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PHOTOCROSSLINKING OF SILICONES. PART 11. RADICAL PHOTOPOLYMERIZATION UNDER OXYGEN–SILICONE ACRYLATES AS MODEL SYSTEMS†

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ABSTRACT

Silicone acrylates were used as model systems for radical photopolymerization under oxygen with commercial photoinitiators of the α-cleavage type. From calorimetric results, it is inferred that oxygen inhibits and terminates the chain process. The reaction rate, the final conversion, and the inhibition time of polymerization are proportional to the air pressure, to the intensity of the incident light, and to the quantum yield of the initiator photolysis. We show that the reaction starts if all oxygen is consumed in the silicone layer. Only oxygen which diffuses into the system determines the termination reaction. By means of the first Fickian diffusion law, it is demonstrated that the oxygen which diffuses into the silicone layer also determines the final conversion of double bonds in the system. However, in the absence of oxygen, the observed final conversion of double bonds is approximately 1. The high final conversion is combined with a high reaction rate.

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†For Part 10, see Reference 1. Part 11 was partially presented at the Aspects of Photoinitiation Conference, Egham, England, 1993.

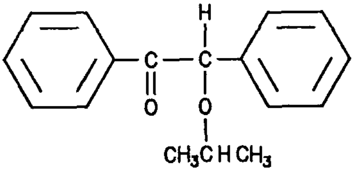
INTRODUCTION

Silicone acrylates combine the favorable material properties of silicones and the fast crosslinking rates of acrylates. The drawback of such silicone derivatives is their high oxygen permeability. However, in the absence of oxygen, the observed final conversion of double bonds x_∞ is approximately 1 [1, 2]. The high final conversion is combined with a high reaction rate. A thermal postcrosslinking of such products is not necessary.

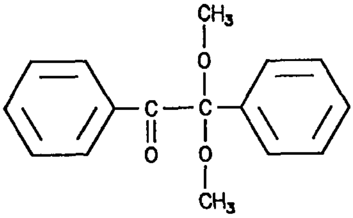
Our investigation of the photocrosslinking process also shows that silicone acrylates represent not only a special type of polymers, but they are also useful as model systems for investigation of the crosslinking process in bulk. The high oxygen permeability allows us to investigate the inhibition and the termination of the radical chain process by oxygen, the oxygen diffusion into the silicone layer, and the quenching of the excited photoinitiator by oxygen.

EXPERIMENTAL

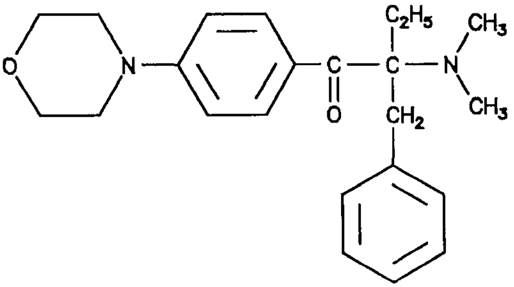
Several photoinitiators which differ in their quantum yields, Φ, were applied in the present kinetic investigations: 2-isopropoxy-2-phenyl acetophenone (benzoin isopropyl ether, BIPE), $\Phi = 0.33$ [2]:



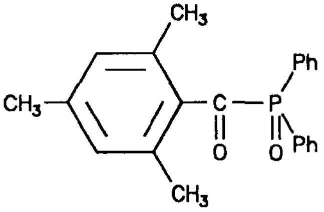
2,2′-dimethoxy-2-phenyl acetophenone (benzil dimethyl ketal, BDMK), $\Phi = 0.52$ [2]:



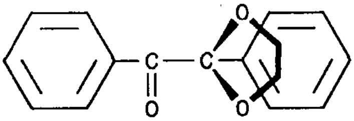
2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (BDMB), $\Phi = 0.22$ [3]:



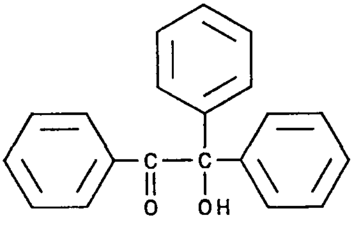
2,4,6-trimethylbenzoyldiphenylphosphinoxide (TMPE), Φ = 0.80 [2]:



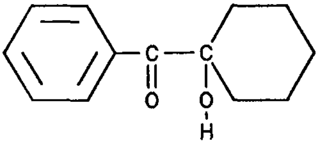
phenyl-(2-phenyl-1,3-dioxolan-2-yl) methanone (benzil mono(ethylene glycol) ketal, BGK), Φ = 0.11 [2]:



2,2-diphenyl-2-hydroxy acetophenone (α-phenyl benzoin, α-PhB), Φ = 0.10 [2]:

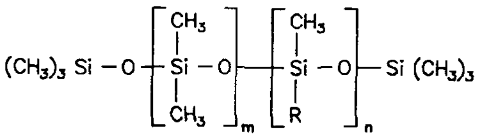


1-hydroxy-cyclohexyl phenyl ketone (HCPK), Φ = 1.0 [2]:



BIPE (Schönert, Leipzig), TMBP (BASF), BDMK, HCPK, and BDMB (I 651; I 184 and I 369, Ciba Geigy) are commercial products and were recrystallized three times. The synthesis of BGK and α-PhB has been described elsewhere [4, 5].

The silicone acrylates **1** (polymer with monofunctional pendant acrylate groups) were applied in the present kinetic investigations. For several special investigations the silicone acrylates from TH Goldschmidt AG **2a** (TEGO 705, polymer with polyfunctional pendant acrylate groups) and **2b** (TEGO 720, polyfunctional α,ω-terminated silicone acrylate), as well as a silicone derivative of Wacker-Chemie GmbH (laboratory product SLM 443022; polymer with monofunctional pendant acrylate groups, see Ref. 6), were also applied. The synthesis of the silicone acrylate **1**



$$(CH_3)_3Si-O\left[\begin{matrix}CH_3\\ |\\ Si-O\\ |\\ CH_3\end{matrix}\right]_m\left[\begin{matrix}CH_3\\ |\\ Si-O\\ |\\ R\end{matrix}\right]_n Si(CH_3)_3$$

by a hydrosilylation reaction with $R = (CH_2)_3-O-(CH_2)_2-O-CCOCH{=}CH_2$ and [acrylate] = 1.2 mol/kg for **1a**, 0.8 mol/kg for **1b**, 0.5 mol/kg for **1c**, and 2.2 mol/kg for **1d** (experimentally determined), has been described elsewhere [7]. For the silicone derivative, **1c**, a H-siloxane of Wacker-Chemie with 0.05% (Si)H and 60–70% Si—O units was used. The reactive silicone derivatives were free of any inhibitors.

The construction of the isoperibolic calorimeter used for kinetic measurements was described previously [7, 8]. The light intensity (I_0) was controlled by a selenium photoelement calibrated with a VTH-10 thermocouple (ZWG of Academy of Sciences of the G.D.R.).

The filter combination 1602 and 810 (Jenaer Glaswerke Schott und Gen.) was used to supply the 340 to 380 nm wavelength region from the emitted light of a 200-W high-pressure Hg lamp (Narva, Berlin), The silicone acrylate/photoinitiator mixture was treated in an ultrasonic bath for 10 minutes in order to obtain a homogeneous solution. For measurements, 50 μL of this mixture was dropped at the probe thermistor; 50 μL of polydimethylsiloxane NM 1-200 (Chemiewerk Nünchritz), containing the same amount of photoinitiator, served as a comparative probe. Further experimental conditions are given in the tables and the figure legends.

RESULTS AND DISCUSSION

Photocrosslinking Kinetics

The crosslinking process of all investigated silicone acrylates can be described by means of photoinitiated radical polymerization. The photocrosslinking of silicone acrylates in bulk begins with photochemical radical formation. The photochemical formed radical initiates the polymerization of the acrylate groups. The result of this polymerization is a crosslinked silicone acrylate.

$$R_P = -dx/dt = k(x)[\mathrm{M}]\alpha I_0^\beta \tag{1}$$

where x is the conversion of double bonds, $k(x)$ is a conversion-dependent quantity, [M] is the double bond concentration in the silicones, I_0 is the incident light intensity, and α and β are exponents.

Due to the specific kinetic situation in bulk, expression (1) is used to describe the rate of the photocrosslinking process (R_P) under stationary irradiation conditions [7]. For a more qualitative overview on the kinetics in these systems, the following kinetic parameters are useful: limiting conversion (x_∞), maximal crosslinking rate ($R_P^{\max}$), and time of the inhibition period (t_i). Typical examples for deconvoluted conversion-time and reaction rate-time curves for the photopolymerization of silicone acrylate are given in Fig. 1. The examples in Figs. 2 and 3 illustrate the connection of the light intensity and double bond content (limited to the same type of silicone acrylate; mono- or polyfunctional) with the rate of the crosslinking process.

$$\Phi_{-\mathrm{M}} = R_P/\eta_{\mathrm{abs}}\cdot I_0 \tag{2}$$

$$\eta_{-\mathrm{M}} = \Phi_{-\mathrm{M}}/\Phi\alpha \tag{3}$$

where $\Phi_{-\mathrm{M}}$ is the quantum yield of monomer decay, Φ is the quantum yield of primary radical formation, and $\eta_{-\mathrm{M}}$ is the kinetic chain length.

By means of the quantum yield of monomer decay ($\Phi_{-\mathrm{M}}$, see Eq. 2), it is possible to prove the chain process of double bond decay. In Table 1, some $\Phi_{-\mathrm{M}}$ values for silicone acrylate **1a** initiated with several photoinitiators are outlined. In all cases for $\Phi_{-\mathrm{M}}$ or the kinetic chain length $\eta_{-\mathrm{M}}$ (see Eq. 3), values $>>$ 1 were found. The limiting value for a chain process is 2. During photolysis of the initiator, two radicals are formed, and both radicals can hypothetically initiate the crosslinking reaction:

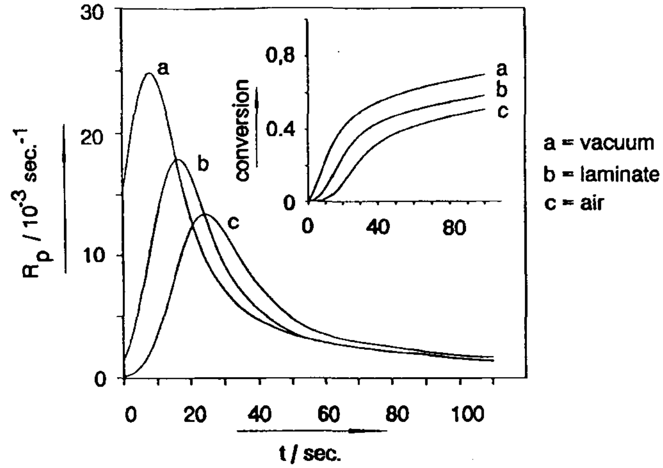


FIG. 1. Conversion (x)/time and reaction rate (R_P)/time curve for the photoinduced polymerization of silicone acrylate **1a** with BDMK as initiator (5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; $I_0 = 3.27$ mW/cm^2; $\lambda = 340 \ldots 380$ nm).

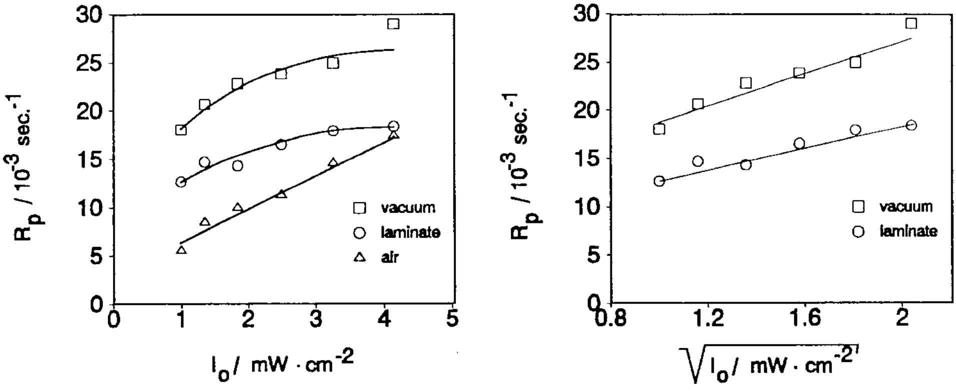
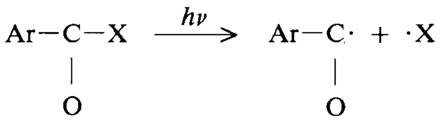


FIG. 2. Plot of reaction rate vs incident light intensity I_0 or vs $(I_0)^{0.5}$ of the photocrosslinking of the system **1a**/BDMK (experimental conditions, see Fig. 1).



$$\mathrm{Ar-\underset{\underset{\displaystyle O}{|}}{C}-X \xrightarrow{h\nu} Ar-\underset{\underset{\displaystyle O}{|}}{C}\cdot + \cdot X} \tag{4}$$

Figure 1 also illustrates the influence of the experimental conditions (vacuum, laminate, open air system) on the typical characteristic points (t_i, R_P^{max}, x_∞). Figure 2 shows for the same system, **1a**/BDMK, plots of R_P^{max} vs I_0 and $(I_0)^{0.5}$. The figure demonstrates that the light intensity exponent β is a function of the experimental conditions. The size of the β value gives information about the termination reaction [9]. In general, the experimental conditions influence the termination reaction of the polymerization process:

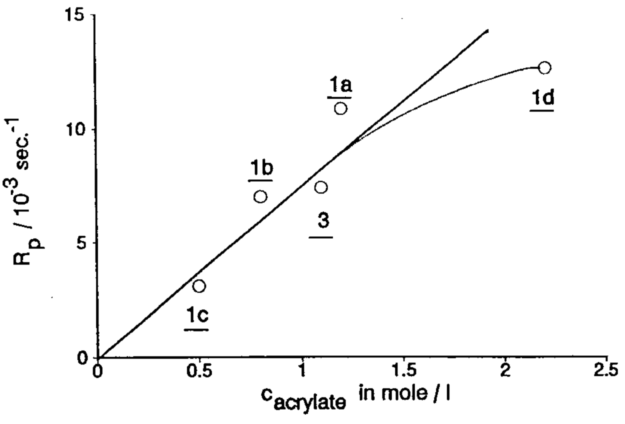


FIG. 3. Plot of R_P vs content of acrylate groups of the silicone acrylate with BIPE as initiator (5×10^{-5} mole photoinitiator per gram of silicone acrylate; I_0 = 3.27 mW/cm^2; λ = 340 . . . 380 nm; laminate).

TABLE 1. Characteristic Data of the Photocrosslinking (silicone acrylate **1a**/initiator; [initiator] = 5×10^{-2} mol/L; 50 μL/sample; I_0 = 3.27 mW/cm^2 = 7.83×10^{-9} Einstein/s)

Initiator, Φ_α	R5, $R_P^{max} \times 100$,[a] mol/L·s	η_{abs}	t_i, seconds	Φ_{-M}[a]	Φ_{ox}	Φ_{-M}/Φ_α[a]	Φ_{ox}/Φ_α
BIPE	0.86	0.55		99		300	
0.33	1.35		16	157	2.2	474	6.7
BDMK	2.19	0.59		237		456	
0.52	3.00		5.5	325	5.9	625	11.3
TMBP	3.15	0.78		258		322	
0.80	3.60		5.3	294	4.6	368	5.8
BGK	0.14	0.49		18		167	
0.11	0.27		52	35	0.75	320	6.8

[a] First value: under air; second value: laminate.

$\beta = 1$	first-order termination
$\beta = 0.5$	second-order termination
$\beta = 0.5, \ldots, 1$	combined first- and second-order termination
$\beta < 0.5$	combined second-order and primary radical termination

Variation of the experimental conditions shows that only the influence of oxygen on the crosslinking process changes (vacuum: inert system; laminate: system with dissolved oxygen; open air system: system with dissolved oxygen and possibility of oxygen diffusion into the silicone layer). In general, oxygen determines the termination process.

A β of 0.5 indicates a biomolecular termination process of the polymer radical; see Eq. (5) (where P· = polymer radical). This order was found under vacuum (oxygen-free system) and in the laminate (system with dissolved oxygen). These experiments show that dissolved oxygen is consumed in the silicone layer. A termination reaction of the polymer radical with oxygen, see Eq. (6), is impossible.

$$\beta = 0.5: \quad P\cdot + \cdot P \longrightarrow \text{product} \tag{5}$$

$$\beta = 1; \text{ by } [O_2] >> [P\cdot]: \quad P\cdot + O_2 \longrightarrow \text{product} \tag{6}$$

Different results were found in the open air system. The order of the β value is 1. Such a value indicates a first- or pseudofirst-order termination of the polymer radical. Typical monomolecular termination reactions are: inclusion of the polymer radical, diffusion-controlled termination, and pseudofirst-order termination with oxygen (see Eq. 6). It is possible that the polymer radical was terminated in a diffusion-controlled process or by inclusion termination in the open air system but not under vacuum and not in the laminate system. In the laminate the order of the β value is 0.5 in the open system 1. From these results it is inferred that only the oxygen which diffused into the open air system can react with the polymer radical when the dissolved oxygen is consumed.

Postpolymerization

Postpolymerization studies were carried out to determine the results from the termination mechanism under stationary irradiation conditions by variation of the experimental conditions. The conversion of monomer in a dark period (x_D) after initiation was measured calorimetrically to describe termination reactions.

The following cases will be discussed [9]:

I. First -order termination:

$$-\ln(1-x_D) = k_p/k_t^m[\mathrm{P}\cdot]_0(1 - \exp(-k_t^m t)) \tag{7}$$

II. Second-order termination:

$$-\ln(1 - x_D) = k_p/k_t^b \ln(1 + [\mathrm{P}\cdot]_0 k_t^b t) \tag{8}$$

III: Mixed first- and second-order termination:

$$-\ln(1 - x_D) = k_p/k_t^b \ln(1 + [\mathrm{P}\cdot]_0 k_t^b/k_t^m)(1 - \exp(-k_t^m t)) \tag{9}$$

where x_D is the double bond conversion in the dark period, $[\mathrm{P}\cdot]_0$ is the polymer radical concentration at the beginning of postpolymerization, k_p is the polymerization rate constant, and k_t is the termination rate constant (^{m} = first order, ^{b} = second order). Postpolymerization was studied for the system **1a**/BDMK under vacuum, in the laminate, and in an open air system. A nonlinear regression program was used to estimate the parameters from Eqs. (7)-(9). In general, the observed postpolymerization courses can be described by the use by one of these three equations. The results lead to the following conclusions:

1. Under vacuum, Eqs. (8) and (9) can be used to describe the course of postpolymerization. The kinetic constants k_p/k_t^b for both models are nearly the same and lead to the conclusion that monomolecular termination is not dominant, see Table 2. A deviation from this general conclusion was found for a short exposure time (t_{ex} = 3 seconds). In this case, the early part of postpolymerization (3-12 seconds) cannot be fitted with the model reaction. The correlation coefficients are low in all cases. After 12 seconds it is possible to fit the observed course of postpolymerization by a bimolecular termination process.
2. In the laminate system it is difficult to discuss one termination model (see Table 2). In general, one can estimate that, after a short exposure time (t_{ex} = 12 or 16 seconds), it is almost possible to describe the observed courses with a first-order termination process; after a long exposure time (t_{ex} = 23 seconds) it is almost possible to describe the observed courses with a second-order termination reaction. Such results are typical if the termination conditions change during the polymerization. In laminate, residual oxygen (which was not consumed in the inhibition period) is consumed by polymer radicals. By means of this theory it is also possible to discuss the postpolymerization results under vacuum after a short exposure time.
3. In the open air system, Eqs. (7) and (9) can be used to describe the postpolymerization courses. The kinetic constants k_t^m for both models are nearly the same and lead to the conclusion that biomolecular termination is not dominant (see Table 2).

TABLE 2. Results of the Postpolymerization of the System BDMK/**1a** ([BDMK] = 5×10^{-5} mol/g; I_0 = 3.27 mW/cm^2)

t_{ex},[a] in seconds	x	x_d	Model I, in s^{-1}		Model II, in s^{-1}		Model III, in s^{-1}		
			k_t^m	$k_P[P\cdot]_0$	k_P/kt^b	$k_P[P\cdot]_0$	k_t^m	k_P/k_t^b	$k_P[P\cdot]_0$
			FQS		FQS		FQS		
			Air				t_P^{max} = 25 s; x = 0.17		
15	0.038	0.08	0.14	0.006	0.016	0.009	0.11	0.066	0.006
15-40			23.12×10^{-6}		108.9×10^{-6}		37.26×10^{-6}		
25	0.16	0.26	0.12	0.012	0.032	0.024	0.11	0.386	0.013
25-65			15.28×10^{-6}		920×10^{-6}		34.93×10^{-6}		
30	0.20	0.30	0.09	0.010	0.032	0.020	0.08	0.639	0.011
30-80			21.45×10^{-6}		791×10^{-6}		17.53×10^{-6}		
40	0.29	0.37	0.075	0.006	0.029	0.011	0.05	0.092	0.007
40-90					138.5×10^{-6}		18.56×10^{-6}		
			Laminate				t_P^{max} = 16 s; x = 0.18		
12	0.045	0.21	0.056	0.010	0.070	0.016	0.028	0.146	0.012
12-72			257.6×10^{-6}		1.500×10^{-3}		500.0×10^{-6}		
16	0.16	0.35	0.067	0.015	0.068	0.031	0.035	0.567	0.019
16-86			1.805×10^{-6}		1.961×10^{-3}		367.9×10^{-6}		
					0.041	0.0042			
30-86					2.201×10^{-6}				
18	0.22	0.38	0.077	0.012	0.046	0.032	0.034	0.582	0.020
18-88			2.435×10^{-3}		654.4×10^{-6}		320.1×10^{-6}		
23	0.26	0.36	0.092	0.009	0.034	0.017	0.032	0.414	0.013
23-65			215.6×10^{-6}		82.12×10^{-6}		17.46×10^{-6}		
			Vacuum				t_P^{max} = 8 s; x = 0.18		
3	0.04	0.34	0.042	0.015	0.134	0.025	0.029	0.453	0.017
3-83			4.351×10^{-3}		1.634×10^{-3}		1.742×10^{-3}		
					0.097	0.009			
13-83					6.123×10^{-6}				
9	0.17	0.45	0.043	0.013	0.103	0.026	0.015	0.152	0.021
9-89			7.981×10^{-3}		230.1×10^{-6}		977.0×10^{-6}		
13	0.27	0.49	0.046	0.011	0.079	0.020	0.008	0.098	0.018
13-93			5.514×10^{-3}		104.6×10^{-6}		399.0×10^{-6}		

[a] Second values: border for the calculation in seconds.

The atmospheric conditions determine the termination reaction of the polymer radical. Oxygen was primarily consumed in the inhibition period, and the residual part was consumed in the early phase of polymerization. In the open air system a first-order termination process was found all the time. All these results lead to the conclusion that oxygen can diffuse into the silicone layer and that the diffused oxygen can react effectively with the polymer radical in a pseudofirst-order reaction.

Figure 4 shows two postpolymerization courses which were initiated under vacuum. The exposure time is the same in both cases. Curve a demonstrates a typical profile under inert conditions. Curve b shows a postpolymerization profile in which the atmospheric conditions were changed during the postpolymerization phase (normal air pressure after 20 seconds; time for the adjustment of the pressure, 0.5 seconds). Figure 4 illustrates that the diffused oxygen determines the termination reaction. In this case the kinetic law of termination changed from second to first order.

Based on the above discussions, the kinetic parameters are dependent on t_{ex} values. With silicone **1a**, at t_{ex} approximately t_P^{max}, the product $k_p[P\cdot]_0$ becomes the highest value and, consequently, the rate constants of termination are the smallest at this point. After this time, the conditions for the polymerization reaction become worse due to the hindered diffusion of the large polymer radicals. Such results are typical if network formation takes place. It was possible to show by means of swelling experiments that network formation depends on the t_P^{max} value (see Fig. 5).

Inhibition Time

Figure 1 illustrates that polymerization starts under air and after an inhibition time t_i in the laminate system. The relations under vacuum demonstrates that oxygen inhibits polymerization (see Fig. 6). The effect of oxygen in radical polymerization can be represented schematically as follows (see also Ref. 10):

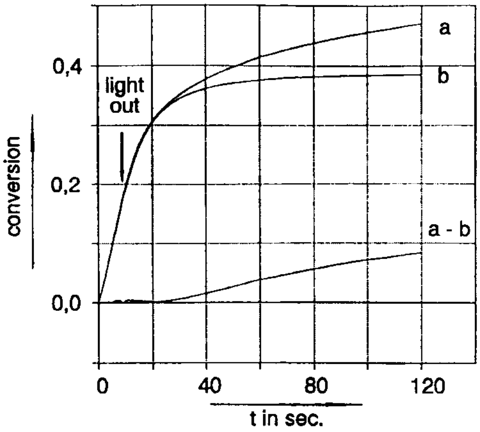


FIG. 4. Conversion degree (x_D) of the postpolymerization of silicone acrylate **1a** with BDMK as initiator [5×10^{-5} mole photoinitiator per gram of silicone acrylate; $I_0 = 3.27$ mW/cm^2; $\lambda = 340 \ldots 380$ nm; exposure time, 9 seconds; Curve a = under 10 mbar; Curve b = normal air pressure after 20 seconds (time for the adjustment of the pressure, 0.5 seconds)].

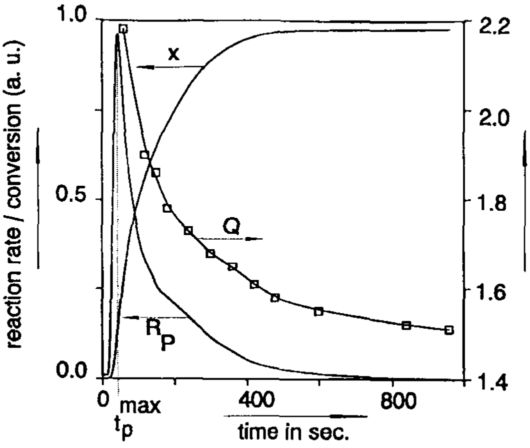


FIG. 5. Conversion/time, reaction rate/time, and swelling degree/time curves for the photoinduced polymerization of silicone acrylate **1b** with BIPE as initiator (5×10^{-5} mole photoinitiator per gram of silicone acrylate; $I_0 = 3.27$ mW/cm^2; $\lambda = 340 \ldots 380$ nm).

$$R\cdot + O_2 \xrightarrow{k_{ox}} R{-}O{-}O\cdot \tag{10}$$

$$R\cdot + C{=}C \xrightarrow{k_{add}} R{-}C{-}C\cdot\ (P_1\cdot) \tag{11}$$

$$P_1\cdot + C{=}C \xrightarrow{k_w} P_2\cdot \tag{12}$$

where R· is an initiator radical (in our cases benzoyl radical), k_{ox} is the rate constant of the radical scavenging by O_2 (5×10^8 L/mol·s [11], 3×10^8 L/mol·s [12]),

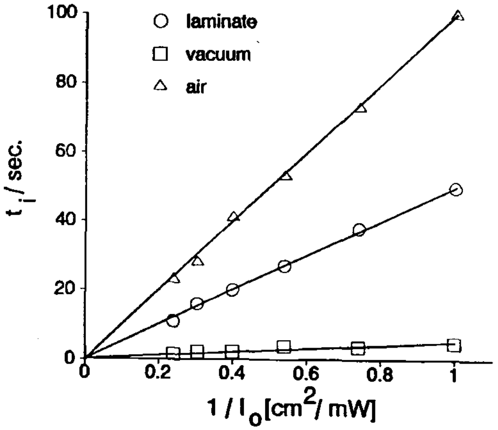


FIG. 6. Plot of the inhibition time t_i vs $1/I_0$ (system **1a**/BIPE; 5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; $\lambda = 340 \ldots 380$ nm; vacuum = 10 mbar).

k_{add} is the addition rate constant (5×10^5 L/mol·s for acrylates [12]), and k_P is the rate constant of propagation (3×10^3 for acrylates [13]).

In an aerated silicone acrylate, where the concentration of dissolved oxygen is of the order of 3×10^{-3} mol/L [14], polymerization cannot develop because the reaction rate of the primary radical is faster with oxygen than with the monomer.

$$k_P[P_1\cdot][M] << k_{ox}[R\cdot][O_2] \qquad ([R\cdot] \geq [P_1\cdot])$$

All the initiator radicals that formed reacted with the oxygen, so oxygen is consumed during this scavenging reaction. The polymerization reaction will only start if the concentration of O_2 is low and the condition of Eq. (13) are realized.

$$k_P[P_1\cdot][M] \geq k_{ox}[R\cdot][O_2] \qquad (13)$$

The steady-state concentration of oxygen during the polymerization process is 1.7×10^{-8} mol/L (calculated by means of the method of Decker [10], see Eq. 14). This low value demonstrates that oxygen is nearly completely consumed in the inhibition period.

$$[O_2]_S = (\Phi I_{abs} k_t^b)^{0.5}(R_P^1/R_P^2 - R_P^2/R_P^1)/k_{ox} \qquad (14)$$

where $[O_2]_S$ is the steady-state concentration of O_2, k_t^b is the rate constant of a biomolecular termination, R_P^1 is the reaction rate under vacuum, R_P^2 is the reaction rate in the laminate [system **1a**/BDMK: $\Phi = 0.52$; $I_{abs} = 10^{-4}$ mol/L·s; $k_t^b \sim 4 \times 10^6$ L/mol·s [10]; $k_{ox} = 5 \times 10^8$ L/mol·s [11]; $R_P^1/R_P^2 = 1.34$ (values for $I_0 = 3.27$ mW/cm^2)].

The overall quantum yield of the oxygen consumption Φ_{ox} can be described by Eq. (15a). In Table 1, some Φ_{ox} values for the silicone acrylate **1a** initiated with several photoinitiators are outlined. In all cases for the kinetic chain length η_{ox} (see Eq. 15b), values $>> 1$ were found. The high values demonstrate a chain process of the oxygen consumption.

$$\Phi_{ox} = \Delta[O_2]/t_i\eta_{abs}I_0 \qquad (15a)$$

$$\eta_{ox} = \Phi_{ox}/\Phi \qquad (15b)$$

For such a process Decker [10] discusses the following mechanism:

$$\begin{array}{llcll}
R\cdot & + O_2 & \xrightarrow{k_{ox}} & R{-}O{-}O\cdot & (10) \\
R{-}O{-}O\cdot & + D{-}H & \longrightarrow & R{-}O{-}O{-}H + D\cdot & (16a) \\
D\cdot & + O_2 & \longrightarrow & D{-}O{-}O\cdot & (17) \\
D{-}O{-}O\cdot & + D{-}H & \longrightarrow & D{-}O{-}O{-}H + D\cdot & (16b) \\
2D{-}O{-}O\cdot & & \longrightarrow & \text{termination} & (18)
\end{array}$$

where R· designates primary radicals, starting radicals, polymer radicals, and donor radicals (D·); D—H is a hydrogen donor.

It follows from the above discussion that the inhibition time t_i must be related both to the oxygen concentration $[O_2]$ and at constant oxygen concentration to the rate of starting radical ($P_1^\cdot$) formation ($R_i = f\Phi\eta_{abs}I_0$). In general, the inhibition time can be described by Eq. (19a). Such dependencies are expected when oxygen inhibits the initiation reaction of the polymerization process [15].

$$t_i = [O_2]/R_i = [O_2]/f\Phi\eta_{abs}I_o \tag{19a}$$

with

$$f = k_{add}[M]/(k_{ox}[O_2] + k_{add}[M] + \Sigma k^R_{des})$$

where R_i is the rate of starting radical formation; Φ is the quantum yield of primary radical formation; $[O_2]$ is the oxygen concentration; f is the addition efficiency of the primary radical to the monomer; k_{add} and k_{ox}, see Eqs. (10) and (11); and Σk^R_{des} = sum of all rate constants of a first- or pseudofirst-order radical termination process.

Our results show that the inhibition time is a function of the incident light intensity and of the oxygen concentration (see Fig. 6). The photoinitiator used (variation of Φ and η_{abs}) also influences the inhibition time (see Table 1). No influence of the acrylate concentration on the inhibition time was found in any case (see Fig. 7).

Figure 6 illustrates the influence of oxygen concentration (oxygen-free system under vacuum, dissolved oxygen in the laminate) and oxygen diffusion (laminate = system without diffusion of oxygen into the layer, open air system = possibility of oxygen diffusion into the layer) on the inhibition period. The t_i values in the laminate and the open air system differ in the systems **1a**/BIPE by a factor of about 2. Using these values and Eq. (19a), one can estimate the difference of the oxygen concentration between the two systems to be a value of about 2. Only by including the oxygen which diffuses into the layer can one explain the double t_i values in the open air system. The inhibition time must be described by

$$t'_i = ([O_2] + [O_2]_{diff})/f\Phi\eta_{abs}I_0 \tag{19b}$$

$$Y = t'_i - t_i = [O_2]_{diff}/f\Phi\eta_{abs}I_0 \tag{20a}$$

$$Yf\Phi\eta_{abs}I_0 = [O_2]_{diff} = \text{constant} \tag{20b}$$

where $[O_2]_{diff}$ is the concentration of oxygen which diffused into the layer.

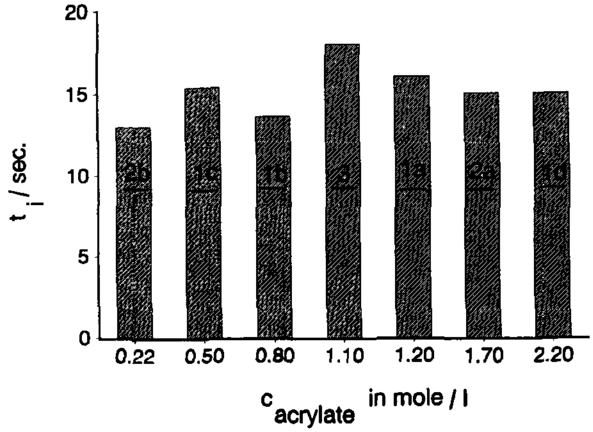


FIG. 7. Plot of the inhibition time t_i (laminate) vs content of acrylate groups of the silicone acrylates with BIPE as initiator (experimental conditions, see Fig. 3).

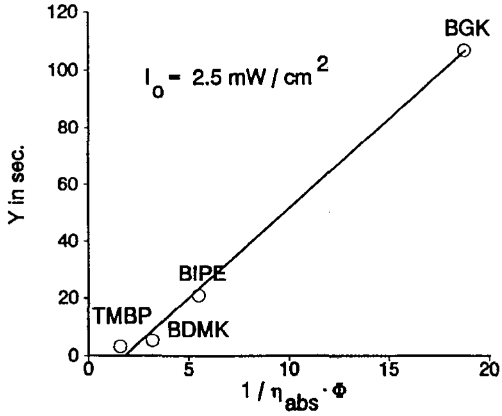


FIG. 8. Plot of the Y-values (see Eq. 20a) vs $1/\eta_{abs}\Phi$ (silicone acrylate **1a**; 5×10^{-5} mole photoinitiator per gram of silicone acrylate; $\lambda = 340 \ldots 380$ nm).

This part of the diffusing oxygen can be calculated from Eq. (20a). The quantity of oxygen which can diffuse into the system is a function of the surface. Only by diffusion of oxygen into the layer from the front side can one expect that the quantity of oxygen which diffuses into the layer will be constant, see Eq. (20b). This means that by variation of the thickness of the layer under equal irradiation conditions ($\Phi\eta_{abs}I_0$ = constant), the Y value will also be a constant. Figures 8 and 9 illustrate the connection of Eqs. (20).

It follows from Eqs. (19) that the inhibition time is a function of oxygen concentration in the layer. In general, the oxygen concentration in a liquid and the diffusion of oxygen into a liquid is, as a first approximation, a linear function of oxygen pressure [16]. If this model describes the real situation, one can estimate

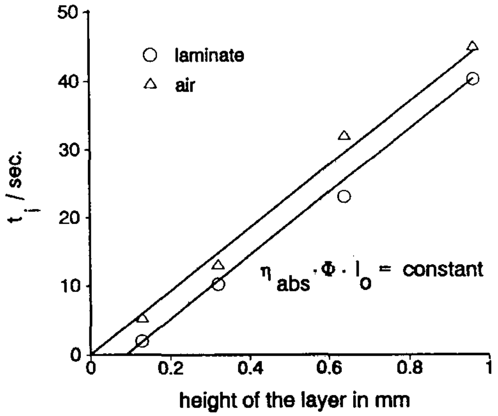


FIG. 9. Plot of inhibition time t_i vs height of the layer (system **1a**/BDMK; 5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; $I_0 = 4.15$ mW/cm^2; $\eta_{abs}\Phi = 0.31$; $\lambda = 340 \ldots 380$ nm).

that t_i is also a function of air pressure. Some results of inhibition time measurements as related to air pressure for several initiators are shown in Fig. 10. Linear relationships were found for the photoinitiators BIPE, BDMK, BGK, and TMBP. A complex relationship was observed for initiation with BDMB.

As a first approximation, we discuss the effect of oxygen by means of Eqs. (10)-(12) only. However, it is well known that excited photoinitiators (A*) can be quenched by oxygen. The overall reaction scheme of primary radical formation in the presence of oxygen may be represented by a set of equations:

$$\mathrm{A}^* \xrightarrow{k_{\mathrm{des}}} \mathrm{A} \tag{21}$$

$$\mathrm{A}^* \xrightarrow{k_{\mathrm{R}}^{\mathrm{m}}} \mathrm{R}\cdot \tag{22}$$

$$\mathrm{A}^* + \mathrm{B} \xrightarrow{k_{\mathrm{R}}^{\mathrm{b}}} \mathrm{R}\cdot \tag{23}$$

$$\mathrm{A}^* + \mathrm{O}_2 \xrightarrow{k'_{\mathrm{des}}} \mathrm{A} + \text{product} \tag{24}$$

The efficiency of primary radical formation is given by

$$\eta_{\mathrm{R}}^{\mathrm{m}} = k_{\mathrm{R}}^{\mathrm{m}}/(k_{\mathrm{R}}^{\mathrm{m}} + k_{\mathrm{des}} + k'_{\mathrm{des}}[\mathrm{O}_2]) \tag{25a}$$

$$\eta_{\mathrm{R}}^{\mathrm{b}} = k_{\mathrm{R}}^{\mathrm{b}}[\mathrm{B}]/(k_{\mathrm{R}}^{\mathrm{b}}[\mathrm{B}] + k_{\mathrm{des}} + k'_{\mathrm{des}}[\mathrm{O}_2]) \tag{25b}$$

where η_{R} designates the efficiency of primary radical formation, the superscript "m" indicates a monomolecular step, and the superscript "b" indicates a bimolecular step.

It follows from Eqs. (21)-(24) that the formation of primary radical competes with oxygen quenching of A*. In this case the influence of oxygen should depend on the lifetime τ [$\tau = 1/(k_{\mathrm{R}}^{\mathrm{m}} + k_{\mathrm{des}})$ or $1/(k_{\mathrm{R}}^{\mathrm{b}}[\mathrm{B}] + k_{\mathrm{des}})$] of the excited photoinitiator. For example, the lifetime of an excited photoinitiator is 10^{-6} second and the k'_{des} value is about 10^{10} L/mol·s. Under these conditions an oxygen quenching of 50% is calculated from an oxygen concentration of 10^{-4} mol/L. In the real case of

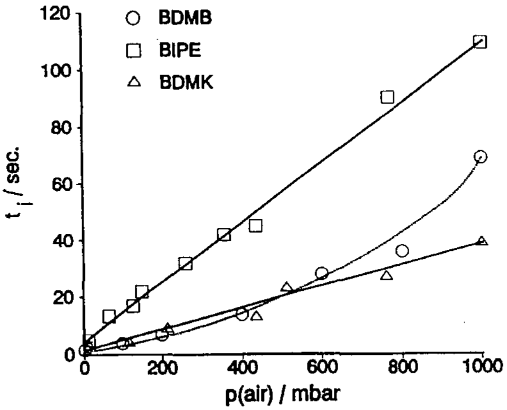


FIG. 10. Plot of inhibition time t_i vs air pressure (silicone acrylate **1a**; 5×10^{-5} mole photoinitiator per gram of silicone acrylate; λ = 340 . . . 380 nm; I_0 = 1.0 mW/cm^2).

silicone layers, the concentration of oxygen is 3×10^{-3} mol/L, so the excited photoinitiator A* should be quenched by more than 97%. In contrast, with a lifetime of 10^{-10} second an oxygen quenching of 50% is calculated using an oxygen concentration of 1 mol/L. O_2 quenching in the silicone layer can be disregarded.

By means of oxygen quenching, one can show that not all long-living photoinitiators cannot be used for the radical crosslinking of silicone acrylates under air and in the laminate. Our results with benzophenone ($\tau > 10^{-6}$ second, $k'_{des} = 9 \times 10^9$ L/mol·s [17], radical formation, see Eq. 23) illustrate this. Benzophenone is able to initiate the crosslinking reaction only under reduced pressure ($<$ 100 mbar), see Fig. 11.

Analysis of the lifetimes of the photoinitiators used demonstrates big differences between BDMB ($\tau = 6 \times 10^{-5}$ second [18, 19]) and the other initiators (10^{-11} second $< \tau^* < 10^{-9}$ second) [20, 21]. As follows from the above discussion, the efficiency of primary radical formation is lower in the aerated silicone layer because of the long-lived triplet state of BDMB. Under the given experimental condition, the η_R value increases by a factor of approximately 6 ($\eta_R^m = 0.22$ [3], 0.037 from Eq. 25a with $k_{des} = 6 \times 10^5\ s^{-1}$ [18, 19]; $k'_{des} = 5 \times 10^9\ s^{-1}$ [18, 19], $k_R^m = 6 \times 10^5\ s^{-1}$ [3], $[O_2] = 3 \times 10^{-3}$ mol/L [14]). BDMB reacts with oxygen by oxygen quenching and radical scavenging by O_2. The other photoinitiators react with oxygen only by radical scavenging, see also Reference 3. These differences help define the complex inhibition time–air pressure relationship.

Limiting Conversion

Qualitatively, the influence of oxygen can be seen in the inhibition period and in the reaction rate. Figure 12 illustrates that the limiting conversion x_∞ is also strongly influenced by oxygen. A comparison of the limiting conversion values

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*τ is not fully correct. For several initiators, one can find only the k_R^m value but $\tau \leq 1/k_R^m$.

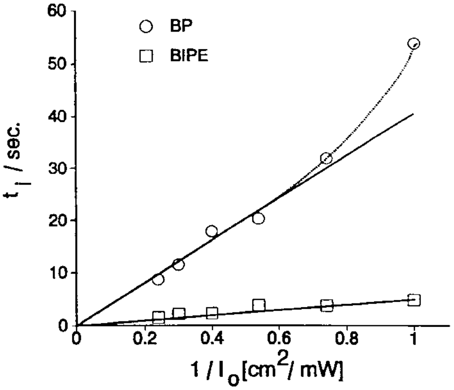

FIG. 11. Plot of the inhibition time t_i vs $1/I_0$ (silicone acrylate **1a**; 5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; λ = 340 . . . 380 nm; air pressure = 10 mbar).

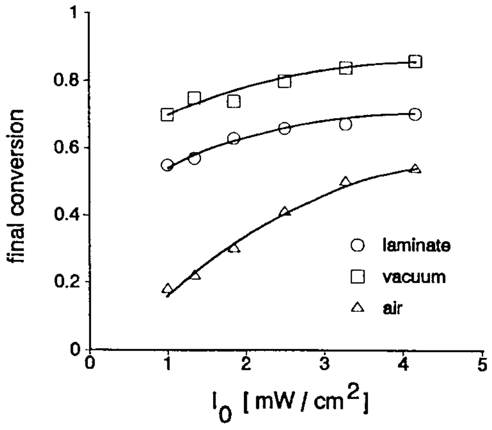

FIG. 12. Final conversion as a function of the light intensity for the photoinduced polymerization of silicone acrylate **1a** with BIPE as initiator (5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; $\lambda = 340 \ldots 380$ nm; vacuum = 10 mbar).

under vacuum and in the laminate (oxygen is consumed in the inhibition period) demonstrates that the lowest traces of oxygen define x_∞. The oxygen diffusion effect can be shown in the open air system. It follows from the above discussion that polymerization starts only in that region of the layer in which both the oxygen initially present is consumed and the number of initiating radicals is higher than the number of oxygen molecules approaching this area via diffusion. Thus, in an air atmosphere, the silicone layers are hardened by exposure beginning at the bottom; see Fig. 13. Throughout the hardening of these layers, high light intensities, i.e., high concentrations of primary radicals, are needed. In contrast, under vacuum (or in inert atmospheres), hardening of the probes begins from the surface [7].

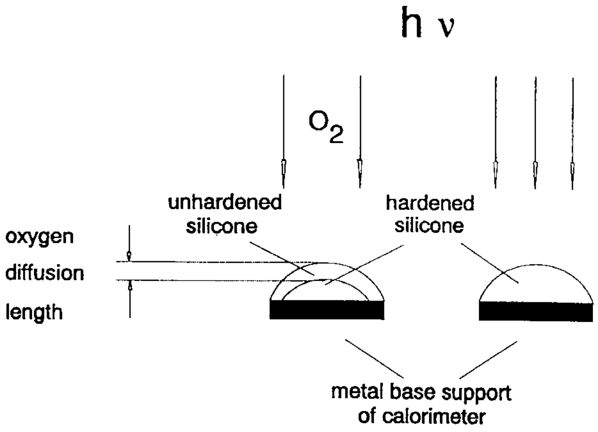

FIG. 13. Photoinduced crosslinking of the silicone acrylates on the thermistor of the calorimeter (left = crosslinking in the presence of air; right = crosslinking under inert conditions).

An example is given in Fig. 14 in which the experimental conditions were changed during the entire crosslinking process. As can be seen, with a low light intensity of $I_0 = 1.0$ mW/cm^2, the limiting conversion becomes $x_\infty = 0.20$. But this value is not caused by topological effects as was shown by further conversion under vacuum and at the same I_0. For this case, the true x_∞ value reaches 0.78. This is the same value found by initiating the crosslinking process under vacuum. Consequently, as was also found with other systems investigated, the acrylate groups are reactive and are not consumed [7].

It follows from these observations that polymerization starts only in that region of the layer in which oxygen is consumed. During the inhibition period the formation of initiating radicals is identical to the consumption of these radicals by oxygen, see Eq. (26). But oxygen concentration is a function of diffusion and a function of the diffusion pathway length l, see Eq. (27):

$$\Phi I_{\text{abs}} = k_{\text{ox}}[\text{R}\cdot][\text{O}_2]_{\text{diff}} \tag{26}$$

$$d[\text{O}_2]/dt = -Dq/V\cdot d[\text{O}_2]/dl \tag{27}$$

$$[\text{O}_2]_{\text{diff}} = Dq/V\cdot[\text{O}_2]_0/l \tag{28}$$

where V is the volume of the sample, q is the surface area of the sample, D is the diffusion coefficient ($D' = q/V$), l is the diffusion pathway, and $[\text{O}_2]_0$ is the maximal concentration of dissolved oxygen in the silicone.

Using the first Fickian diffusion law ($d[\text{O}_2]/dl$ = constant; experimentally realized because the oxygen concentration is zero at the beginning of the diffusion pathway l), one can formulate the expression

$$\Phi I_{\text{abs}} = \text{k}_{\text{ox}}[\text{R}\cdot]D'[\text{O}_2]_0/l \tag{29}$$

The diffusion pathway l is also a function of the volume V' by which the polymerization process is inhibited all the time. In this part of the layer, the conver-

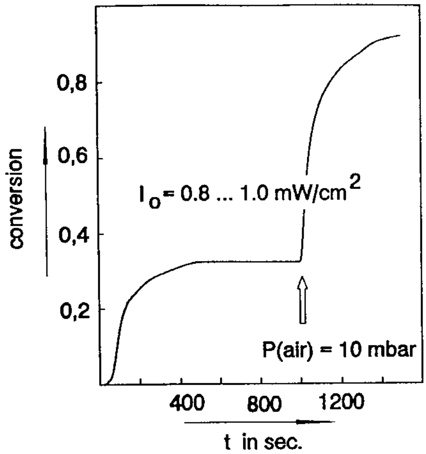

FIG. 14. Conversion/time curve for the photoinduced polymerization of silicone acrylate **1a** with BDMK as initiator under air and under vacuum (after 1000 seconds; 5×10^{-5} mole photoinitiator per gram of silicone acrylate; $I_0 = 0.8 \ldots 1.0$ mW/cm^2; $\lambda = 340 \ldots 380$ nm).

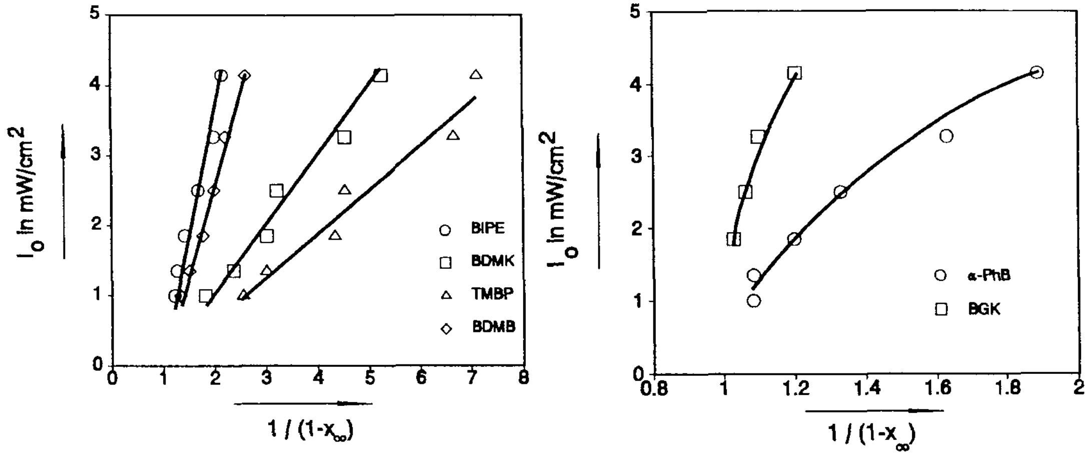

FIG. 15. Plot of $1/(1 - x_\infty)$ vs I_0 for several photoinitiators (5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; normal air pressure; λ = 340 . . . 380 nm).

sion of double bonds is zero. The final conversion is reduced by these unreactive double bonds. The measured limiting conversion x_∞ only defines the final conversion of the reactive part of the layer. Under this assumption, Eq. (29) becomes

$$\Phi I_{\mathrm{abs}} \sim [O_2]_0/l \sim [O_2]_0/V' \sim [O_2]_0/n \sim [O_2]_0/(1 - x_\infty) \qquad (30)$$

which finally yields an expression for the observed limiting conversion as a function of the light intensity, the oxygen concentration, and the quantum yield of primary radical formation, see also Reference 2.

The linear correlation of all these parameters illustrates the legitimacy of the above expression; see Figs. 15–17. However, a linear relationship in the case of BGK and α-PhB was not observed. Both initiators possess low quantum yields of primary

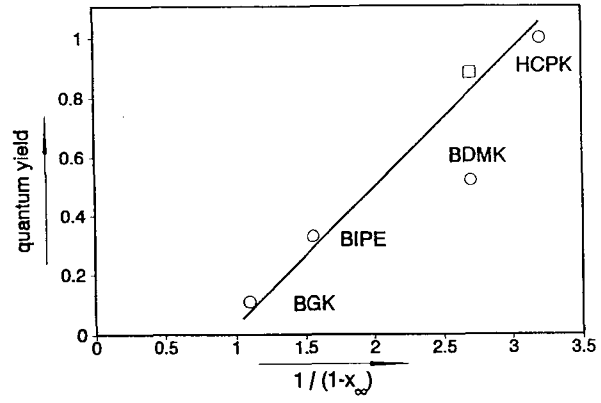

FIG. 16. Plot of quantum yield vs $1/(1 - x_\infty)$ (5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; normal air pressure; λ = 340 . . . 380 nm).

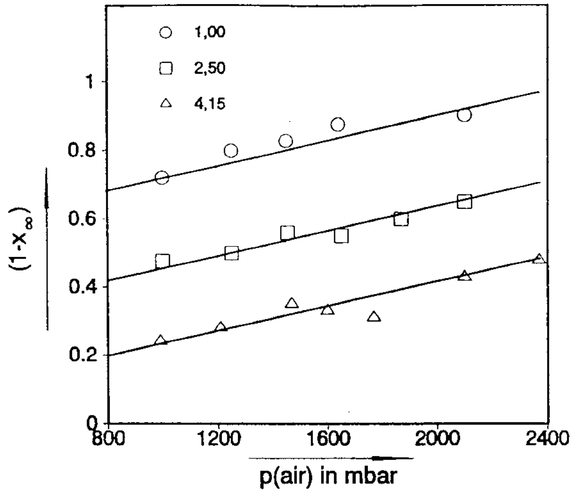

FIG. 17. Plot of $1/(1 - x_\infty)$ vs air pressure (system **1a**/BDMK; 5×10^{-5} mole photoinitiator per gram of silicone acrylate **1a**; I_0 = 1.0 or 2.5 or 4.15 mW/cm^2; λ = 340 . . . 380 nm).

radical formation. Presumably, oxygen was not quantitatively consumed and it can diffuse to the bottom of the layer, so the first Fickian diffusion law is not fully obeyed. That oxygen can diffuse through a 50-μm layer was demonstrated by the following experiment. The system **2a**/BIPE was coated with a silicone oil (NM 1-200) which cannot be mixed with the silicone acrylate **2a**. This system was hardened by UV irradiation. As can be seen in Fig. 18, the measured limiting conversion is a function of the thickness of the silicone oil layer, which is identical with the

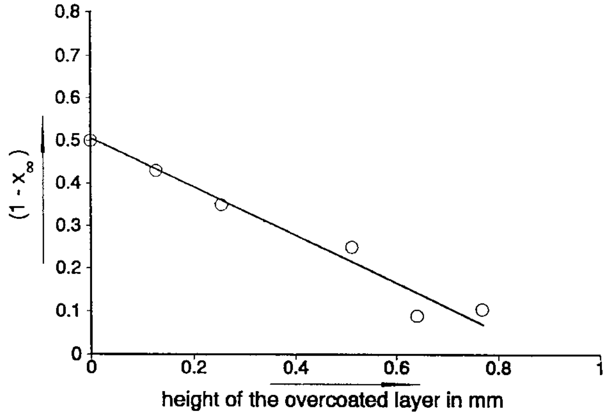

FIG. 18. Plot of $1/(1 - x_\infty)$ vs height of the overcoated silicone oil layer [system **2a**/BIPE; 5×10^{-5} mole photoinitiator per gram of silicone acrylate **2a**; I_0 = 1.0 mW/cm^2; λ = 340 . . . 380 nm; silicone oil = NM 1-200 (Chemiewerk Nünchritz)].

diffusion pathway. This experiment also demonstrates the legitimacy of the assumption $V' \sim (1 - x_\infty)$.

SUMMARY

Silicone acrylates represent not only a special type of polymer, they are also useful as model systems for the investigation of the crosslinking process in bulk. The crosslinking process can be described by means of a radical chain process. The photoinduced radical network formation of silicone acrylates under several experimental conditions (inert gas, vacuum, air-saturated laminate, air) has been investigated in the presence of several photoinitiators. By using two kinetic methods it was possible to show that each initiator used exhibits a different initiating efficiency, the relative order of which has been estimated.

From calorimetric results it is inferred that oxygen inhibits and terminates the chain process. The reaction rate as well as the inhibition time of the crosslinking are proportional to the air pressure, to the intensity of the incident light, and to the quantum yield of the initiator photolysis. Polymerization starts when all oxygen is consumed in the silicone layer.

The final conversion under inert conditions (inert gas, vacuum, air-saturated laminate) is approximately 90%. In the open air system the final conversion is a function of air pressure, of the incident light intensity, and of the quantum yield of radical formation (initiator photolysis). By using the first Fickian diffusion law we showed that in the open air system, only oxygen which diffused into the system determined the final conversion.

O_2 influences the reaction rate, the inhibition time, and the final conversion. Nevertheless, quenching of the excited photoinitiator by oxygen was also observed.

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