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Polymerisation kinetics photoinduced by derivatives of 4-nitroaniline in the presence of *N*,*N*-dimethylaniline studied by Real-Time IR spectroscopy

M. Rodríguez[a], I. García-Moreno[a], O. García[b,*], R. Sastre[b]

[a]*Instituto de Química-Física "Rocasolano", C.S.I.C., Serrano 119, 28006 Madrid, Spain*
[b]*Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain*

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Abstract

The behaviour of nitro-aromatic amines 4-nitro-1-naphthylamine (NNA), *N*-acethyl-4-nitro-1-naphthylamine and *N*,*N*-dimethyl-4-nitroaniline, in the presence of a tertiary amine such as *N*,*N*-dimethylaniline as photoinitiators of the dodecyl acrylate polymerisation has been studied by Real-Time IR spectroscopy upon UV exposure and the results compared with those obtained with 4-nitroaniline (*p*NA). The rate and quantum yield of polymerisation as well as the residual unsaturation in the cured polymer result are strongly dependent on the photoinitiator nature. The formulation based on the NNA compound improves the polymerisation activity of *p*NA exhibiting a reaction rate up to 2.1 M s^{-1} and reaching a conversion of nearly 85%. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photopolymerisation; 4-Nitroaniline derivatives as initiators

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1. Introduction

Increased requests for the improved effectiveness of the photoinitiators of polymerisation and at the same time the reduction in the consumption of the reactives [1,2] motivated our recent investigations on the photochemistry and photopolymerisation activity of a new bimolecular initiator system, based on 4-nitroaniline (*p*NA) in the presence of *N*,*N*-dimethylaniline (DMA) as a reducting agent [3,4].

Although DMA induces the photoreduction of *p*NA with a very low quantum yield, this initiator system exhibits an unexpected high polymerisation efficiency, much higher than well-known bimolecular initiators of industrial importance (i.e. aromatic ketones) [4]. Evidence was found suggesting the existence in this case of a new, more efficient mechanism of bimolecular photoinitiation: the photosensitisation of the first excited triplet state T_1 of DMA through an efficient excitation energy transfer from the first excited singlet state S_1 of *p*NA [5,6]. This mechanism, working concurrently with the photoreduction reaction, generates a cascade of free radicals derived from the coinitiator without the consumption of the initiator in a catalyser-like way. The actual possibilities of this new and promising mechanism encouraged us to extend the investigation to different *p*NA derivatives in order to establish the influence that the energetic, photophysical and structural properties of the initiator have on its polymerisation activity.

To this end, the present paper is devoted to analyse the polymerisation kinetics of dodecyl acrylate monomer, commonly known as lauryl acrylate (LA) monomer photoinitiated by different *p*NA derivatives: 4-nitro-1-naphthylamine (NNA), *N*-acethyl-4-nitro-1-naphthylamine (ANNA) and *N*,*N*-dimethyl-4-nitroaniline (DMNA). The chemical formulae of these initiators are given in Scheme 1.

The polymerisation profiles photoinduced by these initiators in the presence of DMA as the coinitiator were recorded by Real-Time Infrared (RTIR) spectroscopy. This technique has proved to be a method well suited to study the disappearance of a given monomer undergoing ultrafast polymerisation upon UV exposure [7]. The RTIR spectroscopy permits, from the recorded conversion versus time curves, the determination in a single run of the induction period, t_i, the rate of polymerisation, R_p, and the amount of residual unsaturation in the cured polymer, R_u; all these data are of practical and theoretical significance [8].

In a previous paper, by applying this powerful technique, we have analysed in detail the polymerisation kinetics of LA photoinduced by the *p*NA/DMA system and established the

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* Corresponding author. Fax: + 91-5644853.
E-mail address: ictse65@fresno.csic.es (O. García).

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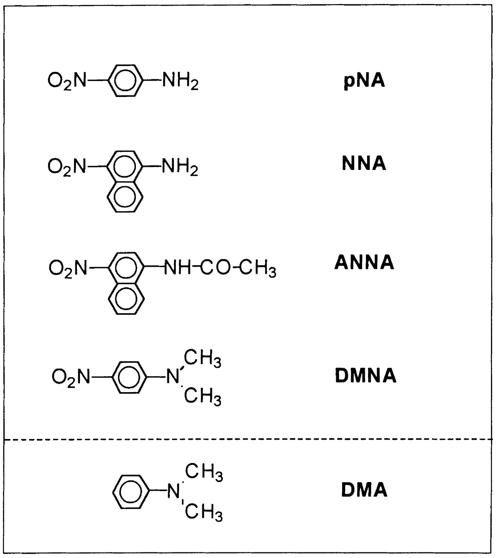

Scheme 1.

Table 1
Influence (experimental conditions: $I_0 = 9.5 \times 10^{-5}$ W/cm^2, $I_a = 6.5 \times 10^{-5}$ W/cm^2, $\lambda_{irr} = 365$ nm, film thickness = 100 μm) of the initiator nature on the polymerisation kinetics of LA photoinduced by *p*NA and its derivatives NNA, ANNA and DMNA, in the presence of a 1/10 molar ratio of DMA

Initiator	[Concentration] (mM)	R_p (M s^{-1})	$\phi_p \times 10^{-3}$
*p*NA	3.2	1.48 ± .05	22 ± 1
NNA	7.9	2.1 ± 0.2	32 ± 2
ANNA	6.1	0.83 ± 0.02	12.8 ± 0.6
DMNA	3.0	2.0 ± 0.1	30 ± 1

influence that both the *p*NA and DMA concentrations and the incident light intensity (I_0) have on the kinetic parameters [5]. The present work is directed to analyse the influence of the photoinitiators' nature on the polymerisation efficiency of these bimolecular systems exposed to UV radiation in the presence of increasing molar proportions of DMA. Besides, although broad photopolymerisation studies are carried out under moderate light intensities and low initiator concentrations, in most industrial photopolymerisation processes both high concentrations and light intensities are commonly used in order to achieve fully cured materials in short exposure times. Therefore, we consider exploring the behaviour of these new nitroaromatic derivatives under the extreme conditions selected in most industrial photopolymerisation processing to be of interest.

2. Experimental part

The photoinitiators *p*NA, NNA and DMNA, all from Aldrich, were recrystallised several times from water (*p*NA) and from ethanol (NNA, DMNA) until impurities were no more detected by conventional analytical methods. ANNA was obtained by the direct reaction of 4-nitronaphthylamine (4 g) with acetic anhydride (150 ml). The mixture was heated at about 100°C for 2 h and on cooling yellow crystals were formed, which were purified by subsequent recrystallisations from chloroform–ethanol mixtures. Its purity was checked by MS, NMR and UV. DMA (Carlo Erba) was dried over potassium hydroxide, distilled under reduced pressure and stored under nitrogen atmosphere in the dark at low temperature. LA monomer (Fluka Chemie, Techn.) was washed three times with portions of 10 vol% aqueous sodium hydroxide to remove the inhibitor, and then twice with distilled water. The monomer, dried over anhydrous $MgSO_4$, was then distilled under reduced pressure prior to use.

The polymerisation reaction was followed in situ by RTIR by using a compact, inexpensive and automatised system developed in our laboratory [5]. A detailed description of the experimental set-up and the methods employed can be found elsewhere [5]. The photopolymerisable formulation was coated onto two polyethylene films, with a typical thickness of 100 μm, which prevents the free diffusion of atmospheric oxygen into the sample. The sample, sandwiched between two NaCl crystals, was placed in the compartment of an infrared spectrophotometer where it was exposed to the UV radiation of a Hanovia medium pressure mercury lamp filtered at 365 nm. The incident light intensity at the sample position was kept constant at 9.5×10^{-5} W/cm^2 as measured by a precalibrated radiometer (International Light Model IL.1700). The disappearance of the monomer was monitored continuously by setting the wavelength of the IR detection at the value where the related double bond exhibits a characteristic peak, such as 812 cm^{-1} for the acrylate ones. By setting the spectrophotometer in the absorbance mode, conversion versus time curves were directly recorded. From the slope of these curves, the actual rate of polymerisation (R_p) can be evaluated at any stage of the process whereas the polymerisation quantum yield, ϕ_p, was evaluated from the ratio R_p/I_a, I_a being the absorbed light intensity.

3. Results and discussion

First, a set of polymerisation experiments in the presence of different *p*NA derivatives were performed, keeping the initiator/DMA ratio at a 1/10 molar proportion constant. In order to record the polymerisation profiles under the same experimental conditions, the concentrations of the initiators were adjusted to ensure the same absorbed light intensity, $I_a = 0.6\, I_0$, at 365 nm. The actual differences between the extinction coefficients at this wavelength constrain the initiator concentrations to range from 3×10^{-3} to 7.9×10^{-3} M (see Table 1). Higher concentrations lead to solubility problems of the initiators in the experimental formulation, being especially serious for the NNA derivative. Fig. 1 shows the polymerisation profiles recorded for LA upon UV-exposure under the aforementioned experimental

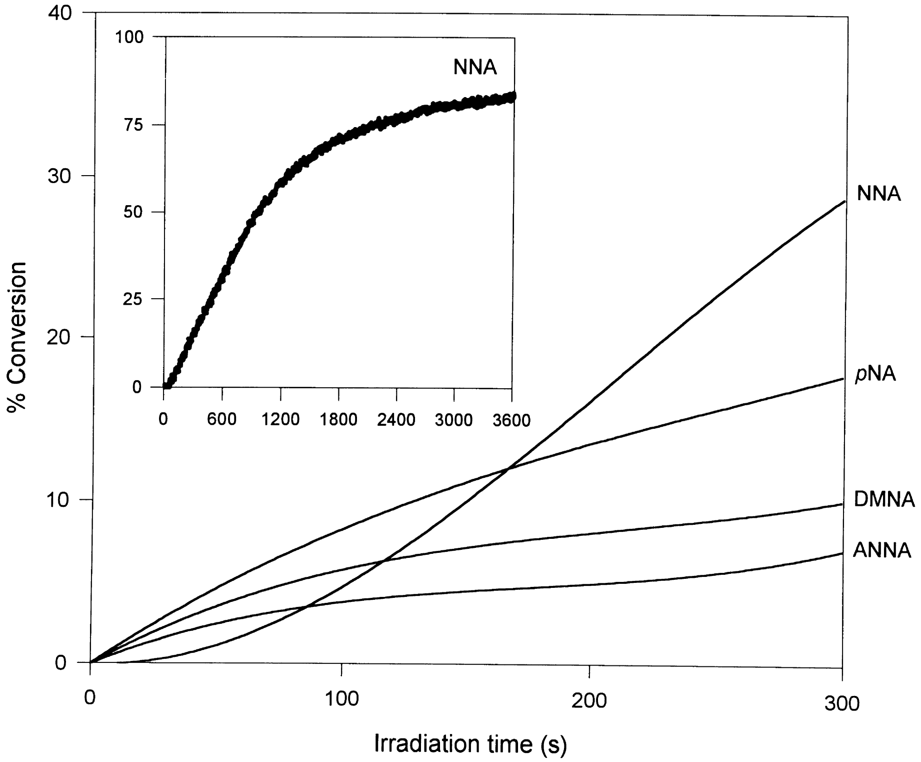

Fig. 1. Polymerisation profiles recorded by RTIR spectroscopy upon UV-exposure of LA monomer photoinduced by *p*NA and its derivatives NNA, ANNA and DMNA in the presence of a 1/10 molar ratio of DMA. The inset shows the RTIR polymerisation profile of LA induced by NNA/DMA system exposed up to 3500 s of UV radiation.

conditions, and the values obtained for R_p and ϕ_p, after 5 min of irradiation, are reported in Table 1.

If all these derivatives induced the free radical generation following the same initiation mechanism, one would expect the LA monomer exhibiting similar polymerisation profiles under UV-exposure. With the exception of the NNA derivative, this prediction is fully confirmed by RTIR experiments although the photopolymerisation activities are dependent upon the structure and the photochemical and photophysical behaviour of each compound. Taking into account that the free radicals derived from DMA are the main and most active species in the initiation mechanism [4], the dependence of the kinetic parameters on the nature of the initiator has to be related to differences in the number of radicals generated by each absorbed photon, which is a direct consequence of both the stoichiometry of the photoreduction reaction and the effectiveness of the photosensisation process of DMA by the corresponding initiator species.

An important fact revealed by the RTIR spectroscopy is the distinct behaviour exhibited by the formulation based on the NNA derivative. In spite of the low initial rate, it has to be pointed out that the polymerisation induced by NNA proceeds at a higher rate reaching a higher conversion degree than those reactions photoinduced by *p*NA, ANNA and DMNA. In addition, the polymerisation process induced by these latter initiators seems time-stable after the initial 100 s of UV-exposure while the polymerisation induced by NNA increases; that is, further doses of UV radiation for up to 2000 s cause the reaction to be autoaccelerated, levelling off at approximately 83% conversion degree because of the severe mobility restrictions existing in the formed polymer. Consequently, these RTIR experiments reveal the significance, from an applied point of view, of this new formulation based on the NNA derivative which improves, under these irradiation conditions, the polymerisation activity exhibited by the *p*NA/DMA system, already found to be a very efficient bimolecular photoinitiator. This enhanced polymerisation efficiency obtained with the NNA/DMA system evidences that new concepts as well as further photophysical and photochemical studies would be required in order to explain the initiation mechanism and its dependence on the nature and position of the substituent in the nitroaromatic molecule since the present results cannot be directly related to the effectiveness of the excitation energy transfer from the S_1 states of these initiators to the T_1 state of DMA. In this way, the ANNA derivative exhibits, under these experimental conditions, the lowest initial polymerisation activity although its S_1 state is the closest one to the T_1 state of DMA [6]. This behaviour could also be related to the kinetics of the α-alkylamino radicals since the generation in a very short irradiation time of a high concentration of primary free radicals, generated directly from the DMA coinitiator, could improve both primary radical recombination reactions and primary radical termination, in which

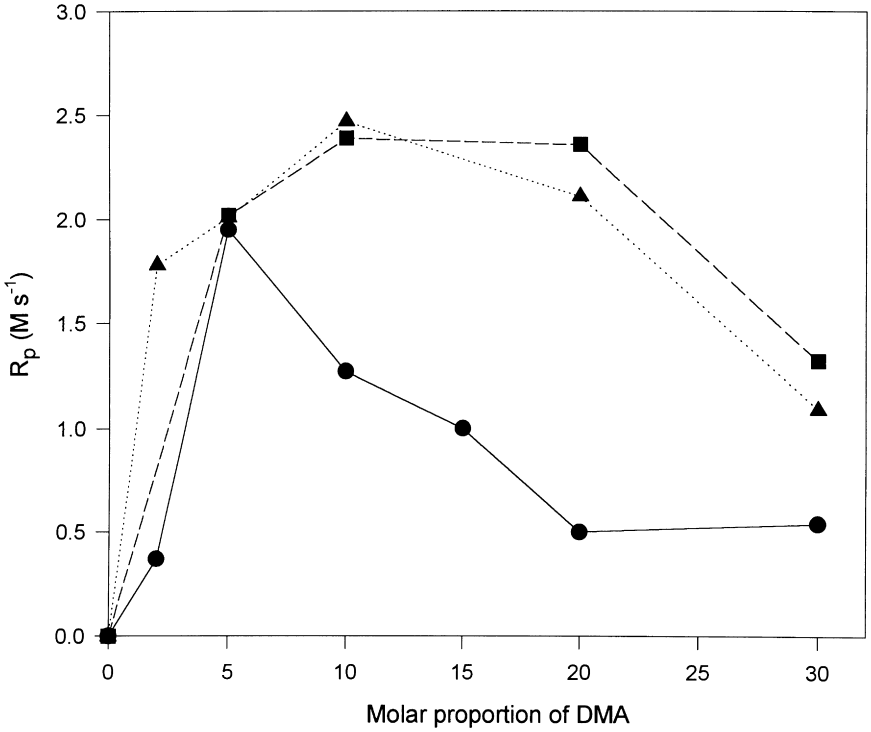

Fig. 2. Dependence of the polymerisation rate R_p on the coinitiator DMA molar proportion added to a constant concentration of the selected initiator: ANNA (● and solid line); DMNA (▲ and dotted line) and NNA (○ and dashed line). The lines represent eyeball fits to the data points.

growing macroradicals are terminated by primary radicals instead of other macroradicals. These primary radical recombination and termination reactions lead to a decrease in the initial polymerisation rate [9] until, as a direct consequence of DMA consumption, the free radical concentration drops to reach a level at which these secondary reactions diminish and the polymerisation rate can progressively increase.

3.1. Effect of the coinitiator concentration

In order to determine the critical concentration of DMA required to optimise the polymerisation rate, a set of experiments were carried out under constant initiator concentration and irradiation intensity, $I_0 = 10.5 \times 10^{-5}$ W/cm^2. For each derivative, we selected the highest concentration which could be totally dissolved in the monomer solution assuring the sample homogeneity. These concentrations were 7.9×10^{-3}, 9.7×10^{-3} and 11.8×10^{-3} M, for NNA, ANNA and DMNA derivatives, respectively, corresponding to absorbances of 0.5, 0.8 and 2.0 at 365 nm. In this way, for each initiator, we analysed the dependence of the polymerisation activity on the DMA concentration although the aforementioned differences make it difficult to establish a proper comparison between the polymerisation kinetics induced by these derivatives.

Under the above experimental conditions, the rate of polymerisation R_p induced by each initiator follows a complex behaviour with the increase in amine concentration (see Fig. 2): first, R_p increases rapidly with the presence of DMA, reaching a maximum value at 1/10 initiator/DMA molar ratio for NNA and DMNA derivatives, and at 1/5 for the ANNA compound. Further increases in the coinitiator concentration result in a drastic decrease of R_p with the exception of the NNA derivative whose polymerisation rate reaches a plateau at 1/20 molar ratio followed by a rapid decrease. In addition, as can be seen in Table 2, the kinetic parameter ϕ_p follows the same dependence on DMA concentration as that exhibited by R_p.

The observed behaviour can be explained by taking into account that the probability of generating initiator radicals increases with the amine concentration up to a point where the deactivation and termination reactions become dominant, leading to a decrease in the polymerisation rate. This

Table 2
Influence (experimental conditions: [NNA] = 7.9×10^{-3} M, [ANNA] = 9.7×10^{-3} M, [DMNA] = 11.8×10^{-3} M, $I_0 = 10.5 \times 10^{-5}$ W/cm^2; $\lambda_{irr} = 365$ nm and film thickness = 100 μm) on the quantum yield (ϕ_p) of the LA polymerisation of the DMA molar ratio added to a constant concentration of the selected initiator

Initiator/DMA Molar ratio	NNA $\phi_p \times 10^{-3}$	ANNA $\phi_p \times 10^{-3}$	DMNA $\phi_p \times 10^{-3}$
1/2	–	4.2 ± 0.2	17 ± 1
1/5	28 ± 1	22 ± 1	19.3 ± 0.9
1/10	33 ± 2	14.4 ± 0.8	23 ± 1
1/15	–	11.3 ± 0.4	–
1/20	32 ± 2	5.7 ± 0.4	20.3 ± 0.9
1/30	18.4 ± 0.9	6.1 ± 0.5	10.5 ± 0.6

behaviour reveals that the known efficiency of amines in retarding the polymerisation process, if their concentrations are large enough, results from a transfer mechanism of the polymer radical to the amine following a standard hydrogen abstraction mechanism [10].

All these *p*NA derivatives follow a different dependence on DMA concentration than that exhibited by *p*NA, which increased continuously with the presence of DMA although it did not follow a linear relationship since up to a molar ratio 1/10 the kinetic parameters became less dependent on the coinitiator concentration [5]. Therefore, it seems that it is the nature of the initiator that determines both the optimum concentration of DMA in the polymerisable formulation and the dependence of its polymerisation activity on the DMA molar ratio. These differences could be ascribed to differences in the effectiveness of the photosensitisation process from the S_1 states of the initiator to T_1 of DMA. In fact, the ANNA derivative whose S_1 state is the closest excited state with respect to T_1 of DMA reaches the maximum efficiency with an ANNA/DMA molar ratio as low as 1/5. Further increase of DMA concentration drastically decreases the polymerisation efficiency of this system since, as was aforementioned, the high concentration of free radicals generated rapidly into the sample would increase the extension of secondary reactions. Consequently, in order to gain more insight on the behaviour observed by RTIR spectroscopy it will be required to analyse in detail the dependence under the present experimental conditions on the initiator nature of both the efficiency and the stoichiometry of the photosensitisation process working concurrently to the photoreduction reaction. Work along these lines is in progress.

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