New Fluorescent Probes for Monitoring Polymerization Reactions: Photocuring of Acrylic Adhesives, 2

Bosch, A; Fernández-Arizpe, F; Catalina, J; Mateo, C; Peinado*

Instituto de Ciencia y Tecnología de Polímeros; CSIC, Juan de la Cierva 3, 28006 Madrid, Spain
E-mail: cpeinado@ictp.csic.es

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Introduction
The versatility and scope of acrylic chemistry has long been exploited in the formulation of a wide variety of commercial products, ranging from the so-called new technologies (microlithography, holography) to the improvement of already established fields, one of the most important being the formulation of coatings, inks, sealants, and adhesives. Among others, acrylic and methacrylic monomers are one of the most used reactive diluents in the formulations of commercial adhesives, given their low price and the facile and versatile chemistry of these materials. The formulation of an acrylic adhesive usually consists on one or more reactive diluents (monomers), a binder (a low to medium molecular weight polymer), and the initiator for the polymerization reaction, the mechanism of which can be thermal or photo-chemical, radical or cationic. Upon polymerization, the formulation will be transformed from a more or less viscous liquid to a rubbery solid, which should stack together the desired objects. These types of photocurable systems are under intensive research because they are solvent-free and environmentally-friendly materials.

The physical and mechanical properties of the adhesive, such as tack, adhesion, surface compatibility, elasticity, or stiffness, will depend critically not only on the chemical formulation, but also on the parameters that govern the polymerization reaction, such as rate of polymerization, final conversion reached by the system, and degree and density of crosslinking. As a result, techniques for monitoring the degree of cure have been a priority in industry for many years as a tool for quality control and process optimization. Several methods have been developed to study the kinetics of polymerization reactions, with DSC and FT-IR being the most widely used. Since...
the beginning of the 1980’s, fluorescence spectroscopy of probes sensitive to their microenvironment has been intensively used,[5] and commercial systems are now available to follow the process on-line. Probe fluorescence changes during polymerization are related to both changes in the microviscosity and the local polarity of the medium, because these changes usually affect the intensity and the position of the fluorophore emission band. Many probes have been recently studied to follow polymerization reactions not only of acrylates,[6] but also of polyurethanes,[7] and epoxies.[8]

We present in this work the study of a new family of fluorescent compounds recently described by us,[9] as probes for monitoring in situ the photopolymerization reaction of acrylic adhesives throughout the entire range of conversion. We have focused our attention on photoinduced polymerization because it is one of the most efficient processes for rapidly producing polymeric materials with well-defined properties.[10] Photopolymerizable systems are easy to formulate and the conditions of the polymerization reaction could be rapidly modified by just changing the intensity of the incident light. In addition, photopolymerizable coatings and adhesives are of commercial interest especially in the field of optics and microelectronics.

In this work, in addition to the quantification of the photopolymerization reaction of the adhesives, attention is also paid to the elucidation of the mechanism of the crosslinking reaction and the role played by the binder depending on the initiator used.

Experimental Part

Materials
Dansylamide (from Aldrich) and Prodan (from Molecular Probes) were used as received. Fluorescent probes, SF1 and SF4 were synthesized as described recently.[9] Photoinitiators 2,2-dimethoxy-2-phenylacetophenone (Irg651) and bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irg819) were generously given by Ciba SC and used as received. Adhesive formulations L312 and L329 were a kind gift from Loctite Corp. and used without further purification.

Analysis
In addition to the technical data supplied by Loctite Corp., qualitative and quantitative analysis were carried out on the adhesive samples and the results are summarized in the next section. The separation of the components was carried out by dissolution of the adhesive formulations in chloroform and further precipitation on cold ethanol. Insoluble fractions were identified in both cases as composed of only one polymer. Soluble fractions were composed of several different components, and product separation was accomplished by column chromatography using hexane/ethyl ether (9:1) as eluent. Complete identification of components was done by spectroscopic (IR, 1H NMR, 13C NMR and UV-vis) and chromatographic analysis (GC-EM and GPC).

Sample Preparation
Samples containing probe (at approximately 0.03 wt.-%), photoinitiator (1 wt.-%) and the adhesive formulation, were prepared by stirring all components in the dark until homogeneous solutions were obtained (not less than 8 h). The photocurable formulations were applied as a uniform layer coating on aluminium foil and covered with a low-density polyethylene film (LDPE, of 40-μm thickness) for the RT-FT-IR experiments, or between two LDPE films for the laser experiments. Previously, it was made sure that the LDPE film does not absorb at the IR frequencies selected to follow the photopolymerization reaction or at the UV-irradiation or emission wavelengths. Photosensitive coatings of 10 μm thickness were obtained by controlled pressing over 1 min using 2 × 107 kg · cm−2 pressure.

UV-Curing, Monitoring and Analysis
Samples have been photopolymerized at room temperature under air atmosphere until their limiting conversion. The irradiation source was a Sylvania 400-W Hg medium-pressure lamp, which provides polychromatic continuous light (MACAM-Flexicure portable system provided with a quartz optical fiberguide). For all samples, the disappearance of double bonds and the fluorescence changes of the probes have been simultaneously monitored in situ by means of RT-FT-IR and real-time luminescence spectroscopy as photopolymerization proceeds as described in Part 1 of this work.[11]

RT-FT-IR spectra (4 cm−1 resolution) were recorded at different irradiation times. The spectrophotometer was operated in the absorbance mode and the detection wavelength was set at 817 cm−1 corresponding to the out-of-plane deformation of the acrylate double bond to monitor its disappearance. The decrease in the absorbance was analyzed by means of a software program to record data in real time. The degree of double bond conversion, a, is expressed by Equation (1):

\[
a = \frac{(A_0 - A_t)}{A_0}
\]

where \(A_0\) is the initial absorbance at the chosen frequency and \(A_t\) is the absorbance value at irradiation time \(t\). The slope of the plot of \(a\) versus irradiation time is proportional to polymerization rate.

Real-Time Fluorescence Spectroscopy
A Nd-YAG pulsed laser (Quanta-Ray from Spectra Physics) emitting at 355 nm was directed through two laser mirrors (Lambda Research Optic Inc.) at 45° to the sample. The laser beam was expanded by using a PCV fused-silica lens to overfill the image of the fluorescent probe (about 4 cm diameter) and an attenuator was used to avoid laser photoinduced polymerization. Laser output was measured by a photocellimeter Scientech model H310D and the laser power reaching the sample was 5 mW · cm−2. Simultaneously the sample...
was polymerized by irradiation at 135° with polychromatic light from the 400-W Hg lamp. The incident light was measured by actinometry using a film of polymethylmethacrylate containing Aberchrome 540, and determined as \( I_0 = 1.47 \times 10^{-10} \text{ Einstein} \cdot \text{s}^{-1} \). In such conditions no polymerization was initiated by the excitation laser beam used for observation. Fluorescence emission was collected to a monochromator (Oriel MS257) by an optical fiber placed at –45° with respect to the sample. A glass filter covering the sample was used to lower the laser intensity preventing a premature polymerization, and an additional cut-off filter (355 nm) coupled to the monochromator was used to eliminate laser beam interference. The spectra were recorded by means of an intensified Charge Coupling Device, Andor camera ICCD-408.

The frequency (v) of laser pulses was adjusted to have a sufficient number of probe emission spectra during the time required to cure the adhesive, but avoiding the photodegradation of the probe. This was \( v = 3.33 \text{ Hz} \) for L312 and \( v = 0.15 \text{ Hz} \) for L329. On decreasing the frequency of the laser pulse repetition the photobleaching of the probe was significantly reduced.

The trigger of the different devices was controlled by a pulse delay generator, Stanford model DG 535. Fluorescence emission was acquired by the ICCD camera (chip of 1024 × 256 pixels) over 1 μs every 0.3–6.8 s, depending on the duration of the experiment and the photostability of the probe. Preliminary manipulation of data was carried out by means of the Oriel software "IntraSpec V".

### Results and Discussion

#### Selection of Materials

The new probes studied in this work are shown in Scheme 1, together with the commercial Dansylamide and Prodan, to which the new results have been compared. Their spectroscopic properties have been described before.\(^9\) All of them correspond to a D-π-A structure and they have been proven to follow accurately photopolymerization reactions of relatively simple systems, such as mono- and difunctional acrylic and methacrylic monomers,\(^{12}\) until the limiting double bond conversion. Their fluorescence band was sensitive both to changes in micropolarity and microviscosity of the medium showing solvatochromic emission band shifts up to 79 nm and an intense increase in emission intensity as the polymerization reaction proceeds.

The commercial adhesives selected, Loctite 329 (hereafter L329) and Loctite 312 (L312) are both acrylic formulations. The product L329 is an acrylic adhesive characterized by its high toughness, which makes it very suitable for use in strong structural joints or in sheet steel where continuous or repeated loads are generated. The analysis of the formulation showed that the rough material is composed of a chlorosulfonated polyethylene polymer (CSPE) as binder and a mixture of two different methacrylic monofunctional monomers identified as methyl methacrylate and 2-hydroxypropyl methacrylate. Although L312 is also an acrylic adhesive, it has a relatively different chemical composition, both in its nature and functional groups. Reactive diluents are monofunctional monomers, identified as 2-hydroxypropyl methacrylate and acrylic acid, and the polymer binder is an aliphatic polyurethane with acrylic terminal functionalities.

Both formulations only include monofunctional acrylic and methacrylic monomers in their composition, and both, upon polymerization, lead to a crosslinked network (Scheme 2). This means that the polymeric binder should
play an important role in the crosslinking reaction. In the case of the formulation containing CSPE (L329), its role can be explained by the participation of the chlorine atoms and the chlorosulfonic groups as reactive centers that could generate, under certain conditions, crosslinking points between the binder chain and the polymerizing acrylic macroradical. In addition, hydrogen atom abstraction on the binder chain could take place, and this is actually an easy process when photoinitiators such as those employed in this work are used as a source of free radicals.

For the functionalized L312 system the crosslinking reaction should mainly occur by reaction of the terminal acrylic groups of the binder with the growing macroradical. The process is shown in Scheme 3. Also, the abstraction of aliphatic hydrogen atoms of the binder could be made by the photoinitiator.

The crosslinking reaction is essential for these systems to reach the mechanical strength and elastic properties that both adhesives possess when fully cured, and to understand the photopolymerization mechanism and kinetics.

**FT-IR Monitoring of the Curing Reaction**

In Figure 1 the FT-IR kinetic profiles for the photopolymerization of L329 and L312 using two different photoinitiators (Irg651 and Irg819) in the presence of the probes are shown. The differences in the rate of polymerization and the limiting double bond conversion should be attributed to the difference in reactivity of the initiating radicals which have been widely studied and described in the literature. The reaction is much faster in the L312 system (less than 100 s for completion) which is a consequence of its composition, having acrylic functional groups of higher reactivity (higher $k_p/k_t^{1/2}$ values) than the methacrylic monomers that constitutes the L329 formulation. For the less reactive system (L329/Irg651) an inhibition period was found in some cases, which has been attributed to oxygen microbubbles that could be present in the sample, given its extremely high viscosity. This initial delay does not affect the rate of polymerization as will be seen below.

The kinetic profiles show, as expected, the conventional behavior of a photocrosslinking curing reaction: a first stage in which the polymerization reaction rapidly progresses with high monomer consumption, followed by a slowly-reached plateau corresponding to the decrease in the rate of polymerization due to the restrictions in mobility as crosslinking takes place. The last step is effective until the photopolymerization reaction ends, due to system vitrification, without reaching total monomer conversion. There are many studies on the mechanism of this free-radical crosslinking reactions, in which explanations of these effects are widely discussed. Rates of polymerization have been obtained as the slope of the initial linear region and the data are compiled in Table 1, together with the limiting conversion reached. The pre-

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Photoinitiator</th>
<th>$R_p [m/s]$</th>
<th>$a$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L329</td>
<td>Irg651</td>
<td>0.4</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>Irg819</td>
<td>0.6</td>
<td>58</td>
</tr>
<tr>
<td>L312</td>
<td>Irg651</td>
<td>2.5</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>Irg819</td>
<td>4.7</td>
<td>60</td>
</tr>
</tbody>
</table>
The presence of the probes does not affect the kinetic profile of the reaction in any case, so they are suitable to be used as sensors of this process.

Real-Time Fluorescence Monitoring of the Curing Reaction

The changes in fluorescence of the probes SF1 and SF4 versus irradiation time have been monitored simultaneously as the curing of the adhesives proceeds. The emission spectra of both probes exhibit an increase in the intensity together with a blue-shift of the band, as occurs for the crosslinking reaction of monomers in bulk (Figure 2). [12]

The variation of fluorescence has been measured as the ratio between the intensities at two given wavelengths. The criteria for the selection of those wavelengths has been previously discussed[12] and the employed values for \( \lambda_1 \) and \( \lambda_2 \) in the different systems are summarized in Table 2.

When the fluorescence variation \( R = I_{\lambda_1}/I_{\lambda_2} \) is plotted versus irradiation time, the kinetic profiles

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>SF1</th>
<th>SF4</th>
<th>Dansilamide</th>
<th>Prodan</th>
</tr>
</thead>
<tbody>
<tr>
<td>L329</td>
<td>373/414</td>
<td>398/442</td>
<td>409/481</td>
<td>373/427</td>
</tr>
<tr>
<td>L312</td>
<td>375/414</td>
<td>399/443</td>
<td>412/474</td>
<td>385/432</td>
</tr>
</tbody>
</table>
obtained by fluorescence are similar to the RT-FT-IR ones, showing the above-mentioned regions of rapid polymerization and the subsequent plateau (Figure 3).

The slope of the non-normalized plots for a given polymerizing system could be defined as the sensitivity of each probe for this particular formulation, and are shown in Table 3. The values for the fluorescence rate of polymerization (\(q\)) have been calculated as the slopes of the normalized fluorescence-time plots\(^{11}\) and they have been also compiled in Table 3. It can be seen that the measured rate of polymerization does not depend on the probe used, this being the main requirement for a probe to be used as a sensor. In addition, these new probes have better sensitivity values than dansylamide and prodan.

The variations of fluorescence with the degree of double bond conversion are shown in Figure 4, and they all correspond with a double-slope plot, as could be expected for a crosslinkable system.\(^{12}\) The inflection point is related to the gelation, and this fact has been also observed by other authors using excimer forming probes.\(^{16}\)

For the flexible L329 formulation, there is some scatter in the inflection points of the plots. No substantial differences are found if the photoinitiator employed is Irg819 or Irg651.

In contrast, the more rigid L312 shows a clear inflection point at around 30% of conversion, independently of the probe used for sensing the reaction. In this case, surprisingly, a different fluorescent response of the probes is observed when the photoinitiator is changed. For Irg651, the slope of region I is higher than the slope of region II, and the opposite occurs when Irg819 is used for initiating the reaction. This is found for both SF1 and SF4 probes and is shown in Figure 5.

As we stated previously\(^{12}\) the slope of the fluorescence-conversion plot is proportional to the rigidity of the medium, so, in the systems studied here, the results strongly suggest that, for the same degree of conversion, a higher degree of crosslinking is being reached in the stage previous to gelation when Irg651 is used as photoinitiator. This could only be due to secondary crosslinking reactions.

Table 3. Fluorescence rates of polymerization (\(\rho\)) and sensitivity values for the probes in the photoinitiated curing of L329 and L312.

<table>
<thead>
<tr>
<th>Probe</th>
<th>PI</th>
<th>L329</th>
<th>L312</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\rho)</td>
<td>Sensitivity (a)</td>
<td>(\rho)</td>
</tr>
<tr>
<td>SF1</td>
<td>0.5</td>
<td>1.1</td>
<td>3.8</td>
</tr>
<tr>
<td>SF4</td>
<td>0.5</td>
<td>1.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Dansylam.</td>
<td>0.4</td>
<td>0.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Prodan</td>
<td>0.5</td>
<td>0.6</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>1.8</td>
<td>4.5</td>
</tr>
<tr>
<td>SF4</td>
<td>0.8</td>
<td>1.5</td>
<td>6.0</td>
</tr>
<tr>
<td>Dansylam.</td>
<td>1.0</td>
<td>1.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Prodan</td>
<td>1.1</td>
<td>1.5</td>
<td>5.7</td>
</tr>
</tbody>
</table>

\(a\) Sensitivity = \(\Delta I/\Delta t\).
(coupling) not involving double bond disappearance, and the inter-chain links must be formed between radicals originated at the binder chain and the growing polymerizing macroradicals. In fact, the higher rigidification is observed for Irg651, which has higher ability than Irg819 to abstract hydrogen atoms at the binder chain.\[17\] This fact, which could not be observed with RT-FT-IR technique, is clearly detected when our fluorescent probes are used, and provides evidence that these new fluorescent probes are useful for following not only the kinetics but also the mechanism of the polymerization reaction.

The monitoring of the secondary crosslinking reactions are important in order to know when an adhesive reached the desired degree of crosslinking, because these processes could not be observed through conventional techniques such as FT-IR and DSC, and are essential in the post-curing reactions.

The process could be also followed by fluorescence when attending only to the position of the maximum wavelength. The fluorescence maxima are blue-shifted up to 38 nm during UV-curing, due to the decrease of polarity from monomer to polymer but also to the increase in rigidity of the system.\[18\] In Table 4 the maximum wavelengths before and after UV-curing are compared, and it can be seen that the solvatochromic shifts for these probes are as high as those for the commercial compounds.
Plots of fluorescence maxima versus time are shown in Figure 6, together with the RT-FT-IR kinetic profile. The beginning of $\lambda_{\text{max}}$ variation is always simultaneous with the onset of the polymerization reaction, and the interval where higher changes are observed practically fit with region I in the kinetic profile. Nevertheless, a detailed examination of the figures reveals that the period of time during which the probes experience variation in their fluorescence (sensing times) are different for each probe (Table 5).

The observed differences in sensing time are a consequence of the molecular size of the probes, being the smallest fluorescent probe of the series, SF1, is always sensitive for longer periods. The Van der Waals volumes of the probes, calculated by means of Cerius$^\text{®}$ computational software, are also enclosed in Table 5.
The fluorescence shifts follow a two-slope variation with conversion as was observed for the intensity ratio (Figure 7). Again, more scatter in the experimental data is found for the flexible L329 system, but the general trend of the variation is clear. In general, the maximum emission wavelength is widely shifted during the first stage of polymerization when more intense changes of both polarity and rigidity are produced. After gelation, $\lambda_{\text{max}}$ becomes a less sensitive parameter.

In these plots the different behaviour of the fluorescence parameter when the photoinitiator is changed in L312 formulation is again observed, and this confirms that higher rigidification of the material (crosslinking reactions) is taking place at the beginning of the reaction with Irg651, which could be detected by fluorescence of probes inserted in the system.

From these results it can be deduced that the wavelength shift of these solvatochromic probes could be also a useful parameter to follow the polymerization reactions of complex systems. Although this parameter is not very sensitive in the last stage of the reaction, which is precisely the most important, it has the advantage of being an absolute method of detection, independently of instrumentation characteristics.

Finally, the variation of the first moment of the fluorescence with both irradiation time and double bond monomer conversion has been checked. This parameter has been proposed by other authors\cite{8a} as very accurate for
following curing reactions. The first moment of the fluorescence is defined as the average value \( \langle \nu \rangle \) of the emission band position (Equation (2)):

\[
\langle \nu \rangle = \frac{\Sigma I_{\nu}(\nu)}{\Sigma I_{\nu}}
\]

(2)

where \( I_{\nu}(\nu) \) is the intensity of fluorescence at a wavenumber \( \nu \).

As can be seen in Figure 8, the plots follow the same behaviour as described above when using the intensity ratio and maximum wavelength. The \( \langle \nu \rangle \)-time plot reproduces the RT-FT-IR kinetic profile and the \( \langle \nu \rangle \)-conversion graph shows the two-slope variation, which confirms that the first moment of the fluorescence is also a good parameter to follow curing reactions of acrylic photopolymerization processes. Very little scatter of the experimental points is observed.

**Conclusions**

Two new fluorescent probes have been used to monitor the curing process of UV-curable adhesive systems. As photopolymerization proceeds, the fluorescence band of the probes showed an increase in intensity as well as a blue shift in its position. This behavior allows the reaction to be followed by the variation of different parameters such as the fluorescence intensity ratio between two wavelengths (\( R \)), the maximum wavelength of the band (\( \lambda_{\text{max}} \)), or the first moment of the fluorescence (\( \langle \nu \rangle \)). Even \( R \) is a sensitive parameter in a wider range of conversion, \( \lambda_{\text{max}} \) is also a very suitable parameter as it is very easy to measure and independent of instrumental conditions, and \( \langle \nu \rangle \) shows very little scatter, hence, depending on the sample and conditions, all the three parameters can be used.

The fluorescent kinetic profiles accurately reproduce those obtained by RT-FT-IR, showing the three steps of the crosslinking reaction: the rapid initial polymerization, gelation, and the termination of the reaction due to vitrification of the system. The rate of polymerization has been measured from the fluorescence-time plots.

Differences in the mechanism taking place have been detected by fluorescence when the photoinitiator is changed from Irg651, in which the hydrogen abstraction is a very important secondary reaction, to Irg819, in which this reaction is practically negligible. These differences could not be observed by RT-FT-IR and this reflects the importance of the fluorescence as a method, and particularly these compounds as fluorescent probes, to follow both the kinetics and mechanism of the polymerization reaction.

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Full Paper: The fluorescence of selected probes is monitored during the entire range of curing of an acrylic-based adhesive. The change of fluorescence parameters are continuously measured during the photo-crosslinking process. Real-time FT-IR spectroscopy is used to quantify the conversion at different irradiation times. The intensity ratio, maximum emission wavelength, and first moment of fluorescence can be used as parameters to determine the conversion. Two-slope plots are obtained, which correspond to the different stages of the reaction (see Figure).

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