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PHOTOCROSSLINKING OF SILICONES. PART XV. CATIONIC PHOTOCROSSLINKING OF α,ω,4-TERMINATED DISILOXANES†

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ABSTRACT

The photoinduced cationic crosslinking of α,ω-terminated disiloxanes (epoxy, vinyl ether, propenyl ether) has been investigated by means of Real-Time IR spectroscopy. A lipophilic iodonium salt and three lipophilic sulfonium salts were used as photoinitiator. The crosslinking rate is influenced by the type of α,ω-terminated disiloxane used and differed by a factor of more than 100 from the aliphatic epoxy to the vinyl ether derivatives. Moreover, the sulfonium salts were found to have a lower initiation efficiency than the

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†For Part 14, See Ref. 1

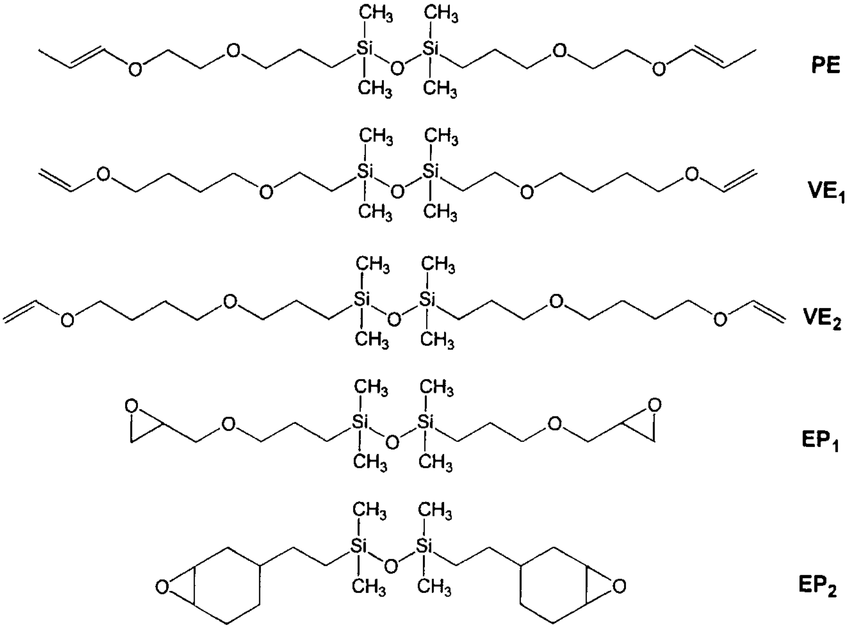
lipophilic iodonium salt in the various systems studied. These results are in good agreement with the quantum yield of proton formation in a hexamethyldisiloxane/dimethoxyethane mixture. The final degree of conversion is larger with the ene derivatives than with the epoxy derivatives. The application of a kinetic method allows us to estimate the rate constant of the termination step (k_t and for the propenyl derivative the rate constant of the propagation step k_P. The termination step can be described by means of a first order reaction. k_t was found to depend on the light intensity and the type of initiators used, whereas k_P is independent of the initiator used.

INTRODUCTION

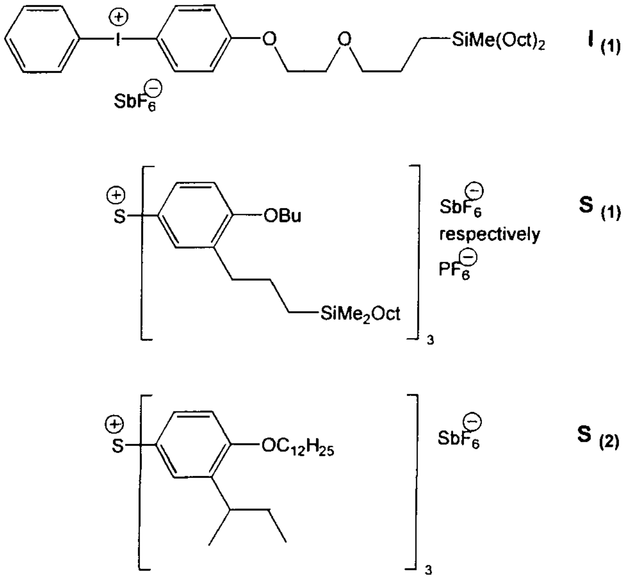
Vinyl ether and epoxy chemistry established more than 50 years ago has finally found its way into the radiation curing technology. Especially, vinyl ethers were known to be among the most reactive monomers in photocuring chemistry [2a]. In silicone chemistry, there has recently been a resurgent interest in the chemistry and technology of photocurable compositions derived from vinyl ether and epoxy silicones. Several types of silicones with vinyl and epoxy groups were designed [2-4] which differ in functionality, spacer group and monomer content. The crosslinking chemistry of such modified silicones involves the well-known cationic crosslinking/polymerization of vinyl ethers and epoxides. Basically, the silicone unit acts as an internal solvent. The initiating species, mainly protons, were formed in a photochemical process from onium type photoinitiators, which are dissolved in the silicones.

EXPERIMENTAL

The α,ω–terminated disiloxane EP_1, EP_2, PE, VE_1, VE_2 (see Scheme 1) and the lipophilic substituted onium salts $I_{(1)}$, $S_{(1)}$, and $S_{(2)}$ (see Scheme 2) were experimental products of WACKER-Chemie. The synthesis of the ene and epoxy terminated dimethyl siloxane and of the onium salts has been described elsewhere [5-8]. The purity of the technical onium salts is greater than 90%. The impurity consists of lipophilic substances caused by the synthesis. The epoxy content of the silicone derivatives were larger than 97% (NMR-spectroscopy). The reactions of the silicone derivative were inhibited by potassium hydroxide.



Scheme 1



Scheme 2

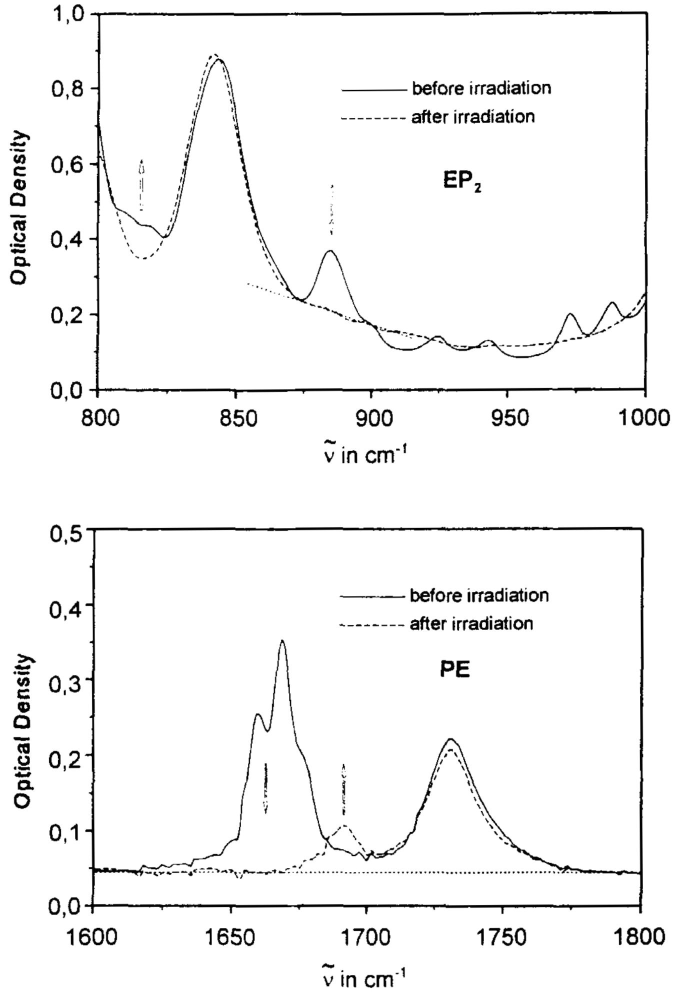


Figure 1. Changes in the IR absorption of EP_2 and PE after UV exposure using $S_{(2)}$ as photoinitiator ([initiator] = $5 \cdot 10^{-5}$ mol per gram of substituted disiloxane, $I_0 >$ 100 mW/cm^2; Δt = 4 minutes, temperature > 70°C).

The experimental set up of Real Time (RT) IR spectroscopy has been described in several recent papers [9-11]. The sample is placed in an IR spectrophotometer (PERKIN ELMER 781) chamber and exposed simultaneously to the polychromatic UV beam (medium pressure mercury lamp from HOYA) and to the analyzing IR beam. The sample is placed between two polypropylene layers to monitor the adhesive power of the sample after irradiation. The thickness of the layer is 12 μm, adjusted with a calibrated wire-wound applicator. The IR spectrometer was set in the absorbance mode and the detection wavelength fixed at a value where the monomer double bond exhibits a discrete and intense absorption. The following wavenumbers were used: 910 cm^{-1} (EP_1), 884.5 cm^{-1} (EP_2), 1676 cm^{-1} (PE), 1620 cm^{-1} (VE_1), and 1622 cm^{-1} (VE_2). The backround absorption on this wavelegth is approximately zero or was corrected by a baseline (base to base), see examples in Figure 1. The degree of conversion (x) can be calculated from:

$$x = 1 - [A_\lambda]_t/[A_\lambda]_o \qquad (1)$$

where $[A_\lambda]_0$ and $[A_\lambda]_t$ is the sample absorbance at the considered wavelength, before and after UV exposure, respectively. The rate of polymerization (R_P) can be determined at any time from the slope of the conversion vs. time curve recorded:

$$R_P = (\Delta x/\Delta t) \cdot [M]_0 \qquad (2)$$

where $[M]_0$ is the initial monomer concentration, and x is the double bond conversion after a given irradiation time.

The incident light intensity (I_0) at the sample position was measured by radiometry (INTERNATION LIGHT TL-390); it could be varied by means of an iris diaphragm.

RESULTS AND DISCUSSION

Monomer and Initiator Influence

Typical examples for conversion-time curves for the photopolymerization of the five α,ω- terminated disiloxanes studied are given in Figure 2. The influence of the type of photoininitiator used on the polymerization of VE_1 is shown in Figure 3. Table 1 summarizes the data obtained in terms of normalized rate of polymerization (R_P/I_0) and allows a quantitative comparison of the effect of both the type of functionalized disiloxane and the cationic photoinitiator on the polymerization kinetics.

It is generally acknowledged that the reaction rate and the final conversion of the epoxy products is lower than the rate and final conversion of the vinyl ether derivatives. Indeed, if the quantum yield of the initiator photolysis is the same for the various systems studied, the low reaction rate of the epoxy is likely to be due to a shorter kinetic chain length, which leads to a low final conversion. The reactivity of

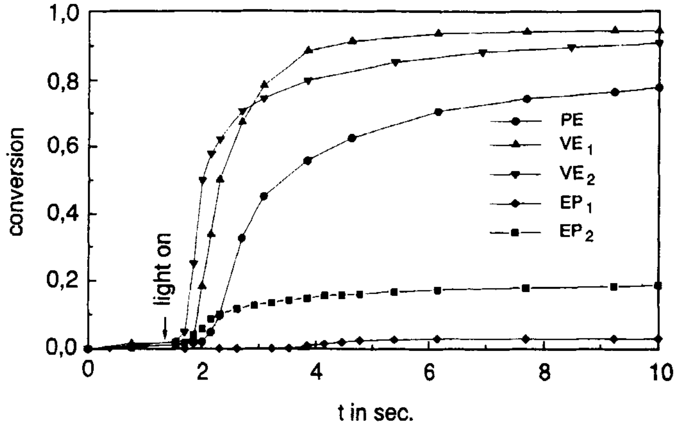


Figure 2. Conversion (x)/time curve for the photoinduced crosslinking of the α,ω-substituted disiloxanes with $S_{(1)}$ as photoinitiator ($S_{(1)}$ as hexafluoroantimonate, [initiator] = $5 \cdot 10^{-5}$ mol per gram of substituted disiloxane, I_0 = 86 mW/cm^2).

EP_1 is very low at room temperature. Nevertheless, at 65°C the polymerization is ten times faster. Moreover, in a given group, the reaction rate and final conversion also differ depending on the chemical structure of the telechelic oligomer. For instance, the polymerization of the ethylene oxide derivative EP_1 is slower than that of the cycloaliphatic derivative EP_2. A reaction ratio larger than 5 was measured for all photoinitiators and light intensities used. This is most likely due to the additional ring strain in the cycloaliphatic system that facilitates the cationic ring opening reaction [3, 12, 13]. Eckberg [3] found a reaction ratio of 8.5 between the two both epoxy monomers. This value is on the same order as the ratio 6.4 determined by Crivello [13] using (4-octyloxyphenyl)phenyl iodonium hexafluoro antimonate as photoinitiator.

Vinyl ethers are known to be among the most reactive monomers in photocuring chemistry [14]. The reaction rate of all olefinic derivatives is more than double the value of the most reactive epoxy product (EP_2). The reactivity of the vinyl derivatives VE_1 and VE_2 being some what higher than that of the propenyl derivative (PE). This result is surprising because, in solution, the propenyl ethyl ether was found to be slightly more reactive than the corresponding vinyl ether [15]. Nevertheless, our RTIR-values agree well with DSC results measured previously by using $I_{(1)}$ as photoinitiator [5].

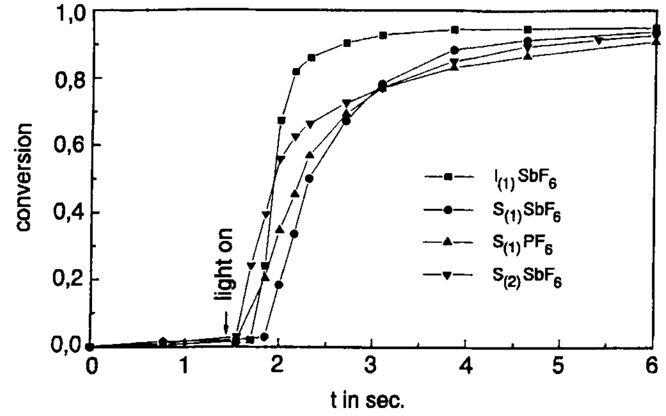


Figure 3. Conversion (x)/time curve for the photoinduced crosslinking of VE_1 with several photoinitiators ([initiator] = $5 \cdot 10^{-5}$ mol per gram VE_1, I_o = 81.3 mW/cm^2).

TABLE 1: Relative Reaction Rate (R_P / I_o) of Several Systems ([On^+X^-] = $5 \cdot 10^{-5}$ mol/g)

Siloxane	$I_o$in mW/cm^2	Rp /I_o in mol· cm^2/(mW· l·s)			
		$I_{(1)}SbF_6$	$S_{(1)}Sb_6$	$S_{(1)}PF_6$	$S_{(2)}SbF_6$
PE	162	0.03	0.02	0.01	0.02
VE_1	162	0.10	0.04	0.04	0.04
VE_2	129		0.05	0.02	0.01
EP_1	134	0.001	0.0002	0.0002	0.0002
EP_2	167	0.01	0.009	0.005	0.01

Qualitatively, the influence of the silicone functionality can be seen on the crosslinking rate as well as on the final conversion x_∞. At an incident light intensity of 63 mW/cm^2, the final conversion increases from 23% for EP_2 to 67% for PE and up to more than 90% for VE_1 and VE_2 (Table 2). Table 2 shows that the final conversion increases with increasing light intensity. Nevertheless, the low degree of conversion for the epoxy monomer EP_2 is not consistent with results reported from Crivello [16], which observed 90% conversion using (4-decyloxyphenyl) phenyl iodonium hexafluoroantimonate as photoininitiator (I_o = 15 mW/cm^2!). Contrary to

TABLE 2: Final Conversion x_∞ as a Function of the Light Intensity I_0 ($[On^+x^-]= 5\cdot10^{-5}$ mol/g)

I_0 in mW/cm^2	x_∞			
	EP_2	PE	VE_1	VE_2
63.0	0.23	0.67	0.90	0.94
61.8	0.25	0.72	0.90	0.95
56.5	0.25	0.68	0.85	0.91
37.5	0.21	0.67	0.80	0.87
22.0	0.14	0.45	0.31	0.24

these findings, we found such high conversion only at 135 mW/cm^2, (Figure 4). It is possible that the temperature in the layer differs between both experiments. Moreover, the low final conversion observed with the cycloaliphatic epoxide EP_2 can result from a lower reactivity of the used onium salt (Φ= 0.7 for (4-decyl-oxyphenyl)phenyl iodonium hexafluoroantimonate [16]; Φ_{H+} = 0.28; 0.15 and 0.21 for the hexafluoroantimonates of $I_{(1)}$, $S_{(1)}$ and $S_{(2)}$, respectively [17]). A fast consumption of the initiator can be excluded, than the initiator loss is lower than 20% at a quantum yield <0.3 (determined by RTIR-technique for benzoin isopropyl ether under similar irradiation conditions, at equal concentration and a similar quantum yield of initiator decay; [1]). Moreover, the sample thickness (which increases the absorbed part of the light) was four times higher in these experiments as given in this paper. The initiator decay differs greatly from the system described in [10], where a strong loss of the initiator (bis[4-(diphenyl-sulphonio-phenyl]-sulfide-bis-hexafluorophosphate) was observed during the crosslinking of a cyclo-aliphatic diepoxy monomer.

The reactivity of the various α,ω-terminated disiloxanes was also tested with several photoinitiators. The sulfonium salts $S_{(1)}$ and $S_{(2)}$ were found to have a lower initiation efficiency than $I_{(1)}$ in the various systems studied (Table 1). These results are in agreement with the quantum yield of proton formation in a hexa-methyldisloxane/dimethoxyethane mixture; Φ_{H^+} = 0.28; 0.15 and 0.21 for the hexafluoroantimonates of $I_{(1)}$, $S_{(1)}$ and $S_{(2)}$,respectively [17]. Moreover, using the sulfonium salt $S_{(1)}$, a larger efficiency was found for the PF_6^- counter ion than for SbF_6^- (Table 1), in full agreement with Tadatomi [18] and Crivello findings [13].

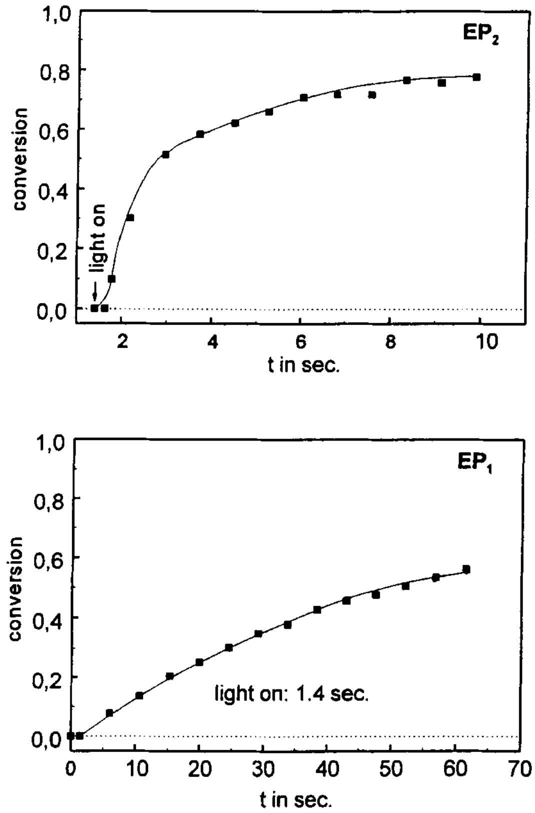


Figure 4. Conversion (x)/time curve for the photoinduced crosslinking of Ep_1 and Ep_2 with $S_{(2)}$ as photoinitiator ([initiator] = $5 \cdot 10^{-5}$ mol per gram of substituted disiloxane, I_o = 135 mW/cm^2).

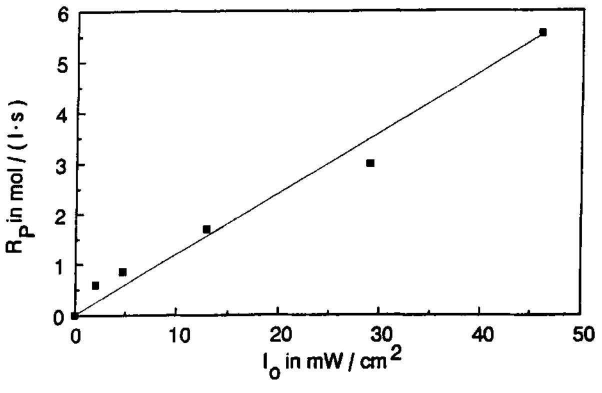


Figure 5. Plot of reaction rate R_P vs. I_o for the system $VE_2/S_{(1)}$ ($S_{(1)}$ as hexafluoroantimonate, [initiator] = $5 \cdot 10^{-5}$ mol per gram of VE_2).

Influence of the Light Intensity - Determination of the β–Value

Qualitatively, the influence of the light intensity can be seen on the final conversion x_∞ as well as on the crosslinking rate. Figure 5 shows a typical connection between the light intensity and the reaction rate for systems containing VE_2 and $S_{(1)}$ as photoinitiator. Due to the specific kinetic situation in the bulk, Equation (3) has to be used for describing the rate of the photocrosslinking process (R_P) under stationary irradiation conditions [19, 20]. Only this general expression and its reduced form (4), reflect the real situation in the polymeric systems investigated in all details, because the viscosity and therefore, the mobility for the reaction partners, is changing with the reaction time.

$$R_p = -\frac{d[M]}{dt} = \frac{dx}{dt}[M]_o = k(x)\cdot[M]^{\alpha}\cdot I_o^{\beta} \tag{3}$$

$$R'_p = \frac{dx}{dt} = k(x)\cdot(1-x)^{\alpha}\cdot I_o^{\beta} \tag{4}$$

where R_P is the molar reaction rate in mol/(l·s) (R'_P indicates the reduced form in s^{-1}), $[M]_0$ is the molar concentration of reactive groups (double bond or epoxy groups) in the uncrosslinked derivative, [M] is the molar concentration of reactive groups at time t, x is the conversion on reactive groups, k(x) is a conversion dependent quantity, I_0 is the intensity of the incident light, α and β are exponents.

The value of the exponent β gives information about the termination reaction. Following relations hold [19, 20]:

β= 1, first-order termination,
β= 0,5 ... 1, combined first- and second-order termination,
β = 0,5, second-order termination.

Figure 5 shows that in the system $VE_2/I_{(1)}$ the reaction rate rises linearly with the light intensity, which indicates that β is on the order of one. The same result was obtained for all the systems studied. Such a linear relationship is expected in photoinduced cationic polymerization, as only one propagation species is involved in the termination step, in contrast to radical type polymerization.

It should be mentioned that the β-value may change during the crosslinking process because of variations in the molecular mobility. Therefore, the dependence of the exponent β on the conversion was studied.

Assuming that α is on the order of one, Equation (4) was integrated into Equation (5), which can be written in its logarithmic form Equation (6).

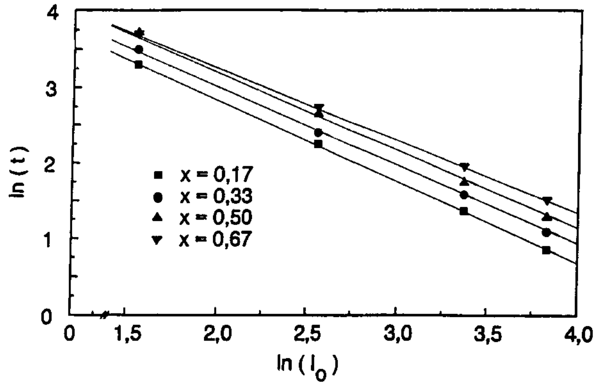


Figure 6. Determination of the β-value for the system $\mathrm{PE}/\mathbf{I}_{(1)}$ according to Equation (6) for several conversions ([initiator] = $5 \cdot 10^{-5}$ mol per gram of PE)

$$-\ln(1-x) = k(x) \cdot I_o^{\beta} \cdot t \tag{5}$$

$$-\ln(t) = \ln\left(\frac{-\ln(1-x)}{k(x)}\right) = \beta \ln \cdot (I_o) \tag{6}$$

where t is the irradiation time (subtracted by the inhibition time), which is necessary to reach a given conversion x at the light intensity I_0.

This complicated procedure is necessary because in highly viscous media the value of k(x) depends on the conversion. A graphic procedure of this algorithm is published in [21]. A logarithmic plot is given in Figure 6 for the system $\mathrm{PE}/\mathbf{I}_{(1)}$. For all the vinylether and propenyl ether systems studied, the value of β was found to be nearly one and to remain almost constant, up to a conversion of about 60% (the conversions of the epoxy derivatives are too low for an exact analysis). This result confirms the finding of the linear dependence of R_P with I_0.

Postpolymerization

Additional information about the kinetics of the crosslinking reaction can be inferred from the RTIR curves recorded upon UV exposure and postcure in the dark. Figure 7 shows, for example, the postpolymerization profiles recorded for the system $\mathrm{PE}/\mathbf{S}_{(1)}$. It can be seen that, after a given exposure time, the polymerization continues to proceed in the dark for up to 30 s. This result was expected due to the living character of cationic polymerization.

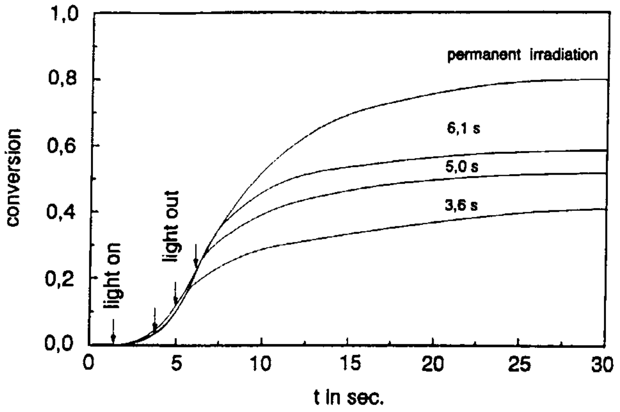


Figure 7. Conversion (x)/time curve for the photoinduced crosslinking and postcure of PE with $S_{(1)}$ as photoinitiator ($S_{(1)}$ as hexafluoroantimonate, [initiator] = $5 \cdot 10^{-5}$ mol per gram of PE, $I_0 = 43$ mW/cm^2, UV exposure for postcure = 3.6, and 5.0 s, respectively).

Determination of the Termination Rate Constant

As no initiating species are produced after UV exposure, the rate equation of the dark polymerizationcan be written as:

$$\frac{d[P^-]}{dt} = -k_t[P^-] \tag{7}$$

$$R_P^D = -\frac{d[M]}{dt} = -k_p[P^-][P^-] \tag{8}$$

where [M] is the monomer concentration, $[P^+]$ is the concentration of the living polymeric carbo cation, k_p and k_t are the rate constants of the propagation and termination steps, respectively.

By integration of Equation (7) between the limits $t_D = 0$ and t, and after combination with Equation (8) (see also [22]), one obtains Equation (9):

$$\ln \frac{[M]_{t_D+t}}{(R_P^D)_{t_D+t}} = k_t t + \ln \frac{[M]_{t_D}}{(R_P^D)_{t_D}} \tag{9}$$

where t_D is the time where the postpolymerization starts.

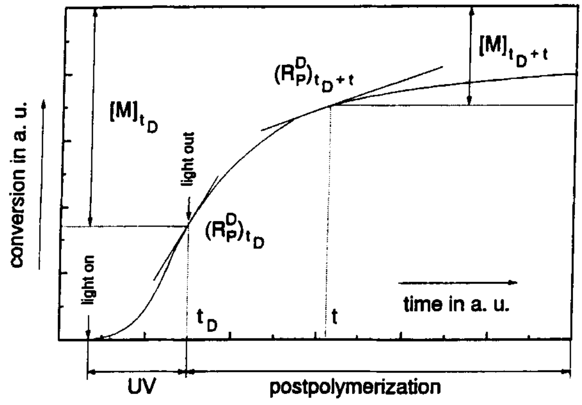


Figure 8. Typical schematic profile for postcure with the terms according to Equation (9).

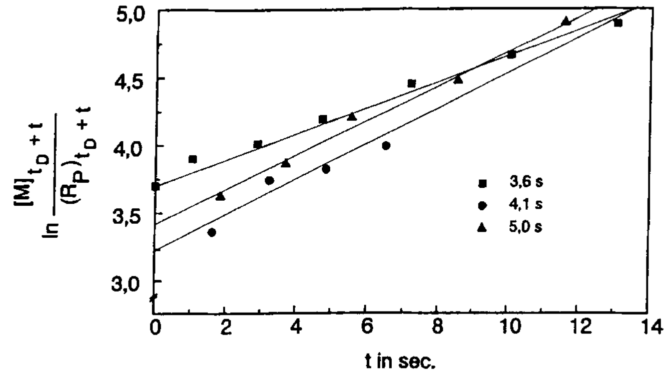


Figure 9 Determination of the k_t-value for the system PE/$S_{(I)}$ according to Equation (9) ([initiator] = $5 \cdot 10^{-5}$ mol per gram of PE I_0 = 43 mW/cm^2, UV exposure for postcure = 3.6, 4.1, and 5.0 s, respectively).

The various quantities of Equation (9) can be determined easily from the RTIR profile recorded (Figure 8) thus allowing the rate constant of the termination step to be determined. Figure 9 shows the variation of the left-hand term of Equation (9) as a function of the dark reaction time, for the PE/$S_{(I)}$ system exposed to UV radiation for 3.6, 4.1 and 5.0 s. The linear relationship observed indicates that the termination step can be described by means of a first order kinetics. It can be seen that the slope of the plot (k_t) depends on the exposure time, i.e. on the conversion.

The results obtained for the silicone derivatives EP_2, VE_1, VE_2, and PE in combination with $I_{(1)}$ and $S_{(1)}$ are summarized in Table 3. The kinetic constants were found to differ for the various silicone derivatives. In the case of VE_1 and VE_2, the k_t-values are also depending on the type of initiator used. In these derivatives, k_t is substantially lower for the sulfonium salt than for the iodonium salt. With PE and EP_2, the k_t-values are on the same order for both initiators. Never theless, an exact comparison of the data is only reasonable at the same conversion x_D (conversion at t_D), because the molecular mobility changes with the conversion. The increasing viscosity leads to an increase of the k_t-value, which was observed in most cases.

Determination of the Propagation Constant

Our results show that the value of the exponent β does not change during the crosslinking process. The linear plot of R_P vs I_0 suggests an ideal crosslinking kinetics of the cationic chain reaction. Moreover, for PE the k_t-value is approximately constant at low conversion. Under this condition, and presuming that the rate of initiation will not decrease during the course of the polymerization, (see above and [1]) the classical crosslinking kinetics is true for the determination of the rate constants. For polymerization in solution Timpe [23] has proposed a simple kinetic procedure to determine the ratio of the propagation and termination rate constant k_P/k_t from the conversion vs. time plot of the reaction under steady state conditions.

Upon UV-irradiation of the photoinitiator, the concentration of the initiating species R^+, and therefore the concentration of active centres P^+, increases up to a stationary state. Under steady state conditions, the rate of formation of initiating species

$$\frac{d[R^+]}{dt} = \Phi_{R^+} I_{abs} \tag{10}$$

is equal to the rate of termination $k_t\,[P^+]$, which leads to

$$[P^+] = \frac{\Phi^{R_+}\, I^{abs}}{k_t} \tag{11}$$

The monomer consumption can be described as:

$$Rp = -\frac{d[M]}{dt} = -k_p[M]\,[P^+] + k_i[M][R^+] \tag{12}$$

TABLE 3: Kinetic Dates of the Postpolymerization for Several Systems ($[On^+X]=5{\cdot}10^{-5}$ mol/g; I_o=43mW/cm^2)

PE

$I_{(1)}^+SbF_6^-$				$S_{(1)}^+SbF_6^-$			
t_D in s	x_D	x_∞	k_t in s^{-1}	t_D in s	x_D	x_∞	k_t in s^{-1}
1.4	0.02	0.44	0.17	3.6	0.01	0.41	0.09
1.7	0.16	0.63	0.17	4.1	0.10	0.52	0.15
				5.0	0.20	0.58	0.14

VE_1

$I_{(1)}^+SbF_6^-$				$S_{(1)}^+SbF_6^-$			
t_D in s	x_D	x_∞	k_t in s^{-1}	t_D	x_D	x_∞	k_t in s^{-1}
1.6	0.02	0.12	1.69	1.7	0.02	0.12	0.50
1.8	0.08	0.24	1.40	2.2	0.08	0.34	0.49
2.0	0.17	0.29	1.40	2.6	0.18	0.36	0.52

VE_2

$I_{(1)}^+SbF_6^-$				$S_{(1)}^+SbF_6^-$			
t_D in s	x_D	x_∞	k_t in s^{-1}	t_D in s	x_D	x_∞	k_t in s^{-1}
1.3	0.03	0.19	1.09	1.9	0.02	0.18	0.14
1.6	0.22	0.41	1.59	2.3	0.22	0.58	0.36
2.4	0.48	0.56	1.79	2.9	0.57	0.76	0.64

Ep_2

$I_{(1)}^+SbF_6^-$				$S_{(1)}^+SbF_6^-$			
t_D in s	x_D	x_∞	k_t in s^{-1}	t_D in s	x_D	x_∞	k_t in s^{-1}
5.3	0.05	0.08	1.57	3.7	0.05	0.08	1.23
6.7	0.09	0.13	1.89	4.2	0.06	0.08	1.49
8.0	0.14	0.16	2.45	5.1	0.08	0.11	1.56

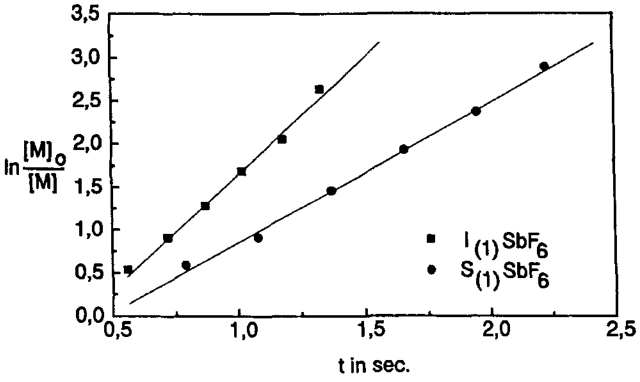


Figure 10. Determination of the k_p/k_t-value for PE according to Equation (14) for several photoinitiators ([initiator] = $5{\cdot}10^{-5}$ mol per gram of PE, I_o = 81 mW/cm$^2 \approx 4{\cdot}10^{-7}$ E·s^{-1}· cm^{-2}.$\eta_{abs} \approx$ 0,07 for both systems).

Integration of this equation results in:

$$\ln\frac{[M]_o}{[M]} = \left(k_p[P^+] + k_i[R^+]\right) t \tag{13}$$

Assuming that (k_p [P^+]) >>(k_i [R^+]) and taking account of Eq (11), it follows,

$$\ln\frac{[M]_o}{[M]} = \frac{k_p}{k_t}\,\Phi_{R^+}\,I_{abs}\,t \tag{14}$$

where $[M]_o$ is the monomer concentration of the uncrosslinked product, [M] the monomer concentration at the irradiation time t, [R^+] the concentration of the initiating species, Φ_{R^+} the quantum yield of the formation of the initiating species, I_{abs} the absorbed light intensity, and R_P the rate of the crosslinking reaction. Figure 10 shows the variation of $\ln[M]_o/[M]$ as a function of the exposure time for the light induced cationic crosslinking of PE with $I_{(1)}$ and $S_{(1)}$ as photo-initiator. The observed linear relationship shows the validity of the kinetic scheme, even in such highly viscous media. From the slope of the straight line, one can estimate the ratio k_p/k_t when the the product Φ_{R^+} I_{abs} is known. Using the known quantum yield of proton formation Φ_{H^+} of both initiators (0.28 for $I_{(1)}$ and 0.15 for $S_{(1)}$ [17]) and the measured intensity‡of the absorbed light as $1.4{\cdot}0^{-2}$ einstein·l^{-1}·s^{-1} (I_{abs}=$1.7{\cdot}10^{-5}$

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‡einstein possesses the unit mol quanta.

einstein·s^{-1} ·cm^{-2}, thickness of the layer 1 μm) one obtains for the ratio k_p/k_t 660 l/mol and 750 l/mol for $\mathbf{I}_{(1)}$ and $\mathbf{S}_{(1)}$,, respectively. By taking the above determined k_t-value (0.17 s^{-1} and 0.15 s^{-1} for both initiators), k_p was evaluated to be 110 l·mol^{-1}·s^{-1}. Both initiators give the same k_p-value, which is typical for the chain reaction of the considered monomer.

In the literature it is difficult to find rate constant values to compare the results of our experiments. The cationic polymerization in bulk, in hydrocarbons, or in other low polarity media is largely controlled by the solvation of the propagation cations by the polymer chain [24, 25]. The rate decreases with increasing solvent polarity [24, 26]. In a recent paper k_p-values were reported for the photocuring of a divinylether derivative using a iodonium salt initiator system [27]. The values determined, between 5 and 30 l·mol^{-1}·s^{-1}, are somewhat lower than our value. The result is in good agreement with the larger reactivity of the propenyl derivatives. But since the k_t-value of the divinyl product (10^{-3} s^{-1}) is also less than for the propenyl ether, the ratio k_p/k_t is overall larger for the vinyl product than for propenyl product.

CONCLUSION

The photoinduced cationic crosslinking of α,ω–terminated disiloxanes (functionalized with epoxy, vinyl ether, and propenyl ether groups) has been investigated by means of Real-Time IR spectroscopy. A lipophilic iodonium salt and three lipophilic sulfonium salts were used as photoinitiator. The crosslinking rate is influenced by the type of α,ω-terminated disiloxane used and differed by a factor of more than 100 from the aliphatic epoxy to the vinyl ether derivatives. The final degree of conversion is larger for the ene derivatives than for the epoxy derivatives. Moreover, the sulfonium salts were found to have a lower initiation efficiency than the lipophilic iodonium salt in the various systems studied. These results are in good agreement with the quantum yield of proton formation in a hexamethyldisiloxane/dimethoxyethane mixture. The crosslinking rate depends on the anion (SbF_6^-, PF_6^-), a slowing down of the crosslinking reaction being often observed with the PF_6^- salt.

The application of a kinetic method allows us to estimate the rate constant of the termination step and for the propenyl derivative, the rate constant of the propagation step. The termination step can be described by means of a first order reaction.

The k_t -value depends on the light intensity, and on the type initiator used. For the propenyl derivative, k_p was evaluated to be 110 l·mol^{-1}·s^{-1}, irregardless of the photo-initiator (lipophilic iodonium salt or lipophilic sulfonium salt), thus showing the importance of the chain reaction in this monomer.

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