Macromolecules **1993,** *26,* 6284–6288

Photopolymerization in Aqueous Solutions Initiated by the Interaction of Excited Pyrene Derivatives with Aliphatic Amines

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Received August 26, 1992; Revised Manuscript Received December 4, 1992⊗

ABSTRACT: The photolysis of pyrene derivatives in the presence of amines has been employed as a source of free radicals in the polymerization of 1-vinyl-2-pyrrolidinone in aqueous solution. The photoinitiation efficiency strongly depends on the amine and the sensitizer employed. With regard to the amine, only tertiary amines are efficient cocatalysts, hydroxyethanolamines being particularly efficient. For a given amine the initiation efficiency is high for pyrene and its cationic derivatives, while pyrenebutyric acid is a poor photoinitiator and pyrenesulfonic acid does not initiate the polymerization. The active radicals are produced in the interaction between the singlet excited state and the additive, the photoinitiation rate being proportional to the fraction of singlets quenched by the amine. The photoinitiation efficiency at total singlet quenching correlates with the rate constant of the quenching process, the photobleaching rate, and the pyrene radical anion yield. Photobleaching yield and the lifetime of the pyrene-derived radical anion decrease in the presence of 1-vinyl-2-pyrrolidinone. All these results are compatible with an initiation mechanism involving the interaction of the pyrene radical anion with the monomer.

Introduction

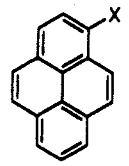
Water-soluble photoinitiators have received increasing interest due to their widespread applications in the grafting of monomers onto natural polymers and UV curing of water-based ink systems. Among the most studied photoinitiator systems are those that act by a bimolecular process comprising an excited chromophore and a coinitiator that behaves as an electron donor. The chromophores generally used are aromatic carbonyl compounds whose water solubility is increased by introduction of ionizable groups, such as alkyltrimethylammonium or sulfonic acid. Aliphatic tertiary amines are generally employed as coinitiators.[1-7]

In previous papers we have reported the free radical polymerization of vinyl monomers in organic media photoinitiated by the system excited pyrene/triethylamine.[8,9] We have showed that the photoinitiating activity of this system is due to the interaction of the excited singlet state of pyrene with the amine and that the species involved in the initiation step is the pyrene radical anion. In the present work, we extend our previous studies to the polymerization of 1-vinyl-2-pyrrolidinone (VP) in aqueous solution. The chromophore employed were pyrene and pyrene ionic derivatives with different charge and size in the alkyl side chain (Chart I). The amines employed were aliphatic alkylamines and hydroxyalkylamines. These studies are carried out with the aim of establishing relationships between the polymerization initiation efficiencies of these systems in aqueous media and the structure and photochemical properties of the chromophores and the cocatalyst.

Experimental Section

Materials. 1-Vinyl-2-pyrrolidinone (VP) (Aldrich) was purified by distillation under nitrogen. Triethylamine (TEA) and all the other amines employed (Aldrich) were vacuum distilled. Pyrene (Py) (Aldrich) was recrystallized twice from ethanol. The ionic pyrene derivatives were purchased from Molecular Probes and used without further purification.

Chart I. Formulas of the Pyrene Ionic Derivatives



Py, X = H

$PyMe^+$, X = $CH_2N^+(CH_3)_3$

$PyBut^+$, X = $(CH_2)_4N^+(CH_3)_3$

$PyBut^-$, X = $(CH_2)_3COO^-$

$PySO_3^-$, X = SO_3^-

Polymerizations. Initial polymerization rates were measured dilatometrically, in arbitrary units, under anaerobic conditions. The experiments were carried out at 25 °C in monomer:water (1:1, v:v). The pH of the solutions was adjusted to 11 with NaOH. The samples were irradiated with a medium-pressure mercury lamp. Matched solutions of the pyrene derivatives were irradiated under identical conditions. Low absorbances (≤ 0.3) were used to avoid inhomogeneous free radical distributions.[10]

Photochemical Measurements. Photoconsumption experiments were carried out under the same conditions of the polymerizations. The pyrene chromophore consumption was evaluated from the decrease in its near-UV absorption band using a Shimadzu 160 spectrophotometer. Quantum yields were determined employing the photobleaching of pyrene by triethylamine in acetonitrile as reference.[8] The absorption band shape does not change with the irradiation time, rendering support to the procedure employed.

Fluorescence quenching experiments were carried out by measuring the fluorescence intensity and/or fluorescence lifetimes. Steady-state measurements were performed with a Perkin-Elmer LS-5 spectrofluorimeter, and fluorescence time-resolved measurements were made by the phase shift and demodulation techniques, using a GREG 200 multifrequency phase fluorometer, or by monitoring the fluorescence decay after excitation with a pulsed nitrogen laser as previously described.[11] Transient absorption experiments were carried out by using as an excitation

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⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1993.

0024-9297/93/2226-6284$04.00/0

Table I. Quenching Rate Constants for Singlet Excited States of Pyrenes by Amines in VP:Water (1:1) Mixture[a]

	k_q, 10^8 M^{-1} s^{-1}				
amine	$PyMe^+$	Py	$PyBut^+$	$PyBut^-$	$PySO_3^-$
triethanolamine	5.4 (12.9)	1.9	1.5	1	0.44
triethylamine	3.4 (13.6)	1.6 (3.9)	1.2 (3.1)	0.7 (1.8)	0.44 (1.0)
N-methyldiethanolamine	3.0 (8.1)	0.9	0.6	0.5	0.3
N,*N*-dimethylethanolamine	0.7 (2.5)	0.37	0.20	0.13	0.15
diethylamine	(1.2)				

[a] Values in acetonitrile:water (1:1) are given in parentheses.

source a pulsed nitrogen laser. The detection system has been described elsewhere.[12]

Results and Discussion

Photoinitiation can arise from the interaction of an excited chromophore with the monomer and/or the cocatalyst.[13] Singlet lifetimes in the absence of amines (τ°) were measured in acetonitrile (AN) and dimethylformamide (DMF) aqueous mixtures. Dimethylformamide is a solvent whose solvatochromic parameters can be considered to resemble those of VP.[14] The singlet lifetime values obtained in AN/water (1:1) and DMF/water (1:1) under anaerobic conditions were similar. However, the lifetime is considerably shorter in VP/water (1:1) mixture, a difference that can be attributed to the quenching by the monomer. The quenching rate constant was estimated from the lifetime differences

$$k_q = [(1/\tau_{VP}) - (1/\tau^\circ)]/[VP] \qquad (1)$$

where τ_{VP} is the pyrene derivative lifetime in VP/water and [VP] is the 1-vinyl-2-pyrrolidinone molar concentration in the 1:1 (v/v) solvent mixture. From eq 1, values of 4.2×10^6, 6×10^6, and 1.8×10^5 M^{-1} s^{-1} were obtained for $PySO_3^-$, $PyMe^+$, and $PyBut^+$, respectively. If it is considered that the aromatic group acts as an electron acceptor,[15] the cationic substituent in the vicinity of the pyrene ring should favor the formation of the charge transfer complex. The apparently anomalous high value for the $PySO_3^-$ quenching constant by VP could be explained in terms of a stabilization of the partial charge localized in the pyrrolidinone moiety by interaction with the proximal negative charge.

The previous data imply that VP traps nearly 65% of the singlet excited state of $PyMe^+$ under our experimental conditions. In spite of this, no significant polymerization is observed in the absence of the cocatalyst, showing that the interaction of the excited singlet/VP does not produce active free radicals. The polymerization readily takes place in the presence of the cocatalyst. This effect has to be due to an increase in the initiation rate since addition of TEA up to 0.2 M does not modify the polymerization rate of VP photoinitiated by 2′,2′-azobis(2-amidinopropane), a photoinitiator that produces radicals by a noncatalyzed unimolecular photocleavage.[16]

An interesting feature of the present results is the strong dependence of the polymerization rate both on the amine and on the sensitizer structures. The singlet excited state of aromatic hydrocarbons is efficiently quenched by amines through a mechanism that involves charge transfer from the amine to the aromatic.[17-20] Then the rate of the process depends on the electron donor capacity of the amine, the electroaffinity of the aromatic compound, and the characteristics of the solvent.[18,19,21] Quenching rate constants were obtained by measuring the decrease of the steady-state fluorescence intensity as a function of the amine concentration. Since the rate of the process is pH dependent, all measurements were carried out at pH = 11. The quenching rate constants obtained are given in Table I. Quenching rates at pHs below 8, where most of the amines are protonated, become negligible. The k_q values reported in Table I show that the quenching efficiency is considerably dependent on the amine structure and on the nature of the pyrene substituent. Thus, for alkyl-substituted amines, the quenching rate constant increases when the ionization potential of the amine decreases. For the tertiary amines, the rate of the process increases when methyl groups are substituted by the 2-hydroxyethyl group, as expected from the enhanced electron donor capacity of the hydroxyethyl group. Triethanolamine presents a quenching efficiency slightly higher than that of triethylamine, in spite of the lower ionization potential reported for the latter.[6] An enhanced reactivity of hydroxyl-substituted amines also has been reported in the quenching of aromatic carbonyl compounds,[6,22,23] and it has been interpreted in terms of the polar microenvironment provided by the hydroxyl group at the reaction site.

For a given amine, the cationic derivative, $PyMe^+$, shows the higher quenching efficiency, and the smaller value was obtained for the anionic derivative, $PySO_3^-$. This trend reflects the contribution of electrostatic effects of the ionic substituents close to the skeleton of the pyrene, as expected from the donor–acceptor properties of the intermediate exciplex formed in the quenching process.

Quenching rate constants in acetonitrile:water (1:1, v:v) for $PyMe^+$ by several amines, as well as the results obtained for the different Py derivatives employing TEA as quencher, are included in Table I. These data show that k_q values are considerably higher in AN/water than in VP/water. Nevertheless, even at relatively low amine concentrations, the quenching by tertiary amines is more important than that by the monomer, allowing almost total quenching by the cocatalyst. k_q values obtained in DMF/water (1:1, v:v) were also significantly smaller than those measured in AN/water (data not shown). These solvent effects on the quenching rate can be understood in terms of the high tendency of VP and DMF to accept a proton in a solute-to-solvent hydrogen bond, as measured by the solvent β parameter.[14] A value of $k_q = 3 \times 10^9$ M^{-1} s^{-1} was determined for Py quenching by TEA in acetonitrile.[8] This value is considerably higher than that measured in aqueous mixtures and supports the conclusion that hydrogen bonding in the amine decreases its capacity to donate an electron to the excited aromatic compound.

From the $k_q\tau_s$ values it is possible to obtain the fraction of excited singlets (*f*) that are deactivated by the amine:

$$f = \frac{k_q\tau_s[\text{amine}]}{1 + k_q\tau_s[\text{amine}]} \qquad (2)$$

If the photoinitiation is due to the interaction of the singlet excited pyrene–amine, the initiation rate will be proportional to *f* and hence

$$R_p^{\,2} - (R_p)_0^{\,2} \propto f \qquad (3)$$

where $(R_p)_0$ stands for the polymerization rate in the absence of the amine.

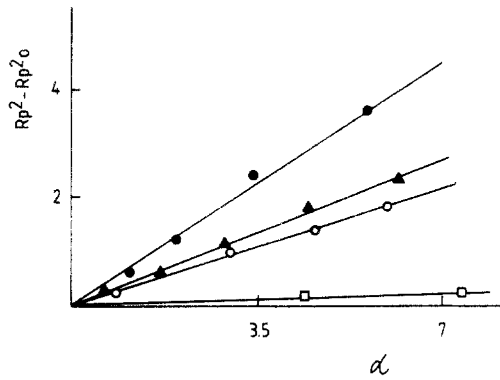

Figure 1. Polymerization rates as a function of the fraction of PyMe$^+$ singlets deactivated by different amines (VP:water (1:1 v:v): triethanolamine (●); *N*-methyldiethanolamine (▲); triethylamine (○); *N,N*-diethylethanolamine (□).

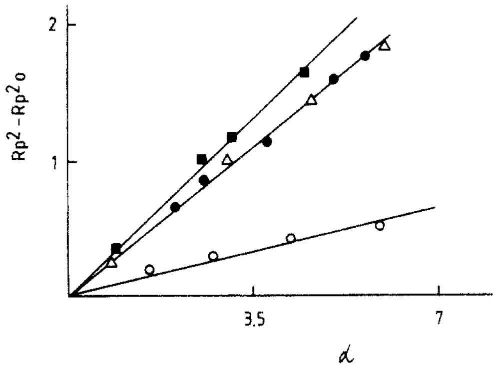

Figure 2. Polymerization rates as a function of the fraction of pyrene derivatives deactivated by triethylamine (VP:water (1:1 v:v): PyBut$^+$ (■); PyMe$^+$ (△); Py (●); PyBut$^-$ (○).

Table II. Polymerization Efficiencies at Total Singlet Quenching[a]

	$R_p^2 - (R_p)_0^2$ (arbitrary units)			
amine	PyMe$^+$	Py	PyBut$^+$	PyBut$^-$
triethanolamine	6.4	6.8	6.2	0.6
triethylamine	3.2	3.2	3.3	0.9
N-methyldiethanolamine	3.8	4.3	4.1	0.46
N,N-dimethylethanolamine	0.4		1.9	0.14
diethylamine	<0.1			

[a] In VP:water (1:1 v:v); the value of R_p^2 measured in matched solutions of MHB was 4.4.

Plots of $R_p^2 - (R_p)_0^2$ as a function of f for PyMe$^+$ and several amines are shown in Figure 1. Figure 2 shows the data obtained employing several sensitizers and TEA as quencher. The plots were linear for all the systems considered, indicating that the photoinitiation arises from the interaction of the excited singlet with the amine. In particular, the proportionality between the initiation rate and the fraction of singlet quenched by the amine allow us to discard possible photoinitiation from the triplet state and would indicate that primary radicals do not participate in the termination of the polymerization chain. Also, extrapolation of the data at $f = 1$ leads to the polymerization efficiency at total singlet quenching by the cocatalyst, thus allowing an estimation of the fraction of active radicals produced in the quenching process. These data are summarized in Table II and show that pyrene and its cationic derivatives are efficient photoinitiators of the VP polymerization in the presence of triethanolamine, triethylamine, and *N*-methyldiethanolamine. However, *N,N*-dimethylethanolamine is a poor photoinitiator, and secondary amines do not initiate the polymerization, even under conditions of total singlet quenching by the amine. For all the amines considered, PyBut$^-$ leads to lower polymerization rates and PySO$_3^-$ does not act as a photoinitiator.

Table III. Photobleaching Quantum Yields in 1:1 Water:AN[a]

amine	PyMe$^+$	Py	PyBut$^+$	PyBut$^-$
triethylamine	0.08	0.07	0.08	0.05
triethanolamine	0.042	0.024	0.022	0.02
N-methyldiethanolamine	0.034	0.021	0.020	0.007
N,N-dimethylethanolamine	0.017	0.02	0.015	0.009
diethylamine	0.005			

[a] Values measured under conditions of total singlet quenching by the amine.

Allen et al.[5,24] have reported a different dependence of the polymerization rate with the amine structure, employing benzophenone derivatives as photoinitiators and acrylates as monomer. However, these experiments employed a constant amine concentration expressed in % (w/v) and did not consider possible changes on the radical behavior with the amine structure. Thus, it is well known that ground-state carbonyls react with α-aminoalkyl radicals[23,25–28] in a process that could be dependent on the amine structure.

To obtain an estimation of the polymerization efficiency under the same experimental conditions, we measured the polymerization rate photoinitiated by 3-methyl-3-hydroxy-2-butanone (MHB), a compound whose photocleavage can be considered as almost quantitative in aqueous media.[29] For this compound, a value of 4.4 was obtained for $R_p^2 - (R_p)_0^2$. Since it can be considered that amines do not modify $k_p/k_t^{1/2}$, the data of Table II indicate that the interaction of Py or its cationic derivatives with tertiary amines is an extremely efficient photoinitiator system. In particular, for triethanolamine, the most efficient coinitiator, the photoinitiation efficiency is ca. 1.5 times higher than that obtained with MHB. Similarly, the addition of TEA or *N*-methyldiethanolamine leads to polymerization efficiencies similar to those obtained employing MHB.

The irradiation of Py, its cationic derivatives, and PyBut$^-$ in the presence of tertiary amines leads to the aromatic consumption. The photobleaching quantum yield was evaluated in acetonitrile:water (1:1) solution following the decrease in the absorbance at the longest wavelength band. In all cases the pyrene consumption follows a good first-order kinetics, and its yield increases proportionally to the singlet fraction quenched by the amine. These results indicate a photobleaching mechanism involving the excited singlet. Table III summarizes the photobleaching quantum yields obtained using several amines as coreactants under conditions of total deactivation of the singlet excited state. Photobleaching quantum yields follow the order

$$\mathrm{PyMe^+} > \mathrm{Py} \simeq \mathrm{PyBut^+} > \mathrm{PyBut^-} \gg \mathrm{PySO_3^-}$$

These data show that photoconsumption yields, for a given amine, follow a trend similar to that of the singlet quenching rate constant. The same conclusion is reached if the data obtained employing different hydroxylamines are considered. For all the pyrene derivatives studied, secondary amines, even when extrapolated to total singlet quenching, do not photobleach the pyrene and, for hydroxylamines, the photoconsumption increases with the number of hydroxyl groups. In all systems considered, substitution of acetonitrile either by water or by VP decreases the photobleaching quantum yields. Thus, a value of 0.22 has been previously reported for Py photobleaching by TEA in acetonitrile.[8] This value is consid-

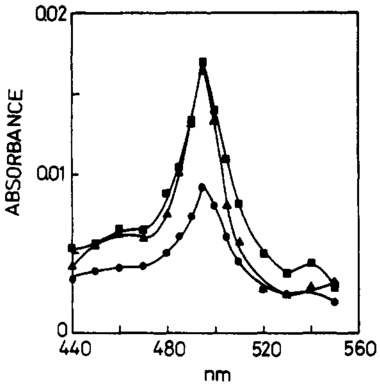

Figure 3. Transient absorption spectra of pyrene derivatives–TEA in VP:water (1:1): PyBut$^+$ (■); Py (▲); PyBut$^-$ (●). The delay time after the laser pulse was 500 ns.

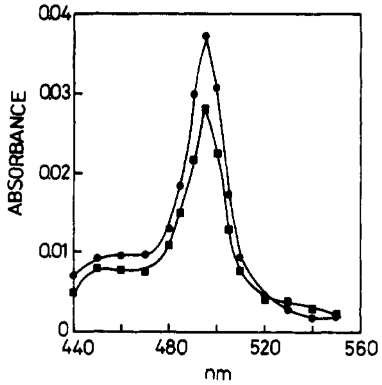

Figure 4. Transient absorption spectra of PyBut$^+$–amines (acetonitrile:water (1:1)): TEA (■); triethanolamine (●). The delay time after the laser pulse was 1 μs.

erably higher than that measured in the present work in AN:water (1:1). Furthermore, addition of the monomer reduces the photobleaching, and in VP:water (1:1) the consumption yields are ca. 50% smaller than those measured in AN:water.

The photoinitiation, as in organic media,[9] could be represented by a mechanism involving the interaction of the pyrene anion, either free or as an ion pair, with the monomer, followed by initiation by the amine-derived radicals (eqs 4–6)

$$Py^- + VP \rightarrow Py + VP^- \qquad (4)$$

$$VP^- + A^+ \rightarrow VP(H)^\bullet + A^\bullet \qquad (5)$$

or

$$(Py^- A^+) + VP \rightarrow Py + A^\bullet + VP(H)^\bullet \qquad (6)$$

where A stands for the amine and $A^\bullet$ is the amine-derived α radical. Both $A^\bullet$ and $VP(H)^\bullet$ radicals should be able to initiate the polymerization chain. If it is considered that Py^- reactions lead to bleaching in the absence of the monomer,[9,20] the occurrence of reaction 4 accounts for the protection afforded by VP addition. The proposed mechanism implies that the efficiency as photoinitiator of a given pyrene/amine pair must reflect the capacity of the system to give the pyrene anion.

The time-resolved absorption spectra of the transients generated in the interaction of the pyrene derivatives and TEA in VP:water (1:1) and acetonitrile:water (1:1) mixtures were measured in the 450–550-nm region, where the absorbance of the pyrene radical anion prevails[20,30,31] (Figure 3). In agreement with the low efficiency as photoinitiator of $PySO_3^-$, no transient could be observed for this compound. This reflects the electrostatic repulsion between the negative charge localized in the pyrene ring and the vicinal SO_3^- anion.

Transient spectra were similar in the two solvent mixtures and similar to that previously reported in nonaqueous media. The intensity of the absorption, monitored at 495 nm, decays monoexponentially with a shorter lifetime in VP:water than in AN:water. The decrease in lifetime due to the VP addition depends on the aromatic compound considered, and the smallest value was observed for PyBut$^-$. Furthermore, assuming that ϵ_{495} for the anions of PyBut$^-$, PyBut$^+$, and Py are similar, the relative intensities of the initial absorbances correlate with the relative photopolymerization initiation efficiencies, supporting an initiation mechanism involving the interaction of VP with the pyrene-derived radical anion. A similar conclusion can be deduced from a comparison of the initiation efficiencies with TEA and triethanolamine as cocatalyst. Figure 4 shows that the interaction of PyBut$^+$ with triethanolamine leads to a higher pyrene anion radical quantum yield than the interaction with TEA. This result is in agreement with the higher initiation efficiency of the hydroxyalkylamine.

In conclusion, the present data indicate that the Py/amine system is a highly efficient source of active radicals in aqueous solutions and that the mechanism of the process involves, as in nonaqueous solutions, the production of the pyrene-derived radical anion. Also, they show that the rate of singlet quenching, the photopolymerization efficiency, and the bleaching rate in the absence of monomer are mostly determined by the capacity of the pyrene/amine pair to generate the pyrene-derived radical anion.

Acknowledgment. This work was supported by FONDECYT (Grant 464-91) and DICYT (Universidad de Santiago de Chile). The use of the GREG 200 phase/modulation fluorometer was made possible through an Interuniversity Grant (FONDECYT, Grant 4012/86).

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