

New fluorescent probes for monitoring the polymerization reaction Part 3: pulsed-laser polymerization of acrylic adhesives

P. Bosch*, A. Fernández-Arizpe, J.L. Mateo, T. Corrales, C. Peinado

Institute of Polymers, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

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Abstract

The pulsed-laser polymerization of acrylic photocurable adhesives has been investigated by following the fluorescence emission of several commercial and non commercial probes inserted in the system. Photopolymerization profiles, rates of polymerization, and the effect of the laser pulse intensity and frequency on the kinetics of the reaction have been studied.

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1. Introduction

Laser-assisted processing of polymers is one of the most efficient methods to induce ultrafast chemical reactions in photosensitive materials [1]. The spatial coherence of the laser emission provides a great directivity so that the laser beam can be focused down to a micronic spot. The temporal coherence of the laser emission, which occurs at a well-defined wavelength, reduces the extent of undesirable secondary reactions induced by polychromatic wavelength. The large power output leads to high light intensities, thus drastically increasing the overall rate of the photochemical processes considered.

During the past two decades many reports have been published describing the kinetics and mechanisms of laser-induced polymerization of monomers in solution or in bulk, most of them devoted to the calculation of propagation and termination rate constants of the polymerization reaction [2]. Other mechanistic and kinetic effects as chain-length dependent termination [3], oxygen inhibition [4] and final conversion [5] have also been studied. Usually, these studies are performed in conjunction with molecular weight analyzing techniques, such as SEC or MALDI-TOF, which has been excellently reviewed by Buback et al. [6].

In addition to basic knowledge of the polymerization reaction, several applications of this technology have ap-

peared in various industrial sectors, especially in areas where speed, selectivity and spatial resolution are of prime importance, in particular stereolithography, holography, optoelectronics and microlithography [7]. One of the major drawback of the study of these systems is the impossibility of analyzing the obtained material in terms of molecular weight, because the formulations always are composed by multifunctional monomers or prepolymers, then rendering a crosslinked network.

One of the important challenges in laser-induced polymerization is to find a reliable method capable of analyze quantitatively and in real time those reactions which occur at high speed. This could be currently done by means of RT-FTIR, analyzing the decrease of the band corresponding to the acrylic double bond as polymerization proceeds [8]. This method has the inconvenience that this band could be difficult to measure in thick films (saturation of the band), in the last steps of the reaction (problems with baseline) or in complex formulations (in which the band could overlap with others).

Fluorescence sensing of dynamic processes taking place in polymeric media have attracted considerable attention during the last two decades, especially those concerning the monitoring of the polymerization reaction through measuring the fluorescence of a probe molecule inserted in the system. Probe fluorescence changes during polymerization are related to both changes in microviscosity and local polarity of the medium, because those changes usually affect the intensity and the position of the fluorophore emission

* Corresponding author. Tel.: +34 91 562 29; fax: +34 91 564 48 53.
E-mail address: pbosch@ictp.csic.es (P. Bosch).

band. Many probes have been studied to follow polymerization not only of acrylics, but also of polyurethanes [9], and epoxies [10]. Given the advantages of this technique (sensitivity, in-situ monitoring) it has also been applied to follow laser-induced polymerizations [11], but up to now, few works have been published.

Recently we have developed a new series of fluorescent probes [12] which have proven to follow accurately the conventional photoinitiated polymerization of acrylic monomers and adhesives [13] and thermal polymerization of epoxy-anhydride systems [14].

The aim of this work is to check the ability of our probes to follow fast processes as those taking place in pulsed-laser induced polymerization of complex systems such as acrylic photocurable adhesives. In addition, the information obtained from following in real time the changes in the fluorescence emission allows the study of the kinetics and mechanism of the reaction taking place in these crosslinkable system. A comparison is due between the sensitivity and stability of our probes and common commercial fluorophores as dansylamide and prodan.

2. Experimental

2.1. Materials

Dansylamide (from Aldrich) and Prodan (from Molecular Probes) were used as received. Fluorescent probes, SF1 and SF4 were synthesized as described [12]. Fluorescent probe *p*-(1',2',2'-tricyanovinyl)-*N*-ethyl-*N*-(2'-acryloxyethyl)aniline (S3F) was synthesized by first obtention of *p*-(1',2',2'-tricyanovinyl)-*N*-ethyl-*N*-(2'-hydroxyethyl)aniline as reported elsewhere [15,16]. Subsequent reaction of the hydroxyl group was performed by addition of a 10% excess of acryloyl chloride in methylene chloride solution at 0 °C, in the presence of equimolecular amount of triethylamine. The reaction temperature was maintained during 3 h, afterwards allowing the reaction to reach ambient temperature. After conventional workup (neutralization with a 5% (w/w) sodium hydroxide solution, evaporation of the solvent at reduced pressure and recrystallization in *n*-hexane/ethanol 3:1), S3F was obtained as a blue solid in a 59% yield.

Analytical data:

¹H NMR (δ_{ppm} , CDCl₃): 8.08 (d, 2H, H_{meta}); 6.75 (d, 2H, H_{ortho}); 3.21 (s, 6H, N(CH₃)₂).

¹³C NMR (δ_{ppm} , CDCl₃): 155.0; 137.4; 132.9; 117.4; 114.4; 113.7; 112.2; 40.3.

IR (KBr): 2220 (CN st); 1605 (C_{Ar}–C st); 1390 (–N(CH₃)₂ δ si); 820 (C=C δ oop).

Photoinitiators 2,2-dimethoxy-2-phenylacetophenone (Irg 651) and bis-(2,4,6-trimethylbenzoyl)-phenylphosphine (Irg 819) were generously given by Ciba SC and used as received. Adhesive formulation Loctite 312 (L312) was a kind gift from Henkel Loctite and used without further purification.

2.2. Sample preparation

Samples containing probe (approximately 0.03% (w/w)), photoinitiator (1% (w/w)) and the adhesive formulation were prepared by stirring in the dark all components until homogeneous solutions were obtained (not less than 8 h). The photocurable formulations were applied as a uniform layer coating between two LDPE films for the laser experiments. Previously, it has been made sure that the LDPE film does not absorb at the UV-irradiation and emission wavelengths. Photosensitive coatings of 10 μm thickness were obtained by controlled pressing during 1 min with $2 \times 10^3 \text{ kg cm}^{-2}$ pressure.

2.3. Laser curing and analysis

Samples have been photopolymerized at room temperature under air atmosphere. 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° of the sample, simultaneously producing the cure of the adhesive and the excitation of the probe inserted. The laser beam was expanded by using a PCV fused silica lens to overfill the area of the sample (about 5 cm²). An attenuator was used to modify the energy reaching the sample. Laser output was measured by a photocalorimeter Scientech model H310D and the laser power reaching the sample was varied between 0.5 and 5.2 mW/cm². Fluorescence emission was collected to a monochromator (Oriel MS257) by an optical fiber placed at –45° respect to the sample. A 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 (chip of 1024 pixels \times 256 pixels) during 1 μs every 0.3–6.8 s, depending on the duration of the experiment.

Frequency of laser pulses was varied between 0.2 and 3.33 Hz. The trigger of the different devices was controlled by a pulse delay generator, Stanford model DG 535. Manipulation of data was carried out by means of the Oriel software “IntraSpec V”.

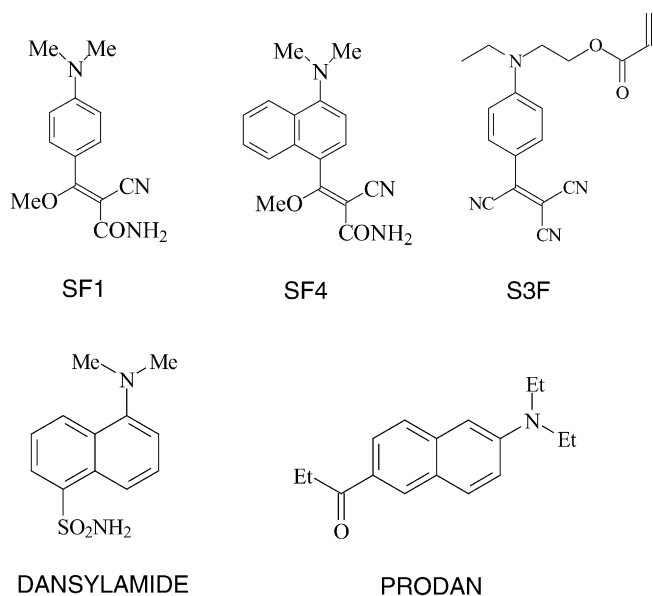
2.4. Conventional curing and analysis

Samples were prepared and irradiated with a conventional Hg lamp, and analyzed by means of RT-IR as described before [12,13].

3. Results and discussion

The structures of the probes studied in this work are shown in Scheme 1.

The spectroscopic properties of SF1 and SF4 have been described before, and Prodan and Dansylamide are well



known in the literature. Spectroscopic properties of S3F have not been described before and are summarized in Table 1.

All the probes correspond to a D- π -A structure and they have been proven to follow accurately photopolymerization reactions of relatively simple systems, as mono- and difunctional (meth)acrylic monomers, and steady-state photopolymerization of acrylic adhesives, until limiting double bond conversion. The fluorescence band of Dansylamide, Prodan, SF1 and SF4 was sensitive both to changes in micropolarity and microviscosity of the medium showing emission band shifts up to 79 nm and an intense increase in emission intensity as polymerization reaction proceeds.

The probe S3F does not show a band shift during polymerization, and only an increase in the intensity of the band occurs throughout the reaction.

The commercial adhesive selected, L312, is a very polar formulation composed by an end-capped acrylic-aliphatic polyurethane binder and hydroxypropyl methacrylate and acrylic acid as monomers which, upon polymerization, leads to a crosslinked network.

Table 1
Maximum wavelengths of absorption and emission, and fluorescence quantum yield of S3F in solvents

Solvent	λ_{abs}	λ_{em}	ϕ_f
Cyclohexane	483	520	$<10^{-3}$
Diethyl eter	498	564	
Chloroform	510	561	
THF	507	565	
Ethyl acetate	505	560	
Acetone	513	568	
Methanol	510	574	

Table 2
Wavelengths used for monitoring fluorescence variations for probes

Probe	Wavelengths (nm)
SF1	371/414
SF4	394/440
Dansilamide	411/470
Prodan	383/427
S3F	597

3.1. Photopolymerization profile, variation of the pulse frequency

For following the polymerization reaction two different fluorescence parameters have been chosen as discussed in previous papers [13]: the relationship between the intensity at two different wavelengths, for those probes which are blue shifted during polymerization, and the intensity at λ_{max} for S3F, whose fluorescence spectrum does not change its maximum wavelength during pulsed laser polymerization. The wavelengths used in the study are shown in Table 2.

Fig. 1 shows, as example, typical polymerization profiles recorded by fluorescence spectroscopy of the solvatochromic probes at frequencies of 3.33 Hz, using Irg819 as photoinitiator, and 0.2 Hz, using Irg 651, respectively. In Fig. 2 the variation in emission intensity of the fluorescence maximum of S3F as a function of the total irradiation time (laser pulses and dark period) during polymerization is also shown. The obtained curves are similar to those described by us for conventional irradiation. During the irradiation time, it is observed good photostability for all the probes except for Prodan. Prodan suffers significant photobleaching at relatively short stages of the reaction, even at low pulse frequency, so it is not adequate to be used for following this process, at least at these irradiation doses.

In Table 3 the fluorescent rates of polymerization (ρ_{fluor}) are shown, obtained from the slope of the normalized plots. As can be seen, within experimental error, calculated value of R_p is independent of the probe employed, as it is the beginning of the plateau. The only parameter which changes from probe to probe is the total increase of fluorescence during reaction, parameter which is taken as the sensitivity of the probe towards the increase in rigidity of the medium (S^*). The sensitivity of SF1 is higher than that of SF4 as it corresponds to the lower molecular volume of SF1. The same behaviour was found for continuous irradiation, this is, sensitivity is higher for the probe with lower molecular volume [13].

Probe S3F showed less sensitivity than the solvatochromic probes for low conversions, but the value obtained for the maximum rate of polymerization is similar to that calculated from the data of the other probes. Data for S3F have been not included since they are calculated from different fluorescent parameter (fluorescence intensity instead fluorescence intensity ratio), and they could not be normalized in the same way.

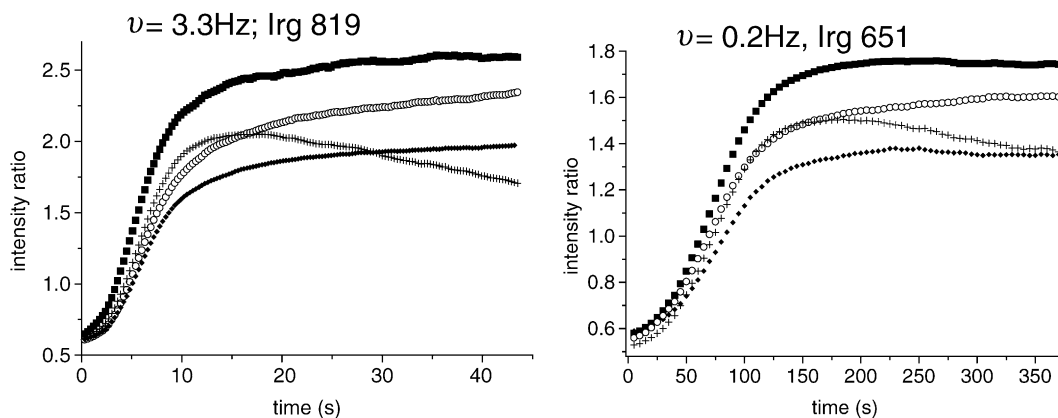


Fig. 1. Polymerization profiles of L312 recorded by fluorescence spectroscopy of the solvatochromic probes at different frequencies and photoinitiator. (■) SF1, (◆) SF4, (○) dansylamide, (+) prodan.

Moreover a remarkable feature of pulsed laser polymerization has to be noted. The total incident energy decreases as the frequency of the pulses does, although the energy per pulse is maintained. Therefore, polymerization rates slow down and induction period become longer.

Similar polymerization runs were performed using Irgacure 819 as photoinitiator, and no substantial differences in the shape of the polymerization profiles were found (Fig. 1). The scattering of polymerization rates obtained with this photoinitiator has been attributed to the reaction between the primary radicals and some fluorescent probes. As mentioned before, this feature is more markedly observed when the time between pulses increases (pulse frequency = 0.2 Hz).

Nevertheless, some differences could be marked analyzing the data of Table 2. Comparing the results for both frequencies, the increase in the fluorescence parameter studied in each case (intensity or intensity ratio) when the reaction has reached the limiting conversion, is always higher in the

experiments carried out at a frequency of 3.3 s^{-1} . This seems to indicate that the rigidity reached by the system is higher as higher is the frequency of the laser pulse.

Given the experimental set-up, it has not been possible to measure in situ the double bond conversion in these polymerizations. Nevertheless, we stated previously [13] that the fluorescent response of these probes was, for a given monomer/probe/photoinitiator system, only dependent on the rigidity reached in each moment by the system. For the estimation of the double bond conversion reached in each case for this adhesive system we have irradiated the samples with continuous UV light and measured double bond conversion by RT-IR and the fluorescence changes during the process, as described previously [13]. As an example, the results for L312/Irg 651 are shown in Fig. 3. Similar plot is obtained for L312/Irg 819.

We have used these fluorescence/conversion data to obtain an estimation of the conversion reached when pulsed laser initiation is used, and the results are shown in Fig. 4.

It is necessary to mention here that this approach is only valid if the reactions taking place in the system are the same

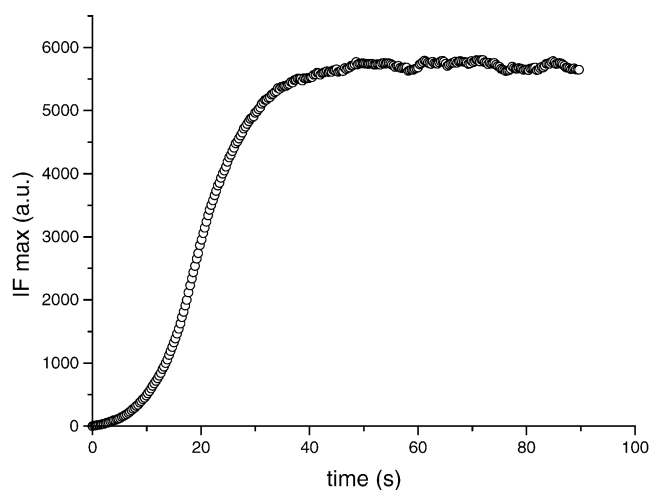


Fig. 2. Polymerization profile for the photopolymerization of L312 recorded by fluorescence spectroscopy of S3F probe. Photoinitiator: Irg651.

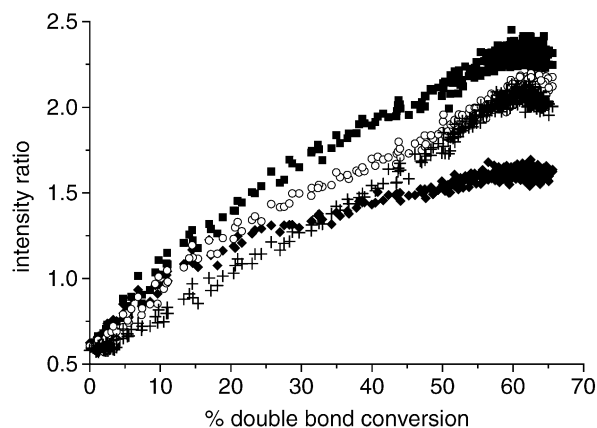


Fig. 3. Variation of fluorescence emission vs. degree of conversion for the photopolymerization of L312 under continuous irradiation. (■) SF1, (◆) SF4, (○) dansylamide, (+) prodan. Photoinitiator: Irg651.

Table 3

Rates of polymerization, emission wavelength shift and probes sensitivity factor for the photopolymerization of L312 at different pulse laser frequencies

Probe	PI	$\rho_{\text{fluor}} (\text{s}^{-1})$				S^*
		$\nu = 3.3 \text{ Hz}$	$\nu = 0.2 \text{ Hz}$	$\Delta\lambda_{3.3 \text{ Hz}}$	$\Delta\lambda_{0.2 \text{ Hz}}$	
SF1	Irg651	0.107	0.010	23	19	1.8
SF4		0.109	0.008	25	18	1.4
Dansilamide		0.110	0.009	34	28	1.8
Prodan		0.110	0.008	23	19	1.9
SF1	Irg819	0.151	0.017	25	22	
SF4		0.117	0.011	24	15	
Dansilamide		0.124	0.014	35	27	
Prodan		0.105	0.016	23	19	

with both types of irradiation, this is, if there are not differences in the rigidity reached by the system occasioned by reactions of the binder other than polymerization of double bonds (secondary reactions). Given the complexity of this system and the mechanism of the polymerization in the conditions employed here, it is not possible to assess the truth of this, and the degree of conversion shown in Fig. 4 has been given only as estimative.

However, some features of the polymerization could be induced from the plot. It is observed higher degree of conversion at higher frequency of the pulses, as expected, and for the same frequency employed, higher degree of conversion for the more efficient photoinitiator (Irg 819). In addition, the limiting conversion increases as the rate of polymerization increases, and reaches the limiting conversion described for polyfunctional monomers in bulk [17]. Longer inhibition period is found for the less efficient photoinitiator at the lower frequency.

3.2. Repetition rate effect

For a deeper analysis of the reaction it is necessary to compare the behaviour of the system at equal irradiation doses. We have previously observed the influence of the repetition rate on the mechanism of pulsed laser polymerization [11c].

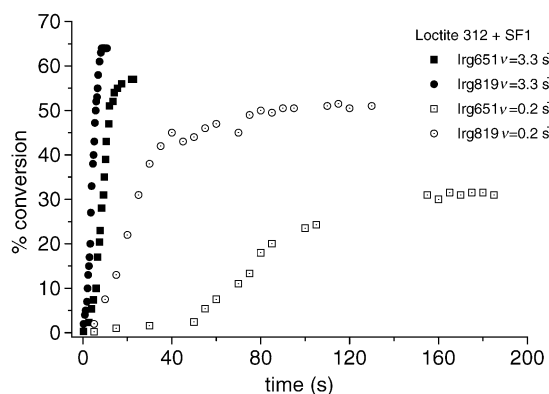


Fig. 4. Estimation of double bond conversion vs. irradiation time for the photopolymerization of L312 under pulsed laser irradiation.

By decreasing the frequency from 3.3 to 0.2 Hz the time between pulses increases from 0.3 to 5 s. Given the laser pulse lasts only 6 ns, the polymerization reactions take place almost exclusively during the dark period between pulses, so secondary reactions (such as recombination and/or reaction with oxygen) should be considered. In this sense, the longer induction period observed when Irg651 is used as photoinitiator may indicate a lower production of efficient radicals than that when Irg819 is used. In addition, this behaviour is in accordance with the higher reactivity expected for phosphinoyl radicals (Irg819).

In Figs. 5 and 6 the variation of fluorescence of the different probes versus the number of pulses received by the sample are shown. Prodan shows again photodegradation for a relatively low number of pulses.

The behaviour observed is unequivocal: at the same number of pulses received the degree of conversion reached by L312 is higher when the system is irradiated at lower repetition frequency, and the limiting conversion obtained is lower.

This effect is known as repetition rate effect and is due to the high lifetime of the macroradicals in viscous media compared to the delay time between pulses [18]. Working at relatively high frequencies, each new laser pulse injects in the system a high concentration of newly generated photoinitiator primary radicals which react with the growing macroradicals generated by the former pulse and prematurely terminate the growth of the chain. Then, the efficiency of polymerization (conversion) decreases. This effect is found for both photoinitiators but it is more evident as the reactivity of the primary radicals coming from the initiator is higher. Then, as expected, the higher difference in conversion per pulse is found for the system with the more efficient photoinitiator (Irg 819, Fig. 6).

The higher limiting conversion found for the higher repetition rate is usually attributed to the higher polymerization rate obtained at his frequency, which allows polymerization to actually precede the contraction process which accompanies crosslinking [19]. This fact has been also described by Kloosterboer and Bowman for continuous irradiation [20] and attributed to creation of a temporary excess free volume

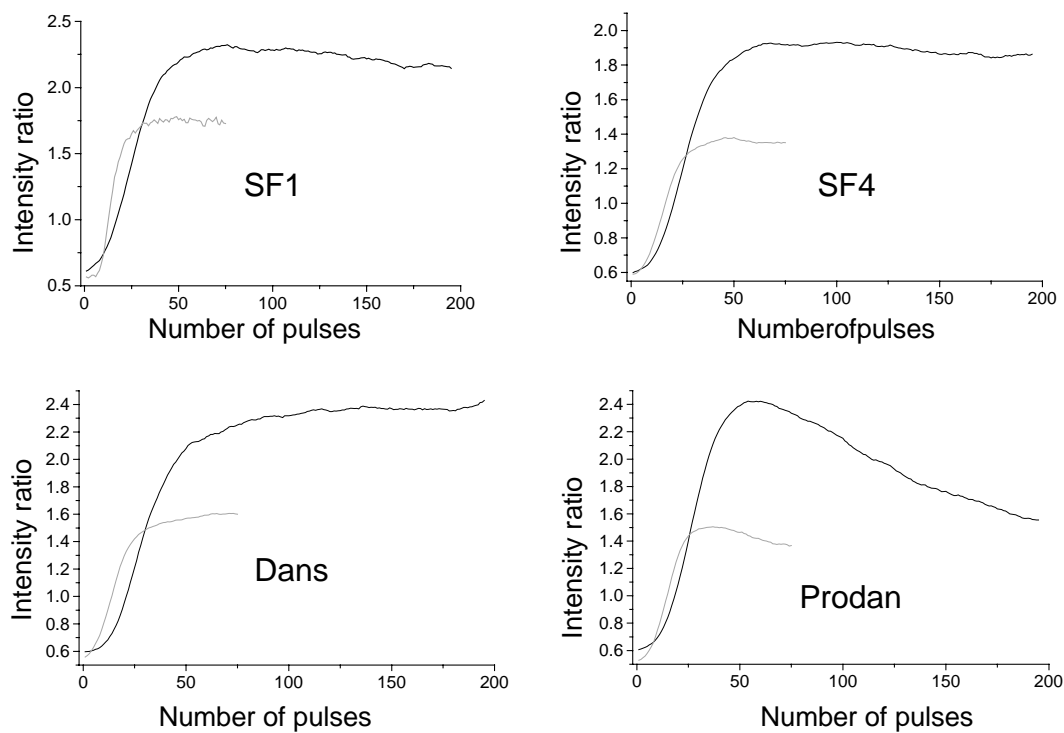


Fig. 5. Variation of fluorescence of the different probes during photopolymerization of L312 vs. the number of pulses received by the sample. Frequencies: (—) 3.3 Hz; (---) 0.2 Hz. Photoinitiator: Irg651.

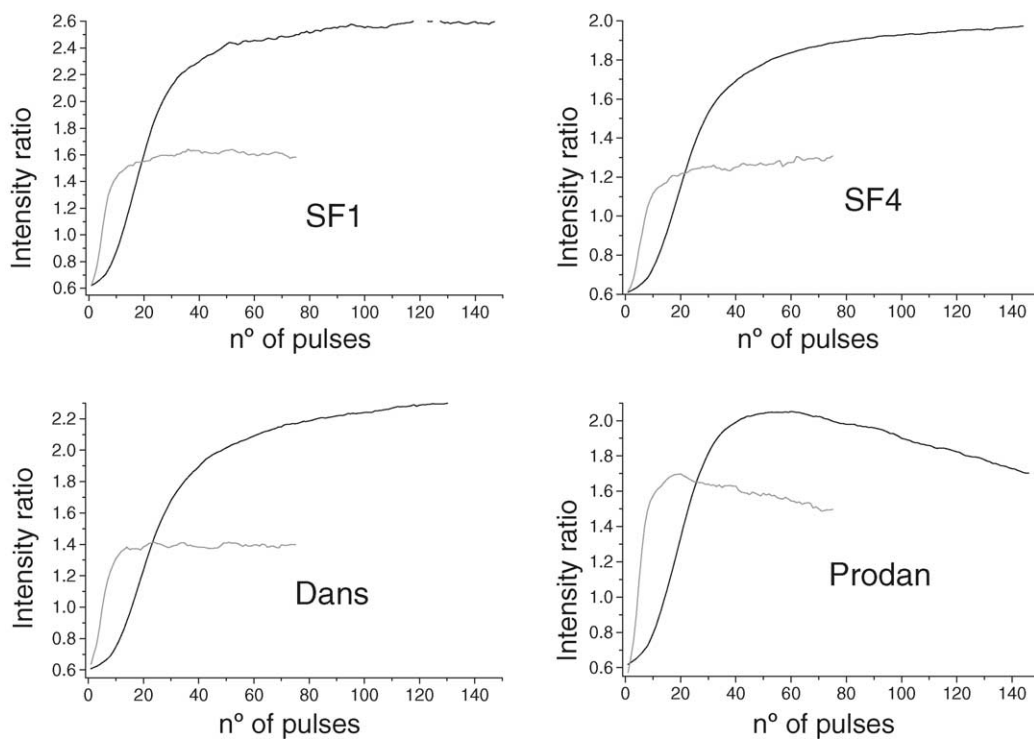


Fig. 6. Variation of fluorescence of the different probes during photopolymerization of L312 versus the number of pulses received by the sample. Frequencies: (—) 3.3 Hz; (---) 0.2 Hz. Photoinitiator: Irg819.

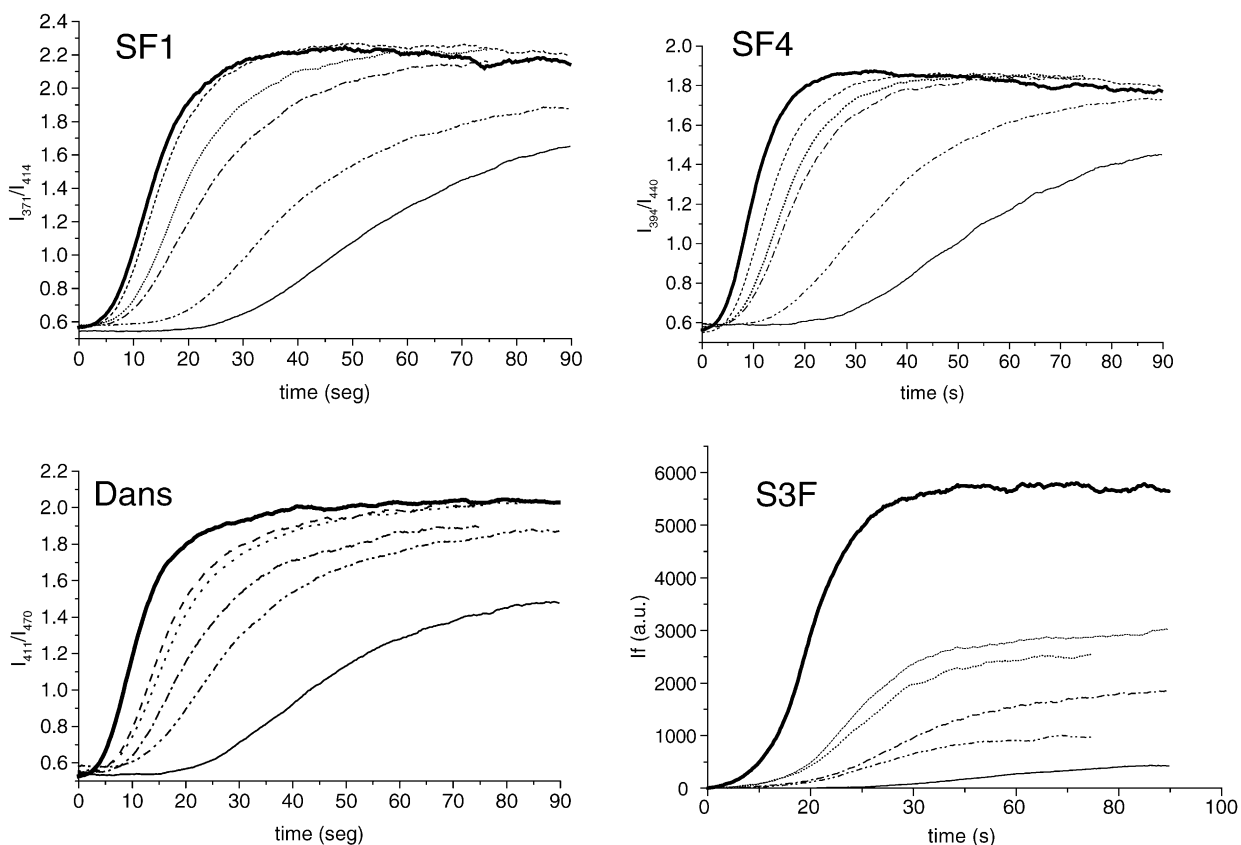


Fig. 7. Fluorescence photopolymerization profiles of L312 obtained with the probes under different intensities of the laser pulse. ((—) 5.2 mW/cm²; (---) 4.6 mW/cm²; (···) 3.7 mW/cm²; (-·-·-) 2.9 mW/cm²; (-·-·-·) 1.8 mW/cm²; (—) 0.5 mW/cm²). Photoinitiator: Irg651.

resulting in increased diffusion rates of reacting acrylate groups.

Finally, it has to be mentioned that the degradation observed for Prodan probe occurs at different number of pulses depending on the photoinitiator used. It always takes place much faster when Irg 819 is used, what means that degradation takes place through reaction of Prodan with the primary photoinitiating radicals simultaneously to direct photochemical bleaching.

3.3. Variation of the laser pulse intensity

The incident light intensity per pulse has been varied from 0.5 to 5.2 mW/cm², keeping constant the frequency at 3.3 Hz, using a beamsplitter for attenuate the energy den-

sity per pulse. The fluorescence kinetic profiles are shown in Fig. 7. All profiles, except for Prodan, showed not significant photodegradation of the probes for pulse doses up to 5.2 mW/cm². Prodan suffer important photobleaching of the fluorescence emission at relatively short stages of polymerization for pulse intensities higher than 1.8 mW/cm².

From the data of Fig. 3, the fluorescence rate of polymerization for the system could be calculated at the different light intensities, and values obtained for the different probes are shown in Table 4.

Polymerization rates increase with incident pulse energy. No saturation rate effect was observed in the range of incident energies employed, as expected for Irg651 [19].

In addition, the variation of the rate of the polymerization of the system could be plotted versus the square root of the

Table 4
Fluorescent rates of polymerization of L312 at different pulse laser intensities

Probe	ρ (s ⁻¹)					
	5.2 mW/cm ²	4.6 mW/cm ²	3.7 mW/cm ²	2.9 mW/cm ²	1.8 mW/cm ²	0.5 mW/cm ²
SF1	0.107	0.096	0.074	0.054	0.034	0.022
SF4	0.109	0.084	0.067	0.058	0.028	0.016
Dans	0.110	0.082	0.066	0.051	0.037	0.021
Prodan	0.110	0.081	0.072	0.060	0.038	0.016

Photoinitiator: Irg 651.

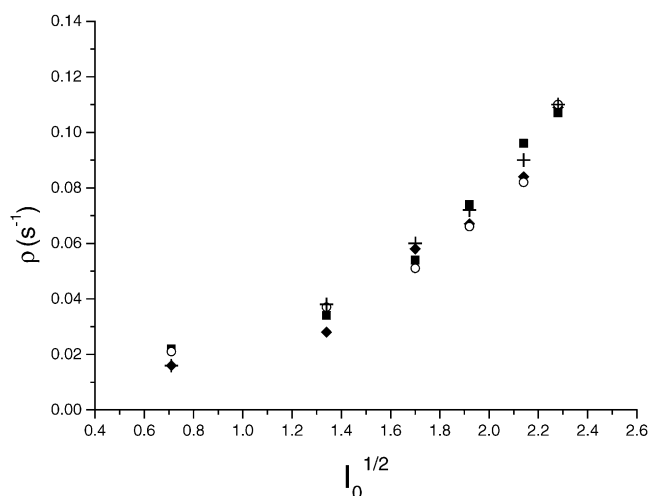


Fig. 8. Fluorescence rates of polymerization of L312 as a function of the laser pulse intensity. (■) SF1, (◆) SF4, (○) Dansylamide, (+) Prodan. Photoinitiator: Irg651.

incident light intensity, showing a non-linear fit, as expected for a system polymerizing in conditions far from the stationary state (Fig. 8). Nevertheless, data for all probes show that the obtained R_p is independent of the probe used for its determination, in the interval of dose pulses investigated.

4. Conclusions

Fluorescence measuring of pulsed-laser initiated polymerization of acrylic adhesives has been described, following the emission of D- π -A probes synthesized by us. The results have shown that fluorescence is a valuable tool for following the kinetics and mechanism of the reaction taking place, and the new probes are sensitive and photostable enough to be employed in the characterization of this type of reaction even at the high intensity doses and frequencies as those used here.

Rates of polymerization calculated by fluorescence are independent of the probe employed in the measurements, then indicating that the method provides adequate kinetic measurements of the events taking place in polymerization reaction.

Estimation of the double bond conversion reached by the system shows, as expected, higher degree of reaction when the more efficient photoinitiator is used.

The laser pulse frequency has been varied, and the kinetics of the polymerization at equal irradiation doses were followed by probes fluorescence. The results reflect that both degree of conversion and limiting conversion reached by the system depends on it (repetition rate effect).

When the intensity per pulse is varied, a non linear dependence of the polymerization rate measured by fluorescence

with the square root of light intensity is found, as expected for a system in conditions far from the stationary state. The results of ρ_{fluor} obtained are again independent of the probe used, for the range of intensities checked.

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