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Kinetic Approach of O_2 Inhibition in Ultraviolet- and Laser-Induced Polymerizations

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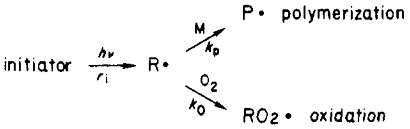
ABSTRACT: The inhibition by oxygen of the photopolymerization of multi-acrylate systems was investigated by IR spectroscopy. Both conventional and laser UV irradiations were used to initiate the reaction; the effect of the light intensity on polymerization kinetics was followed over a 4-orders-of-magnitude range. Based on a simple kinetic scheme, the equation of the steady concentration of O_2 was calculated as a function of the initiation rate and of the ratio of the polymerization rates with and without oxygen; under the conditions employed, the $[O_2]_s$ value was found to be on the order of 5×10^{-6} mol L^{-1}. The less-than-first-order dependence of the inhibition period on the reciprocal light intensity indicates that O_2 is consumed by a chain peroxidation process with kinetic chain lengths between 1.6 and 16, depending on the light intensity.

Introduction

Molecular oxygen is known strongly to inhibit radical-induced polymerizations because of its high reactivity toward radical species. This inhibition effect is particularly pronounced for photopolymerizations which are usually carried out in thin films because of the limited penetration of UV light. The effects of oxygen on the UV curing of coatings and photoresists have thoroughly been investigated.[1-4] By scavenging the initiator radicals, O_2 not only reduces the rate of the polymerization, thus requiring longer exposure times, but also leads to a partial loss of the optical and surface properties of air-cured coatings. Several methods have been proposed to overcome O_2 inhibition in photopolymerization[5-10] but, except for the expensive nitrogen-blanketing technique, none of them appear to be fully satisfactory as far as efficiency is concerned.

The effect of oxygen in light-induced polymerization can schematically be represented as follows:



where r_i is the rate of production of initiating radicals R• by photolysis of the initiator, k_p the rate constant of propagation ($\sim 10^3$ L mol^{-1} s^{-1} for acrylate monomers[11]), and k_0 the rate constant of the radical scavenging by O_2 molecules ($\sim 5 \times 10^8$ L mol^{-1} s^{-1} [12]). In a well-aerated medium, where the concentration of dissolved oxygen is of the order of 10^{-3} mol L^{-1}, the photopolymerization cannot develop because $k_0[O_2] \gg k_p[M]$, so that all the initiator radicals formed are reacting with the oxygen dissolved in the monomer. As a consequence of this scavenging reaction, O_2 is progressively consumed and its concentration in the irradiated monomer drops steadily during the inhibition period. The polymerization process will only start once the monomer molecules are able to compete successfully with O_2 for the scavenging of the initiator radicals, i.e., when $k_0[O_2]_s \sim k_p[M]$. In open systems, a stationary concentration of dissolved oxygen is then reached where O_2 consumption is just compensated by O_2 diffusion from the atmosphere through the surface of the film.

The objective of the present work was to evaluate the steady-state concentration of dissolved oxygen at which photopolymerization takes place in aerated systems. Multi-acrylate monomers were selected for this study because they are the most commonly used UV-curable coatings and their kinetics of polymerization in condensed phase have been thoroughly investigated in our laboratory.[13-15] Both conventional UV lamps and high-power lasers were used as excitation sources in order to cover a broad range of light intensity. It was thus possible to demonstrate the interference of a chain oxidation process for the consumption of oxygen from the dependence of the inhibition period on the light intensity.

Experimental Section

The photopolymerizable system used in this work consisted of three basic components: an epoxy–diacrylate oligomer derived from the glycidyl ether of bisphenol A (Ebecryl 605 A from UCB), a di- or triacrylate monomer that acts as a reactive diluent (TPGDA or TMPTA from UCB), and 2,2′-dimethoxy-2-phenylacetophenone as photoinitiator (Irgacure 651 from Ciba-Geigy). The photosensitive formulation contained equal proportions of monomer and oligomer and 2–5% of photoinitiator. The resin was applied as a uniform layer of 20-μm thickness on a NaCl disk with a calibrated wire-wound applicator. Samples were exposed to the UV source or to the laser beam for various durations up to 0.1 s by means of a camera shutter. The irradiation was carried out either in air or in a nitrogen-saturated reactor.

Two types of UV sources were used:

One was a 2000-W, medium-pressure mercury lamp (Mazda UV 8200) which has its maximum emission at 365.5 nm. The light emitted was concentrated by means of a semielliptic reflector; at the focus point, the light intensity was measured to be 1.5×10^{-6} E s^{-1} cm^{-1} or 9×10^{17} photons s^{-1} cm^{-2}.

The second was an argon ion laser (Spectra Physics Model 170) tuned to its emission line at 363.8 nm; the power available in the continuous-wave mode was 40 mW, which corresponds to a light intensity of 7.6×10^{-6} E s^{-1} cm^{-2}. By focusing the laser beam, we could reach extremely high values of the light intensity: $I_0 = 8 \times 10^{-4}$ E s^{-1} cm^{-2} for a 100-μm spot and 1.2×10^{-2} E s^{-1} cm^{-2} for a 8-μm spot.

The fraction (f) of the incident light absorbed by the sample was determined either by differential actinometry or from the absorbance of the coating at the wavelength of the relevant laser emission. The absorbed light intensity (I_a) was calculated from eq 1

$$I_{a(\mathrm{E\ L^{-1}\ s^{-1}})} = I_{0(\mathrm{E\ s^{-1}\ cm^{-2}})}[1 - \exp(-2.3\ \epsilon e c)]\frac{10^7}{e_{(\mu\mathrm{m})}} \quad (1)$$

where e is the thickness of the film, c the concentration of the photoinitiator, and ϵ its molar extinction coefficient at the laser emission wavlength.

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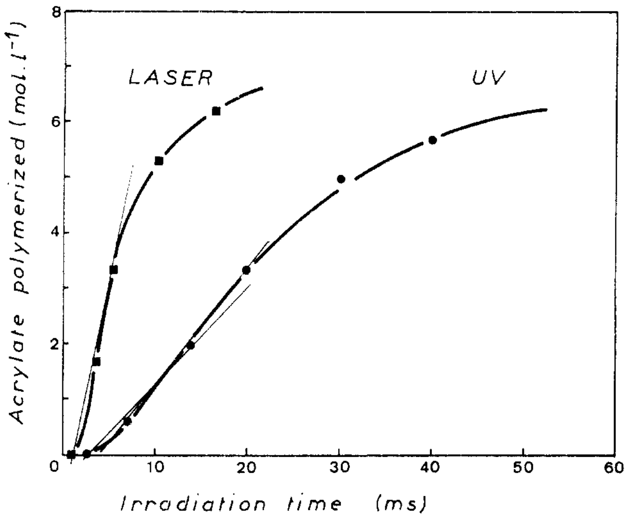


Figure 1. Kinetics of the polymerization of an epoxy–acrylate film (20 μm) under UV (●) or laser (■) irradiation in the presence of air.

The extent of the photopolymerization was evaluated either from the thickness of the insoluble polymer film which is recovered after exposure and solvent development or from the decrease of the IR absorption of the acrylic double bond at 810 cm^{-1} ($CH_2{=}CH$ twisting). The rate of polymerization at a given time was evaluated from the observed variation of the sharp peak at 810 cm^{-1}, by using eq 2

$$R_p = \left(\frac{A_1 - A_2}{A_0}\right)\left(\frac{[M]_0}{t_1 - t_2}\right) \tag{2}$$

where $[M]_0$ is the initial concentration in acrylate function of the formulation ($\sim$8.6 mol L^{-1}) and A_0, A_1, and A_2 are the IR absorbances at 810 cm^{-1} before and after light exposure for times t_1 and t_2, respectively. R_p values reported here were calculated from the slope of the linear portion of the kinetic curve obtained by plotting the number of acrylate double bonds polymerized as a function of the irradiation time (Figure 1).

Reaction Scheme

Upon UV irradiation of the photosensitive resin, the photoinitiator molecules are promoted to excited singlet and triplet states which are highly unstable and cleave into radical fragments. Unlike most triplet ketones, these excited states are not quenched by oxygen during their very short lifetime ($<10^{-9}$ s^{16}) so that the observed air inhibition effect is essentially due to the scavenging of the initiator radicals by the dissolved oxygen molecules. The free radicals that escape O_2 scavenging will react with the surrounding monomer molecules, thereby initiating the polymerization. The relative efficiency of the two competitive processes will depend primarily on the relative concentration of O_2 and of monomer and on the corresponding rate constants (k_0 and k_p).

The overall reaction scheme of the photopolymerization of a monomer in the presence of air may be represented by the set of equations

$$\text{In.} + h\nu \rightarrow \text{In.}^1 \rightarrow \text{In.}^3 \tag{I}$$

$$\text{In.}^3 \rightarrow R\cdot \tag{II}$$

polymerization

$$R\cdot + M \xrightarrow{k_i} RM\cdot \tag{III}$$

$$RM_n\cdot + M \xrightarrow{k_p} RM_{n+1}\cdot \tag{IV}$$

$$RM_n\cdot + RM_m\cdot \xrightarrow{k_t} \text{termination} \tag{V}$$

oxidation

$$R\cdot + O_2 \xrightarrow{k_0} RO_2\cdot \tag{VI}$$

$$RO_2\cdot + DH \rightarrow RO_2H + D\cdot \tag{VII}$$

$$D\cdot + O_2 \rightarrow DO_2\cdot \tag{VIII}$$

$$DO_2\cdot + DH \rightarrow DO_2H + D\cdot \tag{IX}$$

$$RM_n\cdot + O_2 \rightarrow RM_nO_2\cdot \tag{X}$$

$$RM_nO_2\cdot + DH \rightarrow RM_nO_2H + D\cdot \tag{XI}$$

$$DO_2\cdot + DO_2\cdot \rightarrow \text{termination} \tag{XII}$$

where R· designates the radical fragments of the photolyzed initiator (In.), M the acrylic monomer or oligomer, and DH a donor molecule which can be the monomer itself or an added tertiary amine. Since no polymerization occurs in air-saturated systems, the peroxide radicals generated by steps VI, VIII, and X must be considered as ineffective for initiating the polymerization and are likely to disappear essentially by H abstraction to the substrate (DH) or through bimolecular terminating interactions. Although the rate of reaction of a radical with a monomer molecule is expected to depend on the particular type of radicals, it will not affect the overall rate if the polymerization chain is long so that reactions III and IV can be treated as a single set, as a first approximation.

At the beginning of the irradiation, oxygen is consumed by a chain peroxidation process (reactions VI–IX). The scavenging of polymeric radicals by O_2 (reaction X) can only occur at the end of the inhibition period, once the O_2 concentration has been sufficiently lowered to allow reaction III to compete with reaction VI for the scavenging of the initiator radicals R·. Under these steady-state conditions, the rate of O_2 consumption is then equal to the rate of O_2 diffusion. Figure 1 shows some typical kinetic curves of the polymerization of an epoxy–diacrylate resin induced by conventional or laser UV irradiation in the presence of air.

Reaction Kinetics

The rate of formation of the initiating radicals is given by

$$r_i = \phi I_{abs} = \phi I_0[1 - \exp(-2.303\epsilon e c)] \tag{3}$$

where ϕ is the quantum yield of formation of initiating radicals, I_0 the incident light intensity, and $\epsilon e c$ the absorbance of the monomer film.

Letting [X·] represent the sum of concentrations of all $RM_n\cdot$ species (including R· radicals) and assuming that steady-state conditions are reached, i.e., $d[X\cdot]/dt = 0$, one obtains the following equation for polymerizations, carried out in the absence of O_2:

$$r_i = k_t[X\cdot]^2 \tag{4}$$

The rate of polymerization $(R_p)_{N_2}$ takes then the usual form:

$$(R_p)_{N_2} = -d[M]/dt = k_p[X\cdot][M] = k_p(r_i/k_t)^{1/2}[M] \tag{5}$$

If oxygen is present in the system, the steady-state equation becomes

$$r_i = k_t[X\cdot]^2 + k_0[X\cdot][O_2]_s \tag{6}$$

where $[O_2]_s$ is the stationary concentration of oxygen in the monomer undergoing polymerization. Solving this second-order equation gives

$$[X\cdot] = \frac{((k_0[O_2]_s)^2 + 4r_ik_t)^{1/2} - k_0[O_2]_s}{2k_t} \tag{7}$$

Table I
Kinetic Data on the Polymerization of Epoxy–Acrylate Resins Exposed to Conventional UV and Laser Beam

UV source	medium-press. Hg source	argon ion laser	
		unfocused	focused
$10^6 I_0$, E cm^{-2} s^{-1}	1.5	7.6	800
r_i,[a] radical L^{-1} s^{-1}	0.025	0.11	20
$(R_p)_{N_2}$,[b] mol L^{-1} s^{-1}	1760	4000	1.6×10^5
$(R_p)_{O_2}$,[c] mol L^{-1} s^{-1}	230	800	1.2×10^5
$(R_p)_{N_2}/(R_p)_{O_2}$	7.7	5	1.3
$10^6(O_2)_s$,[d] mol L^{-1}	4.2	5.4	8

[a] Rate of production of initiating radicals: $r_i = \phi I_a$. [b] Rate of polymerization in nitrogen-saturated systems. [c] Rate of polymerization in the presence of air. [d] Steady-state concentration of O_2 in the film undergoing polymerization. $[O_2]_s = 3.46 \times 10^{-6}\, r_i^{1/2}[(R_p)_{N_2}/(R_p)_{O_2} - (R_p)_{O_2}/(R_p)_{N_2}]$.

for the steady-state concentration of radical chains.

We can then express the rate of polymerization when air is present:

$$(R_p)_{O_2} = (k_p[M]/2k_t)[(k_0{}^2[O_2]_s{}^2 + 4r_ik_t)^{1/2} - k_0[O_2]_s] \quad (8)$$

The ratio of the rates of polymerization with and without oxygen can be calculated from eq 5 and 8:

$$\frac{(R_p)_{O_2}}{(R_p)_{N_2}} = \frac{(k_0{}^2[O_2]_s{}^2 + 4r_ik_t)^{1/2} - k_0[O_2]_s}{2(r_ik_t)^{1/2}} \quad (9)$$

Rearranging eq 9 gives

$$\frac{(R_p)_{O_2}}{(R_p)_{N_2}}k_0[O_2]_s = (r_ik_t)^{1/2}\left\{1 - \left(\frac{(R_p)_{O_2}}{(R_p)_{N_2}}\right)^2\right\} \quad (10)$$

which finally yields an equation for the steady-state concentration of O_2 as a function of the rate of initiation, the rate constants k_0 and k_t, and the rates of polymerization with and without oxygen:

$$[O_2]_s = \frac{(r_ik_t)^{1/2}}{k_0}\left[\frac{(R_p)_{N_2}}{(R_p)_{O_2}} - \frac{(R_p)_{O_2}}{(R_p)_{N_2}}\right] \quad (11)$$

In order to evaluate the steady-state concentration in O_2, we only need to know the absolute values of k_0 and k_t since the other terms can be determined experimentally. The scavenging of alkyl radicals by O_2 is a very fast reaction which occurs at a rate constant (k_0) of the order of 5×10^8 L mol^{-1} s^{-1}.[12] For the polymerization of monoacrylate monomers, the rate constant of termination is typically of the order of 3×10^6 L mol^{-1} s^{-1};[11] for neat diacrylates, like hexanediol diacrylate, k_t was found to vary between 2×10^6 and 6×10^6 L mol^{-1} s^{-1} in the 18–25% conversion range where our R_p measurements were made.[17]

Determination of the Steady-State Concentration of O_2

From our kinetic data, we can now evaluate $[O_2]_s$ under the two types of irradiation conditions used for the photopolymerization of epoxy–acrylate systems.

Conventional UV Irradiation. For the high-intensity mercury lamp ($I_0 = 1.5 \times 10^{-6}$ E s^{-1} cm^{-2}), the amount of photons absorbed per second by a 20 μm thick film was found to be 2.5×10^{-1} E L^{-1} s^{-1}, which leads to an initiation rate (r_i) of 2.5×10^{-2} radical L^{-1} s^{-1} taking ϕ as 0.1.[16] Kinetic measurements have shown[15] that the rate of polymerization in N_2 is then about 8 times higher than the rate of polymerization in aerated systems (Table I). Introducing those values in eq 11 allows the stationary concentration of O_2 to be calculated:

$$[O_2]_s = \frac{(2.5 \times 10^{-2} \times 3 \times 10^6)^{1/2}}{5 \times 10^8}(8 - 0.125)$$

$$[O_2]_s = 4.2 \times 10^{-6} \text{ mol L}^{-1}$$

This means that, under the given experimental conditions, the concentration of oxygen dissolved in the system has to drop by a factor of about 300 before polymerization can actually start. $[O_2]_s$ will be even lower if the value of k_t decreases during the polymerization because of viscosity and matrix effects, as was found by Tryson and Schultz.[17] By contrast, if the rate constant of the scavenging of alkyl radicals by O_2 is reduced because of some viscosity effects or lower intrinsinc reactivity, $[O_2]_s$ will be increased to the same extent.

Continuous Laser Irradiation. When the photosensitive resin was exposed to the 363.8-nm emission line of an argon ion laser, polymerization proceeded 4 times faster than previously, mainly because of the concomitant increase of the light intensity. The ratio $(R_p)_{N_2}/(R_p)_{O_2}$ was found to be close to 5, which leads to a value of the O_2 steady-state concentration quite similar to that determined for conventional UV irradiation: $[O_2]_s = 5.4 \times 10^{-6}$ mol L^{-1} (Table I).

By focusing the laser beam down to a 100-μm spot, the light intensity was increased by 2 orders of magnitude while the exposure time dropped from 5 to 0.1 ms. In spite of the extremely high rates of radical production that are then reached, the polymerization process was found to develop quite extensively with kinetic chain lengths as long as 4000 mol/radical.[18] It was recently suggested[19] that this unexpected high efficiency at large initiation rates is due to the fact that, in the polymerization of neat multifunctional acrylic monomers, the growing polymer radicals become progressively isolated in the polymer matrix, which reduces the probability of terminating interactions. The decrase of the quantum yield of chain propagation observed at high light intensity[18] may partly result from recombination reactions of primary radicals that are then no more available for chain initiation.

When the focused laser beam is employed as a radiation source, the rate of polymerization of epoxy–acrylate resins irradiated in the presence of air becomes close to the R_p value found in N_2-saturated systems (Table I). Under these conditions, the steady-state concentration of O_2 in the film was calculated to be 8×10^{-6} mol L^{-1}. It thus appears that the concentration of O_2 at which polymerization occurs is only slightly dependent on the light intensity, the increase in $r_i^{1/2}$ being compensated by the drop in the ratio $(R_p)_{N_2}/(R_p)_{O_2}$ (eq 11).

If diffusion of atmospheric oxygen into the film were taking place to a large extent during the exposure to the laser beam, one would expect the stationary concentration of oxygen to decrease under high light intensity since the irradiation time is then drastically shortened. Our findings that $[O_2]_s$ is little affected by a 100-fold increase of the light intensity and follows rather the opposite trend therefore suggests that O_2 diffusion is not playing an important role when irradiation times as short as 5 ms or less are involved.

Chain Peroxidation Process

An interesting parameter that can be inferred from the duration of the inhibition period, usually observed in the photopolymerization in air of these acrylic monomers, is the efficiency of the oxygen consumption by the initiator radicals. By comparing the number of radicals produced during the inhibition period to the number of O_2 molecules consumed, one can estimate the kinetic chain length of the peroxidation process (steps VI–XI). Table II reports the

Table II
Evaluation of the Peroxidation Kinetic Chain Length in the Photopolymerization of Epoxy–Acrylate Resins in the Presence of Air

UV source	medium-press. mercury lamp		argon ion laser	
		+ amine[c]	unfocused	focused
I_a, E L^{-1} s^{-1}	0.25	0.25	1.1	200
t_i, ms	5	2.5	2	0.03
10^4N,[a] radical L^{-1}	1.25	0.625	2.2	6
kinetic chain length,[b] mol/radical	8	16	4.5	1.6

[a] $N = \phi I_a t_i$. [b] O_2 molecules consumed per initiating radical = (10^{-3} mol L^{-1})/(N radical L^{-1}). [c] 10% of dimethylethanolamine.

values of the inhibition period (t_i) under various conditions of irradiation and the calculated number (N) of initiating radicals produced during this lapse of time:

$$N = \phi t_i I_0[1 - \exp(-2.3\epsilon e c)]$$

In the laser experiments, the duration of the inhibition period was evaluated by measuring the lowest scanning rate S where no polymer could be detected: for the unfocused beam of 1.7-mm cross section, $S = 0.85$ m s^{-1} and $t_i = 1.7 \times 10^{-3}/0.85 = 2 \times 10^{-3}$ s; for the 100-μm focused beam $S = 3.3$ m s^{-1} and $t_i = 10^{-4}/3.3 = 3 \times 10^{-5}$ s.

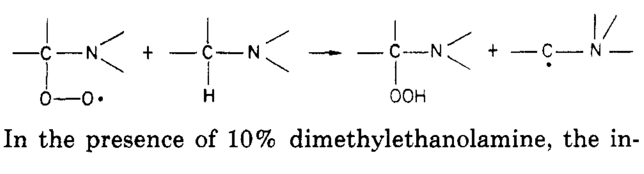
As expected, the value of the induction period decreases as the light intensity is increased. If oxygen were consumed by a nonchain oxidation process, t_i should be inversely proportional to the rate of initiation, i.e., to I_0. Actually, the observed kinetic law is less than first order in reciprocal light intensity, which implies that a chain oxidation process develops during the induction period. As shown by Figure 2, a logarithmic plot of t_i vs. I_0 yields a straight line with a slope of −0.88. The dashed line corresponds to the curve that would be expected if no chain process were operative, i.e., if each initiating radical were consuming only one O_2 molecule: $N = [O_2]_{air} = 10^{-3}$ mol L^{-1} and $t_i = 10^{-3}/r_i$.

Since we have shown that the steady-state concentration of oxygen is over 2 orders of magnitude lower than the O_2 concentration in air-saturated systems, the number of O_2 molecules consumed during the inhibition period can be approximated to the initial amount of oxygen dissolved in the film:

$$[O_2]_{air} - [O_2]_s \simeq [O_2]_{air} = 10^{-3} \text{ mol L}^{-1}$$

From the ratio $N/[O_2]_{air}$, we can then directly evaluate how many O_2 molecules have been consumed per initiating radical during the inhibition period. The values reported in Table II show that the chain peroxidation process develops quite efficiently in these systems, each initiating radical inducing the consumption of as many as eight molecules of O_2.

It is possible further to reduce the length of the induction period by introducing into the formulation some highly oxidizable compounds, such as tertiary amines which generate α-amino radicals that are known to consume oxygen by a chain process:[20]



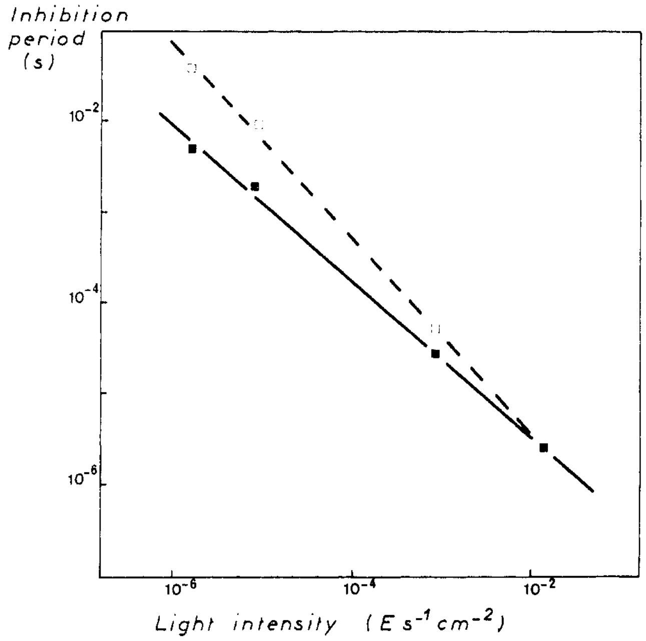


Figure 2. Dependence of the inhibition period (t_i) on the light intensity in the photopolymerization of an epoxy–acrylate resin in the presence of air. The dashed line corresponds to the inhibition period expected in the absence of a chain peroxidation process.

In the presence of 10% dimethylethanolamine, the inhibition period was cut by half and the overall kinetic chain length of the peroxidation was estimated to be 16 O_2 molecules per radical.

As the initiation rate is increased by increasing the light intensity, the kinetic chain length drops steadily, as expected for a chain reaction process with bimolecular termination. When a highly focused laser beam (10-μm spot) was used as radiation source, the chain peroxidation did not develop anymore, even in the presence of amines; each initiating radical then consumes only one O_2 molecule during the inhibition period. A very similar result was obtained in our recent investigation on ultrafast polymerizations of epoxy–acrylate resins by pulsed laser irradiation.[14]

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