The decay of photoinitiators in thin layers—a real-time infrared study [1]

U. Müller

Martin–Luther–Universität Halle–Wittenberg, Institut für Organische Chemie, Geusaer Straße, D-06217 Merseburg, Germany

Abstract

Many initiators used in radical photopolymerization are carbonyl compounds. During the photolysis of the initiator radicals are formed which initiate the crosslinking reaction. Moreover, the photolysis results in a disappearance of the carbonyl group or in a shift of the frequency of the C=O stretching vibration. This work presents results of the initiator photolysis (benzoin type) in a polydimethylsiloxane and in a silicone acrylate layer measured by means of real-time infrared (RTIR), IR, and gas chromatography/mass spectrometry techniques. The rate of initiator photolysis in both media is larger under air than in the absence of oxygen. The calculated quantum yield of initiator decay in the layer correlates well with the quantum yield determined in solution. Nevertheless, the absolute values differ in both systems. Moreover, one can show that oxygen reacts effectively with the radicals formed during the photolysis. This results in an inhibition of the polymerization. The paper shows correlations between the polymerization rates and rate of initiator photolysis.
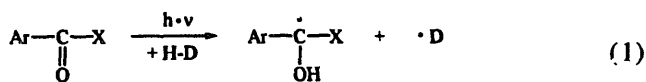
1. Introduction

Real-time infrared (RTIR) spectroscopy was used to study the photopolymerization of many olefinic and epoxy systems [2–5], simply by monitoring the disappearance of the monomer reactive function, owing to the polymerization reaction. Moreover, the crosslinking of an acrylate can be studied also on the carbonyl frequency [5,6]. The crosslinking reaction involves the opening of C=C double bonds, which are conjugated to C=O bonds in the uncrosslinked state. This results in a rise of the frequency of the C=O stretching vibration.

Many initiators used in radical photopolymerization are carbonyl compounds. It is well known, that the frequency of the carbonyl group changes strongly in dependence on the substituent. During the photolysis of the initiator radicals are formed (benzoyl radical or donator radical ˙D) (Eqs. (1) and (2)), which initiates the crosslinking reaction. All in all, this results in the disappearance of the carbonyl group (Eqs. (1)–(3)) or in a shift of the frequency of the C=O stretching vibration (Eq. (4)). Nevertheless, such types of reactions are suitable to monitor the disappearance of the initiator, owing to the initiator photolysis.
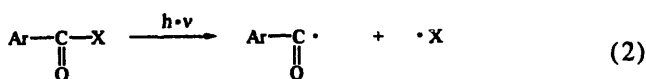
This work presents results of the initiator photolysis (benzoin type) measured by means of RTIR, IR, and gas chromatography/mass spectrometry (GC/MS) techniques,

correlations between the polymerization rates and the only evidence of the oxygen quenching of the benzoyl radical.
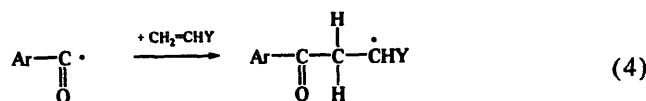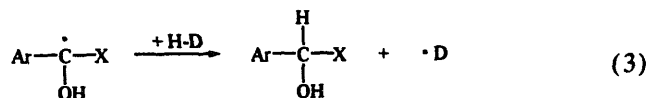
H-abstraction (or e^--transfer followed by H^+-transfer):

$$\text{Ar—}\underset{\overset{\|}{O}}{C}\text{—X} \xrightarrow[+\ \text{H-D}]{h\cdot v} \text{Ar—}\underset{\overset{|}{OH}}{\overset{\bullet}{C}}\text{—X} + \ \cdot\text{D} \tag{1}$$

α-Cleavage:

$$\text{Ar—}\underset{\overset{\|}{O}}{C}\text{—X} \xrightarrow{h\cdot v} \text{Ar—}\underset{\overset{\|}{O}}{C}\cdot + \ \cdot\text{X} \tag{2}$$

Secondary reactions:

$$\text{Ar—}\underset{\overset{|}{OH}}{\overset{\bullet}{C}}\text{—X} \xrightarrow{+\text{H-D}} \text{Ar—}\underset{\overset{|}{OH}}{\overset{H}{C}}\text{—X} + \ \cdot\text{D} \tag{3}$$

$$\text{Ar—}\underset{\overset{\|}{O}}{C}\cdot \xrightarrow{+\ \text{CH}_2\text{=CHY}} \text{Ar—}\underset{\overset{\|}{O}}{C}\text{—}\underset{\overset{|}{H}}{\overset{H}{C}}\text{—}\overset{\bullet}{\text{CHY}} \tag{4}$$
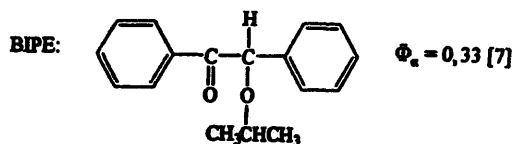
2. Experimental details

In the present kinetic investigations several photoinitiators were applied, which differ in their quantum yields of α-cleavage Φ_α.

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[1] Photochross-linking of silicones Part 14. For Part 13 see Ref. [1].

2-Isopropoxy-2-phenyl acetophenone (benzoin isopropyl ether) (BIPE)

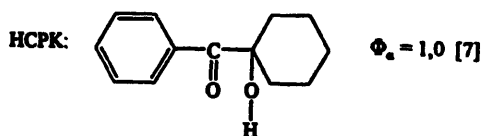BIPE: [structure] $\Phi_a = 0.33$ [7]

CH₃CHCH₃

2,2'-Dimethoxy-2-phenyl acetophenone (benzil dimethyl ketal) (BDMK)

BDMK: [structure] $\Phi_a = 0.52$ [7]
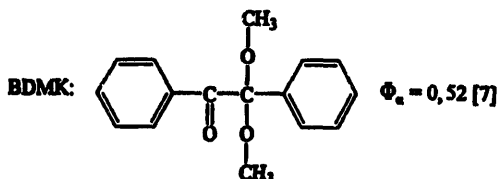
2,2-Diphenyl-2-hydroxy acetophenone (α-phenylbenzoin) α-PhB

α-PhB: [structure] $\Phi_a = 0.10$ [7]
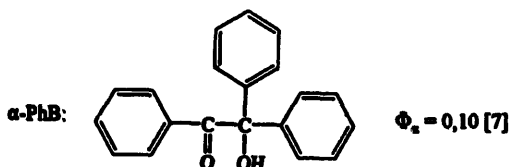
1-Hydroxy-cyclohexyl phenyl ketone (HCPK)

HCPK: [structure] $\Phi_a = 1.0$ [7]

BIPE (Schönert Leipzig), BDMK and HCPK (I 651 and I 184; Ciba Geigy) are commercial products and were recrystallized three times. The synthesis of α-PhB has been described elsewhere [8].

The silicone acrylate (polymer with monofunctional pendant acrylate groups (see Scheme 1)) was applied in the present kinetic investigations. The synthesis of the silicone acrylate by a hydrosilylation reaction, with R=(CH₂)₃–O–(CH₂)₂–O–COCH=CH₂ (see Scheme 1) and acrylate content for $l=0.5$ mol kg⁻¹ (experimentally determined), has been described elsewhere [9]. The silicone acrylate was prepared using a H-siloxane of the Wacker–Chemie with 0.05% (Si)H and 60–70 Si–O units. The reactive silicone derivatives were free from any inhibitors. The polydimethylsiloxane NM 200 (Chemiewerk Nünchritz) was used as inert media.

The experimental set-up of RTIR spectroscopy has been described in several recent papers [2–4]. The sample is placed in an IR spectrophotometer (Perkin–Elmer 781) chamber and exposed simultaneously by a UV beam (medium pressure arc lamp (HOYA) with quartz fibre

[Scheme structure]

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

Scheme 1.
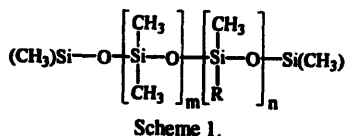
optic). The IR spectrophotometer must be set in the absorbance mode and the detection wavelength fixed at a value where the monomer double bond and the carbonyl group, respectively, exhibit a discrete and intense absorption.

The degree of conversion (x) of the monomer as well as the initiator can be calculated from:

$$x = 1 - [A_\lambda]_t / [A_\lambda]_o \tag{5}$$

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

The rate of initiator photolysis (R_α) can be determined anytime, simple from the slope ($\Delta x / \Delta t$) of the kinetic curve:

$$R_\alpha = -(\Delta x / \Delta t) \cdot [In]_o = R'_\alpha \cdot [In]_o \tag{6}$$

where $[In]_o$ is the initial initiator concentration, x is the conversion on double bonds, t is the irradiation time.

For the GC/MS (Varian 3400-Varian Saturn II) study the photolysis products were extracted in an ultrasonic bath with a methanol/heptane mixture (2:3) from the silicone layer, which contained 5×10^{-2} mol l⁻¹ initiator, where the methanolic phase was used for the analysis (sample thickness of the layer approximately, 200 μm; sample surface, 3.14 cm²; irradiation time, 15 min; $I_o = 4.15$ mW cm⁻²; $\lambda = 330...380$ nm; under atmospheric conditions or 20 mbar). The long chain polydimethylsiloxane NG 100 (Chemiewerk Nünchritz) was used as a medium in order to reduce the part of cyclic and short chain siloxanes, which are partly soluble in methanol. By means of the silicon acrylate no clear methanolic extract was formed, so that only the NG 100 was used for the GC/MS study.

3. Results and discussion

3.1. Initiator photolysis in inert medium

The photolysis of all initiators investigated can be described by means of α-cleavage (see Eq. (2)). The primary products of the photolysis are the benzoyl radical and the corresponding substituted benzil radical. In solution the chemistry of the primary formed radicals is well known [10–12]. For example, the main products of the benzoin methyl-ether photolysis (at 10% conversion) in oxygen free-benzene are: benzyl (37%), benzaldehyde (6%), benzophenone (4%) and the combination product of the substituted benzyl radical (40% of photolysis products [13]). In oxygen-free methanol the results are: benzil (14%), benzaldehyde (7.5%), methylester of the benzoic acid (15%) and the combination product of the benzyl radical (41% of photolysis products [10]). Moreover in ethanol, the ethylester of the benzoic acid is formed which indicates that the ester was produced from the benzoyl group [10].

In Fig. 1 one can see typical changes in the IR absorption spectrum of benzoin isopropyl ether after various exposure durations in a polydimethylsiloxane laminate. Beside the decreases of the peak centred at 1683 cm⁻¹, a new weak
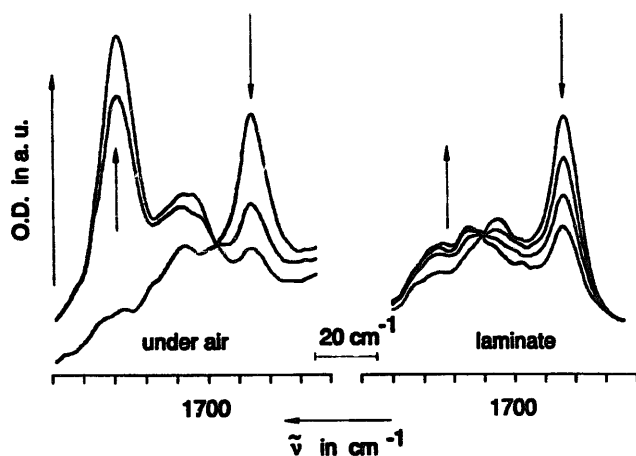
Fig. 1. Changes in the IR absorbtion of a silicone oil layer containing 5×10^{-2} mol 1^{-1} BIPE in the carbonyl range of the initiator by irradiation with polychromatic light ($\Delta t = 20$ s, $I_0 = 32.2$ mW cm^{-2}, thickness of the layer $= 50$ μm, laminates indicates the layer is coated between two polypropylene layers, and air indicates the layer is coated on a polypropylene layer).

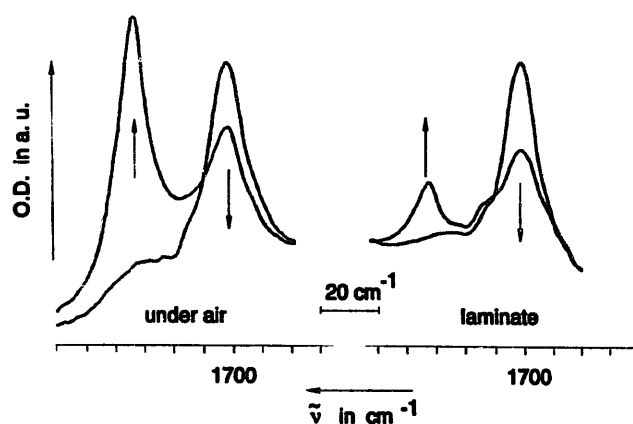Fig. 2. IR absorbtion of a silicone oil layer containing 5×10^{-2} mol 1^{-1} BDMK in the carbonyl range of the initiator before and after irradiation with polychromatic light ($\Delta t = 20$ s, $I_0 = 32.2$ mW cm^{-2}, thickness of the layer $= 50$ μm, laminates indicates the layer is coated between two polypropylene layers, and air indicates the layer is coated on a polypropylene layer).

Fig. 3. IR absorbtion of a silicone oil layer containing 5×10^{-2} mol 1^{-1} HCPK in the carbonyl range of the initiator before and after irradiation with polychromatic light ($\Delta t = 20$ s, $I_0 = 32.2$ mW cm^{-2}, thickness of the layer $= 50$ μm, laminates indicates the layer is coated between two polypropylene layers, and air indicates the layer is coated on a polypropylene layer).
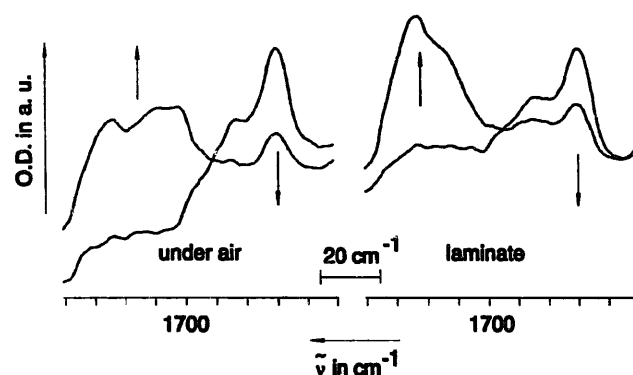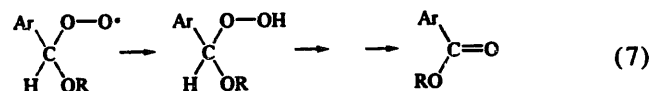
absorption appears at higher wavenumbers (1725 and 1715 cm^{-1}) due to photoproducts. The formation of the peak at 1715 cm^{-1} indicates benzaldehyde ($\tilde{\nu} = 1712$ cm^{-1} in polydimethylsiloxane). The observed weak absorption [2] corresponds to the observation from Adam of a small benzaldehyde formation during the photolysis of benzoin methylether in benzene [10]. Contrary to all expectations, no benzil ($\tilde{\nu}$(benzil) = 1677 and 1657 cm^{-1} in polydimethylsiloxane) or other aromatic benzoyl radical products (derivatives from benzophenone [3] ($\tilde{\nu}$(benzophenone) = 1668 cm^{-1} in polydimethylsiloxane)) can be detected using the IR spectroscopy. This result was surprising, because our own measurements show that benzil and benzophenone are photostable in polydimethylsiloxane under the irradiation conditions used. Therefore photolysis of the formed photoproducts is improbable under the used conditions (see also Refs. [13,14]).

Similar decreases of the IR absorption were also observed in an open air polydimethylsiloxane layer (see Fig. 1). Against the results in the laminate one can also observe a strong increase of a peak at 1727 cm^{-1}. Moreover, this formation is combined with a new weak absorption at 1705 cm^{-1}. The increase of the peak at 1727 cm^{-1} shows presumably the formation of a sequence product of a peroxy radical. Possibly, this is the formation of isopropyl benzoate ($\tilde{\nu} = 1725$ cm^{-1} for benzoic acid methylester in polydimethylsiloxane) formed from the hydroperoxy product of the α-ether radical (see Eq. (7)). In contrast, in the laminate the formation of this peak is very reduced, presumably limited by the content of dissolved oxygen. The experiments under air demonstrate the influence of oxygen of the product for-
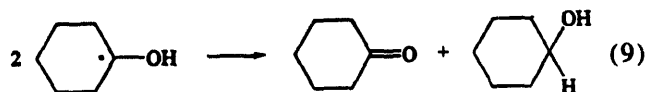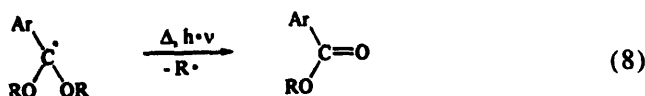
mation and the strong oxygen diffusion into the silicone layer. The discussed ester formation is comparable to the photolysis of the benzoin methylether in oxygen-containing methanol [11], where the main product of the α-methoxysubstituted benzyl radical is the methylester of the benzoic acid (85%). Nevertheless, the nature of the H-donor and the mechanism of ester formation is unknown in the silicone matrix. The mechanism in Eq. (7) is only one possible reaction under the used irradiation conditions.
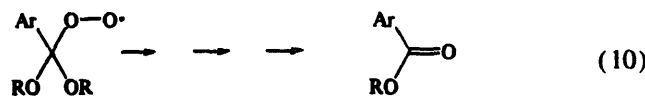
$$\underset{\substack{| \\ H}}{\overset{\substack{Ar \\ |}}{C}}\overset{O-O\cdot}{\underset{OR}{}} \longrightarrow \underset{\substack{| \\ H}}{\overset{\substack{Ar \\ |}}{C}}\overset{O-OH}{\underset{OR}{}} \longrightarrow \longrightarrow \underset{RO}{\overset{Ar}{}}C=O \qquad (7)$$

A similar decrease of the IR absorption of the carbonyl group is observed for BDMK (1704 cm^{-1}) (see Fig. 2) and HCPK [4] (1671 cm^{-1}) (see Fig. 3) in polydimethylsiloxane. In both cases benzil formation was not observed. Contrary to the behaviour of BIPE in the laminate, a new strong absorp-

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[2] Under the assumption of comparable absorption coefficients of all carbonyl groups containing photolysis products and the used benzoin ether.

[3] Combination product with the starting benzoin ether and cross-combination products of benzoyl and α-ether radical [10,13].

[4] The solubility of α-PhB in polydimethylsiloxane is too low.

tion due to photoproducts appears at higher wavenumbers (BDMK, 1735 cm^{-1}; HCPK, 1725 and 1713 cm^{-1} (shoulder)). Using BDMK, the formation of the product peak at 1735 cm^{-1} is possible by formation of methyl benzoate from the dimethoxybenzyl radical (see Eq. (8) and also Ref. [14]). Using HCPK, the nature of the new carbonyl bond formation is more complex than by means of BDMK. Two products are formed, perhaps the formation of the peak at 1713 cm^{-1} converts by a cyclohexanone formation (see Eq. (9), $\tilde{\nu}$ (cyclohexanone) = 1718 cm^{-1} in polydimethylsiloxane).

$$
\underset{\substack{RO\quad OR}}{\overset{Ar}{\diagdown}}\!\!C\cdot \xrightarrow[-R\cdot]{\Delta,\,h\cdot\nu} \underset{\substack{RO}}{\overset{Ar}{\diagdown}}\!\!C{=}O \tag{8}
$$

$$
2\;\langle\!\!\rangle\!\!-OH \longrightarrow \langle\!\!\rangle\!\!=O \;+\; \langle\!\!\rangle\!\!\overset{OH}{\underset{H}{<}} \tag{9}
$$

A related IR decrease was observed for both initiators under air. No benzil formation could be detected. Contrary to the results in the laminate one can observe a stronger increase of the peak at 1735 cm^{-1} (BDMK), and at 1715 cm^{-1} (HCPK) was found. Both findings agree with an imaginable effective ester respectively cyclohexanone formation via the peroxy radical of the dimethoxy benzyl radical (from BDMK, see Eq. (10)) and the ketyl radical of cyclohexanone (HCPK, see Eq. (11)). Moreover, using HCPK more than two new carbonyl products are formed.

$$
\underset{\substack{RO\quad OR}}{\overset{Ar}{\diagdown}}\!\!\overset{O-O\cdot}{\diagup} \longrightarrow \longrightarrow \longrightarrow \underset{\substack{RO}}{\overset{Ar}{\diagdown}}\!\!{=}O \tag{10}
$$

$$
\langle\!\!\rangle\!\!\overset{O-O\cdot}{\underset{OH}{<}} \longrightarrow \longrightarrow \longrightarrow \langle\!\!\rangle\!\!{=}O \tag{11}
$$

3.2. Initiator photolysis in a reactive medium

Fig. 4 represents typical changes in the IR absorption spectrum of benzoin isopropyl ether after exposure duration in a silicone acrylate laminate. Beside the decreases of the carbonyl frequency centred at 1683 cm^{-1}, a new absorption due to a photoproduct appears at 1695 cm^{-1}. The formation of the peak at 1695 cm^{-1} points out acetophenone derivatives (acetophenone $\tilde{\nu} = 1695$ cm^{-1} in polydimethylsiloxane) produced by means of the addition of a benzoyl radical on an acrylate double bond (see Eq. (4)). This reaction initiates obviously the polymerization process of the acrylate group, which is detectable by the loss of the absorption band at 1191 cm^{-1} (associated with the stretching mode ν(C–O) and the skeletal mode γ(C–CO–O) in an ester with olefinic conjugation [15]). Moreover, the crosslinking reaction involves the opening of C=C double bonds, which in the uncrosslinked state are conjugated to C=O double bonds. This results in a
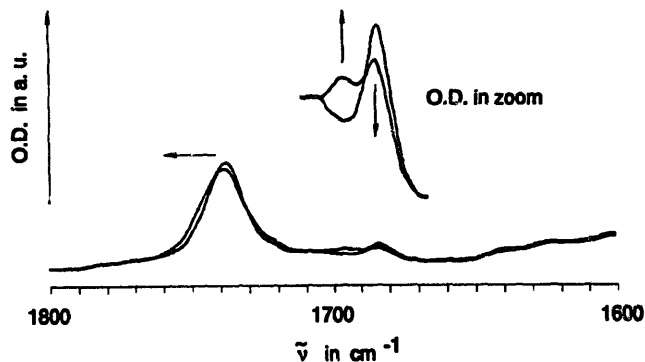

Fig. 4. IR absorbtion of a silicone acrylate laminate layer containing 5×10^{-2} mol l^{-1} BIPE before and after irradiation with polychromatic light ($\Delta t = 20$ s, $I_0 = 32.2$ mW cm^{-2}, thickness of the layer = 50 μm, in zoom = carbonyl range of BIPE).

small increase of the frequency of the C=O stretching vibration of the acrylate group from 1736 to 1738 cm^{-1} combined with the formation of a stronger asymmetric band shape for the crosslinked silicone acrylate. A helpful analysis of these characteristics is given in Ref. [6].

A similar behaviour of the IR absorption of the silicone acrylate–initiator mixture resulting from irradiation (decrease of the carbonyl frequency of the initiator combined with an increase of a new absorption at 1695 cm^{-1}, decrease of the absorption at 1191 cm^{-1} and shifts of the C=O stretching vibration of the acrylate group) was observed in all silicone acrylate laminates containing BDMK, HCPK, respectively, and α-PhB as initiator.

In contrast, in an open air silicone acrylate–initiator mixture no polymerization of the acrylate group was observed by irradiation, provable by constant IR absorption of the characteristic acrylate bands at 1191 and 1736 cm^{-1}. Moreover, the decrease of the carbonyl frequency of the initiator is not combined with the formation of a new absorption at 1695 cm^{-1} (see Fig. 5). Rather, one can observe a tailing of the carbonyl frequency of the silicone acrylate between 1730 and 1720 cm^{-1} (BIPE, BDMK, α-PhB) respectively between 1730 and 1700 cm^{-1} (HCPK) presumably well-founded by the formation of carbonyl products (ester of ben-
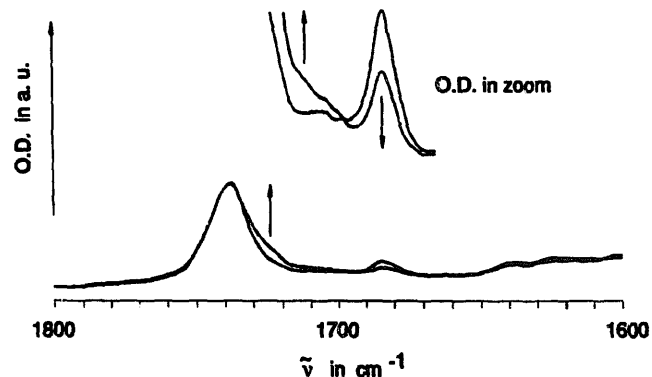

Fig. 5. IR absorbtion of a silicone acrylate layer containing 5×10^{-2} mol l^{-1} BIPE under air before and after irradiation with polychromatic light ($\Delta t = 20$ s, $I_0 = 32.2$ mW cm^{-2}, thickness of the layer = 50 μm, in zoom = carbonyl range of BIPE).
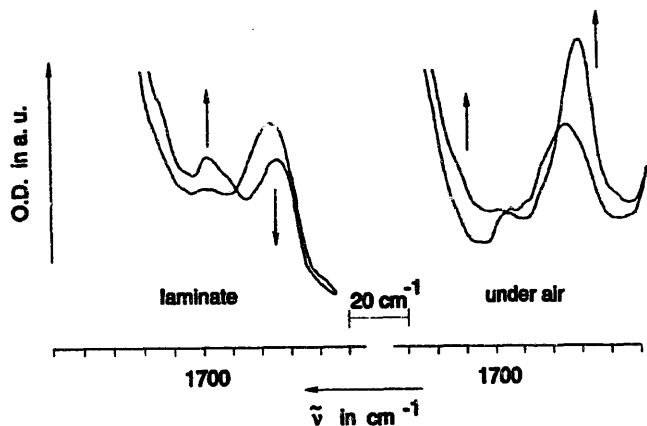
Fig. 6. IR absorbtion of a silicone acrylate layer containing 5×10^{-2} mol l^{-1} α-PhB in the carbonyl range of the initiator before and after irradiation with polychromatic light ($\Delta t = 20$ s, $I_0 = 32.2$ mW cm^{-2}, thickness of the layer = 50 μm, laminates indicates the layer is coated between two polypropylene layers, and air indicates the layer is coated on a polypropylene layer).

zoic acid, cyclohexanone) as result of oxygen addition on the primary formed radicals. Additionally, using α-PhB as initiators (see Fig. 6) one can observe under air the increase of a new absorption at 1670 cm^{-1} due to a photoproduct appear. The formation of this peak at 1670 cm^{-1} points out benzophenone ($\bar{\nu} = 1668$ cm^{-1} in polydimethylsiloxane), presumably produced from the ketyl radical.

These experiments prove that under air the initiator radical R$^{\cdot}$ is trapped by oxygen, which can diffuse very quickly into the layer. All in all, this oxygen diffusion leads to an inhibition of the crosslinking all over the time.

3.3. GC/MS study of the photolysis products

Undisputedly, many discussed photolysis products are imaginary. For that reason a GC/MS study was carried out to support the IR results. In the methanolic extract of an under vacuum irradiated polydimethylsiloxane layer, containing BIPE, was found traces of the isopropyl benzoate, traces of benzil and traces of 1,2-diisopropoxy-1,2-diphenyl ethane besides several dimethylsiloxanes and the starting BIPE (basic peak). On the contrary, under air irradiation conditions, in the methanolic extract of the irradiated polydimethylsiloxane layer was found a strong increase of the ester formation combined with a lower formation of benzil and a strong reduction of the pinacol ether formation.

Results similar to BIPE were obtained with HCPK as the initiator used. Under inert conditions a small benzil formation was observed, which was reduced under air. Interestingly, no other photolysis products (cyclohexanone, dimer of the ketyl radical, etc.) can be detected under the used conditions of analysis.

Some different GC/MS results to BIPE were observed with BDMK in polydimethylsiloxane under identical irradiation conditions. Under inert irradiation conditions one can detect (comparable to BIPE) besides traces of methyl benzoate, traces of benzoic acid, traces of 4-benzoyl benzoic acid

methyl ester, the silicones and the starting benzil dimethyl-ketal. Contrary to the behaviour of BIPE a strong benzil formation was observed. Furthermore, no dimer of the dimethoxybenzyl radical was found using the GC/MS technique.

Similar to BIPE, using BDMK as the initiator under air irradiation an increase of the ester formation and benzoic acid formation was observed. Surprisingly, using BDMK one can also observe under air a strong benzil formation.

$$K \cdot F_{benzyl} / F_{initiator} = [Bz] / [In] = 0.5 \cdot x / (1 - x) \qquad (12)$$

where F is the peak area, K is a factor (experimentally determined as 1.19 (BDMK) and 1.26 (BIPE)), [Bz] is the concentration of formed benzil, [In] is the residual initiator concentration and x is the conversion of the initiator.

Supposing no side reactions takes place one can formulate that one mole initiator gives half a mole of benzil. Under this assumption one can estimate the consumption of the initiator using the ratio of the peak areas of the residual initiator and the benzil formed (see Eq. (12)). By means of Eq. (12) one can estimate that approximately 50% of the BDMK is consumed under vacuum during the irradiation, using BIPE as an initiator one calculates that only 10% of BIPE is consumed under the same inert irradiation conditions (time and absorption [5]). This value is too low which is easy to deduce from the quantum yields of initiator photolysis (Φ(BDMK) = 0.52; Φ(BIPE) = 0.33). By means of these values and a conversion degree of 50% for BDMK a consumption of approximately 30% of BIPE was estimated. All findings result in the formation of benzil for BIPE being too low. This conclusion agrees with Adam's results of the reduction of the benzil formation at higher conversion [10].

By means of the GC/MS technique one can prove many postulated IR products. Moreover, a strong benzil formation was found using BDMK as the photoinitiator. This result was surprisingly, no benzil formation was detected using the IR detection.

3.4. Rate of initiator decay—polymerization rate

The IR spectroscopy is suitable to detect the initiator decay in the silicone layer. A typical example for the conversion–time curve of the photolysis of BIPE was given in Fig. 7. The curve shows that the reaction starts without inhibition time. The final conversion of the initiator decay tends to 1 (independent of the light intensity). Moreover, the reaction rate is a linear function of the light intensity (see Fig. 8). All these findings are typical for an α-cleavage.

Furthermore the results show that the rate of the initiator decay depends on the initiator used and the oxygen content in the layer. For BDMK and BIPE in the silicone oil the reaction rate is faster under air then in the laminate. This observation agrees with our own results [7,16] and findings

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[5] BDMK and BIPE possess, under the used condition, approximately the same light absorption, HCPK absorbs only 10...20% of BIPE under the given condition [7].
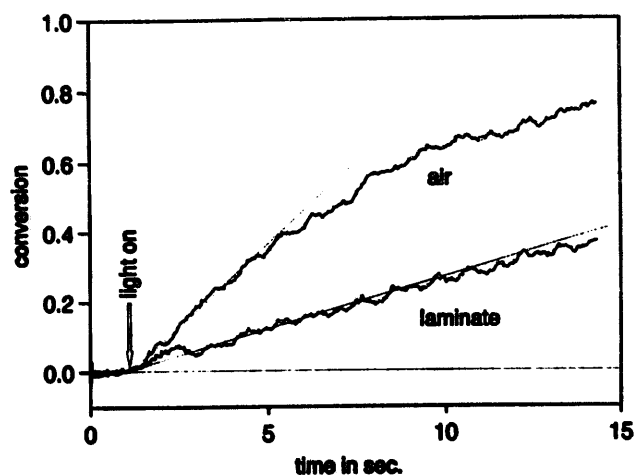
Fig. 7. Conversion (x)/time for the photoinduced decay of BIPE in the silicone oil ([BIPE] $=5 \times 10^{-2}$ mol l^{-1}, $I_o = 77$ mW cm^{-2}, thickness of the layer $= 50$ µm, laminates indicates the layer is coated between two polypropylene layers, and air indicates the layer is coated on a polypropylene layer).
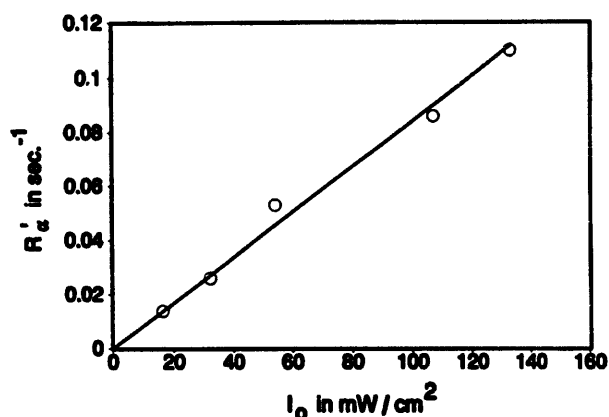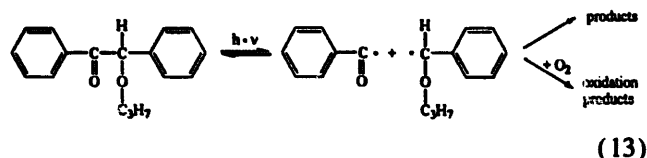

Fig. 8. Plot of reaction rate R'_α vs. I_o of the photoinduced decay of BIPE in the silicone acrylate (for experimental conditions see Fig. 7, laminate).

from Adam et al. [10,11] and is based on a reduced back formation of the initiator from the primary formed cleavage products in the presence of oxygen [10,11] (see Eq. (13)).

(13)

For BDMK and BIPE, the reaction rate is approximately the same in silicone oil as in silicone acrylate under the same irradiation conditions. On the contrary, for HCPK larger differences were found between the inert silicone and the reactive acrylate. Moreover, the rate of the initiator decay (R_α) in the silicone acrylate correlates to the well-known quantum yield of the initiator photolysis in hexamethyldisiloxane (see Fig. 9). Nevertheless, the linear correlation does not fit the origin. Obviously, the quantum yields differ in both the systems used.

Using Eq. (14) one can estimate the quantum yield of photolysis in the silicone acrylate from the R_α value by knowledge of the absorbed part of the incident light,

$$\Phi_\alpha = R_\alpha \cdot l / (I_o \cdot \eta_{abs})$$

(14)

where l is the sample thickness, η_{abs} is the absorbed part of the incident light (I_o) and R_α is the rate of initiator decay.

The results corresponding to Eq. (14) are summarized in Fig. 10. As expected, the Φ_α values of BIPE, BDMK, and α-PhB differ in silicone acrylate from the values obtained in hexamethyldisiloxane. Nevertheless, Φ_α for HCPK is approximately 1 in both the solution and silicone acrylate used.

Kinetic studies have shown that the photoinitiated radical crosslinking of silicone acrylates can be considered as a polymerization process [5–7]. A typical polymerization profile of the silicone acrylate used is given in Fig. 11. The figure shows that the polymerization starts after an inhibition period; reaction rates (slope of the plot) and inhibition times are functions of the initiator used.

Due to the specific kinetic situation in bulk, Eq. (15) can be used for describing the rate of the photocrosslinking process (R_P) under stationary irradiation conditions [5–7,9].
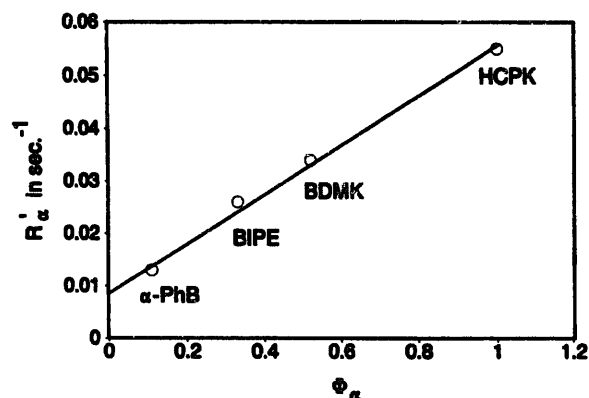

Fig. 9. Plot of R'_α of the photoinduced decay of several photoinitiators in the silicone acrylate vs. quantum yield of initiator decay Φ_α determined in oxygen-free hexamethyldisiloxane (see Ref. [7]) (for experimental conditions see Fig. 7, laminate).
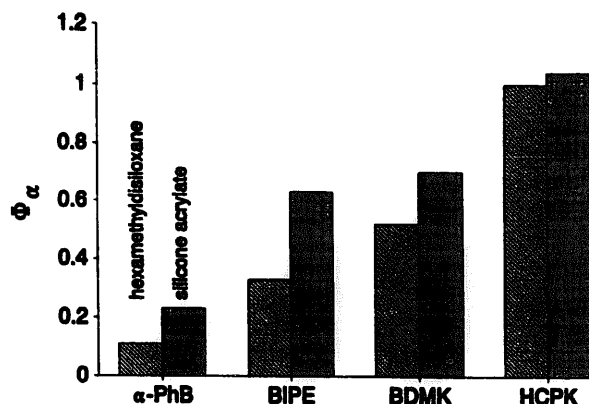

Fig. 10. Comparision of the quantum yield of initiator decay Φ_α determined in oxygen-free hexamethyldisiloxane and in a silicone acrylate laminate layer (for experimental conditions see Fig. 7).
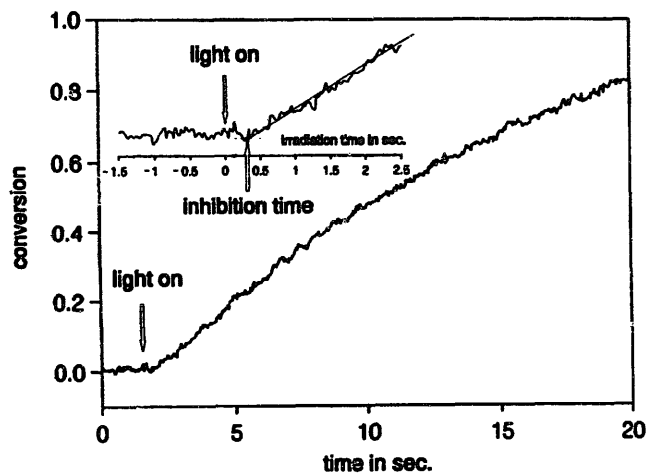
Fig. 11. Conversion (x)/time for the photoinduced polymerization of the silicone acrylate initiated with BIPE ([BIPE] = 5×10^{-3} mol 1^{-1}, I_o = 32.2 mW cm^{-2}, thickness of the layer = 50 μm, laminate).

Only this general expression reflects the real situation in the polymeric systems investigated in all details, because the conditions (viscosity, concentration of oxygen, monomer concentration, etc.) for the reaction partners are changed at each time. The kinetics of the photoinduced radical crosslinking corresponds to a thermal reaction except the initiation step. According to Eq. (15), the dependence of R_P upon I_o, can only be deduced from the rate of start radical formation and all in all from the rate of the α-cleavage. Under this assumption one can formulate the equations:

$$R_P = (-dx/dt) \cdot [M_o] = k(x) \cdot [M]^\alpha \cdot I_o^\beta \qquad (15)$$

$$R_P = k'(x) \cdot [M]^\alpha \cdot (R_\alpha)^\beta \qquad (16a)$$

or the reduced form

$$R'_P = R_P/[M_o] = -dx/dt = k''(x) \cdot [X]^\alpha \cdot (R_\alpha)^\beta \qquad (16b)$$

where $[M]$ is the molar concentration of double bonds, $[M_o]$ is the starting concentration of double bonds, t is the time, $k(x)$, $k'(x)$ and $k''(x)$ are conversion (x) dependent quantities, I_o is the intensity of the incident light, R_α is the reaction rate of the α-cleavage, and α and β are exponents.

According to Eq. (16), it is also to be expected that the photoinitiator used influences the rate of crosslinking via R_α. Fig. 12 shows such dependence for the silicone acrylate and photoinitiators used. The plot R_P vs. R_α is nearly linear, which shows that the light intensity exponent β is in the order of 1, typical for a polymerization with a first-order termination step. Such termination behaviour was observed for the polymerization of silicone acrylates where traces of oxygen influence the radical termination [5,7,17].

Radical-induced polymerizations are known to be strongly inhibited by atmospheric oxygen, an excellent scavenger of both the initiator and the polymer radicals. The inhibition time (t_i) based on oxygen scavenging can be described by Eq. (17):

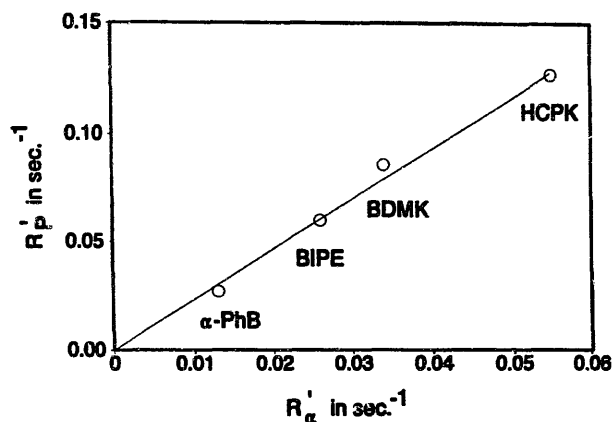$$t_i = [O_2]/\eta \cdot R_\alpha = [O_2]/\eta \cdot \Phi_\alpha \cdot \eta_{abs} \cdot I_o \qquad (17)$$

Fig. 12. Plot of R'_P vs. R'_α for the photoinduced polymerization of the silicone acrylate initiated with several initiators ([initiator] = 5×10^{-2} mol 1^{-1}, I_o = 32.2 mW cm^{-2}, thickness of the layer = 50 μm, laminate).
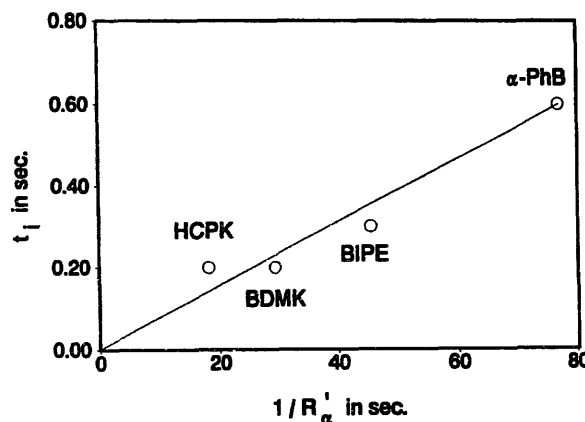

Fig. 13. Plot of t_i vs. $1/R'_\alpha$ for the photoinduced polymerization of the silicone acrylate initiated with several initiators ([initiator] = 5×10^{-2} mol 1^{-1}, I_o = 32.2 mW cm^{-2}, thickness of the layer = 50 μm, laminate).

where R_α is the rate of the α-cleavage, $[O_2]$ is the sum of the dissolved oxygen and of oxygen, which can diffuse into the layer, η_{abs} is the fraction of the absorbed light, Φ_α is the quantum yield of the primary radical formation, η is the addition efficiency of the primary radical to the monomer.

According to Eq. (17), it is also to be expected that the photoinitiator used influences t_i and the crosslinking rate via R_α. Fig. 13 shows such a dependence for the silicone acrylate and photoinitiators used.

Acknowledgements

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