UV Curing of Epoxy Functional Hybrid Silicones

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ABSTRACT: Several epoxy difunctional hybrid alkylene-silicone telomers with different silicone characters and organic spacers (linkers) were prepared via the platinum-catalyzed polyhydrosilylation of α,ω-dihydrosiloxanes and α,ω-dienes. Thereafter, the resulting Si—H-terminated prepolymers were terminally functionalized with 4-vinyl-1,2-epoxycyclohexane or allyl glycidyl ether. In the presence of a lipophilic cationic photoinitiator, the terminally epoxy-functionalized hybrid alkylene–silicone telomers were photopolymerized to give crosslinked, soft, elastomeric, and transparent films. The progress of the photoinitiated cationic ring-opening epoxide polymerizations was monitored using optical pyrometry. Potential applications for these novel photocurable epoxy-functional telomers are as modifiers for UV curable coatings, printing inks, adhesives, and release coatings. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: epoxy functional hybrid alkylene-silicone telomers; hydrosilylation; cationic photopolymerization; optical pyrometry

INTRODUCTION

Hybrid poly(alkylene-siloxanes) are a comparatively new class of polymeric materials combining the chemical properties of silicones and organic polymers such as paraffins or polyethers in a unique way. They have potential applications as thermally stable elastomers with enhanced chemical resistance, as wetting agents, surfactants, and as hydrophobic coatings.[1,2] In addition, such low-surface energy UV-curable hybrid alkylene silicones are of special commercial interest for use in release coatings.

The platinum-catalyzed hydrosilylation reaction provides a convenient route for the synthesis of these new functional materials. Suitable α,ω-Si—H functional polysiloxanes and simple organic α,ω-dienes were combined in a step-growth polyaddition reaction. By variation of the stoichiometry of the two starting materials, the chain length and, thus, the molecular weight can be varied at will.[3] In all cases, the stoichiometry of the two starting materials was adjusted to afford intermediate oligomers bearing terminal Si—H groups. Thereafter, these oligomers were subsequently end-capped with an epoxide bearing a terminal C=C bond to give the targeted hybrid alkylene silicone telomers bearing reactive epoxy-functional groups. A wide variety of noble metal complexes are known to catalyze the addition of hydrosilanes to carbon–carbon multiple bonds. Among these, [Pt$_2$(*sym*-tetramethyldivinyldisiloxane)$_3$] ("Karstedt's catalyst") and hexachloroplatinic acid (H$_2$PtCl$_6$, "Speier's catalyst") are two of the most commonly used catalysts for the hydrosilylation reaction.[4]

The preparation of epoxy-functional siloxane monomers and oligomers and their reactivities in photoinitiated cationic polymerization were first examined by Crivello and Lee in 1990.[5] Monomers and oligomers bearing terminal cycloaliphatic epoxy groups were found to be especially reactive in cationic ring-opening polymerization, and these materials were suggested as attractive candidates for use in photocurable coatings, printing inks, adhesives, and elastomers. Since then, interest and research activity in photoinitiated cationic crosslinking polymerizations of multifunctional epoxide monomers and oligomers have increased rapidly as this technology has found broad use in many industrial applications.
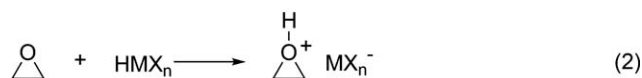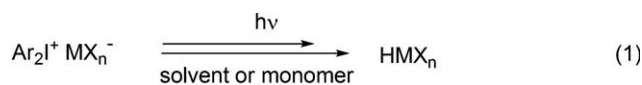
Scheme 1 Generalized mechanism for the photoinitiated cationic ring-opening polymerization of epoxide monomers.

Depicted in Scheme 1 is a generalized mechanism for the photoinitiated cationic ring-opening polymerization of epoxide monomers using a diaryliodonium salt cationic photoinitiator.[6] Irradiation of the photoinitiator with wavelengths in the range of 250–360 nm generates a number of reactive species that subsequently react with the solvent or monomer to give the strong protonic acid, HMX_n (1). Ring-opening polymerization takes place by protonation of the monomer (2) followed by the repetitive addition of monomer molecules to the growing oxonium ion polymer chain end (3).[7]

There are several major motivating factors driving the adoption of this technology. First, the ability to conduct these crosslinking polymerizations very rapidly, with low energy and without the use of an inert atmosphere, provides important economic incentives. Second, because solvents are not used, there are no emissions, and the environmental consequences of these polymerizations are minimal. Last, the thermal, mechanical, and chemical resistance, low shrinkage, and adhesion characteristics of the network polymers that are formed are excellent. The industrial impact of photoinitiated polymerizations in general and photoinitiated cationic polymerizations in particular is predicted to markedly increase in the future as this technology undergoes further maturation.[8,9]

This article describes the synthesis of a novel series of epoxy-functional hybrid alkylene-silicone oligomers. It is well known that epoxy functional silicone monomers such as **I** shown in Figure 1 undergo efficient cationic ring-opening photopolymerization to give crosslinked materials with excellent thermal and chemical resistance.[10] Unfortunately, such low-molar mass difunctional monomers produce hard, brittle, glass-like materials with little elongation and minimal flexibility.[7] For this reason, attempts were made to expand the range of mechanical properties obtained in this class of monomers by the preparation of epoxy–silicone oligomers with a variety of different flexible backbone structures interposed between the two crosslinkable epoxide

groups. A synthetic procedure, originally developed for the preparation of atomic oxygen-resistant epoxy-functional hybrid alkylene-silicone oligomers,[11] was used for the synthesis of the analogous oligomers described in this article.

EXPERIMENTAL

Materials

1,1,3,3,5,5-Hexamethyltrisiloxane (HexMTS) was purchased from ABCR GmbH, Karlsruhe and used as received. α,ω-Dihydropolydimethylsiloxane (PDMS, $M_n = 580$ or 680 g/mol), 4-vinyl-1,2-epoxycyclohexane (VCO), allyl glycidyl ether (AGE), 1,4-butanediol divinyl ether, and triethylene glycol divinyl ether were used as received from Sigma Aldrich. 1,3-Diisopropenyl benzene was received from Sigma-Aldrich and was purified by vacuum distillation before use. 1,9-Decadiene was obtained from Acros. Karstedt's catalyst [Pt$_2$(*sym*-tetramethyldivinyldisiloxane)$_3$] and Pt(PPh$_3$)$_4$ were purchased from Sigma Aldrich and used, respectively, as diluted solutions in hexane and dichloromethane at a concentration of 1 mg Pt/mL.

The photoinitiator, "bis(4-dodecylphenyl)iodonium hexafluoridoantimonate" (UV 9380C), provided as a 50% solution in propylene carbonate, was a gift from the Silicones Department of the General Electric Corporation. This photoinitiator was prepared by the reaction of potassium iodate with a mixture of C10-C14 alkylated benzenes in which the alkyl groups are highly branched.[12] For this reason, photoinitiator UV 9380C consists of a complex mixture of related di(alkylphenyl)iodonium hexafluoridoantimonate salts. (4-*n*-Octyloxyphenyl)phenyliodonium hexafluoridoantimonate (IOC-8) and diphenyliodonium tetrakis(pentafluorophenyl)borate (DPI-TFPB) were prepared as described in earlier publications.[13]

All hydrosilylation reactions were carried out in argon atmosphere using standard Schlenk techniques. Karstedt's catalyst was used in the hydrosilylation reaction for the synthesis of oligomers **IIa–IVb** and **Ve**, while Pt(PPh$_3$)$_4$ was used as the catalyst for the synthesis of oligomers **Va–Vd**.

^{1}H and ^{29}Si-NMR spectra were recorded in CDCl$_3$ using a Bruker Avance 400 MHz nuclear magnetic resonance spectrometer. Gel permeation chromatography (GPC) was conducted on a Waters 2695
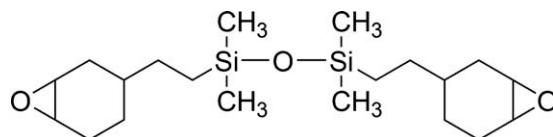

Figure 1 Structure of epoxy-functional silicone monomer **I**.

TABLE I
Composition and Molecular Weight of Hybrid Silicone Telomers

Compound	Siloxane	Diene	Epoxide	m^a	M^a (g/mol)	$M_n{}^b$ (g/mol)
IIa	HexMTS	1,4-Butanediol divinyl ether	VCO	5.65	2,770	3,190
IIb	PDMS	1,4-Butanediol divinyl ether	VCO	1.68	3,130	2,950
IIc	HexMTS	1,4-Butanediol divinyl ether	AGE	6.44	3,050	3,770
IIIa	HexMTS	Triethylene glycol divinyl ether	VCO	4.10	2,550	2,670
IIIb	PDMS	Triethylene glycol divinyl ether	VCO	1.53	3,160	2,980
IVa	HexMTS	1,3-Diisopropenyl benzene	VCO	6.06	3,050	2,950
IVb	PDMS	1,3-Diisopropenyl benzene	VCO	1.80	3280	3,280
Va	HexMTS	1,9-Decadiene	VCO	1.31	1,260	1,780
Vb	PDMS	1,9-Decadiene	VCO	1.28	2,470	3,320
Vc	HexMTS	1,9-Decadiene	VCO	15.48	6,170	6,210
Vd	PDMS	1,9-Decadiene	VCO	21.73	17,150	19,400
Ve	HexMTS	1,9-Decadiene	AGE	1.36	1,260	1,710

[a] Determined by ^{1}H-NMR spectroscopy, error: ±5%.
[b] Determined by GPC.

alliance system using tetrahydrofuran as the mobile phase.

Synthesis of Si—H-terminated hybrid alkylene-silicones by hydrosilylation condensation

Under an atmosphere of argon, $m + 2$ equivalents of HexMTS or PDMS were placed into a 250-mL three-necked round-bottomed glass flask equipped with a reflux condenser, magnetic stirrer, temperature sensor, and dropping funnel and heated to 60°C. Into the dropping funnel there were placed $m + 1$ equivalents of the designated diene linker mixed with a sufficient amount of a 1 mg Pt/mL hexane solution of Karstedt's catalyst or a 1 mg Pt/mL dichloromethane solution of Pt(PPh$_3$)$_4$ to achieve 10 ppm Pt per total substrates. The above mixture was added dropwise with vigorous stirring to the siloxane over the course of ~1 h. The reaction was highly exothermic and the temperature of the reaction mixture was controlled at 60–85°C using an ice bath. After completing the addition, the pale yellow mixture was stirred for an additional 1 h at 75°C and was then allowed to cool to 60°C. The chain length of the oligomers that were formed was determined by ^{1}H-NMR spectroscopy. The integrals of the areas of peaks due to several groups within the molecule are a function of the degree of polymerization m when the integral of the Si—H moiety at 4.7 ppm is set to 2. The average degree of polymerization m was used for the calculation of the molecular weight.

Functionalization with 4-vinyl 1,2-epoxycyclohexane

Using the same apparatus as described above, a stoichiometric amount (2 equiv) of VCO was slowly added to the Si—H-terminated hybrid alkylene-silicone oligomer at 60°C via the dropping funnel. The reaction was slightly exothermic and the mixture

was heated to 75°C for 1 h to allow complete conversion. Thereafter, volatiles and isomerized allyl glycidyl ether were removed in vacuo at 60°C. The final products were obtained as pale-yellow oils, and their molecular weights were determined using ^{1}H-NMR spectroscopy and GPC.

Functionalization with allyl glycidylether

Using the above-described apparatus, an excess (2.5 equiv) of AGE was slowly added to the Si—H-terminated hybrid silicone oligomer at 60°C via the dropping funnel. The reaction was exothermic, and the temperature was maintained at 75°C for 1 h to complete the reaction. Thereafter, the reaction was allowed to cool to room temperature, and the volatile excess starting AGE and isomerized AGE were removed *in vacuo* at 60°C. The final products were obtained as pale-yellow oils. The molecular weights of the oligomers were determined by ^{1}H-NMR spectroscopy and GPC.

Table I gives an overview of the composition and molecular weights of all epoxy functional hybrid alkylene-silicone telomers prepared during the course of this work.

Synthesis of telomer IIa

Under an atmosphere of argon, 100.0 g (0.48 mol, 6 equiv) HexMTS were placed into a 250-mL three-necked round-bottomed glass flask equipped with reflux condenser, magnetic stirrer, temperature sensor, and dropping funnel and heated to 60°C. 56.0 g (0.40 mol, 5 equiv) 1,4-butanediol divinyl ether were mixed with 1.57 mL of a 1 mg Pt/mL hexane solution of Karstedt's catalyst and placed into the dropping funnel. With vigorous stirring, the mixture was added dropwise to the siloxane over the course of ~1 h. The reaction was highly exothermic and the

temperature of the reaction mixture was controlled using an ice bath. The maximum temperature attained by the reaction mixture was 84°C. After the addition, the pale yellow oil was stirred for an additional 1 h at 75°C and was then allowed to cool to 60°C. It was added slowly via the dropping funnel 14.0 g (0.11 mol, 2 equiv) of VCO. The reaction was slightly exothermic and the mixture was heated to 75°C for 1 h to allow complete conversion. Thereafter, the reaction was allowed to cool to room temperature and any volatile materials were removed by stripping under high vacuum. There were obtained 169.0 g of the final product as pale-yellow oil. Molecular weight (determined by ^{1}H-NMR) = 2770 g/mol; MW (by GPC) = 3190 g/mol.

^{1}H-NMR (400 MHz, CDCl$_3$, δ): 0.05 (m, 139H, Si—CH$_3$), 0.50 (m, 4H, epoxy-CH$_2$—Si), 0.80–2.24 (m, 18H, cHex, and cHex-CH$_2$), 0.99 (m, 26H, Si—CH$_2$), 1.62 (m, 26H, CH$_2$), 3.12 (m, 4H, epoxy—CH), 3.39 (m, 27H, CH$_2$—O), and 3.50 (m, 27H, CH$_2$—O) ppm.

^{29}Si-NMR (80 MHz, CDCl$_3$, δ): −21.2 (—SiO—Si—OSi—), −20.9 (epoxy—SiO—Si—OSi—), 5.67 (epoxy—SiO—Si—OSi—CH$_2$), 5.80 (Si—CH$_2$), and 7.45 (epoxy—SiO—Si—OSi) ppm.

The synthesis, NMR data, and determination of the molecular weights for all other epoxy functional hybrid silicone oligomers are given in the Supporting Information.

Monitoring of the photopolymerizations by optical pyrometry

The apparatus and methods employed for the monitoring of the photopolymerizations carried out in this investigation using optical pyrometry were described in an earlier communication.[14] Samples (usually 0.5 g of the epoxy functional oligomer were used) for analysis were prepared as follows: homogeneous solutions of the desired epoxy functional oligomer with the designated photoinitiator (2 wt%) were prepared. A 10-μm thick-fluorinated polyethylene film was first laid down, and a thin polyester fiber mesh, serving as a spacer, was placed on top of the polymer film. The liquid sample was placed onto this assembly, and an identical layer of fluorinated polyethylene film was placed over the top. The resulting sample sandwich was mounted in a 2.0-cm × 2.0-cm plastic slide holder and irradiated with UV light from a UVEX SCU-110 mercury lamp and directed via a 95-cm liquid optic light guide onto the sample. The wavelengths transmitted through the liquid optic light guide are from 220 to 650 nm. The end of the wand was placed at a predetermined distance and directed at an incident angle of 45° onto the sample window. A Raytek Marathon Series MM Infrared Thermometer (Raytek, Champlain, NY) was used to monitor the temperature of

the sample in real time. This instrument has a sensitivity of ±0.5°C with an operating temperature range of −40 – 800°C, a response time of 120 ms, and the capability of up to 10 temperature measurements per second. The instrument is responsive to infrared radiation in the range of 8–14 μm. Using a laser aligner, the focal point of the sensor of the OP instrument was centered in the middle of the sample window. All optical pyrometry experiments performed in this investigation were conducted at ambient temperature (21–25°C). In each case, the samples were allowed to equilibrate and establish a flat baseline for 20 s before the start of the UV irradiation. Temperature data were collected at a rate of one measurement per second and were directly recorded and downloaded to a Lenovo ThinkPad personal computer for analysis. All experiments were performed at a light intensity of 2340 mJ/cm^2 min.

RESULTS AND DISCUSSION

Synthetic approach

Twelve different epoxy functional hybrid alkylene silicones were prepared via the platinum-catalyzed polyhydrosilylation reaction. To obtain a set of different hybrid materials, the silicone character of the polymers was varied as well as the alkylene spacer. For a broad variation of the properties of the polymers with respect to polarity and structure, we chose 1,4-butanediol divinyl ether, triethylene glycol divinyl ether and 1,3-diisopropenyl benzene, and 1,9-decadiene as alkylene spacers. The silicone content was varied through the use of two different types of siloxane building blocks, HexMTS and α,ω-dihydropoly (dimethylsiloxane) (PDMS, MW = 580 or 680 g/mol) with different chain lengths. Figure 2 shows the structures and designations of the hybrid silicones used in this study.

In the first step of the synthesis, α,ω-Si—H-terminated oligomers were synthesized by the platinum-catalyzed polyhydrosilylation reaction of HexMTS or PDMS (MW = 580 or 680 g/mol) with the above-mentioned spacers using Karstedt's catalyst or Pt(PPh$_3$)$_4$. Karstedt's catalyst was used for the synthesis of the oligomers **IIa–IVb** and **Ve**, while Pt(PPh$_3$)$_4$ was used for the synthesis of oligomers **Va–Vd**.

In a second hydrosilylation reaction using the same catalyst, the synthesized α,ω-Si—H-terminated oligomers were further functionalized with epoxy groups by reacting them with VCO or AGE to provide the desired epoxy-functionalized oligomers. As an example, Scheme 2 shows the synthesis of oligomer **IIa** from HexMTS and 1,4-butandiol divinyl ether.
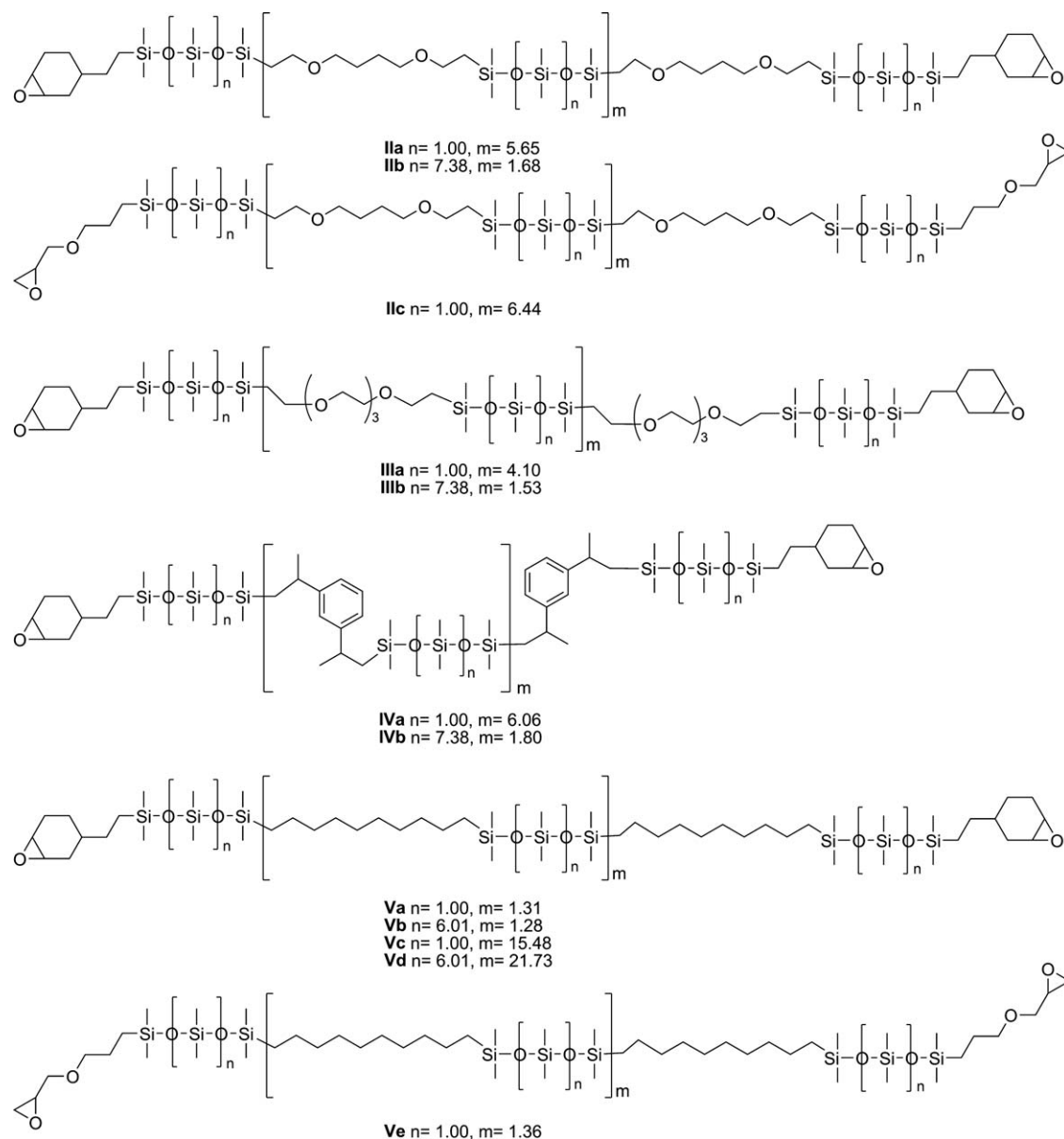
Figure 2 Structures of epoxy-terminated hybrid silicones used in this study.

Previously, it was reported that during platinum-catalyzed hydrosilylations of VCO, ring-opening epoxide polymerization can occur as a side reaction. This side reaction is especially prone to take place when the platinum-containing Karstedt's catalyst is used. In the present case, this reaction leads to the spontaneous gelation of the epoxy-terminated oligomer.[15] This undesired side reaction can be inhibited by adding a small amount of a Lewis base such as PPh$_3$ to the reaction mixture. It was reported that the active species for this side reaction is colloidal platinum formed by the *in situ* reduction of the catalyst by Si—H-containing organosilanes.[16] In the case of 1,4-butanediol divinyl ether, triethylene glycol divinyl ether and 1,3-diisopropenyl benzene Karstedt's catalyst could be used for the hydrosilylation reactions as well as for the subsequent

functionalization with VCO or AGE. We suggest that the presence of the weakly Lewis basic oxygen atoms or aromatic groups within the polymer backbones effectively inhibits the formation of colloidal platinum and also the gelation reaction. Less-reactive glycidyl ether systems do generally not undergo this platinum catalyzed ring-opening polymerization. Therefore, oligomers **IIa–IVb** and **Ve**-containing such groups could be prepared using Karstedt's catalyst without the need for an inhibitor.

In contrast, when 1,9-decadiene was condensed with various α,ω-Si—H functional siloxanes and followed by attempted terminal functionalization with VCO, gelation was observed in every case in which Karstedt's catalyst was used. For this reason, Pt(PPh$_3$)$_4$ was used successfully as the catalyst for
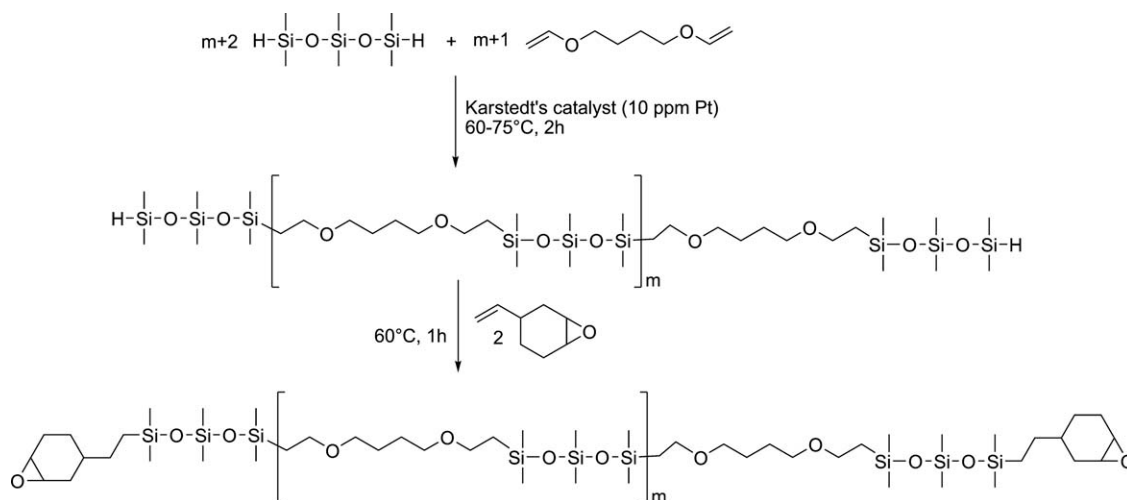
Scheme 2   Synthesis of epoxy-functionalized hybrid silicone telomer **IIa**.

the synthesis of hybrid alkylene silicone oligomers **Va–Vd**.

The chain lengths and also the molecular weights of the copolymers were determined by ^{1}H-NMR-spectroscopy, and these values were independently verified by GPC measurements. Figure 3 shows the ^{1}H-NMR spectrum of oligomer **IIa**. The assignment of the signals and the results of the chain length calculation based on integration of the areas of the indicated resonances are given in Table II.

The molecular weight for this oligomer was determined using the following equation:

$$M = 2 \times M(\text{siloxane}) + M(\text{diene}) + m[M(\text{siloxane}) + M(\text{diene})] + 2 \times M(\text{epoxy component}).$$

Thus, for oligomer **IIa**:

$$M = 2 \times 208.48\,\text{g/mol} + 142.20\,\text{g/mol} + 5.65 \times 350.68\,\text{g/mol} + 2 \times 124.18\,\text{g/mol} = 2770\,\text{g/mol}$$
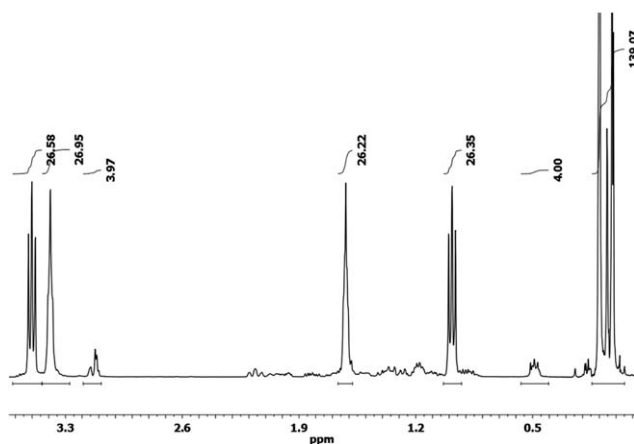
Figure 4 shows the inverse-gated ^{29}Si-NMR spectrum of telomer **IIa**.

The strong signal at 5.80 ppm was assigned to the Si atoms directly bonded to carbon atoms in the oxyalkylene spacer group. The strong signal at -20.9 ppm is produced by the Si atoms located between two other silicon atoms in the polymer chain. The signal at 7.4 ppm is assigned to the Si atoms at the very ends of the oligomer, linked to the group containing the epoxy moiety (epoxy-Si—O—Si—). The low-intensity signals at -21.2 and $\overline{5.67}$ ppm can be assigned to the silicon atoms in immediate vicinity to the very last silicon atoms (epoxy-Si—O—$\underline{\text{Si}}$—O—Si— and epoxy-Si—O—Si—O—$\underline{\text{Si}}$—).

Figure 5 shows the ^{1}H-NMR spectrum of oligomer **IIc**.

Photoinitiated cationic polymerization

As noted at the outset of this article, there is considerable interest in epoxy-functional monomers and oligomers that undergo rapid photoinduced cationic polymerization and also give good mechanical and thermooxidative properties. It was, therefore, particularly interesting to us to evaluate the rates of the

Figure 3 ^{1}H-NMR spectrum of **IIa**.

TABLE II
Assignment of ^{1}H-NMR Signals and Determination of the Chain Lengths for Oligomer IIa

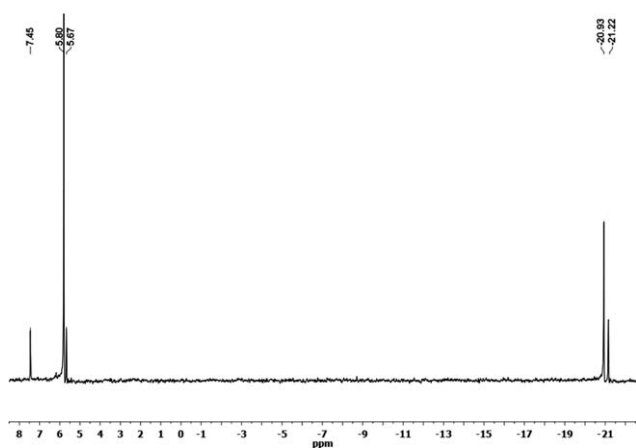| Group	Signal (ppm)	Integral	Degree of polymerization (m)
Si—CH$_3$	0.05	139 =18 m + 36	5.73
Epoxy—CH$_2$—Si	0.5	4	–
CH$_2$—Si	0.99	26.35 = 4 m + 4	5.59
CH$_2$	1.62	26.22 = 4 m + 4	5.55
Epoxy—CH	3.12	4	–
CH$_2$—O	3.39	26.95 = 4 m + 4	5.74
CH$_2$O	3.50	26.58 = 4 m + 4	5.65

Figure 4 Inverse gated ^{29}Si-NMR spectrum of oligomer **IIa**.

photopolymerizations of several representative oligomeric monomers prepared during the course of this investigation to determine whether relationships between their structures and reactivity could be established. In this investigation, the rates of photopolymerization were measured using optical pyrometry. This method involves following the course of the temperature of a monomer or oligomer sample during a photopolymerization in real time with an infrared camera (optical pyrometer). The greater the rate of increase in the temperature of the sample, the more reactive the monomer or oligomer.

As a first step in this study, three different onium salt cationic photoinitiators were tested in the photopolymerization of telomer **IIa**. Figure 6 shows the
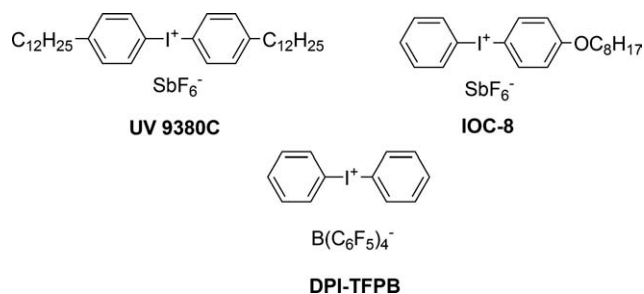

Figure 6 Structures and abbreviations for the photoinitiators used in this study.

structures and short-hand designations for the three different diaryliodonium salt cationic photoinitiators. Photoinitiator **UV 9380C** was used as 50% solution in propylene carbonate.

Figure 7 shows a study of the course of the polymerization of oligomer **IIa** with 2 wt % of the three different photoinitiators as determined by optical pyrometry.

The best results were obtained with **UV 9380C**, which is a very lipophilic photoinitiator having good solubility in the oligomer **IIa**. **IOC-8** is a somewhat more polar photoinitiator and less soluble in **IIa**. The borate initiator, DPI-TFPB, is even less soluble and, as a result, displays very poor photoinitiation activity. With **UV 9380C** and **IOC-8**, soft, elastic, and transparent rubber-like films were obtained after photopolymerization. When the borate initiator was used, inhomogeneous, red inclusions of undissolved photoinitiator were observed within the polymer film. Because of the overall better performance of
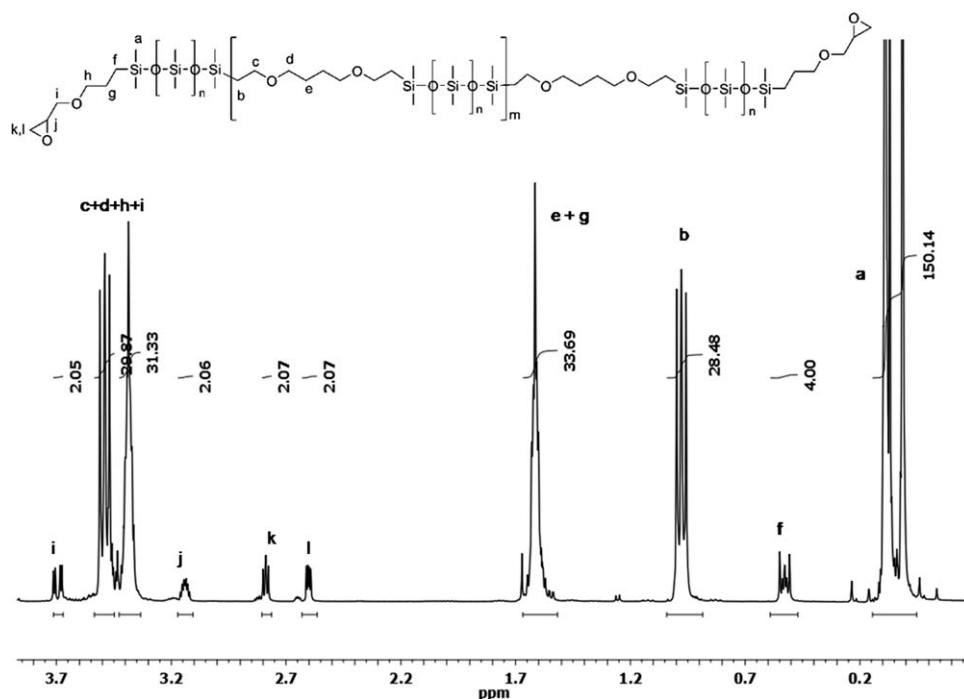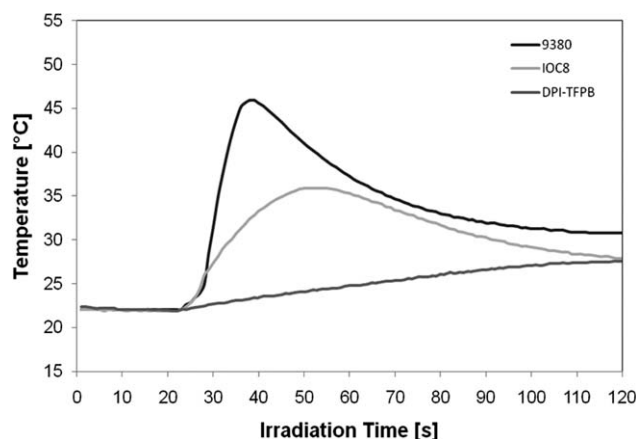

Figure 5 ^{1}H-NMR spectrum of **IIc**.

Figure 7 Progress of photopolymerization of **IIa** with different photoinitiators at a light intensity of 2340 mJ/cm² min.

UV 9380C, this photoinitiator was used in all subsequent photopolymerization studies.

Figure 8 shows a study of the effect of the variation in the amount of photoinitiator **UV 9380C** used in the UV-induced crosslinking polymerization of **IIa**.

Because there was very little difference in the photopolymerization rates using 3 and 2 wt % **UV 9380C** photoinitiator and because 1% gives somewhat lower photopolymerization rates, 2 wt % photoinitiator **UV 9380C** were used in all subsequent photopolymerization experiments.

Figure 9 shows a study of the reactivities of the six oligomers **IIa–IVb** bearing epoxycyclohexane terminal groups with different siloxane lengths and different organic linking groups.

The most rapid rate of temperature increase along with the highest ultimate sample temperature was observed with the oligomer, containing HexMTS as a short siloxane block and triethylene glycol divinyl ether as the organic spacer (**IIIa**). It is likely that the
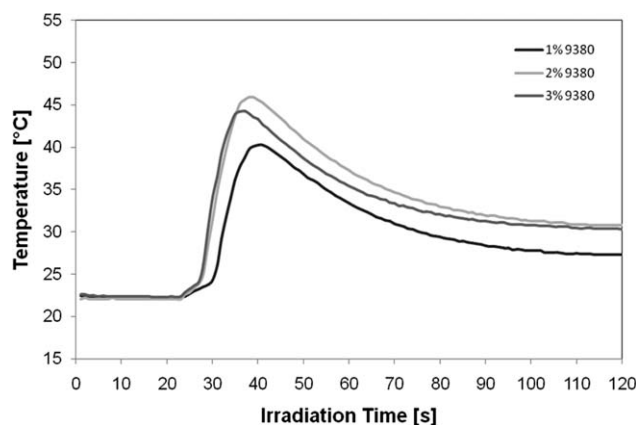

Figure 8 Variation of the amount of **UV 9380C** used in the photopolymerization of **IIa** (all concentrations are given as weight percent).
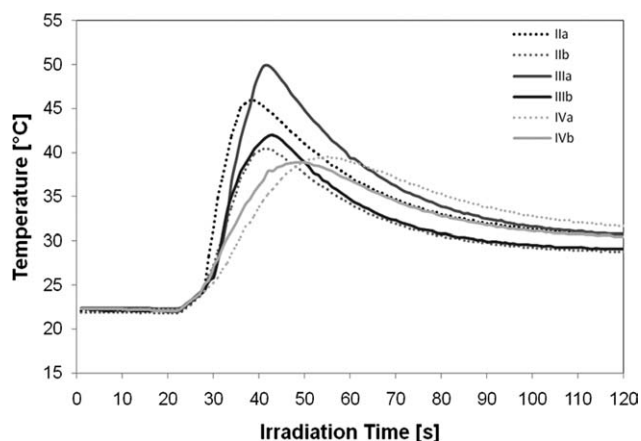

Figure 9 Comparison of cationic photopolymerizations of the six difunctional epoxycyclohexane monomers **IIa–IVb** with different siloxane lengths and different organic linking groups.

polarity of the triethylene glycol building block leads to a better solubility of the ionic photoinitiator, and consequently, fast polymerization was observed. When 1,4-butandiol divinyl ether was used as the organic linking group in combination with HexMTS as the siloxane unit (**IIa**), polymerization was somewhat slower due to the decrease in polarity and resulting poorer photoinitiator solubility. When a longer siloxane chain (PDMS) was used, the photopolymerization was also slowed due to a further decrease in the polarity of the polymer and thus poorer solubility of **UV 9380C**. Thus, **IIIb** that contains both, triethylene glycol and PMDS units was less reactive than its HexMTS analogue **IIIa**, but faster than the very nonpolar **IVb**, which contains the aromatic ring as a spacer group in the chain. As already observed for the short-siloxane-containing systems **IIIa** and **IIa**, the polymerization rate decreased when 1,4-butandiol divinyl ether (**IIIb**) was used instead of triethylene glycol divinyl ether (**IIIb**) as the diene component. The very nonpolar oligomers containing 1,3-diisopropyl benzene units in combination with HexMTs (**IVa**) and PDMS (**IVb**) displayed the lowest reactivity.

In summary, the rate of polymerization increases with increasing polarity of the oligomer. The polarity decreases in the order: **IIIa** > **IIa** > **IIIb** > **IIb** > **IVa** > **IVb**.

In all cases, a short induction period was observed. We suggest that this may be due to the presence of small amounts of basic or nucleophilic impurities that inhibit the cationic ring-opening polymerization. The induction period is the longest for those telomers with the poorest reactivity. In the oligomers **IVa** und **IVb**, a competing light absorption due to the aromatic rings present in the oligomer could also contribute to the observed low rates of polymerization.
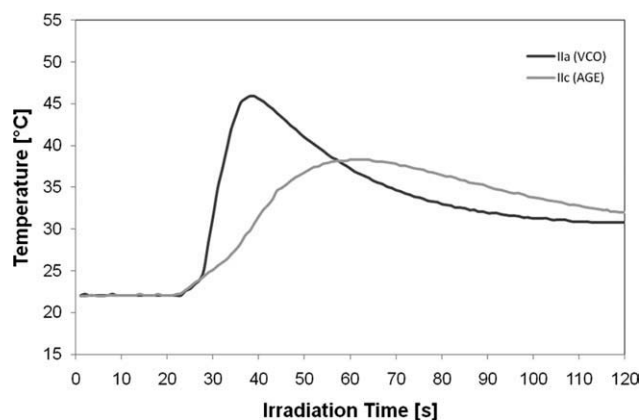
Figure 10 Comparison of epoxycyclohexyl- and glycidyl ether-terminated HexMTS-1,4-butandiol divinyl ether oligomers **IIa** and **IIc**.

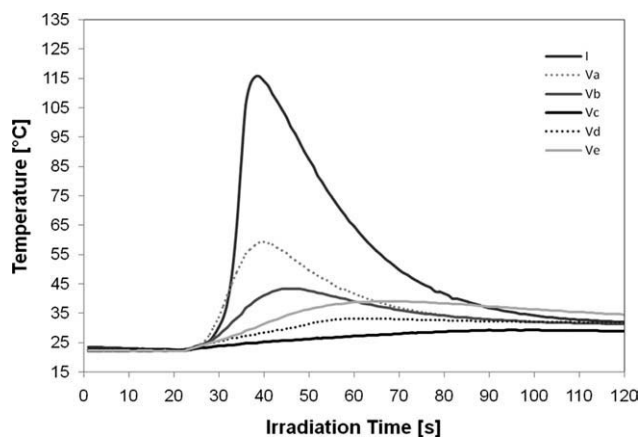**Figure 11** Comparison of difunctional hybrid silicones with different siloxane lengths using 1,9-decadiene as the organic spacer.

In Figure 10, the reactivity of the epoxycyclohexyl- (**IIa**) and glycidyl ether-terminated (**IIc**) telomers derived from HexMTS with 1,4-butandiol divinyl ether spacers is compared.

In accord with the data already described in literature,[6] the epoxycyclohexyl-terminated oligomer **IIa** is much more reactive than its glycidyl ether-terminated analogue **IIc**. We attribute the rather poor reactivity of this and other glycidyl ethers in photo-induced and thermally induced cationic polymerizations to two factors. First, the ring strain of the glycidyl ether is lower than in the epoxycyclohexyl functional system. Second, the presence of the two oxygen atoms of the glycidyl ether moiety provides a means for the stabilization of the protonated species through simultaneous coordination to both oxygen atoms via the formation of a pseudo five-membered ring.

The rates of photopolymerization $R_p/[M_0]$ for the six epoxycyclohexyl-terminated oligomers **IIa–IVb** and the glycidyl-terminated oligomer **IIc** are given in Table III. They were determined from the linear portions of the slopes of the irradiation time/temperature curves depicted in Figure 9. Previously,[14] we have demonstrated that there is a direct correlation between the $R_p/[M_0]$ values determined by OP

TABLE III
Rates of Polymerization ($R_p/[M_0]$) for the Six Epoxycyclohexyl-Terminated Oligomers IIa–IVb and the Glycidyl Ether-Terminated Telomer IIc

Oligomer	Rate of polymerization $R_p/[M_0]$ (°C/s)
IIa	2.83
IIb	1.56
IIIa	3.00
IIIb	1.98
IVa	1.05
IVb	0.97
IIc	0.73

and by real-time infrared spectroscopy measurements. The order of the rates is as expected, with the highest polymerization rate for the most polar oligomer and the lowest rate for the least polar one.

Figure 11 shows a comparison of the reactivity of **I** with five difunctional hybrid silicones **Va–Ve** with 1,9-decadiene as the organic spacer and different siloxane spacer lengths, having either epoxycyclohexyl or glycidyl ether functional groups.

The most rapid rate of temperature increase along with the highest ultimate temperature was observed with oligomer **I**, possessing a very short difunctional siloxane with epoxycyclohexyl end groups. The most reactive hybrid silicone was **Va** with a molecular weight of ~1500 g/mol bearing epoxycyclohexyl end groups. Increasing the silicone character of the system by using a longer siloxane unit decreases the rate of the photopolymerization (**Vb**). The same telomer containing glycidyl ether end groups (**Ve**) showed a further substantial reduction in the photopolymerization rate. When the chain length, and thus the molecular weight, was further increased, very low rates of polymerization were observed due to the very low concentration of epoxy groups present in the oligomers (**Vc** and **Vd**).

The rates of polymerization $R_p/[M_0]$ for **I** and the five hybrid silicone oligomers **Va–Ve** are given in Table IV. These values were determined from the linear portions of the slopes of the irradiation time versus temperature curves depicted in Figure 11.

The order of the polymerization rates is as expected, with the highest rate observed for the oligomer with the shortest polymer chain and very low rates for the longer polymer chains. This is reasonable, because the density of the epoxy-functional groups decreases in the same order (**I** $\gg$ **Va** > **Vb** > **Vc**). It is noteworthy that the very long hybrid silicone telomer, **Vd**, containing PDMS as the siloxane building block was slightly more reactive than its

TABLE IV
Rates of Photopolymerization for I and Telomers Va–Ve

Oligomer	Rate of polymerization $R_p/[M_0]$ (°C/s)
I	18.97
Va	3.68
Vb	1.45
Vc	0.25
Vd	0.43
Ve	0.54

HexMTS analogue **Vc**, probably due to solubility effects. Despite its lower molecular weight, the glycidyl ether-terminated system **Ve**, containing 1,9-decadiene, was slightly less reactive than its 1,4-butanediol divinyl ether analogue **IIc**. Again, this is apparently due to the better solubility of the photoinitiator in the ether-containing oligomer **IIc**.

Photopolymerized films of **I** are hard and brittle. In contrast, the photocrosslinked polymer films of **Va**, **Vb**, and **Ve** are soft, elastic, rubber-like transparent materials. In the case of oligomer **Vd**, a translucent, very soft but completely crosslinked film was obtained. For oligomer **Vc**, incomplete crosslinking was observed, leading to a sticky gel.

CONCLUSIONS

Twelve hybrid silicone oligomers with different silicone characters and different organic linking groups were prepared via the platinum-catalyzed polyhydrosilylation of α,ω-dihydrosiloxanes and α,ω-dienes and further functionalized with VCO or AGE. For a broad variation of the properties of the oligomers with respect to polarity, structure, and molecular weight, we chose 1,4-butanediol divinyl ether, triethylene glycol divinyl ether, 1,3-diisopropenyl benzene, and 1,9-decadiene as the organic spacer groups. The silicone content was varied through the use of two different siloxane building blocks, HexMTS and α,ω-dihydropoly(dimethylsiloxane) (MW = 580 or 680 g/mol). In the presence of a lipophilic cationic photoinitiator, the epoxy-functionalized hybrid silicones were cured to give soft, elastomeric, and transparent films. The course of curing was monitored using optical pyrometry. It was determined that the rate of photopolymerization increases with the increasing polarity of the oligomers, possibly due to the better solubility of the ionic photoinitiator. When the molecular weight of the oligomers was varied, the highest polymerization rate was observed for the shortest polymer chain. Furthermore, when identical hybrid oligomers were compared having either epoxycyclohexyl or glycidyl ether functional end groups, it was observed that the rate of polymerization of those oligomers bearing glycidyl ether end groups was substantially lower than that of their counterparts bearing epoxycyclohexyl groups.

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