The mechanism of the photoinitiation of methyl methacrylate polymerization by the neutral red/triethylamine system

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Abstract

The photoinitiation of the polymerization of methyl methacrylate by the dye neutral red in the presence of triethylamine was studied in order to determine the mechanism that leads to the formation of the initiating radicals. An expression for the yield of free radicals was deduced from that mechanism, and the experimental values for the equilibrium and reaction constants of the ground, singlet and triplet states of the dye in the presence of the other components of the formulation, were used to calculat the behaviour of the system when varying the concentration of the co-initiator triethylamine. The observed dependence fits closely the global polymerization rates obtained directly from polymerization kinetics studied by dilatometry. On the other hand, inhibition times showed a behaviour which follows inversely the polymerization rates, confirming that most of the inhibition is originated from the consumption of residual oxygen.
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1. Introduction

The interest in the dye-initiated photopolymerization of vinyl monomers arises because of the possibility of using visible light fonts (arc lamps or lasers) in applications such as the manufacture of printed circuits, encapsulation of electronic components, decorative coating, dental filler composites, stereolithography, the manufacture of contact lenses, etc. [1–4].

The use of dyes is especially interesting because of their high molar absorptivities, which allow the use of minimal amounts of the absorbing species, and their relatively low oxidation potential, which increases the initiating radical yields. In many cases, the dye is photoreduced by amines, as originally proposed by Chen in the study of the photopolymerization of acrylamide by methylene blue in the presence of triethanolamine [5]. In recent years, many studies were performed in order to provide a better insight into the photo-

physical and photochemical processes involved in the global photopolymerization process [6–9]. The ultimate aim being the development of better and more efficient photoinitiator systems adapted to different problems and applications with the aim of elucidating the overall mechanisms as a function of the elemental reactions involved.

In the present work, continuing our work on dye-initiated photopolymerizations [7,10–13] we present results for the polymerization of methyl methacrylate (MMA) photoinitiated by neutral red (NR) in the presence of triethylamine (TEA) as co-initiator in MMA and ethyl acetate solutions. The photoinitiation mechanism is described in terms of the elemental reactions involved in the processes that lead to polymerization initiating radicals.

2. Experimental part

2.1. Chemicals

The monomer, methyl methacrylate (Merck), was distilled from an ice bath at reduced pressure in the presence of hy-

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droquinone, washed with 5% NaOH in water and dried over CaCl$_2$. Triethylamine (Fluka, 99.5%) was vacuum-distilled before use. The dye neutral red (Sigma, 92%) was used as received.

2.2. Photopolymerization procedure

The light induced polymerization of MMA (pure monomer, ∼9 M) in the presence of the photoinitiator system (NR–TEA) was followed in a dilatometer [14,15]. The solution was thoroughly deoxygenated by bubbling oxygen-free nitrogen for 40 min. The dilatometer was constructed by attaching two capillaries (internal diameter 0.18 cm) to a cylindrical reaction vessel (internal diameter 2.2 cm, volume 8.5 ml), which was placed in a constant temperature bath (25 °C) in front of the irradiation source. The reaction cell was placed in front of a 200 W Hg(Xe) lamp in an Oriel Universal Arc Lamp source. In our systems, a 395 nm cut-off filter was placed between the lamp and the reaction cell.

The polymerization rates (R_p) were calculated using Eq. (1)

$$R_p = \frac{\Delta V}{Fft}[\text{MMA}] \, (\text{M/s}) \tag{1}$$

where ΔV is the contraction in volume in the capillary (calculated from the variation in a cathetometer) at time t, f the volume fraction of monomer MMA in the solution, F the volume contraction related to the densities of polymer and monomer in solution, $F = [(d_p - d_m)/d_p]$, and [MMA] corresponds to the monomer molar concentration.

After irradiation, the polymers (poly-MMA) were precipitated, washed with ice-cold methanol, dried in a desiccator and characterized by gel permeation chromatography on a Shimadzu LC-10 AD HPLC chromatograph with a refraction index detector. A combination of two Styragel HR4 and two Styragel HR5 columns were used and the M_n were calculated comparing with a poly-MMA kit of the American Polymer Standards Corp.

Actinometry was performed using ferrioxalate/phenanthroline salt. The quantum efficiency of this actinometer is ∼1.0 at wavelengths below 405 nm [16].

2.3. Photochemical measurements

The fluorescence decays and lifetimes were measured using the single-photon timing technique on a CD-900 Edinburgh spectrometer, operating with a Ti-Sapphire laser, at room temperature (25 ± 1 °C). The excitation wavelength was 400 nm and the emission was monitored at 560 nm.

Static fluorescence quenching experiments were carried out at room temperature using a Hitachi F-4500 spectrofluorimeter. NR was excited at 480 nm and the emission was determined at the maximum of the emission peak. Absorption spectra were measured on a Hitachi U-2000 spectrophotometer.

Transient absorption spectra and triplet quenching were determined with an applied photophysics kinetic laser spectrometer. Excitation at 532 nm was accomplished with Nd-YAG laser (Spectron). Detection was done with a Hamamatsu R928 photomultiplier.

For the fluorescence quenching experiments, the solutions were air-equilibrated. For the triplet studies the solutions were degassed using up to five freeze-thaw vacuum cycles with liquid nitrogen.

3. Results and discussion

In order to establish the mechanism that leads to the photopolymerization of MMA in the presence of neutral red and the co-initiator TEA, it is necessary to evaluate all the possible elemental reactions that may happen in the system. Therefore, interactions between the three components of the systems were studied in the ground and excited states.

3.1. Ground state interactions

The dye neutral red presents two different protonation states when changing the pH. In slightly acid solutions it is protonated and has a maximum absorption around 520 nm. In neutral and higher pH, the solutions become yellow with a maximum at 435 nm [17] (Fig. 1). This means that in the experiments performed in this study, when reasonable amounts of amines (acting as co-initiators) were added to the dye, the prototropic form present in the solution was always the yellow unprotonated dye.
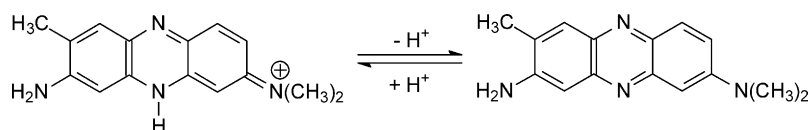
Although it is well known that many cationic dyes, like neutral red itself, aggregate in concentrated solution [18], in the present case there is no aggregation because dimerization processes are restricted to charged dyes. Thus, only the monomeric deprotonated form of the dye has to be considered as active in this study.

3.2. Singlet state processes

The lifetimes of the singlet excited state of NR in the absence and presence of TEA were obtained from fluorescence decay times and the changes in the emission intensity. The Stern–Volmer plots obtained by both methods can be assumed to be within the experimental errors, as shown in Fig. 2. The
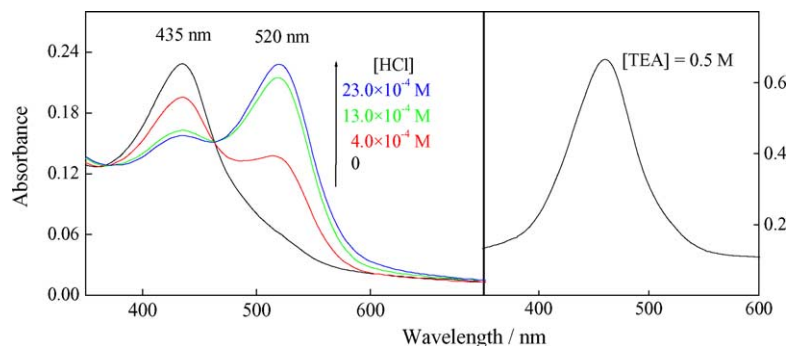
Fig. 1. Spectra of neutral red in ethyl acetate in the presence of different concentrations of HCl and in TEA 0.5 M.

lifetime of NR was determined as 4.4 ns, in good agreement with the values (3–5 ns) reported in the literature for various solvents [17]. The Stern–Volmer constant obtained from that plot is $0.18 \, M^{-1}$. Using this value together with the lifetime indicated above, ^1k_q can be estimated to be in the range of $\sim 4 \times 10^7 \, M^{-1} \, s^{-1}$.

There does not seem to be any significant interaction between the dye and the amine, so that there is no need to consider a ground state complex in the overall reaction mechanism.

3.3. Triplet state processes

The transient absorption spectrum of neutral red (5×10^{-5} M) in ethyl acetate is shown in Fig. 3. In the absence of amine, there is a region of absorption from 300 to 400 nm, which is attributed to the triplet–triplet absorption. The spectrum was registered from 300 to 800 nm, immediately after the laser pulse. The spectrum is similar to that found for the same dye in water and methanol solutions [19]. Some slight shift in the maxima can be ascribed to solvent effects.

Bimolecular quenching rate constants were obtained from the decay of the triplet at 350 nm as a function of amine concentration (Fig. 4). The Stern–Volmer plot for the quenching of the NR triplet is shown in Fig. 5 and corresponds to a rate constant of $5.70 \times 10^4 \, M^{-1} \, s^{-1}$.

The rate constant for the quenching of the triplet state of neutral red by MMA has been found to be $2.17 \times 10^2 \, M^{-1} \, s^{-1}$, i.e. about 2–3 orders of magnitude less than that for quenching by TEA. Therefore, even at the lowest amine concentration, most of the excited triplet dye molecules will react with the amine.
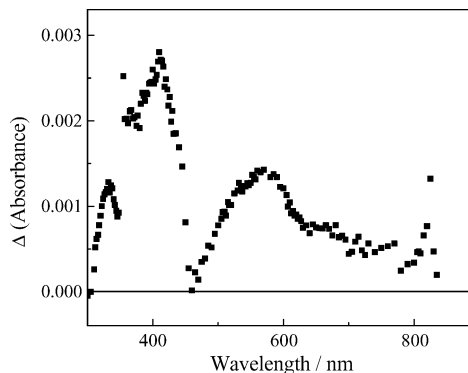

Fig. 3. Transient absorption spectrum of neutral red 5×10^{-5} M in ethyl acetate taken 8 μs after excitation.
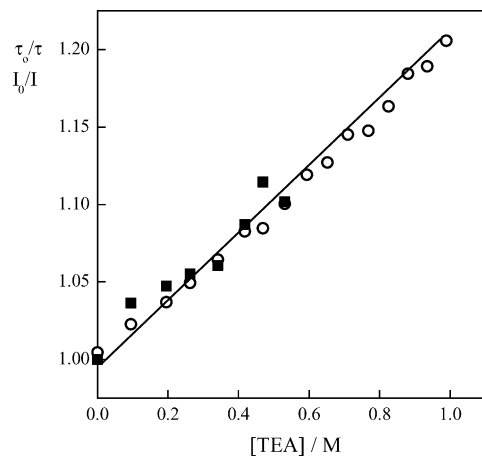

Fig. 2. Stern–Volmer plots for the quenching of neutral red singlet by triethylamine in ethyl acetate.
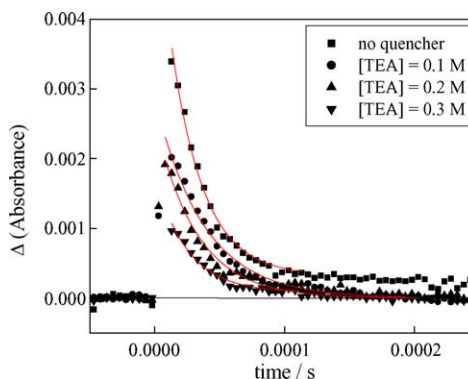

Fig. 4. Decay of the transient absorption of neutral red at 350 nm as a function of TEA concentration in ethyl acetate.
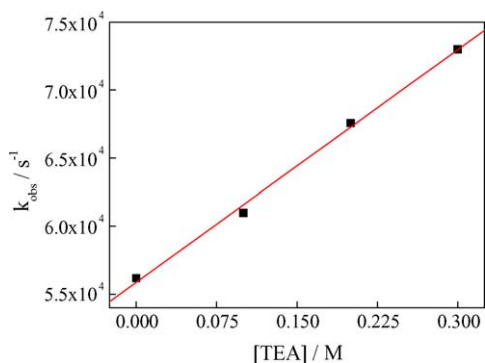
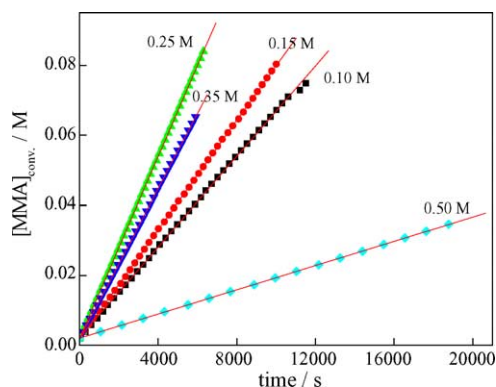Fig. 5. Stern–Volmer plot for the quenching of neutral red triplets by TEA.

Fig. 6. Monomer conversion in the photopolymerization of MMA in the presence of NR at various TEA concentrations.

3.4. Polymerization

The dye photoinitiated polymerization of MMA in pure monomer solution could only be achieved in the presence of an appropriate co-initiator and using a 395 nm cut-off filter. The rates of polymerization of MMA using the photoinitiating NR/TEA system were determined as a function of monomer concentration (Fig. 6) and of amine concentration (Fig. 7).
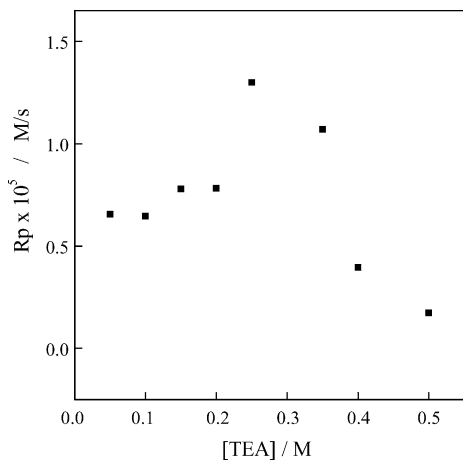

Fig. 7. Dependence of the MMA photopolymerization rates with TEA concentration.
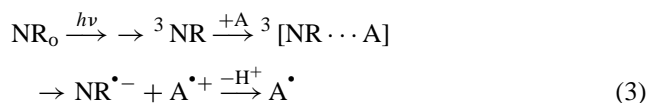
3.4.1. Effect of the co-initiator concentration

In order to determine the concentration of amine required to optimize the polymerization rate, experiments using different concentrations of the co-initiator were carried out under constant irradiation intensity. The initiator concentration was kept constant at 1.0×10^{-5} M. Under anaerobic conditions, the rate of polymerization R_p follows a complex behaviour with the increase in amine concentration (Table 1 and Fig. 7): first, the polymerization rate increases rapidly with amine concentration, reaching a maximum (~ 0.3 M). Further increase in the co-initiator concentration results in a decrease in the rate of the polymerization process.

This behaviour can be explained assuming two different processes. On one side, the increase in amine concentration will increase the interaction between the singlet state dye and the amine, forming singlet exciplexes that will, preferentially, be deactivated to its ground state components.

$$NR_o \xrightarrow{h\nu} {}^1NR \xrightarrow{+A} {}^1[NR \cdots A] \rightarrow NR_o + A \qquad (2)$$

On the other hand, a large excess of amine radical might contribute to deactivate the triplet NR–TEA exciplexes, and consequently the concentration of initiator radicals leading to a decrease in the polymerization rate.

$$NR_o \xrightarrow{h\nu} \rightarrow {}^3NR \xrightarrow{+A} {}^3[NR \cdots A]$$
$$\rightarrow NR^{\bullet -} + A^{\bullet +} \xrightarrow{-H^+} A^{\bullet} \qquad (3)$$

$${}^3[NR \cdots A] \xrightarrow{+A} NR + A \qquad (4)$$

This behaviour reveals the known efficiency of amines in retarding the polymerization process if their concentrations are large enough [7,10].

3.4.2. Role of oxygen

The polymerization process showed a significant inhibition period, even for the degassed solutions. It can be seen that the inhibition times decrease with amine concentration down to a minimum (~ 0.3 M), after which it increases again (Fig. 8).

These inhibition periods should be related to the residual molecular oxygen dissolved in the solution even after degassing. Molecular oxygen is known to inhibit radical-induced polymerization because of its high reactivity with radical species. Taking into account that the photo-oxidation rate is 10^5 times larger than that of polymerization propagation, the initiating radicals will react mainly with oxygen, and polymerization would only start when the oxygen concentration drops to a level low enough for the monomer to be able to compete with the oxygen molecules in the reaction with the initiator radicals.

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \xrightarrow{X-H} ROOH \qquad (5)$$

Thus, when oxygen is present, the tertiary amine seems to act not only as a co-initiator but also as an oxygen consumer through a well known chain process in which the α-

Table 1
Inhibition times, polymerization rates, quantum yields for the photopolymerization of MMA and molecular weights

TEA (M)	Inhibition time (min)	R_p (M s^{-1})	Φ_m (10^3 mol einstein^{-1})	Mn (Da)
0.05	90	6.55×10^{-6}	1.06	15,100
0.10	78	6.46×10^{-6}	1.04	17,200
0.15	40	7.80×10^{-6}	1.26	18,300
0.20	35	7.82×10^{-6}	1.26	63,500
0.25	30	1.30×10^{-5}	2.10	124,200
0.30	15	1.44×10^{-5}	4.73	191,300
0.35	27	1.07×10^{-5}	1.73	166,700
0.40	50	3.95×10^{-6}	0.64	33,400
0.50	145	1.73×10^{-6}	0.28	32,600

aminoalkyl primary radicals are rapidly scavenged by oxygen generating peroxy radicals which, in turn, will abstract other hydrogens to form hydroperoxides. After the consumption of the oxygen, the interrupted chain propagation is restored [20]. This is clearly observed when comparing the polymerization rates with the inhibition times, shown in Fig. 8. The faster the reaction, the sooner the residual oxygen will be consumed and the effective polymerization will start to be able to propagate.

3.4.3. Polymerization mechanism

A mechanism consistent with the results of photochemical behaviour of the singlet and triplet states of NR in presence of TEA in ethyl acetate solution is shown in Fig. 9.

At the concentrations used in this work, there seems to be no association between the amine and the dye in the ground state. The exciplexes formed by the interaction of the dye singlet with amine will not form free radicals due to spin restrictions [10,12,13].

On the other hand, the triplet exciplexes will rapidly form free radicals by an electron transfer mechanism between the triplet dye and the amine. The formation of these radicals can
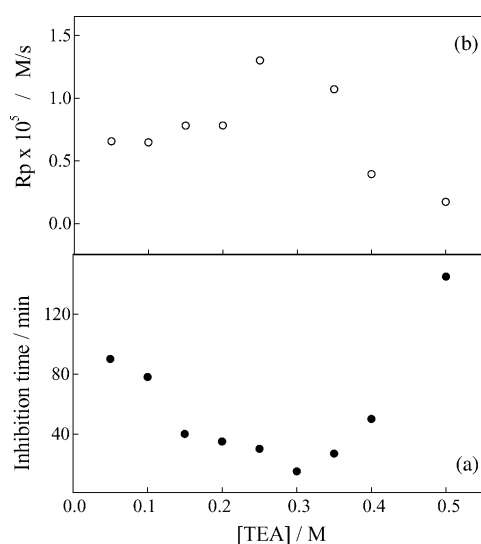
be inferred from the ingrowth of the semi-reduced radical that absorbs in the 350 nm region, as shown in Fig. 10.

The large amount of amine in the system might also contribute to the deactivation of the exciplex, competing with the formation of formation of free radicals [21–23]. This effect found also for the polymerization of MMA in the presence of the thionine/TEA photoinitiating system [7], has also been suggested by Sastre and co-workers to explain the same effect in the photopolymerization of lauryl acrylate [24]. On
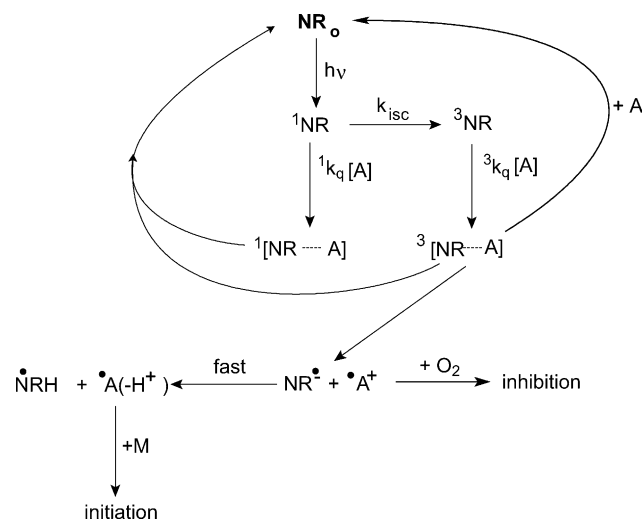

Fig. 9. Mechanism for the production of photoinitiating free radicals in the NR/TEA system.

Fig. 8. Dependence of the inhibition times (a) and photopolymerization rates (b) with TEA concentration.
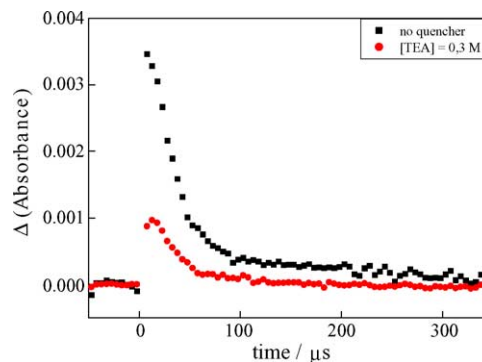

Fig. 10. Decay of the absorption of the semi-reduced specie of neutral red (350 nm) in the absence and presence of TEA.
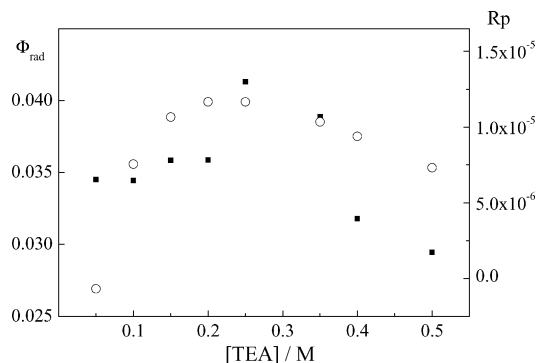
Fig. 11. Calculated free radical yields (○) and experimental polymerization rates (■) for the photoinitiated polymerization of MMA by the NR/TEA systems.

the other hand, in a recent paper, Previtali and co-workers [25] proposed that the decrease in the Safranine-initiated photopolymerization rates at high amine concentrations is due to the photobleaching of the dye. Nevertheless, no photobleaching was observed during the polymerization experiments in the NR system.

In general, it is found that large radicals, with the free electron delocalized over a large π-system, are not good initiators. As the initiation by semi-reduced NR would lead to a polymer with yellow/red colour, and the polymers obtained in these experiments are colourless, it may be concluded that the initiation pathway by the dye radical can be discarded.

The amine radical loses a α-hydrogen to form a secondary C-centered radical, which is the initiating species

$$\overset{+\bullet}{N}(C_2H_5)_3 \rightarrow (CH_3CH_2)_2 - N - \overset{\bullet}{C}H - CH_3 + H^+ \qquad (6)$$
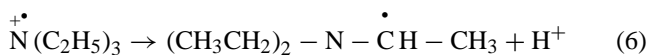
On the other hand, when residual oxygen is present, it will scavenge the free radicals, and inhibit the polymerization process by forming hydroperoxides and other similar unreactive species. As oxygen is consumed by this process, the inhibition times parallel the polymerization rates as can be seen comparing Figs. 7 and 8.

Using the reactions in the scheme of Fig. 9, an expression for the yield of free radicals can be deduced (Eq. (7)).

$$\Phi_{rad} = \beta \frac{\Phi_{isc}}{1 + {}^1K_{SV}[A]} \times \frac{{}^3K_{SV}[A]}{1 + {}^3K_{SV}[A]} \times \frac{1}{1 + k_d[A]/k_{et}} \qquad (7)$$

where k_{et} corresponds to the rate constant for the effective electron transfer inside the exciplex to form initiating radicals, k_d the constant for the deactivation of the exciplex by amine and β is the efficiency of the radicals to initiate the polymerization process. The yields of free radicals calculated using ${}^1K_{SV}$ and ${}^3K_{SV}$ obtained above (0.18 and 1.02 M^{-1}, respectively), and 12 M^{-1} for the k_d/k_{et}, show a trend qualitatively similar to that of the polymerization rates, as can be observed in Fig. 11.

4. Conclusions

The photoinitiation of MMA polymerization by neutral red/TEA system is efficient and maximum conversion rates are found for amine concentrations around 0.3 M. A mechanism is proposed for the photoinitiation process that includes the deactivation of the exciplex in the presence of high amines concentrations. This mechanism accounts well for the observed results up to the maximum conversion rate. Other processes, active at higher amine concentrations do decrease the concentration of initiating amine radicals.

Acknowledgements

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