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PHOTOCROSSLINKING OF SILICONES. PART 12. UV-CURING OF SILICONE ACRYLATES IN THIN LAYERS—A REAL TIME INFRARED STUDY†

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ABSTRACT

Silicone acrylates are useful as model systems for the investigation of the crosslinking process in bulk. The photocrosslinking of silicone acrylates is studied by both RT-IR spectroscopy and a photocalorimetric set-up using a laminate technique. The influence on the polymerization kinetics of light intensity, exposure time, and type of photoinitiator are described. The parameters of the kinetic equation are determined. It is shown that oxygen acts as an inhibitor. Only oxygen which diffuses through the polypropylene protecting layer into the system determines the termination reaction. The experimental results received with calorimetric and infrared methods show analogous results. However, because the experimental conditions differ in the two experimental set-ups, the results are influenced.

INTRODUCTION

The photoinduced radical crosslinking of silicones containing pendant acrylate groups has been investigated by calorimetric, ESR, and infrared measurements [1–4]. The investigation of the photocrosslinking process of such silicone acrylates shows that they represent not only a special type of polymer, but they are also useful

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†For Part 11, see Ref. 1.

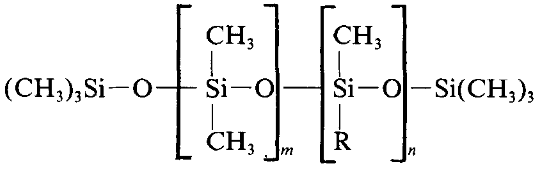
as model systems for the investigation of the crosslinking process in bulk. The high oxygen permeability of silicones allows us to investigate the inhibition and termination of the radical chain process by oxygen, oxygen diffusion, and quenching of the excited photoinitiator by oxygen.

From calorimetric results [1-3] it is inferred that oxygen inhibits and terminates the chain process. The reaction rate, the final degree of conversion, and the inhibition time of polymerization are functions of the partial pressure of oxygen. One can show that crosslinking of acrylate groups starts after the consumption of all dissolved oxygen, and that the oxygen which diffuses into the system determines the termination reaction and the final degree of conversion.

For a more quantitative overview on crosslinking kinetics in the region of oxygen diffusion, a real time infrared study was used. By means of the polypropylene laminate technique it was possible to separate the region of oxygen diffusion and to measure the crosslinking kinetics in this region. This study demonstrates that sample thickness influences the kinetic result.

EXPERIMENTAL

The synthesis of the silicone derivative SIAC used,

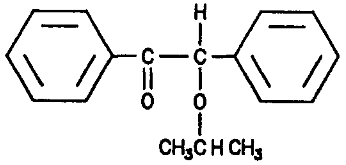


$$(CH_3)_3Si-O-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\right]_m-\left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ R \end{array}\right]_n-Si(CH_3)_3$$

(where R = $(CH_2)_3-O-(CH_2)_2-O-COCH=CH_2$ and [acrylate] = 1.2 mol/kg as experimentally determined), has been described elsewhere [3]. The molar mass of SIAC was about 5 kg/mol. The reactive silicone derivative was free from any inhibitors.

Several photoinitiators which differ in Φ, their quantum yields of photolysis, were applied in the present kinetic investigations. They were 2-isopropoxy-2-phenyl acetophenone (*b*enzoin *i*so*p*ropyl *e*ther),

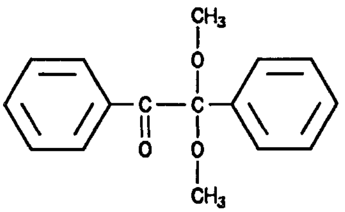
BIPE:



Φ = 0.33 [2]

2,2′-dimethoxy-2-phenyl acetophenone (*b*enzil *dim*ethyl *k*etal),

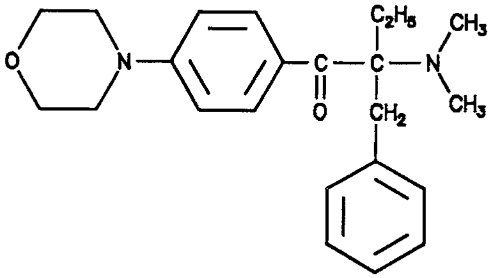
BDMK:



Φ = 0.52 [2]

2-*b*enzyl-2-*d*imethylamino-1-(4-*m*orpholinophenyl)-*b*utanone-1,

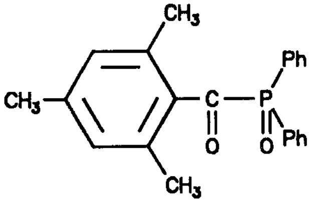
BDMB:



$\Phi = 0.22$ [5]

2,4,6-*t*ri*m*ethyl*b*enzoyldiphenyl*p*hosphinoxide,

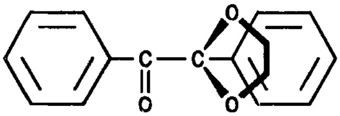
TMBP:



$\Phi = 0.80$ [2]

phenyl-(2-phenyl-1,3-dioxolan-2-yl) methanone (*b*enzilmono(ethylene *g*lykol) *k*etal),

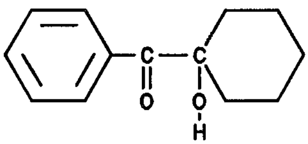
BGK:



$\Phi = 0.11$ [2]

and 1-*h*ydroxy-*c*yclohexyl *p*henyl *k*etone,

HCPK:



$\Phi = 1.0$ [2]

BIPE (Schönert Leipzig), TMBP (BASF), BDMK, HCPK, and BDMB (I 651, I 184 and I 369, Ciba Geigy) are commercial products. They were purified by recrystallization three times. The synthesis of BGK has been described elsewhere [6].

The experimental set-up of real time (RT)-IR photospectroscopy has been described in several recent papers [7-9]. The structure and geometry of the sample is described in the Fig. 1. The sample is placed in an IR spectrophotometer (Perkin-Elmer 781) chamber and exposed simultaneously to a UV beam [medium pressure arc lamp (HOYA) with quartz fiber optics]. The IR spectrophotometer must be set in the absorbance mode, and the detection wavelength must be fixed at a value where the monomer double bond exhibits a discrete and intense absorption. In the case of SIAC, 1193 cm^{-1} was used [4]. The degree of conversion can be calculated from:

$$x = 1 - [A_\lambda]_t/[A_\lambda]_0 \tag{1}$$

where $[A_\lambda]_0$ and $[A_\lambda]_t$ are the sample absorbance at this wavelength before and after UV exposure, respectively.

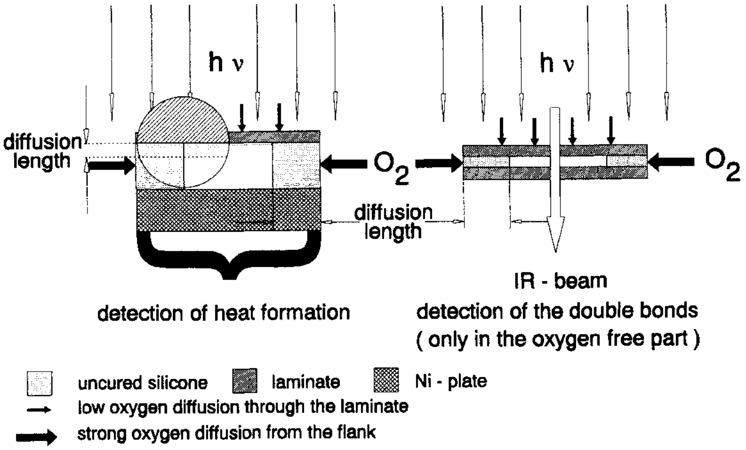


FIG. 1. Structure and geometry of the calorimetric (left) and RTIR sample (right) (sample thickness 640 μm and 12 μm, respectively).

The rate of polymerization (R_p) can be determined at any time from the slope of the kinetic curve:

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

where $[M]_0$ is the initial monomer concentration, x is the conversion on double bonds, and t is the irradiation time.

The construction of the isoperibolic calorimeter has been schematically described previously [3, 10]. 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 arc lamp (HBO 200, Narva). The structure and geometry of the sample are described in Fig. 1.

The heat flow generated by the crosslinking reaction is directly recorded as a function of time. The rate of polymerization and the degree of conversion can be derived at any moment from the heat flow value, provided that the standard reaction heat for the system used is known. The reaction rate is given by Eq. (3), and the conversion is given by integration of Eq. (3):

$$R_p = -(dx/dt)\cdot[M]_0 = -(dH/dt)\cdot[M]_0/\Delta H_0 \qquad (3)$$

where $[M]_0$ is the initial monomer concentration and dH/dt is the heat flow value. For the standard heat of polymerization of acrylate (ΔH_0), a value of 83 kJ/mol [8] was used.

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

RESULTS AND DISCUSSION

General Kinetics

Kinetic studies have shown that the photoinitiated radical crosslinking of silicone acrylates can be considered to be a polymerization process [1–4]. Radical-induced polymerizations are known to be strongly inhibited by atmospheric oxygen, an excellent scavenger of both initiator and polymer radicals. This effect is more important for silicone derivatives because oxygen is very soluble and exhibits a large diffusion coefficient [12]. Therefore, the photoinduced crosslinking of silicone derivatives also strongly depends on the oxygen concentration in the polymeric layer and in the surrounding atmosphere.

Due to the specific kinetic situation in bulk, Eq. (4) has to be used to describe the rate of the photocrosslinking process (R_p) under stationary irradiation conditions [3, 13]. Only this general expression or the reduced form (Eq. 5)

$$R_p = -d[\mathrm{M}]/dt = -(dx/dt)\cdot[\mathrm{M}]_0 = k(x)\cdot[\mathrm{M}]^{\alpha}\cdot I_0^{\beta} \tag{4}$$

$$R_p' = -dx/dt = k(x)\cdot[\mathrm{M}]^{\alpha}\cdot I_0^{\beta} \tag{5}$$

(where [M] is the molar concentration of double bonds, t is is the time, $k(x)$ is a conversion (x) dependent quantity, I_0 is the intensity of the incident light, and α and β are exponents) reflect the real situation in the polymeric systems investigated because the conditions (viscosity, concentration of oxygen, monomer concentration, etc.) for the reaction partners change with time.

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).

The inhibition time can be described by

$$t_i = [\mathrm{O}_2]/R_i = [\mathrm{O}_2]/\eta\cdot\Phi\cdot\eta\mathrm{abs}\cdot I_0 \tag{6}$$

with

$$R_i = \eta\cdot\Phi\cdot\eta_{\mathrm{abs}}\cdot I_0 \tag{7}$$

where R_i is the rate of starting radical formation, $[\mathrm{O}_2]$ is the sum of dissolved oxygen and of oxygen which can diffuse into the layer, η_{abs} is the fraction of absorbed light, Φ is the quantum yield of primary radical formation, and η is the addition efficiency of the primary radical to the monomer.

Such dependencies are expected when oxygen inhibits the initiation reaction of the polymerization process [3]. Oxygen, which can diffuse into the silicone, will determine the observed final conversion.

$$\Phi\cdot I_0\cdot\eta_{\mathrm{abs}} \sim [\mathrm{O}_2]_0/l \sim [\mathrm{O}_2]_0/(1 - x_\infty) \tag{8}$$

where $[\mathrm{O}_2]_0$ is the maximal concentration of dissolved oxygen in the silicone and l is the diffusion pathway.

Using the first Fickian diffusion law, Expression (8) can be formulated for the observed limiting conversion (x_∞) as a function of the light intensity (I_0), oxygen concentration ($[\mathrm{O}_2]_0$), and quantum yield of primary radical formation (Φ). See Refs. 1 and 2.

RT-IR Measurements

Influence of the Light Intensity

It follows from Eq. (4) that the crosslinking rate is related directly to the light intensity. Typical conversion-reaction time curves of the crosslinking from SIAC/BDMK under monochromatic irradiation are shown in Fig. 2 as a function of the

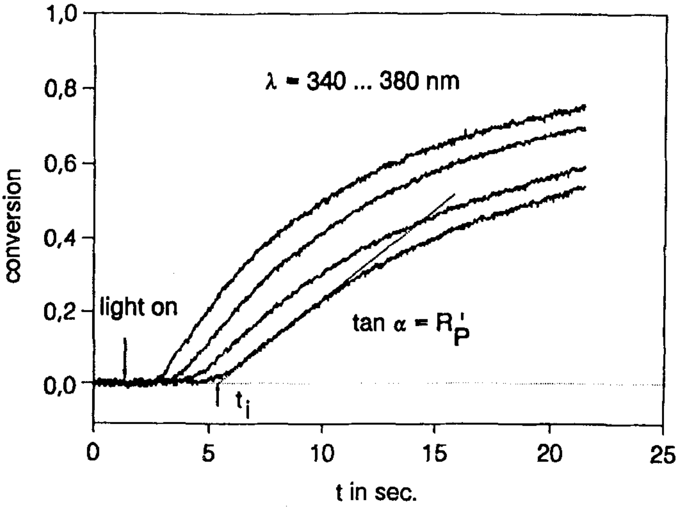


FIG. 2. Conversion (x)/time for the photoinduced polymerization of SIAC with BDMK as initiator [4.4×10^{-5} mol photoinitiator per gram of SIAC; I_0 = 17.5, 11.2, 7.6, and 4.6 mW/cm^2 (left to right); filter 1602].

light intensity. The reaction starts after a certain inhibition time t_i, the reaction rate (slope of the plot) is proportional to the intensity of the incident light, and there is a final conversion of approximately 100% independent of the inhibition time and of the light intensity.

The plot of R_p' versus $(I_0)^{0.5}$ (see Fig. 3) is nearly linear, which demonstrates that the light intensity exponent β is of the order of 0.5, typical for a polymerization with a second-order termination step [13]. However, the linear relationship in Fig.

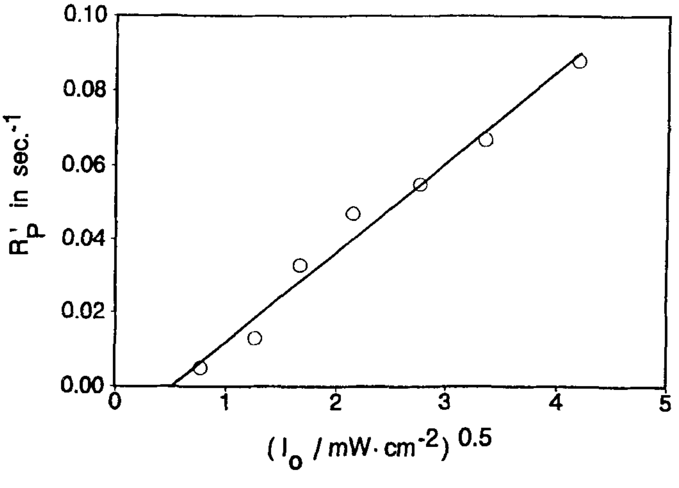


FIG. 3. Plot of reaction rate vs $(I_0)^{0.5}$ of the photocrosslinking of SIAC/BDMK (experimental conditions: see Fig. 2).

3 does not fit such an origin, and therefore an ideal bimolecular second-order termination is not fully obeyed. From the plot of lg(R_p') versus lg(I_0) (see Fig. 4), it can be inferred that the correlation is not linear at lower light intensities. The slope (identical with the β value) varies from approximately 1 to 0.55. These values show that the kinetics of chain termination ($\beta = 1$ indicates a first-order termination [13]) change from a first-order to a second-order termination step with increasing light intensity. Nevertheless, in the case of polychromatic irradiation one can observe that the β value decreases from 1 to 0.2 with increasing light intensity; see Fig. 4. The kinetics of the termination process change from first order (or a complex termination mechanism) to second order and finally to termination by primary radicals ($\beta < 0.5$ [13]).

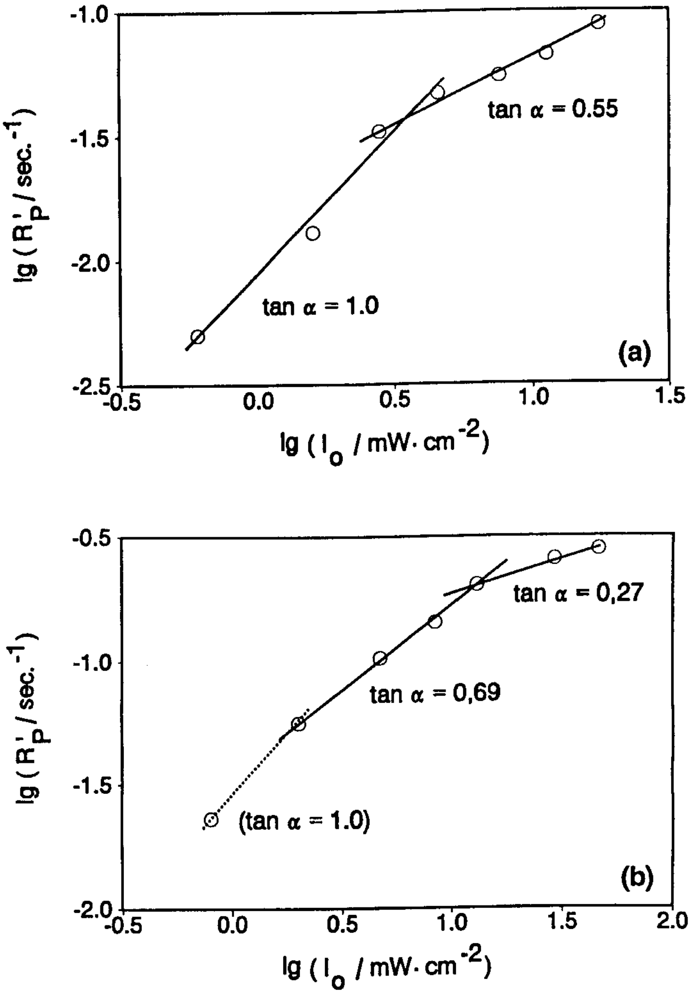


FIG. 4. Double logarithmic plot of reaction rate vs incident light intensity I_0 under monochromatic (a) and polychromatic irradiation (b) (experimental conditions: see Fig. 2; under polychromatic irradiation without filter).

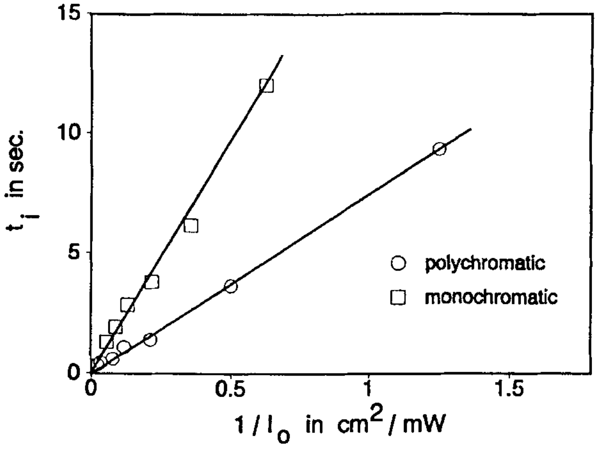


FIG. 5. Plot of the inhibition time t_i vs $1/I_0$ (system SIAC/BDMK; experimental conditions: see Fig. 2; under polychromatic irradiation without filter).

Additional to the dependence of R_p' upon I_0, one can observe an inhibition time t_i proportional to $1/I_0$. Figure 5 shows the dependencies of t_i upon $1/I_0$ under monochromatic and polychromatic irradiation conditions. The linearity of the plot demonstrates that Eq. (6) is fully obeyed. Under this condition it is possible to determine the rate of starting radical formation (R_i) by means of Eq. (6).

Influence of the Photoinitiators

Plots of the inhibition period t_i vs $1/I_0$ for BDMK, BIPE, and BDMB under monochromatic irradiation conditions are summarized in Fig. 6. Linear relationship were found for all the initiators used. It can be seen from Fig. 6 that the slope of the

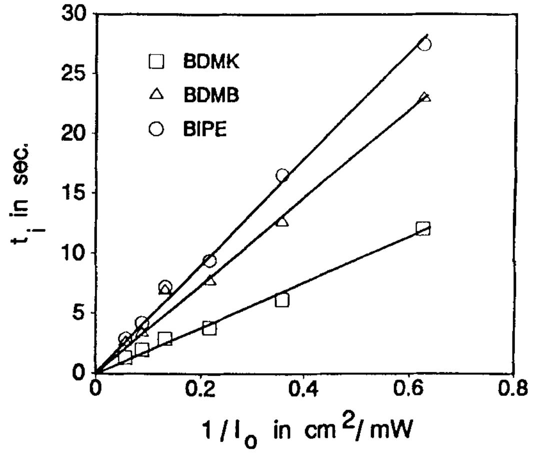


FIG. 6. Plot of the inhibition time t_i vs $1/I_0$ (silicone acrylate SIAC; [*initiator*] = 5 × 10^{-5} mol (BIPE); 4.4 × 10^{-5} mol (BDMK); 7 × 10^{-6} mol (BDMB) per gram SIAC, monochromatic irradiation; η_{abs}(365 nm) = 0.018).

plot is a function of the photoinitiator. The initiator influences the inhibition time via Φ, η, and η_{abs}. By working under the same η_{abs}, it is possible to estimate a relative value for the initiation efficiency ($\eta \cdot \Phi$) for the initiator used. By variation of the initiator concentration it is realized that all initiators absorb at 365 nm, the same fraction of the incident light. The values obtained, referred to BIPE (1), are 2.3 for BDMK and 1.3 for BDMB.

The kinetics of radical photocrosslinking corresponds to a thermal reaction with the exception of the initiation step. According to Eq. (4), the dependence of R_p upon I_0 can only be deduced from the rate of the beginning radical formation. Under this assumption, one can formulate

$$R'_p = k'(x) \cdot [\mathrm{M}]^{\alpha} (\eta \cdot \Phi \cdot \eta_{abs} \cdot I_0)^{\beta} \tag{9a}$$

or by means of eq. (7),

$$R'_p = k'(x) \cdot [\mathrm{M}]^{\alpha} \cdot R_i^{\beta} = k'(x) \cdot [\mathrm{M}]^{\alpha} ([\mathrm{O_2}]/t_i)^{\beta} \tag{9b}$$

where $k'(x)$ is a conversion-dependent quantity.

According to Eq. (9a), it is also to be expected that the photoinitiator used will influence the rate of crosslinking via Φ, η, and η_{abs}. On the contrary, from Eq. (9b) it follows that only R_i determines R'_p, and this strength of this relationship depends on the initiator used.

Figure 7, which shows a plot of R_p vs $(1/t_i)^{0.5}$ for SIAC/BDMK, demonstrates the inhibition period (value of R_i) correlated with the reaction rate in the above manner (Eq. 9b). However, the linear relationship in Fig. 7 does not fit the origin; it is the same effect found for the plot R'_p vs $(I_0)^{0.5}$ (see Fig. 3). Nevertheless, this fact demonstrates that there is no error in the determination of the light intensity. The t_i value is an internal standard.

Nearly identical plots [R'_p vs $(1/t_i)^{0.5}$] were obtained by initiation of the crosslinking by means of BIPE or BDMB. The intersections with the x-axis are indepen-

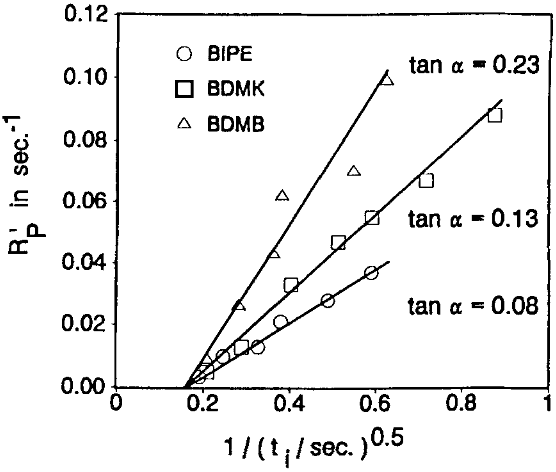


FIG. 7. Plot of reaction rate vs $(1/t_i)^{0.5}$ of the photocrosslinking of SIAC with several photoinitiators (experimental conditions: see Fig. 6).

dent of the initiator used. The slopes of the plot $[k'(x) \cdot [M]^{\alpha} \cdot [O_2]^{-0.5}]$ differ (under the assumption α is constant). The values obtained, referred to BIPE, are 1.3 for BDMK and 2.5 for BDMB. Values from 1.6 for BDMK and 2.6 for BDMB (all values referred to BIPE) were obtained from the slope $[k'(x) \cdot [M]^{\alpha} \cdot (\Phi \cdot \eta)^{0.5}]$ of the plot R_p vs $(I_0)^{0.5}$ through knowledge of the relative values for $\Phi \cdot \eta$. These relative values of $k'(x)$ demonstrates that $k'(x)$ is a function of the initiator used.

Plots of R'_p vs $(1/t_i)^{0.5}$ under polychromatic irradiation conditions are given in Fig. 8, which shows no linear correlation for BDMB, TMBP, and HCPK at higher light intensities. Plots of $\lg(R'_p)$ vs $\lg(I_0)$ demonstrate that the slope (β value) changes in all systems; see Fig. 9. Nevertheless, the correlations between inhibition

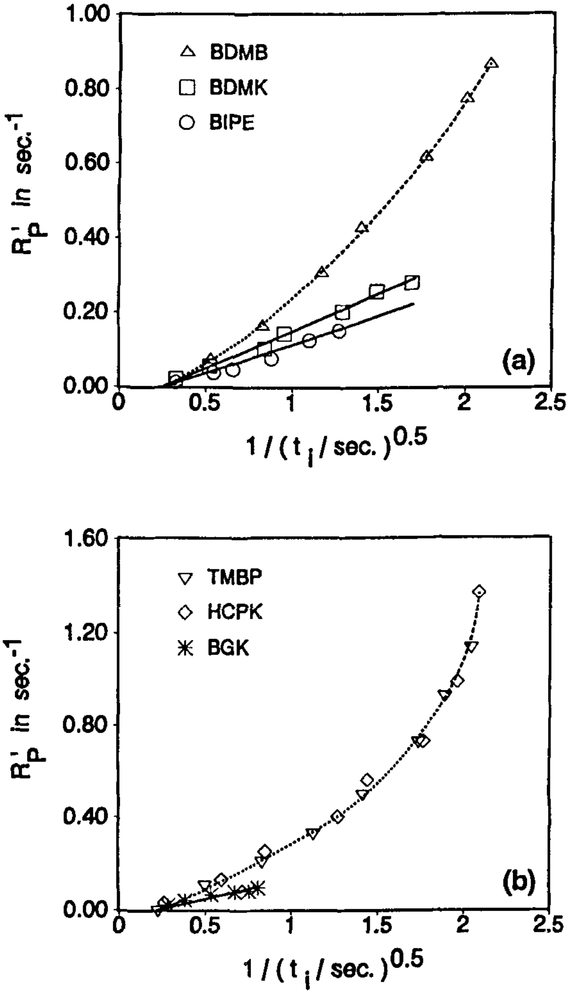


FIG. 8. Plot of reaction rate vs $(1/t_i)^{0.5}$ of the photocrosslinking of SIAC with several photoinitiators (silicone acrylate SIAC; [initiator] = 5×10^{-5} mol (BIPE and BGK); 4.4×10^{-5} mol (BDMK); 7×10^{-6} mol (BDMB); 5×10^{-4} (HCPK); 2.7×10^{-5} (TMBP) per gram SIAC, polychromatic irradiation; $\eta_{abs}(365 \text{ nm}) = 0.018$).

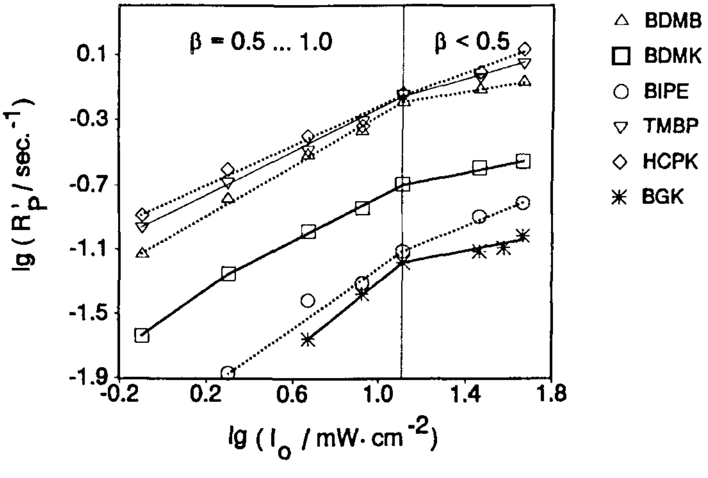


FIG. 9. Double logarithmic plot of reaction rate vs incident light intensity I_0 under polychromatic irradiation (experimental conditions: see Fig. 8).

time and $1/I_0$ are linear, which demonstrates that the inhibition time and $1/I_0$ are linear, which demonstrates that the inhibition kinetics is fully obeyed.

All previous investigations were carry out under light absorption at 365 nm (wavelength of the main emission line). However, a medium-pressure arc lamp also emits light at lower wavelengths. It is well known that the quantum yield of initiator photolysis changes with the irradiation wavelength ($\Phi_{\mathrm{BIPE}} = 0.25$ at 254 nm and 0.55 at 313 nm [14], respectively; 0.49 at 365 nm [15] in methanol under air). In polychromatic irradiation conditions these wavelengths were absorbed from the initiator used. Under these conditions is clear that the slope of the plot t_i vs $1/I_0$ will differ under monochromatic and polychromatic irradiation [values referred to BIPE (1) are given in Table 1].

TABLE 1. Characteristic Points of Polymerization of SIAC under Poly- and Monochromatic Irradiation (O.D. = 0.008, . . . , 0.009 at 365 nm; I_0 = 17.5 mW/cm^2 under monochromatic irradiation; I_0 = 46, 0 mW/cm^2 under polychromatic irradiation)

		Poly			Mono		
Initiator	$c_{\mathrm{initiator}}$, mol/g	R'_p, s^{-1}	t_i, s	tan α[a]	R'_p, s^{-1}	t_i, s	tan α[a]
BIPE	5.0×10^{-5}	0.15	0.63	1.00	0.037	2.87	1.00
BDMK	4.4×10^{-5}	0.28	0.35	0.42	0.088	1.31	0.42
BGK	5.0×10^{-5}	0.10	1.52	3.28	0.020	14.01	–
HCPK	2.0×10^{-4}	1.37	0.23	0.13	0.318	0.98	–
TMPB	2.0×10^{-5}	1.14	0.24	0.18	0.310	0.80	–
BDMP	7.0×10^{-6}	0.87	0.23	0.15	0.099	2.57	0.77

[a] Slope of the plot t_i vs $1/I_0$.

The light absorptions of several SIAC/initiator laminates are summarized in Table 2. The values demonstrate that light absorption differs at a constant initiator concentration (1%) between 0.023 and 0.18. We found that BDMB has the shortest inhibition period and the largest reaction rate under the given polychromatic irradiation conditions.

Influence of Oxygen and the Type of the Laminate Layer

Radical-induced polymerization is known to be greatly inhibited by atmospheric oxygen, an excellent scavenger of both the initiator and the polymer radicals. Furthermore, it is known that traces of oxygen influence radical termination in SIAC systems [1]. The photocrosslinking of a 12-μm layer of SIAC is possible only under a reduced oxygen influence. The decay of double bonds in the laminate starts after an inhibition period. During this period, photochemical radical formation is identical to the consumption of these radicals by oxygen [1-3], see Eq. (10). Polymerization cannot start because the reaction rate of the primary radical is faster with oxygen than with the monomer. All initiator radicals formed may react with oxygen, so oxygen is consumed during this scavenging reaction. The polymerization reaction will start only when the conditions of Eq. (11) are obtained:

$$\Phi\cdot\eta_{\mathrm{abs}}\cdot I_0 = k_{\mathrm{ox}}\cdot[\mathrm{R}\cdot]\cdot[\mathrm{O}_2] \gg k_{\mathrm{p}}\cdot[\mathrm{R}\cdot]\cdot[\mathrm{M}] \tag{10}$$

$$k_{\mathrm{p}}\cdot[\mathrm{R}\cdot]\cdot[\mathrm{M}] \geq k_{\mathrm{ox}}\cdot[\mathrm{R}\cdot]\cdot[\mathrm{O}_2] \tag{11}$$

where k_{ox} is the rate of radical consumption of oxygen, k_{p} is the rate of the propagation, $[\mathrm{R}\cdot]$ is the primary radical concentration in the layer, and $[\mathrm{O}_2]$ is the concentration of the dissolved oxygen.

The crosslinking of SIAC is inhibited under air at all times. From this effect it can be deduced that oxygen diffuses into the layer, and so the conditions of Eq. (11) are never obtained.

One can infer from Fig. 10 that the type of laminate (KBr, polypropylene) influences the crosslinking rate ($R_{\mathrm{p}}^{\mathrm{max}} = 0.04\ \mathrm{s}^{-1}$ for polypropylene and $0.062\ \mathrm{s}^{-1}$ for KBr) under the given conditions. Measurements between two KBr plates were carried out only for the SIAC/BDMB system because the plates were glued together after curing. However, the inhibition time values are the same for both systems, and

TABLE 2. Characteristic Points at Constant Initiator Concentration (1%; $I_0 = 46\ \mathrm{mW/cm}^2$ under polychromatic irradiation conditions)

Initiator	η_{abs}	t_{i}, s	R'_{p}, s^{-1}
BIPE	0.024	0.67	0.10
BDMK	0.024	0.36	0.42
BGK	0.032	1.93	0.08
HCPK	0.023	0.54	0.42
TMBP	0.051	0.23	1.06
BDMP	0.180	0.17	1.75

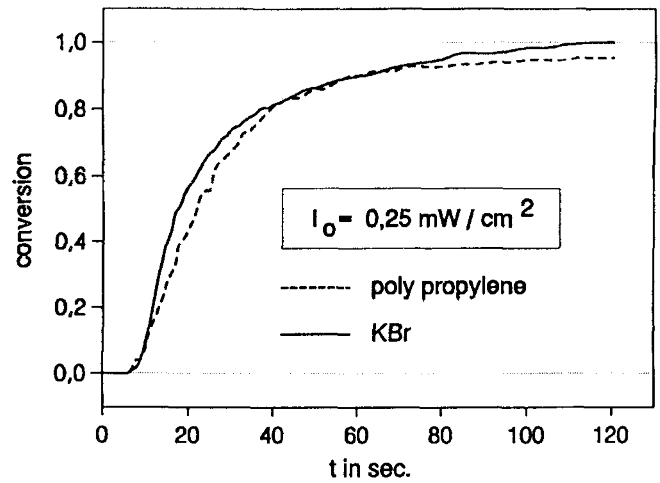


FIG. 10. Conversion (x)/time for the photoinduced polymerization of SIAC with BDMB as initiator (7 × 10^{-6} mol/g SIAC; polychromatic irradiation).

the final degrees of conversion vary only by 0.03 (0.97 for polypropylene and 1 for KBr).

From the above discussion it can be deduced that traces of oxygen may influence the crosslinking kinetics in the propylene laminate system. Under the assumption that no diffusion takes place in the KBr-laminate and the dissolved oxygen in the monomer layer is completely consumed in the inhibition period, it can be estimated by means of the method of Decker [16] (see Eq. 12) that the steady-state concentration of oxygen in the polypropylene SIAC laminate is about 7 × 10^{-8} mol/L. The above assumption is necessary because without the laminate technique an exact record of polymerization under nitrogen is not possible as a consequence of floating of the layer in the vertical experimental set-up during a long irradiation time.

$$[O_2]_s = (R_i \cdot k_t^b)^{0.5}(R_p^1/R_p^2 - R_p^2/R_p^1)/k_{ox} \qquad (12)$$

where $[O_2]_s$ is the steady-state concentration of O_2, k_t^b is the rate constant of bimolecular termination, R_p^1 is the reaction rate between KBr and the laminate, R_p^2 is the reaction rate in the polypropylene laminate [$R_i = 3.75 \times 10^{-4}$ mol/L·s (by means of Eq. 7; with $t_i = 8$ s; $[O_2] = 3 \times 10^{-3}$ mol/L [12]; $k_t^b \approx 4 \times 10^6$ L/mol·s [16]; $k_{ox} = 5 \times 10^8$ L/mol·s [17]; $R_p^1/R_p^2 = 1.55$].

Calculation of the steady-state concentration occurs under the assumption $[O_2]_s = 0$ in the KBr laminate. This means that oxygen can diffuse through the polypropylene into the silicone acrylate under the given experimental conditions and reduce the final crosslinking conversion. However, the rate is low in this case and so differences in the inhibition time cannot be found; see Ref. 1. According to Eq. (8), under conditions for a low start of radical formation (low irradiation intensity and low quantum yield of initiator photolysis), the diffused oxygen dramatically reduces the final conversion.

BGK is one initiator with a low Φ value (0.11). In this system a crosslinking reaction is only seen at light intensities ≥ 4.7 mW/cm^2. Hence, with I_0 < 4.7 mW/

cm^2 the reaction is inhibited at all times ($x_\infty = 0$). Nevertheless, between two KBr plates at $I_0 = 1$ mW/cm^2, a final conversion of 1 can be observed [4]. This dramatic effect proves the diffusion of oxygen into the silicone layer. In Fig. 11 an example of the dependence of x_∞ (from long time measurements) on I_0 is given for the SIAC/BIPE system. The relative high t_i value (see Table 1) in this system indicates a low start of radical formation (see Eq. 6). By irradiation involving two polypropylene protecting layers, a dependence of the limiting conversion on the light intensity can be observed at low light intensities. On the contrary, the final limiting conversion between two KBr plates is 1 [4]! A plot according to Eq. (8) (see Fig. 11) shows a linear relationship between the parameters. Such a dependence is normally observed in open air systems, and it once again proves oxygen diffusion through the laminate into the silicone.

Keeping in mind the oxygen diffusion, the variation of the β value from 1 to approximately 0.5 can be discussed. This change indicates a transition of the polymer radical from first-order to second-order termination with increasing light intensity. From calorimetric results it is inferred that a pseudofirst-order termination process takes place in the presence of oxygen. Oxygen determines the termination reaction of the polymer radical. This result infers the conclusion that in the polypropylene laminate under low irradiation conditions (β approximately 1) the diffused oxygen react with the polymer radical in a pseudofirst-order reaction:

$$\beta = 1 \; ([O_2] \gg [P\cdot]):$$

$$P\cdot + O_2 \longrightarrow P{-}O{-}O\cdot \tag{13}$$

where [P·] is the concentration of polymer radicals.

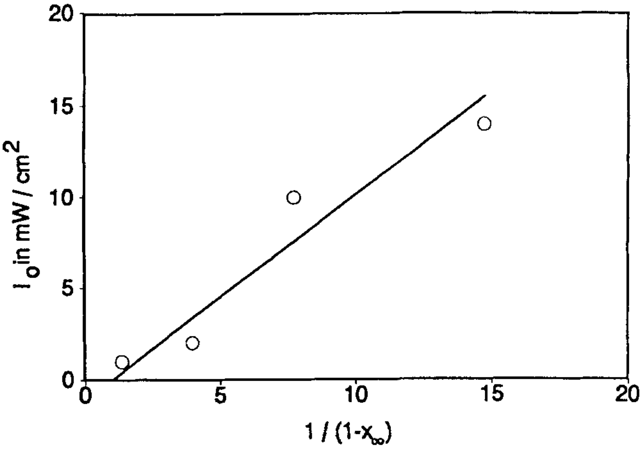


FIG. 11. Plot I_0 vs $1/(1 - x_\infty)$ for SIAC/BIPE (5×10^{-5} mol photoinitiator per gram SIAC, polychromatic irradiation, long time irradiation of 5–15 minutes (the initiator is not consumed under these conditions)).

Comparison with Calorimetric Results

Typical calorimetric examples for deconvoluted conversion–time and reaction rate–time curves for the photopolymerization of silicone acrylate with BDMK in a laminate under monochromatic irradiation (wavelength region 330 to 380 nm from emitted light of a 200-W high-pressure arc lamp) are given in Fig. 12. The plot R_p vs $(I_0)^{0.5}$ (see Fig. 13) is linear, which demonstrates second-order termination kinetics under the given experimental conditions.

Figure 14 shows a plot R_p vs $(1/t_i)^{0.5}$ for SIAC/BDMK and demonstrates that the inhibition period correlates to the reaction rate. However, the linear relationship in the figure does not fit the origin. On the other hand, plots of R_p vs $(1/t_i)^{0.5}$ for SIAC/BIPE and SIAC/BDMB go through the origin, which demonstrates an ideal behavior. The slope of the plot ($k'(x) \cdot [M]^{\alpha} \cdot [O_2]^{-0.5}$; see Eq. 6) differs by a factor of 1.6. Nevertheless, the calorimetric determined factor is lower than the RT-IR value.

Plots of the calorimetric determined inhibition period vs $1/I_0$ for BDMK, BIPE, and BDMB under monochromatic irradiation conditions are summarized in Fig. 15. Approximately linear relationships were found for all the initiator used. The values of the product $\eta \cdot \Phi$ obtained, referred to BIPE ($\eta_{abs} = 0.55$), are 2.3 for BDMK ($\eta_{abs} = 0.59$) and 1.4 for BDMB ($\eta_{abs} = 0.55$). RT-IR and photocalorimetry gives the same results! Using the quantum yields of the initiator photolysis [$\Phi = 0.33$ (BIPE), $\Phi = 0.52$ (BDMK), $\Phi = 0.22$ (BDMB)] with BIPE = 1, the relative initiation efficiencies can be estimated. The values obtained are 1.5 for BDMK and 2.1 for BDMB.

From calorimetric postpolymerization experiments [1, 2] it can be deduced that oxygen, which can diffuse into the layer, determines the termination reaction

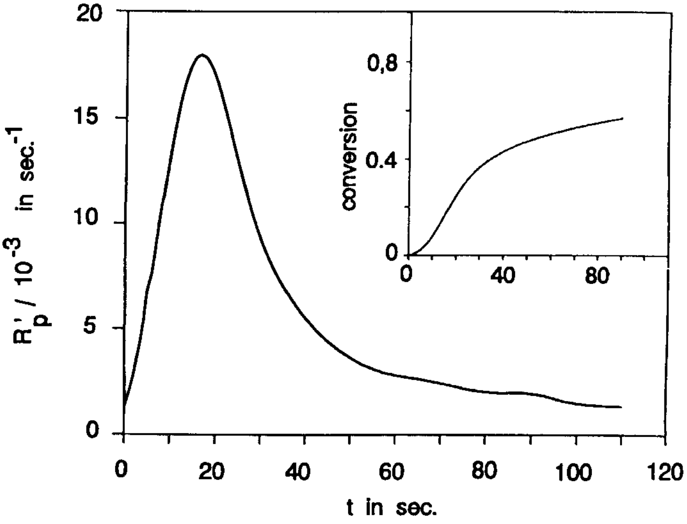


FIG. 12. Calorimetric determined conversion (x)/time and reaction rate (R'_p)/time curve for the photoinduced polymerization of SIAC/BDMK (5×10^{-5} mol photoinitiator per gram SIAC; I_0 = 3,27 mW/cm^2; λ = 340 . . . 380 nm; see also Ref. 1).

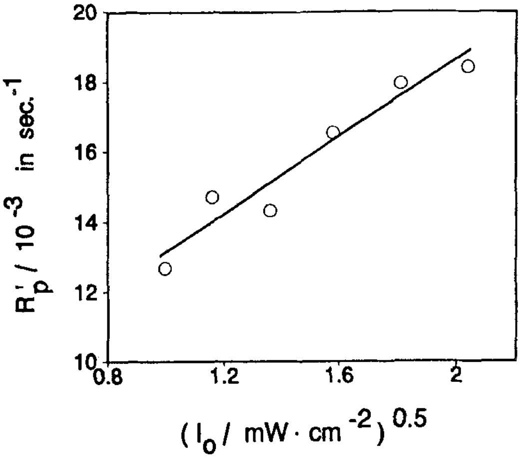


FIG. 13. Plot of reaction rate vs $(I_0)^{0.5}$ of the photocrosslinking of SIAC/BDMK (experimental conditions: see Fig. 12; see also Ref. 1).

of the polymer radical. In an open air system a first-order termination process and in the laminate a second-order termination reaction was found. The observed β value of 0.5 in the laminate indicates that all oxygen is consumed and an effective oxygen diffusion through the polyvinyl alcohol layer into the silicone layer is negligible [RT-IR experiments with the same system using two polypropylene protecting layers show that the β value decreases (1 to 0.5) with increasing light intensity].

Qualitatively, other experimental evidence on the results is given by the limiting conversion x_∞. Figure 16 illustrates that the calorimetric-determined limiting conversion is strongly influenced by the light intensity. The results obtained (see

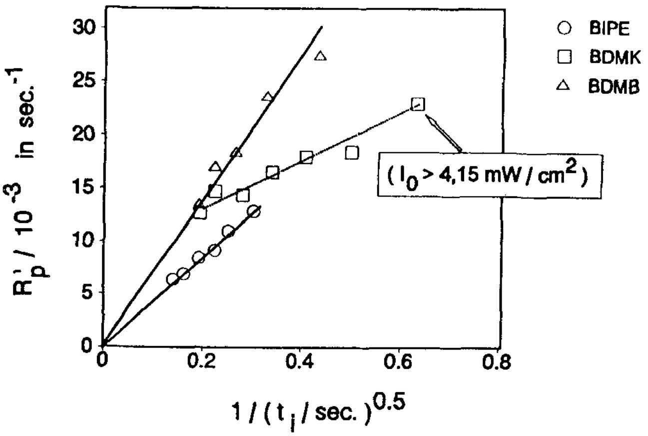


FIG. 14. Plot of reaction rate vs $(1/t_i)^{0.5}$ of the photocrosslinking of SIAC with several photoinitiators (experimental conditions: see Fig. 12; $I_0 = 1.0, \ldots, 4.15$ mW/cm^2).

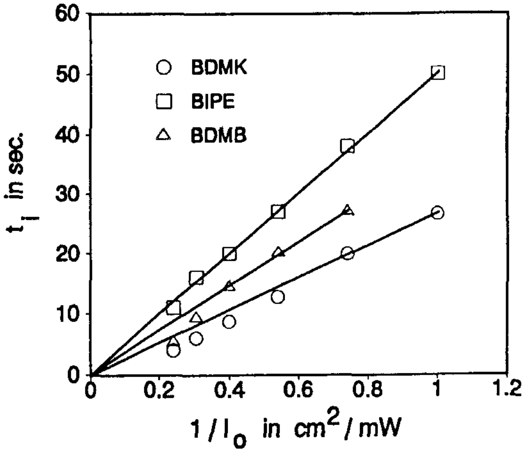


FIG. 15. Plot of the inhibition time t_i vs $1/I_0$ for several photoinitiators (5×10^{-5} mol photoinitiator per gram of SIAC; $\lambda = 340, \ldots, 380$ nm; laminate).

also Refs. 1 and 2) demonstrate that oxygen which diffuses into the silicone acrylate layer limits the final conversion, see Eq. (8). From these discussions it follows that there is strong oxygen diffusion under calorimetric conditions. However, this thesis is contradictory to our discussion of the height of the β value. Nevertheless, RT-IR experiments confirm both positions.

The fundamental questions are: Why are there differences in the evidence using calorimetric measurements? What is the difference between the methods?

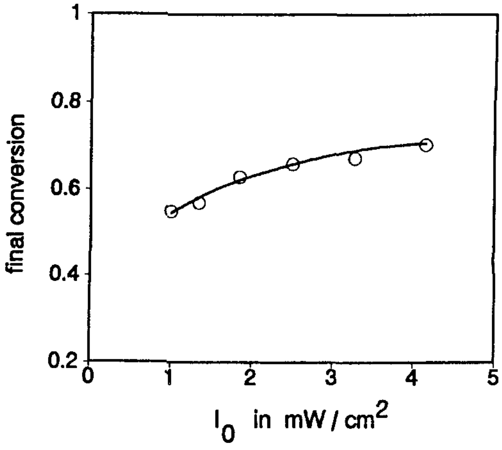


FIG. 16. Final conversion as function of the light intensity for the photoinduced polymerization of SIAC/BDMK (5×10^{-5} mol photoinitiator per gram SIAC; $\lambda = 340, \ldots, 380$ nm; laminate).

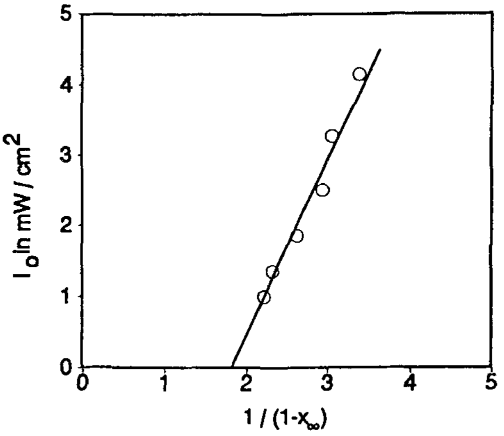


FIG. 17. Plot of I_0 vs $1/(1 - x_\infty)$ for SIAC/BDMK (5×10^{-5} mol photoinitiator per gram SIAC, monochromatic irradiation, laminate).

Figure 1 represents schematically the sample from the RT-IR and the calorimetric measurements under irradiation conditions. Clearly, the difference is the thickness (640 and 12 μm, respectively) of the samples used. Obviously, oxygen may diffuse into the silicone layer of the calorimetric sample from the flank. Under this assumption of a diffusion pathway of 0.5 mm (in this area the polymerization is inhibited at all times [1, 2]), the height of the value is in agreement with experimental results [2]. The reactive polymerization volume was reduced to 81%, but the polymerization heat was measured over the full volume.

On the contrary, in IR detection the IR beam is located in the center of the irradiation window, so oxygen diffusion from the flank cannot influence the window of the detection, which is given by the IR beam of the spectrometer. According to this thesis the calorimetric measured limiting conversion must correlate exactly to the light intensity. Figure 17 is a plot I_0 vs $1/(1 - x_\infty)$ for the SIAC/BDMK laminate system. The linearity of the plot demonstrates that Eq. (8) is suitable to describe the dependence of x_∞ on I_0, but the plot does not fit 1.

From the literature it is well known that oxygen diffusion through polypropylene is more effective than through polyvinyl alcohol [18]. Furthermore, using the second Fickian diffusion law, it can shown that oxygen concentration is a function of the diffusion pathway. Thus, it can be inferred that the influence of oxygen in a thin film (diffusion pathway $\approx$ sample thickness) is larger than in a thick layer (diffusion pathway $\ll$ sample thickness). Oxygen diffusion into silicone through a laminate with a thin silicone layer is significant. We found a β value of 0.5 at high light intensities where many initiating radicals are formed and consume all the oxygen. The observed decrease of β values with increasing light intensity (1, . . . , 0.5 at monochromatic or 1, . . . , 0.2 at polychromatic irradiation) and the dependency of x_∞ on the light intensity is in agreement with our discussion. On the other hand, a β value of 0.5 for a thick layer proves that oxygen diffusion through the laminate is negligible both because of the sample thickness and the diffusion coefficient for polyvinyl alcohol. The observed dependency of x_∞ on I_0 can be attributed to diffusion from the flank.

CONCLUSION

Silicone acrylates are useful as model systems for the investigation of the crosslinking process in bulk. The photoinduced radical network formation of silicone acrylates between polypropylene and KBr protecting layers has been investigated in the presence of several photoinitiators. The crosslinking can be described by a radical chain process.

From RT-IR results it is inferred that oxygen inhibits and terminates the chain process. The reaction rate as well as the inhibition time are functions of both the intensity of the incident light and the photoinitiator used. Polymerization starts when all oxygen is consumed in the layer. In a system without a protecting layer (open air system), crosslinking is inhibited at all times.

The final conversion in the laminate is a complex function of light intensity and the photoinitiator used. By using the first Fickian diffusion law it can be shown that oxygen which diffuses through the polypropylene protecting layer into the system determines the limiting conversion and the termination reaction.

Measurements using a photocalorimeter led to somewhat different results in some cases. These differences can be explained by different experimental set-ups.

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