol-gel procurers. Thus, the inorganic crosslinking reaction can take place by hydrolysis and condensation of the alkoxy groups via a typical sol-gel reaction [1] for example in case of NMTMS according to:



For generating more flexible properties of the products the sol-gel precursors were hydrolyzed and condensed in the presence DMDES yielding a norbornene group containing polycocondensates of the used silanes. After evaporation of the solvent transparent viscous sol monomers are obtained, which can be crosslinked by the reaction with di- or multifunctional thiol compounds.

Table 2 Polymerization shrinkage of various light-cured materials

Monomer mixture	Polymerization shrinkage (%)
HDNC/TMPTMP	5.2
NMIT/TMPTMP	4.3
NMIT/PETMP	2,3
Poly(NMTMS-co-DMDES)/PETMP	0.5
Poly(NMTMS-co-DMDES)/TMPTMP	0.8
Poly(MTMS)	7.5

The main benefit of the thiol-ene polyaddition as crosslinking principle is the low-shrinking behaviour during the setting of the material [13] in opposite to for example resins on the basis of multi(meth)acrylates. This is demonstrated by the crosslinking of norbornene group containing sols starting from NMTMS with the multithiols PETMP and TMPTMP (Table 2). The volume shrinking during the photocrosslinking of the functionalized inorganic nanoscale particles is below 1 %. In case of photocrosslinking of methacryl group containing sols, which are obtained starting from MTMS under analogous conditions, the polymerization shrinkage in result of the photocrosslinking is about 7.5 %. Furthermore, the IR spectroscopic investigations of the thiol-ene polyadducts shown that the norbornene C=C bonds are almost consumed by the polyreaction with the multifunctional thiols. In the opposite to this, in case of the multifunctional (meth)acrylates it is known, that their crosslinking at ambient temperature shows an incomplete conversion [14]. Finally, a advantage of the combination of the sol-gel process with the thiol-ene polymerization is also the possibility to varry the properties of the composites over a wide range, for instance it is possible to generate hard or soft or elastic materials on this way, which is beeing further investigated.

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