Photocrosslinking of Silicones. Part 13. Photoinduced Thiol-Ene Crosslinking of Modified Silicones

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PHOTOCROSSLINKING OF SILICONES. PART 13. PHOTOINDUCED THIOL-ENE CROSSLINKING OF MODIFIED SILICONES†

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ABSTRACT

The photoinduced radical crosslinking of α,ω-ene-terminated silicones (vinyl, vinyloxy, allyl, norbornenyl, etc.) with siloxanes containing pendant mercapto groups has been investigated by means of calorimetry, Raman and swelling measurements. The reaction enthalpy depends on the type of olefin. The values vary from 99.5 kJ/mol (hexenyl) to 209 kJ/mol (norbornenyl). The crosslinking rate is influenced by the type of α,ω-ene terminated silicone used and differs by a factor of 4.5 from the norbornenyl to the allyl product. The final degree of conversion of the double bonds is generally high. Using Raman techniques, one can show that nearly 100% of the thiol groups are consumed. The crosslinking is inhibited and terminated by oxygen. The inhibition period depends on the light intensity, the oxygen pressure, and the type of olefin. Using values of the inhibition time and reaction rate, one can estimate the relative efficiency of several radicals. The application of a modified

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swelling test allows us to estimate the formation of the network density as a function of exposure time, thiol content and type of silicone. The network density of the vinyl product is much higher than other products. Norbornenyl and allyl derivatives formed networks with the lowest cross-link density.

INTRODUCTION

The thiol-ene cure is one of the most efficient methods to produce highly crosslinked polymer networks. In recent years in silicone chemistry there has been a resurgent interest in the chemistry and technology of photocurable compositions derived from blends of alkene and thiol silicones. Several types of thiol-ene–silicones have been designed, not unlike the platinum addition cure system; see Fig. 1. The crosslinking chemistry involves the well-known radical addition of thiol across the double bond of the alkene. The initiating radicals are formed in a photochemical process. The cured products have excellent physical properties and are of commercial interest in a number of areas [2].

One of the distinct advantages of radiation curing is the speed of crosslinking. Currently a number of analytical methods are used to study the kinetics of photocuring (for instance, infrared spectroscopy for the decay of double bonds, Raman spectroscopy for the decay of double bonds and of the thiol groups, respectively, gravimetry for the formation of crosslinked products, calorimetry for the formation of heat, and swelling degree for the formation of the network).

In this paper we present results of our investigations on the photocrosslinking of α,ω-ene siloxanes with silicones containing pendant thiol groups. The crosslinking has been investigated by means of real-time measurements (calorimetry), Raman spectroscopy, and swelling measurements.
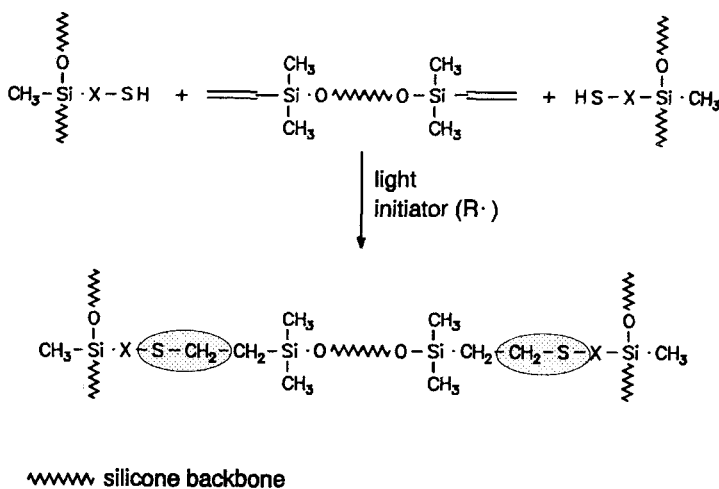

FIG. 1.   Vinyl–thiol system.

EXPERIMENTAL

Materials

All silicones were experimental products of Wacker-Chemie Burghausen (Germany). The synthesis of the ene-terminated dimethylsiloxane and the trimethylsilyl 3-mercaptopropylmethylsiloxy dimethylsiloxy copolymer has been described elsewhere [3]. In Table 1 all polymeric silicone materials used are described and typical data are given for the silicones. The double bond contents were determined iodometrically or by means of the H-NMR spectroscopy. Both methods result in approximately the same values. The reactive silicone derivatives were provided free from any inhibitors.

Several photoinitiators, which differ in their quantum yields of photolysis Φ_α, were used in the present kinetic investigations:

2-isopropoxy-2-phenyl acetophenone (benzoin isopropyl ether),

BIPE:

$\Phi_\alpha = 0.33$ [4]
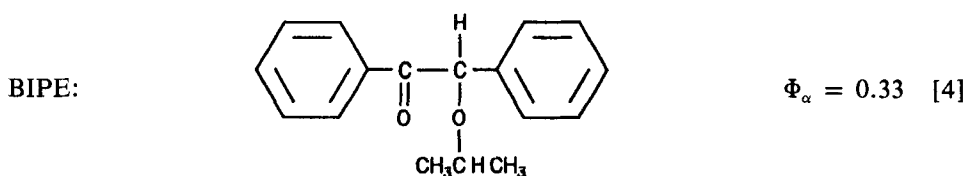
TABLE 1. Characteristic Data of the α,ω-ene-siloxanes

| | | | C=C content, g/mol | | Viscosity, |
Alkene	Endgroup X	Code	Iodometrical	H-NMR	mm^2/s
vinyl	—CH=CH$_2$	VI	6350	—	538
allyl	—CH$_2$—CH=CH$_2$	AL	4500	6300	400
hexenyl	—(CH$_2$)$_4$CH=CH$_2$	HE	5900	6200	361
allyloxyalkyl	—(CH$_2$)$_3$OCH$_2$CH=CH$_2$	AO	6500	6500	400
vinyloxyalkyl	—(CH$_2$)$_3$O(CH$_2$)$_4$OCH=CH$_2$	VO	—	6600	450
norbornenyl	exo/endo-	NO	5900	7000	294
norbornenylethyl	exo-	NE	4600	7000	378

thiol-silicone.

SH-content = 688 g / mol
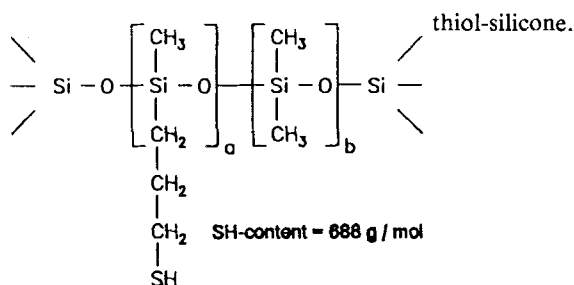
2,2′-dimethoxy-2-phenyl acetophenone (*benzil dimethyl ketal*), .

BDMK:

$\Phi_\alpha = 0.52$ [4]
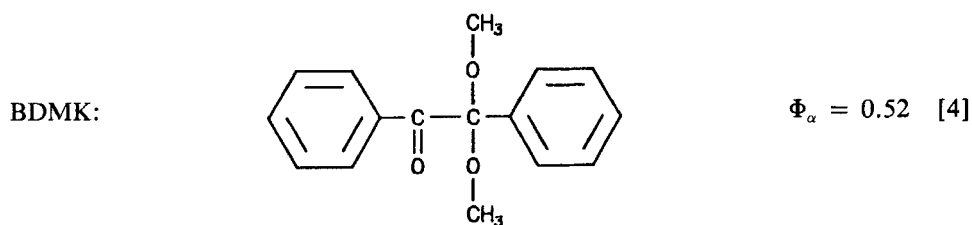
2,4,6-*trimethylbenzoyldiphenylphosphinoxid*,

TMBP:

$\Phi_\alpha = 0.80$ [4]
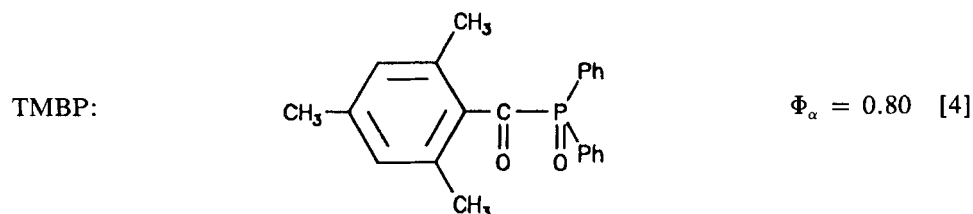
phenyl-(2-phenyl-1,3-dioxolan-2yl) methanone (*benzilmono(ethylene glykol) ketal*),

BGK:

$\Phi_\alpha = 0.11$ [4]
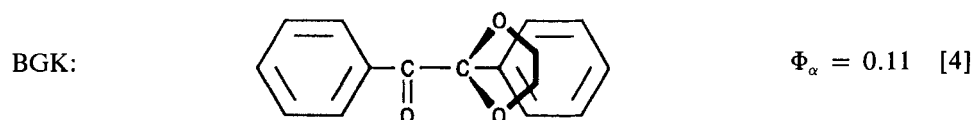
1-*hydroxy-cyclohexyl phenyl ketone*,

HCPK:

$\Phi_\alpha = 1.0$ [4]
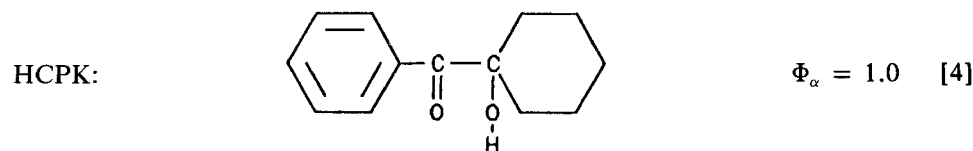
BIPE (Schönert Leipzig), TMBP (BASF), BDMK, and HCPK (Ciba Geigy) are commercial products. They were purified by recrystallization three times. The synthesis of BGK has been described elsewhere [5].

Measurements

The construction of the isoperibolic calorimeter was schematically described previously [6]. The system used is hard- and software modified (K. Rittmeier, Computeranwendungen Merseburg). The filter combination 1602 and 810 (Jenaer Glaswerke Schott und Gen.) was used to select the wavelength region 330 to 380 nm from the emitted light of a 200-W high-pressure mercury arc lamp (HBO 200, Narva). For measurements, 50 μL of mixed silicone derivative and photoinitiator

were dropped at the probe thermistor ($\oslash$ = 1 cm). 50 μL of polydimethylsiloxane NM 1-500 (Chemiewerk Nünchritz), containing the same amount of photoinitiator, served as a comparative sample. The sample thickness was about 640 μm.

All Raman spectra were recorded on a Bruker IFS 66 FT-IR spectrometer with a Raman adapter at 1 cm^{-1} resolution and averaged over 100 scans. A SPECAC variable temperature cell P/N 21.500 was used. The sample was placed between quartz plates, whereby a sample thickness of about 100 μm was realized. The thiol-ene-silicone initiator system was irradiated (15 min I_0 = 4.15 mW/cm^2) with a mercury arc lamp HBO 200 (NARVA Berlin) in the wavelength range from 330 to 380 nm outside the Raman set-up.

The technique for determining the swelling degree has been schematically described previously [7, 8]. 50 μL of the mixed silicone derivative and photoinitiator was coated on special paper ($\oslash$ = 1 cm, ZnO paper, Pecozet Z10, Papierfabrik Penig). The irradiation of the thiol-ene-silicone initiator system was carried out in the calorimetric set-up. During the swelling in toluene (25°C), the swollen silicone layer separates from the paper. The swelling equilibrium was reached in 20 minutes. The change in volume was measured by the change of the sample diameter.

Further experimental conditions are given in the legends to the tables and figures.

RESULTS AND DISCUSSION

Reaction Enthalpy

The heat flow generated by the crosslinking reaction is directly recorded as a function of the time. The rate of polymerization (see Eq. 1) and also the degree of conversion x (by integration of Eq. 1) can be derived at any moment from the heat flow value, provided that the standard heat of reaction is known for the system used.

$$R_p = -(dx/dt) \cdot [M]_0 = -(dH/dt) \cdot [M]_0/\Delta H_0 \qquad (1)$$

where $[M]_0$ is the initial monomer concentration, dH/dt is the heat flow value, and ΔH_0 is the standard heat of the addition reaction.

The reaction enthalpy of the chain process plays the key role in the determination of the conversion–time and reaction rate–time curves. Using the copolymerization parameters r_1 and r_2 of the alkene and the thiol (determined by means of the Q,e scheme of Alfrey and Price), it is obvious that the alkene comonomer does not undergo homopolymerization. The product of the copolymerization parameters (see Table 2) is lower than 10^{-3} (it was impossible to find all the structure parameters for the systems used; in those cases the parameters of olefins with a related olefinic structure were used). Such values are typical for an alternating copolymerization. These theoretical results are in agreement with experimental data from Klemm, which demonstrates a strong alternating structure in crosslinked thiol–vinyl [9] and thiol–allyl systems [10], respectively; see Scheme 1. Under these conditions the reaction enthalpy is given by the heat of the addition of a thiol group onto an olefin. These values, obtained by means of the Hess's law, are summarized in Fig. 2. The values illustrate that the reaction enthalpy of this crosslinking process depends on the type of olefin. The calculated values vary from 99.5 kJ/mol (HE) to 209 kJ/

TABLE 2.   Calculated Copolymerization Parameter Using the
Q,e-Schema

System	Q	e	Parameter r	$r_1 \cdot r_2$
Thiol[a]	1.6	2.44	0.053	3.5×10^{-4}
Si—CH=CH$_2$[b]	0.031	-0.38	6.6×10^{-3}	
Thiol	1.6	2.44	0.017	1.1×10^{-5}
Si—CH$_2$—CH=CH$_2$[c]	0.024	-0.94	6.3×10^{-4}	
Thiol	1.6	2.44	7.7×10^{-3}	0
C$_4$H$_9$—O—CH=CH$_2$	0.087	-1.2	3.1×10^{-4}	
Thiol	1.6	2.44	0.11	6.1×10^{-4}
1-Hexene	0.019	-0.28	5.5×10^{-3}	

[a]n-Hexanthiol.
[b]Trimethoxyvinylsilane.
[c]Allyltriethyoxysilane.

mol (NO, NE). These values are much larger than the experimental values of Klemm (allyl–thiol system $\approx$ 68 kJ/mol [10]) and Jacobine (norbornene–thiol system $\approx$ 100 kJ/mol [11]) measured during photoinduced crosslinking. However, in a later paper [12] Jacobine published some values of the limiting conversion x_∞ of norbornene–thiol systems (0.49–0.76), which show that the published heat value of 100 kJ/mol cannot reflect the complete conversion of double bonds. Our experimentally determined reaction heat (using a Perkin-Elmer DSC-7 and azobisisobutyronitrile as initiator) is lower than the theoretical value in all cases but much larger than the
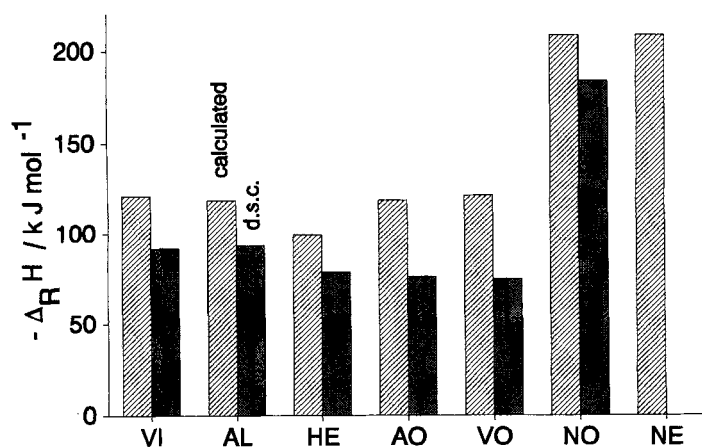

FIG. 2.   Calculated and measured reaction enthalpy.

published values from Jacobine and Klemm. A limiting conversion of <1 can explain this result.

The calculated reaction enthalpy shows that it is impossible to discuss the reactivity of the silicone systems by means of the measured reaction enthalpies only. Therefore a comparison of the individual reactivities has to be made to adjust the reaction rate.

Raman Results

The low double bond content in the system, the strong backbone absorption in the 700-900 cm^{-1} range, and the resulting weak absorption in the 1600 cm^{-1} range made it impossible to record the concentration of double bonds by IR. Raman studies show that the strong absorption of the silicone backbone is reduced in the 700-900 cm^{-1} range, but a double-bond absorption was not found in this range. On the other hand, an S—H vibration was detected at 2580 cm^{-1}; see Fig. 3.

No S—H vibration in this range can be detected in the alkene-thiol system after curing. Consequently, all thiol groups were consumed during irradiation. A complete consumption of the thiol groups was found for all systems.

Reaction Rate

Typical examples for conversion-time and reaction rate-time curves of the thiol-vinyl system (obtained by means of the calculated reaction enthalpy) are given in Fig. 4. For a more quantitative insight into the kinetics of these systems, the following kinetic parameters are useful: limiting conversion of double bonds (x_∞), maximal crosslinking rate (R_p^{max}), inhibition time (t_i). By means of these three parameters, one can describe the inhibition period, the growing phase of the crosslinking process, and the residual unsaturation content of the cured polymer.
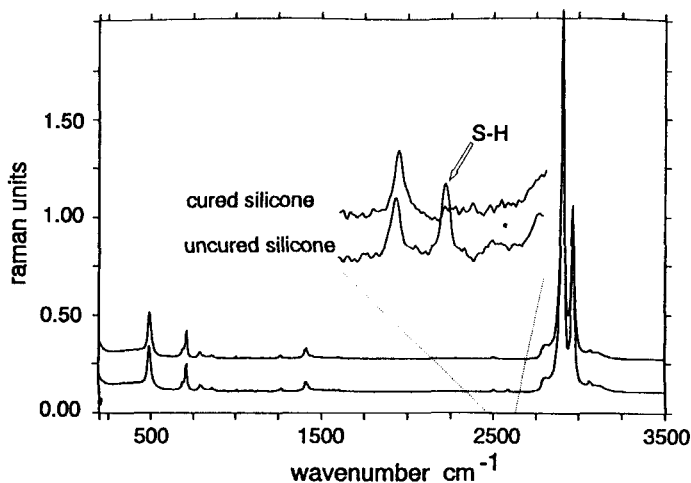

FIG. 3.   Raman spectra of cured and uncured silicone (norbornenylethyl-thiol system; initiator: BIPE; $c_{BIPE} = 5 \times 10^{-5}$ mol/g; $I_0 = 4.15$ mW/cm^2; irradiation time 15 minutes).
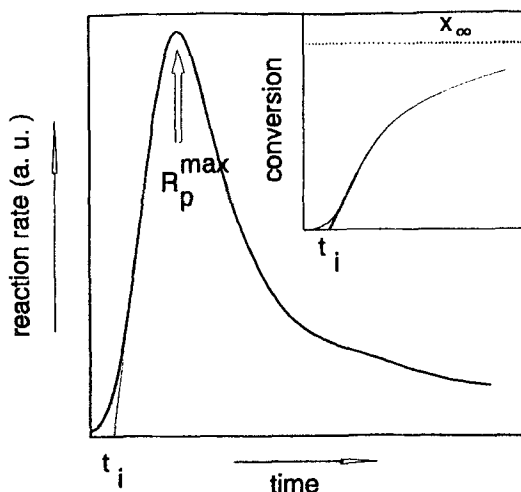
FIG. 4.   Schematic reaction rate- and conversion–time curves.

Due to the specific kinetic situation in highly viscous silicones, Eq. (2a) has to be used to describe the rate of the photocrosslinking process (R_p) under constant irradiation:

$$R_p = -[M]_0 \cdot dx/dt = k(x) \cdot [M]^\alpha \cdot [S-H]^\gamma \cdot I_0^\beta \qquad (2a)$$

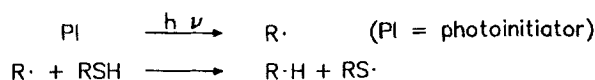$$R_p = -[M]_0 \cdot dx/dt = k'(x) \cdot [M]^\alpha \cdot I_0^\beta \qquad (2b)$$

where x is the conversion of double bonds, $k(x)$ and $k'(x)$ are conversion-dependent quantities, $[M]_0$ is the beginning double-bond concentration in the silicones, $[M]$ is the double-bond concentration in the silicones, $[S-H]$ is the thiol concentration of the system, I_0 is the intensity of the incident light, and α, β, and γ are exponents.

The reduced Eq. (2b) is identical with the equation of photoinduced radical polymerization [13, 14]. Such relations are expected when the light intensity determines the initiation rate of the polymerization process. Insights into the termination mechanism are given by means of the light intensity exponent β. The following relationships hold: $\beta = 1$ reflects a first-order termination, $0.5 \leq \beta \leq 1$ indicates a combined first- and second-order termination, $\beta = 0.5$ is typical for a second-order termination step, and $\beta < 0.5$ is typical for a combined second-order and primary radical termination.

The plot of R_p vs the incident light intensity (see Fig. 5) demonstrates a linear relationship between the light intensity and the reaction rate, and indicates a β-value of 1. Contrary to our results, Morgan [15] reported in an early work a β-value of 0.5 (allyl isocyanate–polythiol system) under no defined atmospheric conditions. However, $\beta = 1$ is typical for a first- or pseudofirst-order termination reaction. Monomolecular termination reactions are: inclusion of the growing radical, diffusion-controlled termination, and pseudofirst-order termination with oxygen.

In the absence of air, a light intensity exponent β of approximately 0.5 was found for photocrosslinking, typical for a second-order termination process. This

initiation:

$$PI \xrightarrow{h\nu} R\cdot \qquad (PI = photoinitiator)$$

$$R\cdot + RSH \longrightarrow R\cdot H + RS\cdot$$

propagation:

$$RS\cdot + \rangle\!\!=\!\!\langle_X \longrightarrow RS\!-\!\!\langle\cdot_X \qquad (P\cdot)$$

$$P\cdot + RSH \longrightarrow P\cdot H + RS\cdot$$

$$P\cdot + \rangle\!\!=\!\!\langle_X \!-\!/\!/\!\longrightarrow \quad r_1 \cdot r_2 < 0.001; \text{ no homopolymerization}$$

termination:

$$P\cdot \text{ or } RS\cdot \xrightarrow{+O_2} \text{peroxy radicals} \quad (\beta = 1)$$
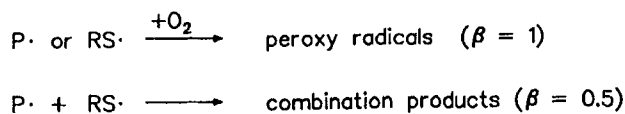
$$P\cdot + RS\cdot \longrightarrow \text{combination products} \quad (\beta = 0.5)$$
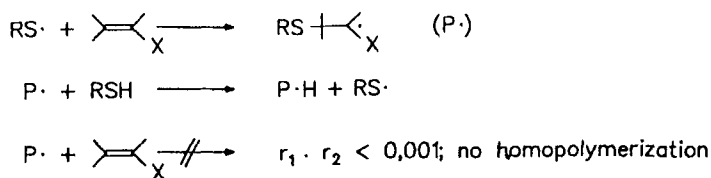
SCHEME 1.

means that the reaction of radicals with oxygen causes pseudofirst-order kinetics; see Scheme 1. A change of the light intensity exponent under air and inert conditions was observed in all the systems used. These results are in agreement with the insights of Szmant and coworkers [16] that dissolved oxygen is incorporated into the polymer by a complex series of steps.

In Table 3 the kinetic values of all a,ω-ene siloxanes used are summarized. The table illustrates that the reaction rate (reduced reaction rate values $(R_p/[M]_0)$ were used to eliminate the differences of the $[M]_0$ value) is influenced by the type of α,ω-ene terminated silicone. The values vary by a factor of 4.5 from the norbornenyl
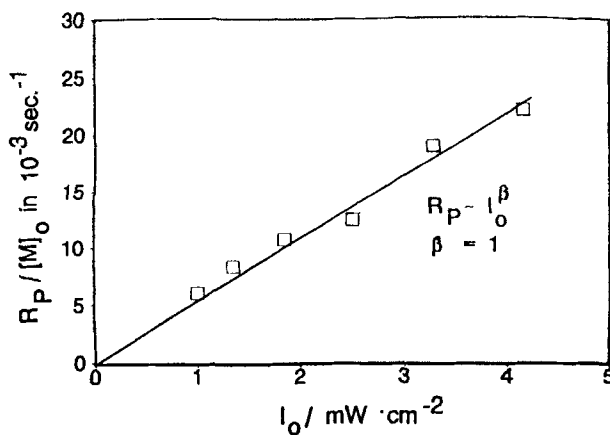

FIG. 5.   Thiol–vinyl system (initiator: BIPE; $c_{BIPE} = 5 \times 10^{-5}$ mol/g, air).

TABLE 3.   Characteristic Points of the Thiol-Ene Crosslinking (initiator: benzoin isopropyl ether; [initiator] $= 5 \times 10^{-5}$ mol/g; light intensity: 4.15 mW/cm^2)[a]

Type	$R_p^{max}/[M]_0$ $[10^{-3}\,s^{-1}]$	x_∞	Φ	Φ/Φ_α	t_i, seconds
Vinyl	22.0	0.98	28	85	11.5
	32.0	0.88	41	124	2.3
Allyl	14.0	0.42	20	61	6.6
	11.3	0.72	16	49	3.9
Hexenyl	20.6	0.60	29	88	6.5
	19.2	0.76	27	82	3.0
Allyloxyalkyl	5.8	<0.2	7.4	22	6.7
	5.4	1.00	6.9	21	6.2
Vinyloxyalkyl[b]	20.0	1.00	25	76	4.9
	21.7	0.90	27	82	0.2
Norbornenyl	26.2	0.56	36	109	1.9
	24.4	0.49	34	103	0.7
Norbornenylethyl	24.3	0.52	42	127	1.9
	27.3	0.69	47	142	0.9

[a]First value under air, second value by 10 mbar.
[b]Second value by 17 mbar.

to the allyl product and 1.2 from the norbornenyl to the vinyl derivative. The limiting conversion is generally high. From the reaction rates the relative reactivity is calculated: norbornenyl ~ norbornenylethyl > vinyl > hexenyl > vinyloxy > allyl > allyloxy.

On the other hand, the measured inhibition time is not in agreement with these reactivities. To describe the kinetics it is useful to classify the process into inhibition period and reaction rate. The order of the above reactivity is in agreement with the results of Jacobine (norbornene (10) > butyl vinyl ether (1) > phenyl allyl ether (0.3); relative rate of reaction [11]). Nevertheless, the exact data are not in good agreement.

$$\Phi = R_p/I_{abs} = R_p/\eta_{abs} \cdot I_0 \qquad (3)$$

where Φ is the quantum yield of monomer decay, I_{abs} is the intensity of the absorbed light, and η_{abs} is the part of the absorbed light.

By means of the quantum yield of monomer decay (Φ, see Eq. 3), it is possible to prove the chain process of double-bond decay. In Table 3 the Φ values of all the systems initiated with BIPE are outlined. In all cases for Φ and the kinetic chain length (Φ/Φ_α, where Φ_α is the quantum yield of the initiator photolysis), values $\gg 1$ were found. The limiting value for a chain process is 2 (two radicals are formed during the initiator photolysis, and both radicals can hypothetically initiate the crosslinking reaction). The measured values confirm a chain process for the crosslinking reaction (see also Ref. 15). Photoactivation of every single step was not found (see Ref. 10).

The kinetics of radical crosslinking correspond to a thermal reaction with the exception of the initiation step. According to Eq. (2b), the dependence of R_p upon I_0 can only be deduced from the rate of the beginning of radical formation. Under this assumption, Eq. (2c) can be formulated:

$$R_p = k''(x) \cdot [M]^\alpha (\eta \cdot \Phi_\alpha \cdot \eta_{abs} \cdot I_o)^\beta \tag{2c}$$

where Φ_α is the quantum yield of the initiator photolysis, η is the initiation efficiency, and $k''(x)$ is a conversion-dependent quantity.

According to Eq. (2c), the crosslinking rate of the silicones investigated must be correlated to the quantum yield of the photoinitiator used. Provided that α and β are of the order of 1 and η_{abs} is the same for all the photoinitiators used, which was experimentally proved under air, Eq. (4) can be formulated [4]:

$$(R_p^1 + R_p^x)/R_p^1 = 1 + \eta^x \cdot \Phi_\alpha^x / \eta^1 \cdot \Phi_\alpha^1 \tag{4}$$

where R_p^1 and R_p^x are the maximal crosslinking rates initiated by the reference photoinitiator 1 (BIPE) and initiator x, Φ_α^1 and Φ_α^x are Φ_α values of the initiators 1 and x, and η^1 and η^x are the initiation efficiencies of the initiators 1 and x ($\eta^1 = 1$ by definition).

This relationship is given in Fig. 6 for several photoinitiators. From this slope it is possible to calculate a relative initiating efficiency of the primary radicals (η) of several photoinitiators. The photolysis of these initiators gives the benzoyl radical in all cases. If only the aroyl radical causes initiation, differences in initiation behavior are not to be expected. This can be explained only by the effect of the radical X˙, which also initiates thiol–ene crosslinking. Values larger than 1 (BDMK) indicate that both radicals initiate crosslinking. Values lower than 1 (TMBP) show that only the radical X˙ initiates the step-by-step reaction. H-abstraction from thiol is the kinetically controlled first step of the primary radicals. It is deduced from this assumption that the relative initiating efficiency describes the efficiency of H-abstraction only.
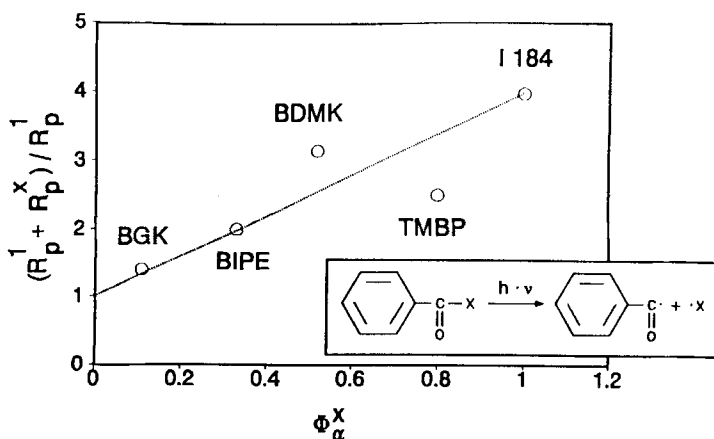

FIG. 6.   Plot of reaction rate vs quantum yield of initiator photolysis ($I_0 = 4.15$ mW/cm^{-2}; $\eta_{abs} = 0.55$ by 365 nm).

The thiol content must influence the efficiency of H-abstraction and also the reaction rate; see Eq. (2a). Figure 7 demonstrates that the reaction rate R_p is a function of thiol content. This rate increases with increasing thiol content. The largest R_p values are achieved in the range of stoichiometric mixtures. Beyond this range, one can observe that the reaction rate decreases with increasing thiol content. In a stoichiometric mixture, $\beta = 1$. On the other hand, for larger thiol contents, a β value of approximately 0.5 has been found, typical for a second-order termination process. We assume that this self-decelerated region is caused by the favored recombination of thiyl radicals under these conditions, where change in the crosslinking kinetics is combined with a decrease of the reaction rate.

In general, radical reactions are strongly influenced by oxygen. This effect is more important for silicone derivatives because oxygen is both freely soluble and exhibits a large diffusion coefficient in many silicones. Therefore, photo-induced crosslinking of silicone derivatives also strongly depends on the concentration of oxygen dissolved in the polymeric layer. On the other hand, it is well known that thiol-ene polymerization is not inhibited by the presence of oxygen [16, 17].

Qualitatively, the influence of oxygen in our systems can be expressed as an inhibition period. Polymerization starts only in that region of the layer in which oxygen has already been consumed. The experimental results do not agree with the statements of Jacobine and Szmant [16, 17]. The reaction rates of crosslinking are nearly the same at 1000 mbar and at 10 mbar. They differ only in the case of the VI systems, see Table 3 (the calculation of the reaction rate was carried out under the assumption of the addition of a thiol group on a double bond; the incorporation of oxygen into the polymer is not consider). From our results for the radical crosslinking of silicone acrylates, we know [13, 18] that the initiator radicals (R·) which are formed react with oxygen first, so oxygen is consumed during this scavenging reaction. The polymerization reaction will start as soon as the concentration of O_2 is sufficiently low and the condition of Eq. (5a) are realized. By combining these findings with our results, it follows that in thiol-ene systems the reaction will start
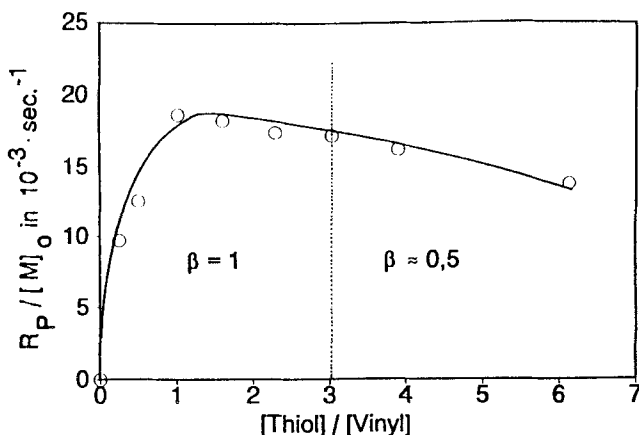

FIG. 7.   Reaction rate vs thiol content (vinyl-thiol system; initiator BIPE; $c_{BIPE} = 5 \times 10^{-5}$ mol/g; $I_0 = 4.15$ mW/cm^2).

when the conditions of Eq. (5b) are realized. The inhibition period reflects only the oxygen scavenging of the initiator radicals.

Radical polymerization:

$$k_{add} \cdot [R_i] \cdot [M] \geq k_{ox} \cdot [R^{\cdot}] \cdot [O_2] \tag{5a}$$

Thiol–ene system:

$$k_{ab} \cdot [R_i] \cdot [SH] \geq k_{ox} \cdot [R^{\cdot}] \cdot [O_2] \tag{5b}$$

k_{ox} is the rate constant of the radical scavenging by O_2, k_{add} is the addition rate constant on monomers, k_{ab} is the rate constant of hydrogen abstraction from a thiol group, $[O_2]$ is the oxygen concentration, $[SH]$ is the thiol concentration, and $[M]$ is the monomer concentration in the silicon layer.

It follows from Eq. (6) that the values of the inhibition period depend on the oxygen concentration and, at constant $[O_2]$, on the incident light intensity, respectively. Correlations between these parameters are given in Fig. 8, and they result in linear relationships for t_i vs $[O_2]$ and $1/I_0$. However, the linear curve in both parts of Fig. 8 do not intersect the origin. Presumably, further inhibiting processes occur, and therefore the ideal equation is not fully obeyed.

$$t_i = [O_2]/R_i = [O_2]/\eta \cdot \Phi_\alpha \cdot \eta_{abs} \cdot I_0 \tag{6}$$

where R_i is the rate of the start of radical formation and $[O_2]$ is the oxygen concentration.

Figure 9 shows the linear relationship of t_i vs $1/I_0$ for several alkene systems with different slopes. The photolysis of the initiator gives the benzoyl radical, which produces a thiyl radical by hydrogen abstraction from the thiol group. The effect of the thiol content on the inhibition time is neglected because the thiol content in all systems is approximately the same. The differences among the slopes can only be explained by the addition of the thiol radical on the double bond. The slopes give the relative addition efficiency of the thiyl radicals on different alkene groups.

In Fig. 10 the addition efficiency of thiol radicals on all the α,ω-ene siloxanes used are summarized. The figure illustrates that the efficiency is influenced by the type of α,ω-ene-terminated silicone used. The values vary by a factor of 5 on norbornenyl to the vinyl derivative. The results agree with flash photolysis studies of the addition of phenylthioradicals to a series of cycloalkenes, cyclodienes, and bicycloalkenes from Ito [19] which showed that [2.2.1] bicyclic olefins have a high affinity to add thiyl radicals.

Taking these findings into consideration, the norbornenyl derivative is the best system. On the other hand, the vinyl system has nearly the same reaction rate as the favored norbornenyl system, and the limiting conversion in the norbornenyl system is lower than in the vinyl system.

Network Characterization

The most important parameter for characterization of the networks is the network density ν_B. This value is a quantity of the concentration of network points per volume of the polymer network.
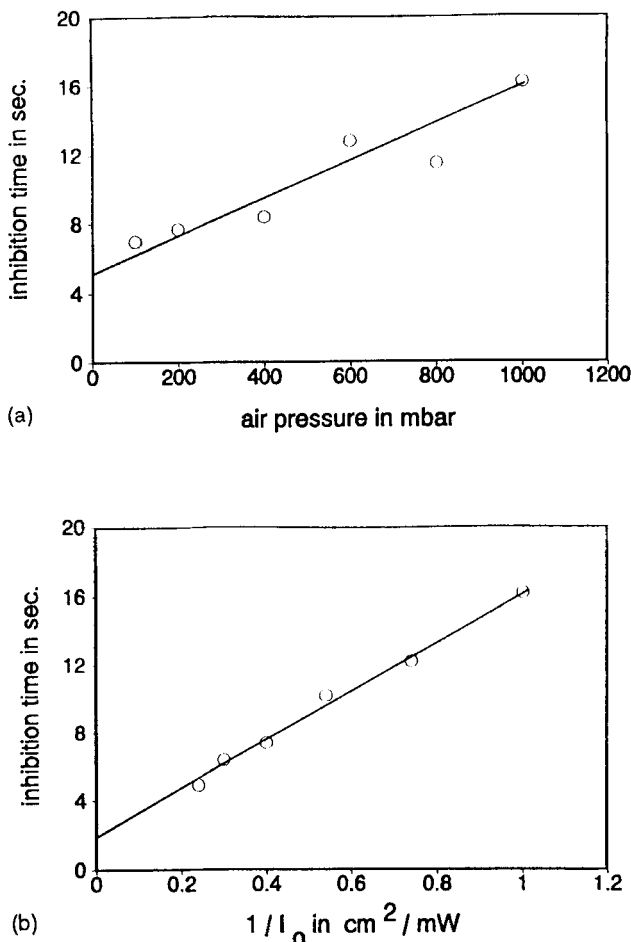
FIG. 8. Plot of inhibition time vs light intensity and air pressure [vinyloxy–thiol system; initiator: BIPE; c_{BIPE} = 5 × 10^{-5} mol/g; (a) p(air) = 1000 mbar, (b) I_0 = 1.0 mW/cm^2].

By means of the Flory–Rehner equation (Eq. 7), it is possible to estimate the density of the polymer network from the swelling degree Q (Eq. 8) if the χ parameter [7] is known. The swelling degree represents a relative value of the inverse network density [7] (Eq. 9). The swelling degree is defined as the ratio of the volume from the sample of the polymer network with and without solvent and is a function of the solvent used.

A plot of swelling degree versus reaction time of several thiol–ene systems is shown in Fig. 11. The swelling degree decreases with increasing reaction time. After a certain period of time, a limiting value can be found. The shape of the curve is nearly the same as the conversion–time curve; see Fig. 4.

Figure 12 shows a kinetic plot of the swelling degree versus the reaction time. We found a linear relationship. The formation of the network correlates with a
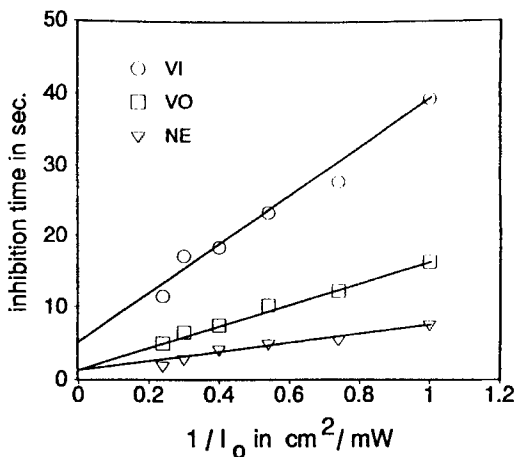
FIG. 9.   Plot of inhibition time light intensity for several ene systems (initiator: BIPE; $c_{BIPE} = 5 \times 10^{-5}$ mol/g; ene/thiol ratio $= 1$).

first-order law. The building of the network and the decrease of double bonds have the same kinetic law.

$$\nu_B = -\frac{\ln[1 - (1/Q)] + 1/Q + \chi/Q^2}{V_A^M(A/Q^{1/3} - B/Q)} \tag{7}$$

$$Q = (V_p + V_Q)/V_p = (d_{eq}/d)^3 \tag{8}$$

$$\log(\nu_b) \sim -\log(Q) \tag{9}$$

where V_A^M = mol volume of the swelling solvents; V_p = volume of the dry polymer network; V_Q = volume of the solvent in the swollen polymer network; d_{eq} = diame-
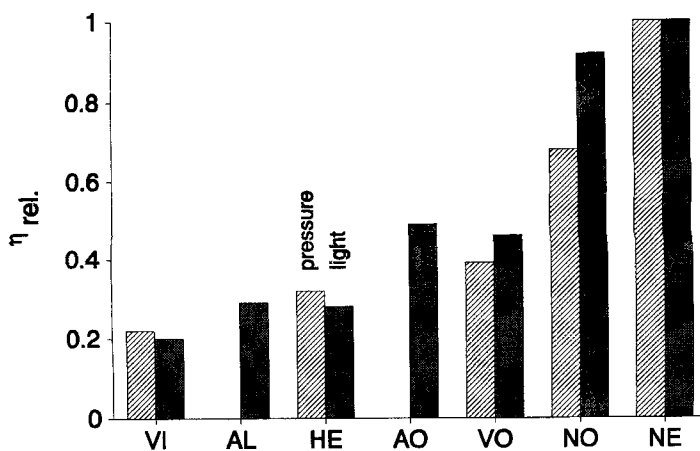

FIG. 10.   Relative addition efficiency of the thiol radicals on double bonds.
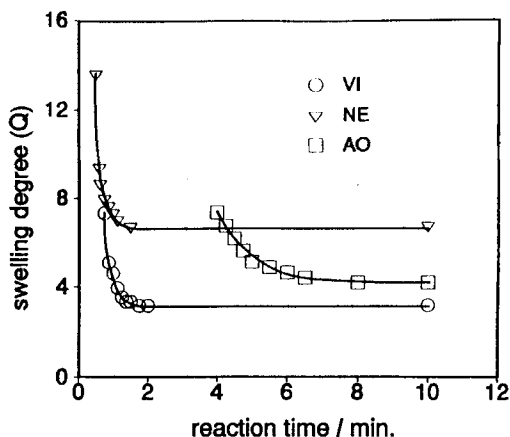
FIG. 11. Plot of swelling degree vs reaction time for several ene systems (initiator: BIPE; $c_{BIPE} = 5 \times 10^{-5}$ mol/g; ene/thiol ratio $= 1$).

ter of the swollen polymer sample; d = diameter of the dry polymer sample; A = a factor of the microstructure (for an affine network, $A = 1$; for a phantom network $A = 1 - 2/a$, where a = functionality; $A = 1/2$ for $a = 4$); B = a factor of the volume (for an affine model, $B = 2/a$; for a phantom model, $B = 0$); and χ = Huggin's parameter.

Furthermore, the alkene type plays an important role in efficient crosslinking. The rate of network formation for the norbornenyl and vinyl systems are nearly the same. The rate of the allyloxy product is the lowest of all. However, the figure also illustrates that the final network density of the norbornenyl system is lower than that of all other products. These results are in agreement with our kinetic experiments.

The thiol content influences the efficiency of H-abstraction and also the reaction rate. Figure 13 demonstrates that the swelling degree and the network density are both functions of the thiol content. The network density increases with increas-
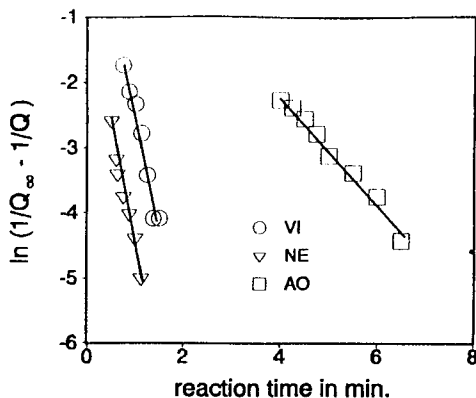

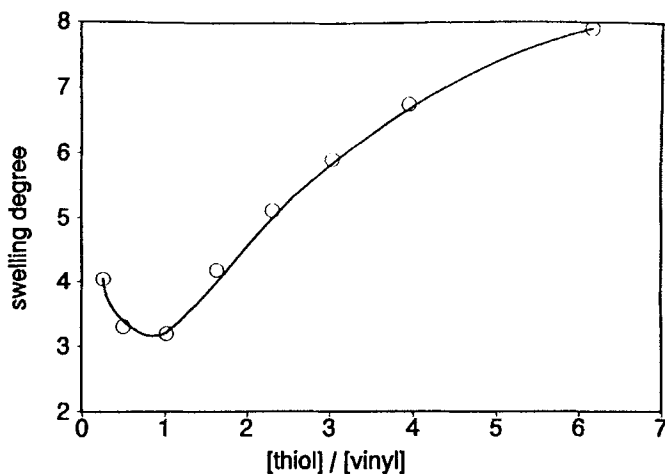FIG. 12. Kinetic plot of swelling degree vs reaction time.

FIG. 13. Plot of swelling degree vs thiol content (initiator: BIPE; $I_0 = 4.15$ mW/cm^2; irradiation time 15 minutes).

ing thiol content, and the highest values are achieved in the range of stoichiometric mixtures. Beyond this range the network density decreases with increasing thiol content.

CONCLUSION

The photoinduced radical crosslinking of α,ω-ene-terminated silicones (vinyl, vinyloxyalkyl, allyl, allyloxyalkyl, hexenyl, norbornenyl, norbornenylethyl) with siloxanes containing pendant mercapto groups has been investigated by means of calorimetry, Raman, and swelling measurements. The reaction enthalpy of the radical step-by-step chain process depends on the type of olefin. The values vary from 99.5 kJ/mol (hexenyl) to 209 kJ/mol (norbornenyl). The reaction enthalpy demonstrates that it is impossible to discuss the reactivity by means of the measured reaction enthalpies only.

The crosslinking rate is influenced by the type of α,ω-ene-terminated silicone used and varies by a factor of 4.5 from the norbornenyl to the allyl product. The final degree of conversion of the double bonds is generally high. By using the Raman-techniques, it can be shown that nearly 100% of the thiol groups are consumed.

The crosslinking of the silicone derivatives is inhibited and terminated by oxygen. Qualitatively, the influence of oxygen can be expressed as an inhibition period. Polymerization begins only in that region of the layer in which the oxygen has already been consumed. The reaction rates of crosslinking are nearly the same for 1000 and 10 mbar. They differ only in the case of the vinyl systems. The inhibition period depends on the light intensity, the oxygen pressure, and the type of olefin. By using values of the inhibition time and reaction rate, the relative efficiency of several radicals can be estimated.

The application of a modified swelling test allowed us to estimate the formation of the network density as a function of exposure time and thiol content and type of silicone. Under our conditions the network density obtained with the vinyl product is much higher than with other products. Norbornenyl and allyl derivatives formed networks with lowest crosslink density.

ACKNOWLEDGEMENTS

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