Fluorescent Probes for Monitoring the Pulsed-Laser-Induced Photocuring of Poly(urethane acrylate)-Based Adhesives

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ABSTRACT: Fluorescence spectroscopy was used to study the kinetics of polymerization of acrylic adhesive formulations exposed to a 355-nm pulsed emission from an Nd-YAG laser. Nine fluorescent probes were used for monitoring the laser curing, showing different sensitivities. In general, the fluorescence intensity emission increased as crosslinking occurred. In addition, solvatochromic fluorescent probes showed a blue-shift in their emission. A relative method was applied for the evaluation of the polymerization rates in three different acrylic systems. Special features of pulsed-laser-induced polymerization were treated in detail, such as the influence of the laser pulse frequency and the incident laser beam intensity. The polymerization rate slowed down as the pulse repetition rate decreased. An inhibition period due to oxygen quenching was observed, and it was highly dependent on the laser repetition rate and the nature of the photoinitiator. The effect of the laser beam intensity on the kinetics of such fast reactions was studied. In general, increasing the laser energy improved the rate of polymerization. The degree of cure improved as the polymerization rate increased as a result of faster crosslinking, rather than relaxation volume kinetics. Moreover, a saturation rate effect occurred that depended on the photoinitiator. The different behaviors of the two photoinitiators in the curing of the same acrylic formulation was explained on the basis of primary radical termination. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 1227–1238, 2004

Keywords: pulsed-laser polymerization; fluorescence; fluorescent probes; kinetics (polym.); primary radical termination; curing; adhesives

INTRODUCTION

The main applications of the technology of laser-induced polymerization have been developed in those areas for which speed\(^1\) (productivity) and selectivity are of crucial importance. Laser-induced polymerization has some advantages, such as (1) high energy, which allows very rapid curing reactions; (2) spatial coherence of the laser beam, which makes it possible to obtain high-resolution images; and (3) monochromatic light, which allows the selective excitation of chromophores, reducing undesirable secondary reactions. Applications have been developed in direct laser writing or patterning, holographic recording, the manufacture of optical elements, various sectors of imaging technology (printed circuit boards and stereolithography), holography, biomedicine, and so forth. Nowadays, the application of laser polymerization in nanotechnology\(^2\) seems to very promising because of the choice of initiating a polymerization reaction focused in very small regions (submicra).

Therefore, the laser-assisted processing of multifunctional systems is a very efficient method for achieving the high-speed curing of photosensitive resins. Pulsed-laser polymerization has been fol-
allowed by Fourier transform infrared (FTIR) in real time and differential scanning calorimetry.\textsuperscript{3,4} Recently, the fluorescence method has become a powerful tool for investigating fast crosslinking reactions, induced by lasers, that occur in a few seconds or less\textsuperscript{5} and, in general, polymerization reactions. Compared with other curing monitoring methods, fluorescence emission offers advantages such as a fast response time, which is crucial in ultraviolet (UV) curing (mainly under intense exposures), high sensitivity, and \textit{in situ} noninvasive analysis. Real-time infrared (RTIR) offers the same advantages and can be particularly useful for following separately the polymerization of monomers with different natures (acrylates and methacrylates). The main difference between the two methods (RTIR and fluorescence) lies in the sensitivity. Although RTIR monitoring follows the disappearance of reactive functional groups, the fluorescence method allows researchers to monitor changes in the local rigidity of the medium. Therefore, the fluorescence method can be useful for the analysis of microstructural changes during UV curing.\textsuperscript{6}

Nevertheless, fluorescence emissions from monomers and oligomers do not show changes that allow the monitoring of curing in most of the cases. Therefore, fluorescent probes have been used as reporters of the degree of cure in polymer matrices. An appropriate selection of the fluorescent probe is needed to avoid its interference with the light-induced reaction. Coupling between the excited state of the probe and polymer is dependent on the microenvironment, and so efficient coupling leads to a more relaxed state of the probe emitting at a lower frequency, whereas the opposite shift of the maximum emission wavelength is observed as the relaxation of the probe becomes more restricted. The exact mechanism of relaxation has not yet been elucidated. However, for twisted intramolecular charge-transfer probes, it is related to the rotation of some moieties of the fluorophore. Therefore, as the polymerization progresses, the free-volume fraction decreases, and depending on the molar volume of the rotating parts, this movement and relaxation are hindered. In general, the fluorescence emission is blueshifted, and the intensity increases, during polymerization.

Here we present a study of the pulsed-laser-induced polymerization of acrylic-based adhesives. The fluorescence method, previously reported,\textsuperscript{6,7} has been used to analyze the kinetics of the curing reaction. An Nd-YAG laser pulse (355 nm and 6 ns) induces the photofragmentation of a photoinitiator, and the photogenerated radical initiates the polymerization reaction. Simultaneously, a laser beam serves as a source of excitation of the fluorescent probes incorporated into the formulation. One of the significant advantages of using a pulsed laser as a radiation source is that the initiation process can be considered instantaneous because it is very rapid in comparison with primary radical addition to the monomer.

**EXPERIMENTAL**

**Fluorescent Probes and Sample Preparation**

The chemical structure, name, and acronym of each fluorescent probe is shown in Figure 1 and Table 1. The probes DMANS, DMANBu, NBD–NEtOH, NBD–NEt\textsubscript{2}, and NBD–NAc were synthesized as previously described,\textsuperscript{8} and Py-1, Sty-7, DMASP–Br, and DMASBT–I, from Aldrich, were used as received.

The adhesive formulations were provided by Loctite España. Loctite 350 (L350) is a UV-curable acrylic adhesive containing a photoinitiator (2,2-dimethoxy-1,2-diphenyl-1-one), whereas Loctite 312 (L312) requires a further addition of an activator for UV curing. Both adhesive formulations are based on polyurethane methacrylic resins and a mixture of acrylic monomers used as reactive diluents. Two commercial photoinitiators, 2-benzyl-2-N,N-dimethylamino-1-(4-morpholino-phenyl)-1-butanone (DBMP; Irgacure 369) and bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide (TMBAPo; Irgacure 819), were provided by Ciba Specialty Chemicals.

Samples of the adhesive formulations containing a fluorescent probe (0.03 wt %) and photoinitiator (1 wt %) were prepared by the stirring of all components for 8 h until homogeneous solutions were obtained. The photocurable formulations were cast as uniform layer coatings (10 \(\mu\)m) between two low-density polyethylene (LDPE) films (40 \(\mu\)m thick). The role of the LDPE was to prevent oxygen diffusion from the atmosphere into the samples during irradiation at room temperature.

**Laser Irradiation**

A Quanta-Ray Nd-YAG laser (Spectra Physics) emitting at 355 nm was directed through two laser mirrors (Lambda Research Optics, Inc.) at
45° to the sample. The laser pulse energy output was 100 mJ, and its duration measured at the half-maximum intensity was 6 ns. The repetition rate of the laser was variable, between 1 and 3.3 Hz, with a Stanford DG 535 pulse delay generator. The laser output was attenuated with a beam splitter before it reached a sample, and the energy was measured with a Scientech H310D photocolorimeter. The laser beam was expanded with a PCV fused silica lens to overfill the image of the UV-curable formulation (ca. 4 cm in diameter).

### Monitoring by Real-Time Fluorescence

The equipment and procedure have been described elsewhere. The fluorescence emission was collected with an Oriel MS257 monochromator, and the spectra were recorded with an Andor ICCD-408 intensified charge coupling device camera. The trigger of the intensified CCD camera and the laser were controlled by a Stanford DG 535 pulse delay generator. The acquisition and preliminary manipulation of data were carried out using custom software.

### Table 1. Names and Acronyms of the Fluorescent Probes

<table>
<thead>
<tr>
<th>Probe</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMANS</td>
<td>4-Dimethylamino-4′-nitrostilbene</td>
</tr>
<tr>
<td>DMANBu</td>
<td>4-Dimethylaminophenyl-4′-nitrophenylbutadiene</td>
</tr>
<tr>
<td>NBD-NetOH</td>
<td>N,N-Diethylamino-7-nitrobenz-2-oxa-1,3-diazole</td>
</tr>
<tr>
<td>NBD-Net₂</td>
<td>N-(2-Hydroxyethyl)-N-methylamino-7-nitrobenz-2-oxa-1,3-diazole</td>
</tr>
<tr>
<td>NBD-Nacr</td>
<td>N-(2-Acryloxyethyl)-N-methylamino-7-nitrobenz-2-oxa-1,3-diazole</td>
</tr>
<tr>
<td>Py-1</td>
<td>Pyridine-1</td>
</tr>
<tr>
<td>Sty-7</td>
<td>Styryl-7</td>
</tr>
<tr>
<td>DMASP-Br</td>
<td>4-[4-(Dimethylamino)styryl]-1-docosylpyridine bromide</td>
</tr>
<tr>
<td>DMASBT-I</td>
<td>2-[4-(Dimethylamino)styryl]-3-ethylbenzothiazol iodide</td>
</tr>
</tbody>
</table>

[Figure 1. Chemical structures and acronyms of fluorescent probes.]
out with the Oriel program IntraSpec V, which allows the storage and processing of data.

**Monitoring by FTIR**

FTIR measurements were carried out in a Nicolet 520 IR spectrophotometer provided with a Fourier transform algorithm. The samples were placed over a specular reflection accessory in the IR spectrophotometer. Because the IR absorbance was proportional to the monomer concentration, the conversion was analyzed on the basis of the decrease in the absorbance at 817 cm$^{-1}$ (corresponding to the disappearance of the acrylate double bond).

**RESULTS AND DISCUSSION**

The laser-induced polymerization of two commercial poly(urethane acrylate) formulations has been followed through the measurement of the changes in the emission spectra of nine fluorescent probes incorporated into these systems. As an example, the variation of the fluorescence spectra of Py-1 at different irradiation times (the laser pulse and the dark period between two pulses) during the pulsed-laser-induced polymerization of L312 is shown in Figure 2. An increase in the intensity and a blueshift of the maximum of fluorescence was observed as the polymerization occurred. The spectrum evolution shows different behaviors depending on the photoinitiator, although the same final conversion was obtained (which was independently measured by the reduction of the acrylic double-bond absorption in FTIR). This reveals that the rigidity of the media during polymerization changes differently in the two systems. A hint of this difference, which could not be detected during the monitoring of curing by means of other techniques such as photocalorimetry, is given in the following sections. Moreover, the simultaneous occurrence of secondary reactions other than crosslinking reactions has to be considered. The incorporation of the fluorescent probe does not change the kinetic profile obtained during the UV curing of the adhesive in the absence of the probe.

The kinetic profiles obtained by fluorescence are shown as characteristic S-shaped curves in Figure 3. First, there is an induction period, which is due to the inhibition effect of oxygen. Then, the fluorescence increases with the irradiation time of the laser, and finally, it comes to a plateau with a time dependence on the adhesive formulation. In a previous article, correlations between the fluorescence changes and the degree of conversion were established during the UV curing of these acrylic formulations under continuous irradiation from a medium-pressure mercury lamp. The slope of the plots of the normalized fluorescence versus the time was demonstrated to be proportional to the rate of polymerization. Moreover, the sensitivity of the fluorescent probes was evaluated from the nonnormalized curves of emission changes. Table 2 summarizes the fluorescence rates, along with the sensitivity of the probes and the shift of the maximum emission wavelength during curing.

The polymerization rates are similar for each adhesive independently of the fluorescent probe,
and this indicates that the presence of the fluorophores does not vary the polymerization kinetics, at least with the concentrations used. As previously reported, the sensitivity of the probes depends on the adhesive formulation, showing broader changes in fluorescence during the curing of L312 with DBMP than during the curing of L350. This fact was interpreted as a result of the lower rigidity of L350. Although DMANS is the most sensitive in L350, DMANBu and Py-1 show the highest fluorescence changes in L312. Among the commercial fluorescent probes, the lowest sensitivity was found for probes containing a benzothiazol group (Sty-7 and DMASBT-I). The probes based on NBD (NBD–NEt₂ and N-alkylamine-7-nitrobenz-2-oxa-1,3-diazo–Acr) behaved similarly to stilbene derivatives (DMANS or DMANBu), but they exhibited lower photostability, which led to a decrease in the fluorescence intensity at long irradiation times as a result of photobleaching.

In a previous article, we reported an interesting feature when the behavior of NBD–NEt₂ and NBD–Acr was compared. The probe containing the acrylic moiety showed lower sensitivity during the final stage of curing under UV continuous polychromatic irradiation as a result of being incorporated into the macromolecular network; therefore, the higher motion restrictions diminished the sensitivity of the label. This effect was reproduced in pulsed-laser-induced curing. This observation can be explained by the assumption that covalent attachment affects the distribution of probes between the rigid environments, presumably highly crosslinked gel particles, and the mobile monomer-rich environments. The enrichment of nonreactive probes in mobile environments is expected because of the diffusion out of the crosslinked regions, whereas reactive probes remain attached to polymer networks. Therefore, the sensitivity toward microrigidity changes is enhanced for a nonreactive probe.

**Influence of the Repetition Rate of the Laser Pulse**

Pulsed lasers have the advantage of being able to modify the time interval between two pulses by modifying the rate of repetition. The pulsing fre-
quency effect on the kinetics of UV curing of the acrylic adhesives was studied by the fluorescence method. The frequency of the pulses was varied from 1 to 3.3 Hz, corresponding to times between successive pulses of 1, 0.7, 0.5, and 0.3 s. Two parameters were used to show fluorescence changes: the ratio between the intensities at two different wavelengths \( \frac{I_{305}}{I_{20855}} \) and the first moment of fluorescence \( \langle \nu \rangle \). Py-1 was used as a probe because it showed good sensitivity to the process. Figure 4 plots the intensity ratio as a function of the total irradiation time (the laser pulse and the dark period between two pulses) during the laser polymerization of the acrylic formulations.

An induction period can be observed at the beginning of the polymerization reaction, becoming more pronounced at low repetition rates. The laser pulse lasts only 6 ns, which is about the time needed to generate the initiating radicals, so the polymerization itself develops mainly in the dark, after the laser shot. The consumption of oxygen dissolved in a sample may lead to a long period of induction (more or less), depending on the rate of radical production. The energy per pulse does not change with a reduction in the frequency of pulses \( f \); however, the average incident intensity \( I_0 \) decreases, and then the polymerization rates \( \rho \) slow down and the time to reach the maximum rate \( t_{\text{max}} \) increases (Table 3).

As shown in Table 3, the inhibition time \( t_{\text{inh}} \) increases as the frequency of repetition of the laser pulse decreases. The longer induction period observed with L350 could result from a greater solubility of oxygen in L350 or to a less efficient production of free radicals by the photoinitiator as suggested by the lower polymerization rates. These periods are also dependent on the nature of the photoinitiator, as shown in Figure 5, which plots \( t_{\text{inh}} \) as a function of the reciprocal of the incident light intensity during the laser curing of L312 with DBMP or TMBAPO.

Laser polymerizations were carried out under a fixed initial oxygen concentration because the LDPE film prevented a further uptake of oxygen.

![Figure 4](image)

**Table 3.** Influence of \( f \) on the Laser-Induced Curing of Acrylic Formulations

<table>
<thead>
<tr>
<th>( f ) (Hz)</th>
<th>L350</th>
<th>L312–DBMP</th>
<th>L312–TMBAPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (s(^{-1}))</td>
<td>( t_{\text{max}} ) (s)</td>
<td>( t_{\text{inh}} ) (s)</td>
<td>( \rho ) (s(^{-1}))</td>
</tr>
<tr>
<td>3.3</td>
<td>0.06</td>
<td>34</td>
<td>5</td>
</tr>
<tr>
<td>2.0</td>
<td>0.04</td>
<td>56</td>
<td>13</td>
</tr>
<tr>
<td>1.4</td>
<td>0.03</td>
<td>74</td>
<td>20</td>
</tr>
<tr>
<td>1.0</td>
<td>0.02</td>
<td>89</td>
<td>28</td>
</tr>
</tbody>
</table>
from the air atmosphere, as explained in the Experimental section. Oxygen molecules are very small in comparison with the other species present and, therefore, extremely mobile, contributing to a great extent to the quenching of primary radicals. Therefore, it can be assumed that oxygen acts as an inhibitor, and the dissolved oxygen in the formulation should be consumed before the polymerization is effectively initiated. The dependence of $t_{inh}$ on the light intensity can be obtained as follows:

$$t_{inh} = \frac{[O_2]}{R_{st}} = \frac{[O_2]}{(\phi \cdot f \cdot n_{abs} \cdot I_0)}$$

(1)

where $R_{st}$ is the rate for production of free radicals that are scavenged by oxygen and, therefore, will consume the oxygen dissolved; $[O_2]$ is the oxygen concentration in the adhesive formulation; $f$ is the number of free radicals formed per photoinitiator molecule photofragmented; $\phi$ is the photolysis quantum yield of the photoinitiator; and $n_{abs}$ is the fraction of absorbed intensity.

$n_{abs}$ is assumed to be similar for both photoinitiators at the irradiation wavelength (355 nm) under the experimental conditions with a high concentration of the photoinitiator. Therefore, from the slopes of the plot, a higher photoinitiator efficiency for DBMP is deduced, being considered the product of $\phi$ and $f$. This result is surprising, given that under irradiation, TMBAPO gives rise to phosphorus-centered radicals that are more reactive toward acrylic double bonds than carbon-centered radicals, such as those obtained from DBMP (Scheme 1). The high reactivity of phosphinoyl radicals has been attributed to a high degree of s character and spin localization on the P atom. However, the change in the primary radical concentration with time in pulsed-laser polymerization may notably differ from that under continuous irradiation, for which a steady-state concentration is produced until the photoinitiator is totally consumed. Secondary in-

**Figure 5.** Plot of $t_{inh}$ as a function of $1/I_0$ during the curing of L312. The photoinitiators were DBMP and TMBAPO, and the fluorescent probe was Py-1.

**Scheme 1.** Photofragmentation mechanisms of photoinitiators DBMP and TMBAPO under UV irradiation.
cage reactions, such as free-radical recombination, may have more influence on pulsed polymerization to the extent that the time between successive pulses is changed by variations in the frequency rate. Hence, the fraction of initiated macroradicals per absorbed photon ($\frac{d\phi}{H_{9278}}$) should decrease with the repetition rate, and this influence should be more pronounced for the more reactive phosphinoyl radicals.

This has also been confirmed from the comparison of the photopolymerization profiles for both photoinitiators shown in Figure 6. At the pulse frequency of 3.3 Hz, a reduction of the autoacceleration effect can be clearly seen when TMBAPo is used instead of DBMP, whereas the initial polymerization rate is independent of the photoinitiator. Under laser-induced polymerization at the lowest frequency, 1 Hz, both the increase of the fluorescence intensity ratio with time and the final value of the intensity ratio are reduced in the case of TMBAPo with respect to DBMP. This behavior agrees with a lower photoinitiation efficiency of TMBAPo, giving rise to longer chained macroradicals.

In pulsed photoinitiated polymerization, the termination rate coefficient ($k_t$) may depend on the free-radical chain length. Termination is diffusion-controlled from the very beginning of a free-radical polymerization and, therefore, may depend on the physical properties of the reaction medium, such as the chain length of the free radicals, the diffusivity of these radical species and their segment mobility, and the microstructure of the produced polymer network. Modeling the termination kinetics of nonstationary free-radical polymerizations$^{14}$ has shown that the variation of $k_t$ with the chain length is particularly pronounced under conditions in which an entanglement network exists and is a decreasing function with the reaction time. Therefore, it seems feasible that a more rapid decrease of the $k_t$ function occurs in laser-induced polymerization photoinitiated with DBMP, for which a higher crosslinking density is expected with respect to TMBAPo, leading to higher polymerization rates.

Figure 6 plots the fluorescence intensity ratio as a function of the number of pulses received, that is, the incident energy reaching the sample. During the UV curing of L312 with TMBAPo, the final value of the intensity ratio at the plateau decreases as the pulse frequency decreases from 3.3 to 1 Hz. This fact points out that the limiting degree of cure decreases as a result of termination reactions between pulses due to the high radical concentration generated in each pulse.$^{15}$ However, no dependence of the final intensity ratio on the pulse repetition rate was observed when L350 (containing 2,2-dimethoxy-1,2-diphenyletan-1-one as a photoinitiator) and L312 (with DBMP) were cured. This feature could be explained by the fact that the time between pulses determines the growth time of a major portion of the chains because biradical termination occurs preferably just after the radical concentration has increased through a subsequent laser pulse. Because the dark periods

![Figure 6](image6.png)

**Figure 6.** Plot of the fluorescence integrated intensity versus the irradiation time during the laser curing of L312 with TMBAPo and DBMP at two laser pulse frequencies: 3.3 and 1.0 Hz.

![Figure 7](image7.png)

**Figure 7.** Plot of the Py-1 fluorescence intensity ratio versus the number of pulses at different frequencies of the repetition of the laser pulse during the UV curing of L312 and DBMP.
change slightly during the interval of the studied frequencies, no differences in the final degree of curing may be expected. The different behavior with TMBAPo may be attributed to the higher influence of secondary in-cage reactions, which play important roles during dark periods. Moreover, oxygen acts as a quencher of primary radicals, giving rise to longer $t_{1/2}$'s with this photoinitiator in comparison with those with DBMP at the same frequency of the laser pulse.

The value of the fluorescence intensity at the maximum depends on experimental factors such as the incident intensity and probe concentration. Baselga et al.\textsuperscript{16} proposed using a new method based on the determination of the first fluorescent moment to monitor both free-radical polymerization and step-growth polymerization. The first moment of emission spectrum $\langle \nu \rangle$ is given by the weighted average wave number:

$$
\langle \nu \rangle = \sum I_\nu \cdot \nu / \sum I_\nu
$$

(2)

In Figure 8, $\langle \nu \rangle$ is plotted as a function of time for the curing of L312 in the presence of Py-1. The mathematical treatment of the experimental data (emission spectra between 450 and 720 nm) for the calculation of $\langle \nu \rangle$ displayed the same behavior as the fluorescence intensity (cf. Fig. 4(b)) but led to a lower scatter of data. Moreover, the intensity method requires an internal standard or normalization to avoid errors due to experimental fluctuations, whereas $\langle \nu \rangle$ gives absolute measurements.

The plots of $\langle \nu \rangle$ versus time show that there are two different behaviors. At the beginning, the initial slope is smaller, and the period of this stage corresponds to the induction period determined by the intensity ratio method. Unlike the intensity ratio, $\langle \nu \rangle$ increases slightly during this period. The origin of the changes in the emission spectra is rather complex. In solvatochromic probes with a strong dipole moment in the excited state, the typical behavior during a curing reaction consists of the average emission energy shifting toward higher energies because of increasingly inefficient coupling between the excited state dipole and the environment, as shown in Figure 8.

**Influence of the Laser Beam Intensity**

The laser photocuring of L312 in the presence of several fluorescent probes was carried out with different incident laser intensities and a constant pulse frequency of 3.3 Hz. The energy density per pulse was attenuated by means of a beam splitter, which allowed the reflection of different fractions of the laser beam. Increasing the incident energy improved the rate of polymerization and the degree of cure and, therefore, also led to lower amounts of the unreacted monomers in the final product (Figs. 9 and 10). It is well known that the extension of a photopolymerization reaction leading to network formation depends on the structure of the monomer. When the glass-transition temperature of the growing polymeric matrix

![Figure 8. Plot of $\langle \nu \rangle$ as a function of the irradiation time during the curing of L312, showing the influence of the repetition rate of the laser pulse. The photoinitiators were DBMP and TMBAPo. The fluorescent probe was Py-1.](image-url)
reaches the polymerization temperature, the mobility of the macroradicals and reactive double bonds is very low, the polymerization rate decreases drastically, and vitrification occurs. It is remarkable that fast reactions such as laser-induced polymerization involve the reaction of more double bonds, and usually higher final degrees of conversion are reached than under thermal or conventional UV curing. In that sense, the polymerization kinetics, as well as the volume relaxation kinetics, should be considered. An excess of temporary free volume is generated because the volume shrinkage process is substantially slower than the polymerization kinetics. Thus, the speed of the reaction plays an important role, and the limiting degree of cure due to vitrification increases in faster reactions.

In general, the polymerization rate scales with the square root of the light intensity, as predicted by classical kinetic analysis. Apparently, a saturation rate effect can be envisioned as the energy increases during the laser curing of L312 with TMBAP (Fig. 9). This phenomenon refers to the decrease in the dependence of the polymerization rate with the light intensity, to the point of the polymerization rate becoming independent of the intensity above a critical value. This effect was not observed during curing with DBMP in the range of light intensities used in this study (up to 30 mW/cm²). Some authors have explained this effect by a simple kinetic model incorporating primary radical termination. Therefore, when the primary radical population is large, primary radical termination will occur with macroradical termination through reaction diffusion. Primary radical termination becomes the dominant mode of termination at high intensities because of the high concentration of primary radicals, whereas a significant fraction of primary radicals may undergo recombination reactions outside of the cage. Again, the reactivity of initiator radicals merits consideration, to the extent that an increase in the kinetic constant of primary radical termination is expected because of the greater reactivity.

Figure 9. Plot of the fluorescence integrated intensity versus the irradiation time at different laser incident energies during the UV curing of L312 and TMBAP. The fluorescent probes were DMASBT–I and NBD–Nac. The frequency of the laser pulse was 3.3 Hz.

Figure 10. Plot of the final degree of conversion versus $I_0$ during the curing of L312. The photoinitiators were DBMP and TMBAP. The frequency of the laser pulse was 3.3 Hz, and the exposure time was 3 min.
of phosphinoyl radicals derived from TMBAPO. This fact may explain why primary radical termination can take place for this particular photoinitiator at relatively low light intensities. With the pseudo-steady-state hypothesis, the following equation can be established:

$$k_i[P_n]^2 + k_{tp}[R\cdot][P_n] = k_i[R\cdot] \cdot [M]$$

where $k_i$, $k_{tp}$, and $k_i$ are the bimolecular termination, primary radical termination, and initiation rate constants; $R\cdot$ and $P_n\cdot$ are the primary radicals and growing macroradicals, respectively; and $M$ is the monomer.

When primary radical termination becomes the dominant mode of termination, the concentration of macroradicals is independent of the primary radical concentration and thus independent of the light intensity. Therefore, the polymerization rate reaches a limit once the kinetics become controlled by the diffusion of the reactive species and not by the initiating rate anymore. Our results agree with those obtained by Decker et al. with another bisarylphosphine oxide (Irgacure 1700) as a photoinitiator. An upper limit value of the light intensity decreases as the pulse frequency and, therefore, the rate of polymerization slow down. Secondary reactions of primary radicals become more favored as the dark period increases, and a dependence on the photoinitiator can be clearly seen.

Moreover, the kinetic study has revealed novel features related to the microstructure of photogenerated networks. With different photoinitiators, the UV curing of an acrylic-based formulation proceeds in few seconds. It is particularly well suited because of its short response and high sensitivity, especially for $\langle \nu \rangle$. From the plots of fluorescence rates, with TMBAPO, the conversion increases, and a dependence on the photoinitiator can be clearly seen.

The influence of the laser repetition rate on the curing of acrylic adhesives has been analyzed. The energy density per pulse is essentially independent of the pulse repetition rate as long as the output of the laser is kept constant, but the average light intensity decreases as the pulse frequency and, therefore, the rate of polymerization slow down. Secondary reactions of primary radicals become more favored as the dark period increases, and a dependence on the photoinitiator can be clearly seen.

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Moreover, the kinetic study has revealed novel features related to the microstructure of photogenerated networks. With different photoinitiators, the UV curing of an acrylic-based formulation proceeds in few seconds. It is particularly well suited because of its short response and high sensitivity, especially for $\langle \nu \rangle$. From the plots of fluorescence rates, with TMBAPO, the conversion increases, and a dependence on the photoinitiator can be clearly seen.
other widely used curing monitoring techniques such as RTIR, can provide complete information for analyzing the kinetics of pulsed-laser polymerization.

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REFERENCES AND NOTES