Polymerization Photoinitiated by Carbonyl Compounds. IX. Methyl Methacrylate Polymerization Photoinitiated by Anthraquinone in Presence of Triethylamine

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Synopsis

Addition of triethylamine (TEA) notably increases the efficiency of anthraquinone (AQ) as photoinitiator of methyl methacrylate (MMA) free radical polymerization in nonpolar solvents. On the other hand, when alcohols or acetonitrile are employed as solvents the addition of TEA decreases the AQ photoinitiated polymerization rate. The polymerization efficiency measured in nonpolar solvents decreases when the MMA concentration increases. These results are explained in terms of quenching of the AQ–TEA charge transfer complex by MMA. This conclusion is supported by the decrease in AQ photoconsumption and AQH_2 formation produced by the monomer addition.

INTRODUCTION

The polymerization of vinyl monomers photoinitiated by aromatic carbonyl compounds in the presence of amines has been a subject of increasing interest.[1-6] A thorough understanding of the factors determining the efficiency of the initiation step has been achieved due to the background provided by several previous studies on the photoreduction of carbonyl compounds by amines.[7-12] The process occurs through a charge transfer intermediate, being one of the decomposition steps a proton transfer from the amine cation to the ketone to give a radical pair. The ketyl radicals formed, as well as the charge transfer intermediates, have been detected in several systems.[9-12] The behavior of the charge transfer complex is highly dependent on the solvent and the nature of the carbonyl compound.[10-13] Consequently, the quantum yield of free radicals capable of initiating the monomer polymerization is also extremely sensitive to changes in these factors.

The above mentioned studies have been carried out employing different types of carbonyl compounds as photoinitiators, such as aliphatic[6] and aromatic[1-3] monoketones and α-dicarbonyl compounds.[4,5] However, no such studies have been performed employing quinones as sensitizers, which are also able to initiate free radical polymerizations in the presence of suitable hydrogen donors. Anthraquinone (AQ) has been shown to be able to initiate free radical polymerization in the presence of hydrogen donating solvents such as hydrocarbons,

alcohols and tetrahydrofuran.[14,15] In particular, Ledwith et al.[14] have given details of the kinetic and the mechanism involved in the AQ sensitized photopolymerization of methyl methacrylate (MMA) in tetrahydrofuran. In the present work, we use the system AQ/triethylamine (TEA) as photoinitiator of the MMA polymerization. A detailed study on the photoreduction of the AQ triplet by TEA has been recently published by Hananoue et al.[12]

EXPERIMENTAL

Anthraquinone (Fluka), was purified by recrystallization. Methyl methacrylate and triethylamine were vacuum distilled prior to their use. All solvents (spectroscopic grade) were used without further purification.

Photopolymerization rates (arbitrary units) were measured in Pyrex dilatometers under nitrogen at 24°C. The samples were irradiated with light from a medium-pressure mercury lamp. tert-Butyl peroxide (TBP) was used as a reference photoinitiator. Matched solutions of the quinone and the reference compound were irradiated under identical conditions. TEA addition to the TBP did not produce any significant change in the polymerization rates. Low absorbances were used to avoid the generation of an inhomogeneous free radical distribution.[16]

Polymer molecular weights were determined viscosimetrically in benzene at 30°C [log MW = 1.31 × log($\eta/5.2 \times 10^{-5}$) with η in g/100 mol].[17]

The photolysis of AQ/TEA solutions were carried at room temperature, under the same irradiation conditions as those employed in the polymerization experiments. Absorption spectra were recorded using a Shimadzu UV-160 spectrophotometer.

RESULTS AND DISCUSSION

MMA polymerization rates (R_p), photoinitiated by the AQ/TEA system, were measured in solvents of different polarities, like benzene, alcohols and acetonitrile. The initiation efficiency, f_{exp}, obtained employing a reference photoinitiator under matched absorbances, is given by eq. (1):

$$f_{exp} = \frac{R_p}{(R_p)_{ref}} f_{ref} \qquad (1)$$

where initial rates must be used since AQ is significantly consumed during the photolysis. The initiation efficiencies obtained using eq. (1), with tert-butyl peroxide as reference photoinitiator, are given in Table I. These data show that AQ, in the absence of TEA and in solvents of low hydrogen donor capacity, is a poor photoinitiator. In solvents of low polarity, amine addition notably increases the photoinitiation efficiency. However, in polar solvents such as acetonitrile and alcohols, the initiation efficiency remains very low even in the presence of added amine. It is interesting to note that in alcohols, the polymerization rate is reduced by the TEA addition. Furthermore, in benzene/acetonitrile mixtures, the increase of the acetonitrile content produces a con-

TABLE I
Photoinitiation Efficiencies by the Anthraquinone–Triethylamine System

Solvent	[TEA] (M)	f_{exp}[a]
MMA	0.086	0.072
Benzene[b]	—	0.008
	0.004	0.07
	0.012	0.09
	0.022	0.19
	0.043	0.22
	0.086	0.25[c]
	0.17	0.22
Ethanol[b]	—	0.08
	0.086	0.03
Isopropanol[b]	—	0.1[d]
	0.086	0.05
Acetonitrile[b]	0.086	0.005
Acetonitrile : benzene $(1:2)$[b]	0.086	0.03

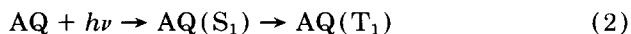[a] Initiation efficiency of TBP taken $= 1$.[18]
[b] Monomer : solvent $(1:1)$ (v : v).
[c] Molecular weight, 3.5×10^4.
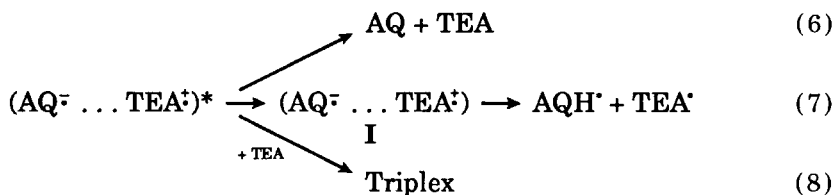[d] Molecular weight, 4.5×10^4.

siderable effect on the polymerization rates. However, the polymerization rate sensitized by *tert*-butyl peroxide (a free radical photoinitiator with a nearly solvent independent photocleavage yield), remains almost constant when the solvent is changed from benzene to acetonitrile or when TEA is added.[19] The decrease of the polymerization rate with the acetonitrile content observed in the AQ/TEA system must be then a consequence of changes in the initiation efficiency.

The quenching of triplet AQ by TEA leads to the quinone photoreduction.[12,13,20] The process takes place by a charge transfer mechanism, and the rate of the primary process is nearly diffusion controlled even in nonpolar solvents.[12] The reaction can be represented by the following mechanism:

$$AQ + h\nu \rightarrow AQ(S_1) \rightarrow AQ(T_1) \qquad (2)$$

$$AQ(T_1) \rightarrow \text{physical deactivation} \qquad (3)$$

$$AQ(T_1) + TEA \rightarrow (AQ^{\overline{\cdot}} \ldots TEA^{\overset{+}{\cdot}})^* \qquad (4)$$

$$AQ(T_1) + SH \rightarrow AQH^{\cdot} + S^{\cdot} \qquad (5)$$
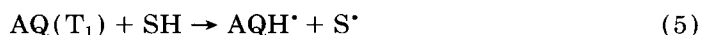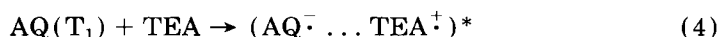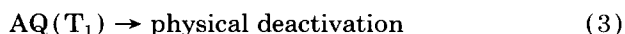
where SH stands for the solvent.

The exciplex formed in step (4) has been well characterized by nano- and picosecond spectroscopy, and the rates of its different deactivation pathways have been determined.[12] According to the mechanism proposed by Hamanoue et al.,[12] the exciplex decomposition can be represented by:

$$AQ + TEA \qquad (6)$$

$$(AQ^{\overline{\cdot}} \ldots TEA^{\overset{+}{\cdot}})^* \longrightarrow (AQ^{\overline{\cdot}} \ldots TEA^{\overset{+}{\cdot}}) \longrightarrow AQH^{\cdot} + TEA^{\cdot} \qquad (7)$$

$$\mathbf{I}$$

$$+ TEA$$

$$Triplex \qquad (8)$$

The intermediate **I** has been characterized as a contact ion pair, whose formation is followed by proton transfer to generate anthrasemiquinone ($AQH^{\cdot}$) and triethylamine free radicals. The semiquinone radicals disproportionate to form AQH_2 and AQ. Process (8), the exciplex quenching by TEA, is considered to be important only in polar solvents.[12]

According to the scheme depicted by eqs. (2)–(8), steps (5) and (7) can be the source of the primary free radicals capable of initiating the polymerization process. The experimentally measured initiation efficiency will be then given by eq. (9):

$$f_{\exp} = \alpha_5 f_5 + \alpha_7 f_7 \qquad (9)$$

where f_i measures the quantum yield of a given process, and α_i is the fraction of free radicals produced.[6]

When benzene is employed as the solvent, the lack of significant polymerization in the absence of TEA indicates that α_5 and/or f_5 are negligible. In presence of TEA, the observed polymerization must result from the occurrence of reaction (7). On the other hand, the addition of amine decreases the polymerization rate observed when ethanol or isopropanol are employed as solvents. This result indicates that, even at high amine concentrations, $\alpha_7 f_7 < \alpha_5 f_5$. The low value of $\alpha_7 f_7$ could be due either to a major contribution of step (8) and/or to a low value of α_7, implying that other reaction paths than proton transfer dominate the contact ion pair decay. At high amine concentration, where f_5 vanishes and f_7 is given by

$$f_7 = k_7/(k_6 + k_7 + k_8[TEA]) \qquad (10)$$

the proposed mechanism implies that $f_{\exp}$ must be independent on the monomer concentration. Nevertheless, the data given in Table I show that the initiation efficiency decreases when the monomer concentration increases.

In order to get further insight on the photoinitiation mechanism, we studied the effect of the MMA concentration on the AQ photoreduction rate by TEA. These effects were measured by changes on the absorption spectra of the photolyzed mixtures. These spectral changes are shown in Figures 1 and 2 in benzene and ethanol as solvents, respectively. These figures show a depletion of AQ absorption and the build up of a photoproduct during the photolysis with λ = 313 nm. The existence of an isobestic point with $\lambda_{\max} = 345$ nm indicates that the photoproduct is a primary product and that it is stable in the time scale of the experiments. These results are essentially the same as those reported for the photolysis of AQ in the absence of MMA and the absorption band with maxima wavelength at 382 nm is well characterized as due to 9,10-dihydroxy-
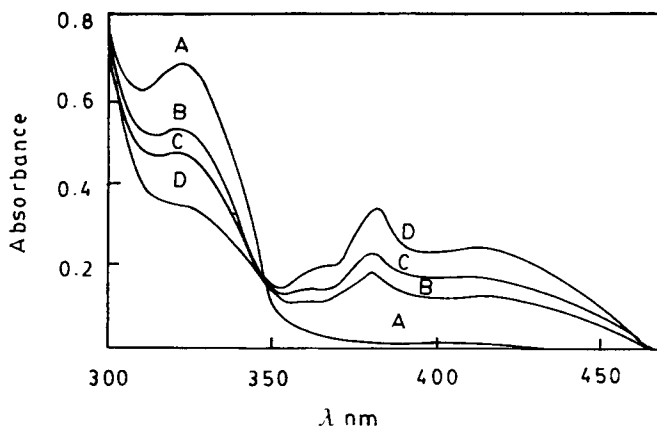
Fig. 1.   Absorption spectral changes of AQ/TEA $(0.2M)$ in the presence of MMA $0.79M$, in benzene upon irradiation with 313 nm light at room temperature: (A) at zero time, (B) after 0.5 min, (C) after 1.5 min, (D) after 3 min.

anthracene, AQH_2.[12,14,21,22] Similar results have been reported by Ledwith et al.[14] for the photoreduction of AQ by tetrahydrofuran in the presence of MMA.

Figures 3 and 4 show the effect of varying MMA and TEA concentrations on the decrease of anthraquinone absorbance at 325 nm and the appearance of the absorption band at 382 nm. These data show that, when benzene is used as solvent, the quinone photoconsumption and the dihydroxyanthracene formation are independent of the TEA concentration, both in the presence or absence of MMA. In the presence of ethanol, however the photoconsumption as well as the product formation are dependent on the TEA concentration. In this point it is noteworthy to indicate that even at the lowest amine concentration used in these experiments, more than 90% of AQ triplets are quenched by the amine. Thus, the TEA dependence can be related to the occurrence of reaction (8) in ethanol.
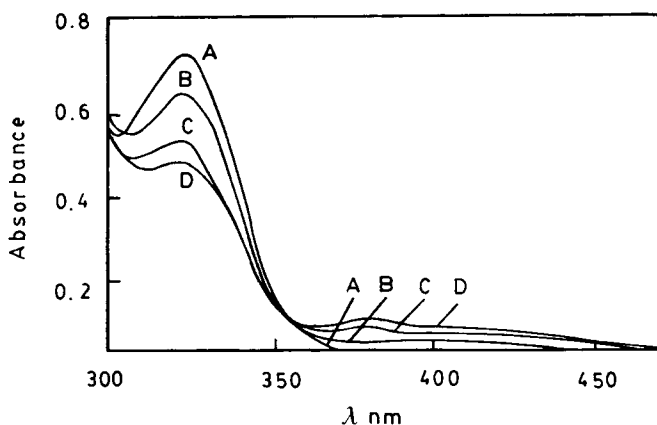

Fig. 2.   Absorption spectral change of AQ/TEA $(0.2M)$ in the presence of MMA $0.79M$, in ethanol upon irradiation with 313 nm light at room temperature: (A) at zero time, (B) 1.5 min, (C) 8 min, (D) 15 min.

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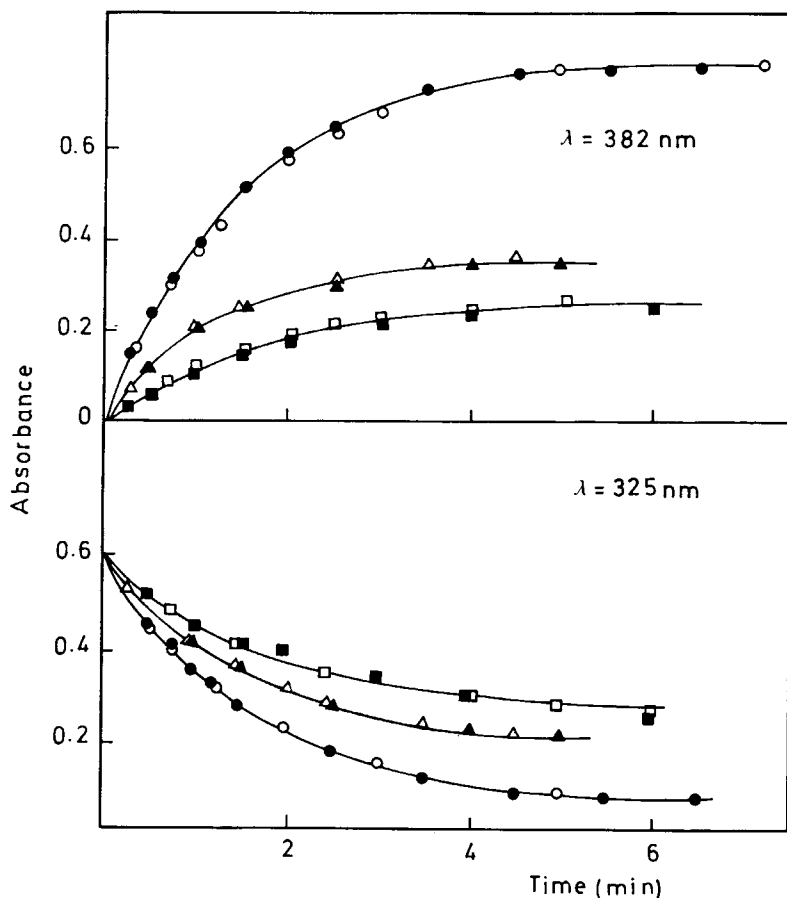

Fig. 3. Absorbances of the AQ/TEA mixtures as a function of irradiation time in benzene, at different TEA and MMA concentrations. Closed symbols [TEA] = $0.036 M$; open symbols [TEA] = $0.2 M$. ($\bigcirc$, $\bullet$) in absence of MMA, ($\triangle$, $\blacktriangle$) [MMA] = $0.79 M$, ($\square$, $\blacksquare$) [MMA] = $3.15 M$.

Figures 3 and 4 show that, in the two solvents considered, the limiting optical densities at 382 nm obtained in the photolysis of AQ/TEA mixtures decrease considerably in the presence of MMA, and the AQ photoconsumption is reduced. The fraction of AQ consumed that produce AQH_2 can be evaluated by plotting $(\Delta A)_{382}$ vs. $(\Delta A)_{325}$ (Fig. 5). In ethanol as solvent, the presence of TEA does not modify the AQH_2 production in the absence of MMA. Nevertheless, addition of MMA drastically decreases the product yield, with a much more important effect in the absence of added TEA. When benzene is employed as solvent, the AQH_2 yield in absence of MMA is similar to that obtained in ethanol. However, the decrease observed on MMA addition is smaller than that elicited when ethanol is employed as solvent. The decrease in AQH_2 formation in the presence of MMA could be attributed to trapping of the $AQ(T_1)$, the exciplex, the contact ion pair and/or the $AQH^{\bullet}$ radical. The triplet quenching by MMA can be disregarded since in the absence of TEA, the photoconsumption yield in ethanol or toluene is not sensitive to the MMA concentration (data not shown). The same conclusion can be reached from the data of Ledwith et al.,[14] that show
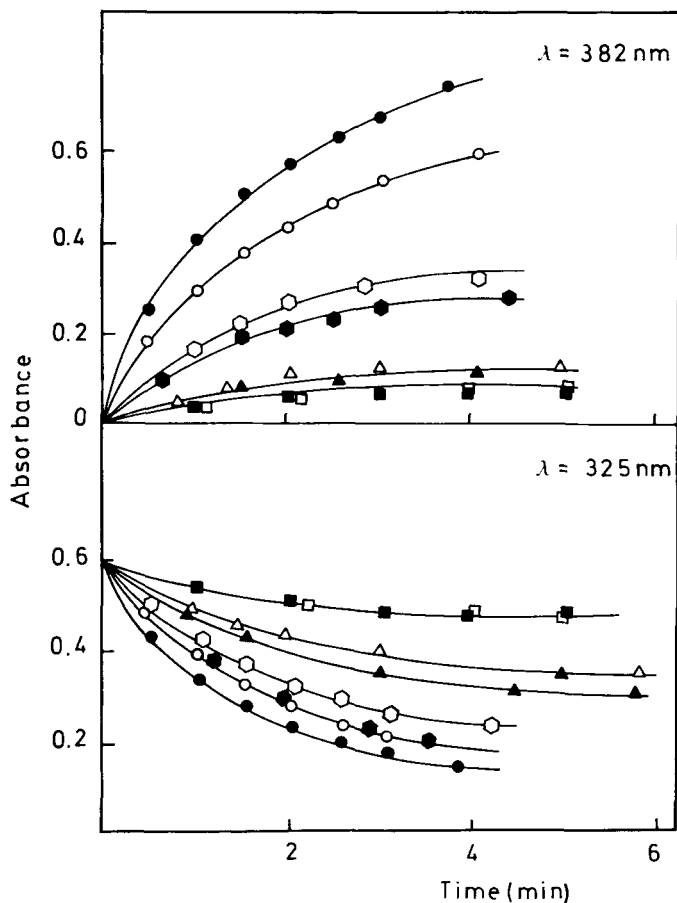
Fig. 4. Absorbances of AQ/TEA mixtures as a function of irradiation time in ethanol, at different TEA and MMA concentrations. Closed symbols [TEA] = 0.036M; open symbols [TEA] = 0.2M. (O, ●) in absence of MMA, (o, ●) [MMA] = 0.22M, (△, ▲) [MMA] = 0.79M, (□, ■) [MMA] = 1.58M.

that the AQ sensitized MMA photopolymerization rate in tetrahydrofuran is proportional to the MMA concentration over a wide concentration range. The decrease of the AQH_2 formation in the presence of MMA can not be explained only in terms of the scavenger of the $AQH^•$ radicals by the growing polymer, as suggested by Ledwith et al.,[14] since the photoconsumption decreases when the MMA concentration increases. These results can be explained in terms of the quenching of the charge transfer intermediate by MMA. Figures 3 and 4 show that the effect of MMA depends on the TEA concentration in ethanol, but is independent on it in benzene, suggesting that MMA interacts with the exciplex according to eq. (11):

$$(AQ^{-•} \ldots TEA^{+•})^* + MMA \rightarrow \text{Deactivation} \tag{11}$$
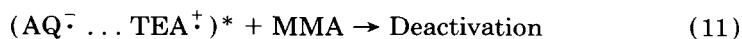
In ethanol, this process competes with reaction (8). In benzene, quenching of
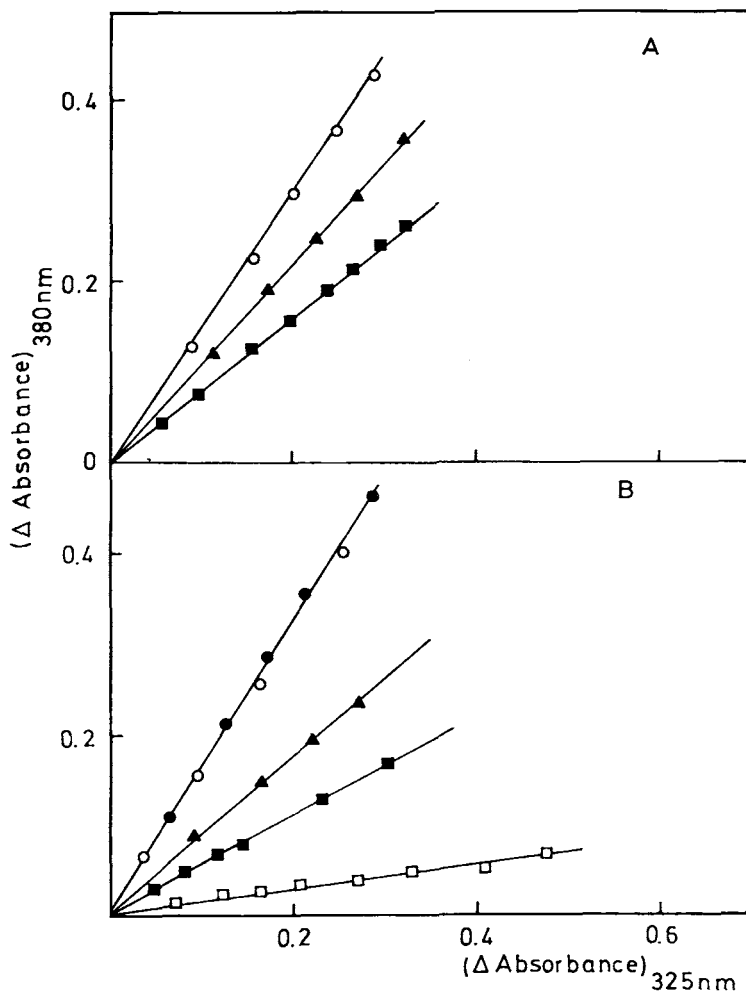
Fig. 5. Relation of the absorbance of the formed product (measured at 382 nm) and AQ consumption (measured at 323 nm) under different MMA and TEA concentrations: (A) in benzene as solvent, (B) in ethanol. (●) in absence of TEA and MMA; (○) in presence of TEA $0.2M$; (▲) [TEA] = $0.2M$, [MMA] = $0.79M$; (■) [TEA] = $0.2M$, [MMA] = $3.15M$; (□) [MMA] = $3.15M$.
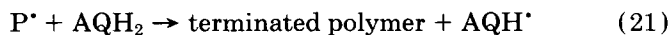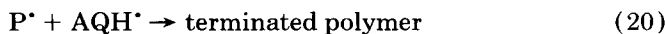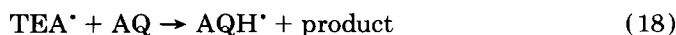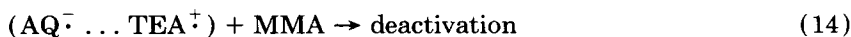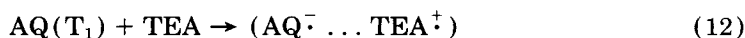
the exciplex by TEA is negligible,[12] and the effect of MMA becomes independent on TEA concentration.

Quenching of exciplexes has been reported both for molecules that can act as electron donors or acceptors, particularly olefins.[23-26] The quenching process involves the formation of a ter-molecular complex. Thus, the exciplex represented by (AQ^- ... TEA^+) could be quenched by MMA, an acceptor quencher, from the AQ side, i.e., $MMA^{\delta-}$ ... $AQ^{\delta-}$ ... $TEA^{\delta+}$. This process becomes more important in ethanol due to the larger exciplex lifetime[12] and the ability of polar solvents to favour charge transfer quenching processes.[27]

The data shown in Figure 5 emphasizes the point that MMA addition not only decreases the AQ photoconsumption yield but also decreases the fraction of it that appears as AQH_2. Furthermore, it is important to note that no other

near UV absorbing product is formed, indicating that anthracene moieties are not formed along the process. The photoaddition of olefins to anthraquinone produces the corresponding oxetans.[28] Since oxetan formation implies an exciplex precursor, its formation could be more likely from the exciplex. Regarding this point, it has been reported that the photocycloaddition of 1-aminoanthraquinone to olefins proceeds efficiently due to the charge transfer character of its excited state.[29]

A simplified photopolymerization mechanism in benzene consistent with the experimental observations is shown in the following:

$$AQ(T_1) + TEA \rightarrow (AQ^{\cdot -} \ldots TEA^{\cdot +}) \tag{12}$$

$$(AQ^{\cdot -} \ldots TEA^{\cdot +}) \rightarrow (AQ^{\cdot -} + TEA^{\cdot +}) \rightarrow AQH^{\cdot} + TEA^{\cdot} \tag{13}$$

$$(AQ^{\cdot -} \ldots TEA^{\cdot +}) + MMA \rightarrow deactivation \tag{14}$$

$$AQH^{\cdot} + TEA^{\cdot} \rightarrow AQ + TEA \tag{15}$$

$$2AQH^{\cdot} \rightarrow AQH_2 + AQ \tag{16}$$

$$TEA^{\cdot} + MMA \rightarrow P^{\cdot} \tag{17}$$

$$TEA^{\cdot} + AQ \rightarrow AQH^{\cdot} + product \tag{18}$$

$$P^{\cdot} + P^{\cdot} \rightarrow Polymer \tag{19}$$

$$P^{\cdot} + AQH^{\cdot} \rightarrow terminated\ polymer \tag{20}$$

$$P^{\cdot} + AQH_2 \rightarrow terminated\ polymer + AQH^{\cdot} \tag{21}$$

where reactions (20) and (21) have been included in order to explain the low molecular weight of the polymer obtained in the absence[14] or presence of added TEA (see Table I).

The proposed initiation mechanism can account for the differences observed in ethanol and benzene, and the dependence of the initiation efficiency on MMA concentration. In ethanol, deactivation of the exciplex by TEA and MMA predominates and the polymerization rate is negligible. In benzene, free-radical formation is more relevant but, due to the occurrence of reaction (11), its yield decreases when the MMA concentration increases. It is interesting to note that an increase in exciplex deactivation by MMA with solvent polarity could explain the decrease in polymerization rate observed by Li et al.[15] at high isopropanol concentrations.

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