Polymerization Photoinitiated by Pyrene in the Presence of Triethylamine: Interaction between Monomers and Pyrene-Derived Reaction Intermediates[1]

M. V. ENCINAS,[*,2] C. MAJMUD,[2] E. A. LISSI,[*,2] AND J. C. SCAIANO[3]

Departamento de Química, Universidad de Santiago de Chile, Casilla 5659, Correo 2, Santiago, Chile, and Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6

Received June 1, 1990;
Revised Manuscript Received September 21, 1990

There have been a number of studies on the photoinitiated polymerization of vinyl monomers using excited carbonyl or aromatic hydrocarbon compounds in the presence of amines.[4,5] It is well established that the production of the radicals that initiate the polymerization proceeds through a charge-transfer mechanism.[4-8] In a recent publication, we examined the polymerization of methyl methacrylate sensitized by the pyrene-triethylamine system;[4] we showed that this system is an efficient photoinitiator in polar solvents and suggested that the active free radicals are produced from the interaction of the monomer with the ion pair and/or the hydropyrenyl radicals. In order to understand better the mechanism of the photoinitiation, we have examined the effect of vinyl monomers on the transients involved in the pyrene-triethylamine system using nanosecond laser flash photolysis techniques.

Experimental Section

Methyl methacrylate (MMA), styrene, vinyl acetate, and triethylamine (TEA), all from Aldrich, were vacuum distilled prior to their use.

Photoinitiation efficiencies under steady-state irradiation were obtained from measurements of polymerization rates. Di-*tert*-butyl peroxide was employed as a reference initiator under conditions of matched absorbances. Polymerization rates were obtained by the dilatometric techniques described previously.[4,7]

All time-resolved experiments were carried out in oxygen-free samples using pulses (337.1 nm, ~8 ns, ≤10 mJ/pulse) from a Molectron UV-24 nitrogen laser for excitation. Transient absorptions were monitored by using a computerized system described elsewhere.[9,10]

Results and Discussion

The time-resolved absorption spectra from irradiated pyrene-TEA mixtures in acetonitrile-ethyl acetate solution are shown in Figure 1. The absorption band with λ_{max} = 488 nm corresponds to the pyrene anion (Py^{-}), while the band at ~400 nm has been assigned to absorption by the 1-hydro-1-pyrenyl radical, $PyH^{\bullet}$.[6,11,12] The relative optical densities of the $PyH^{\bullet}$ and Py^{-} bands lay between those reported[6] when acetonitrile or acetone are employed as solvents. This result is that expected from the dependence of the hydropyrenyl yield on solvent polarity. The transient spectra in acetonitrile-MMA mixtures were quite similar to those determined when ethyl acetate was used as cosolvent. Similar results were obtained with styrene or vinyl acetate.

The pyrene anion band[6,13,14] measured at 488 nm showed, under our experimental conditions, a monoexponential decay with $\tau \sim 1$ μs, and after ca. 6 μs (spectrum B in Figure 1) only the signals due to the long-lived radical remain. The monoexponential behavior of the radical ions in this system is not unprecedented, and it has been attributed to the formation of an ion pair in equilibrium with the free ions.[6] The initial absorption intensity is independent of the addition of monomers, but the anion lifetime can be significantly shortened, particularly by MMA. This effect is less noticeable for styrene and negligible for vinyl acetate. The rate constants for pyrene anion quenching by the vinyl monomers were obtained from a plot of the transient decay rate as a function of the monomer concentration. These data are given in Table I and show that the pyrene anion is efficiently quenched by MMA but it is unaffected by vinyl acetate.

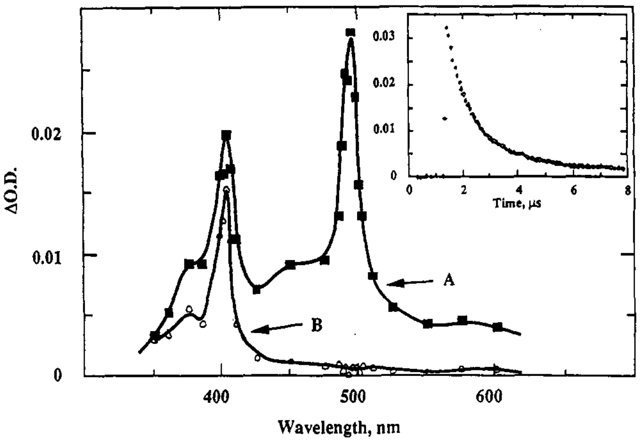

Figure 1. Transient absorption spectrum of pyrene-TEA in an acetonitrile-ethyl acetate solution. Delay time after the laser pulse: 500 ns for A and 6 μs for B. Inset: typical first-order decay trace monitored at 488 nm.

The absorption decay at 400 nm is complex, since at this wavelength both the residual anion and the pyrene radical, $PyH^{\bullet}$, show significant absorption. However, at times longer than 5 μs the remaining decay could be readily fitted with an exponential with a lifetime of ca. 10 μs, which we assign to $PyH^{\bullet}$ radicals and was not significantly affected by the monomer addition. However, its intensity, obtained by extrapolating to zero time the slow-decay component, decreases when the monomer concentration increases. These results are consistent with monomer quenching of the precursor of the radical $PyH^{\bullet}$.

Steady-state photolysis of pyrene in the presence of TEA leads to pyrene consumption.[4] Styrene addition, as previously reported for MMA, decreases the photoconsumption rate. Plots of ln ($[Py]_0/[Py]$) as a function of time were linear, showing that photobleaching follows first-order kinetics.[4] Values of Φ^0/Φ (where Φ^0 and Φ are the pyrene photoconsumption yields in the absence and in the presence of monomer) are shown in Figure 2. This figure shows that the data follow a Stern-Volmer type relationship. The slopes of the plots (K_{SV}) are given in Table I. Under the conditions employed, protection by the monomers cannot be due to singlet quenching and must be related to trapping of the intermediates produced in the excited pyrene-TEA interaction. The time-resolved experiments show conclusively that the species trapped is the pyrene radical anion, Py^{-}. In agreement with this, the relative efficiency of the monomers in reducing pyrene photoconsumption parallels their reactivity toward the pyrene radical anion; i.e., MMA is more efficient than styrene and vinyl acetate is ineffective. However, the K_{SV} value obtained for MMA is larger than that derived from time-resolved experiments (ca. 0.5 M^{-1}). This difference can probably be attributed to some shortening of the pyrene anion due to second-order processes at the rather high concentrations produced under laser irradiation.

Polymerization rates were determined employing acetonitrile as cosolvent. The initiation efficiencies (f_i)

0024-9297/91/2224-2111$02.50/0

Table I
Rate Constants for the Interaction Pyrene-Derived Reaction Intermediates with Monomers and Their Photoinitiation Efficiencies[a]

monomer	k,[b] $M^{-1}\,s^{-1}$	K_{SV},[c] M^{-1}	f_i
MMA	5.3×10^5	3.75	0.28
styrene	1×10^5	1.35	0.15
vinyl acetate			0.006

[a] Initial solvent, acetonitrile–ethyl acetate or acetonitrile–benzene 1:1 (v:v); [TEA] = 0.06 M. [b] Rate constants for Py^- quenching. [c] Stern–Volmer constant for pyrene photoconsumption.

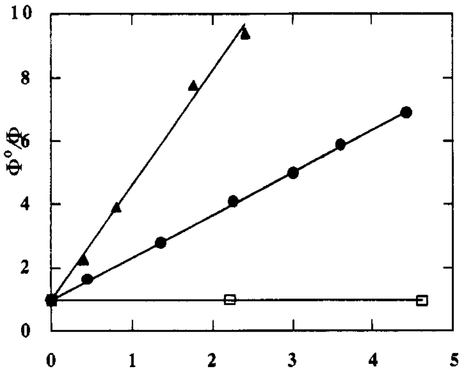

Figure 2. Effect of MMA (▲), styrene (●), and vinyl acetate (□) addition upon the pyrene photoconsumption yield.

obtained employing TEA concentration so as to achieve essentially complete quenching of the pyrene fluorescence are given in Table I. These efficiencies were obtained employing di-*tert*-butyl peroxide as a reference initiator.[15] The data given in Table I show that while pyrene–TEA initiates MMA polymerization efficiently, it is very ineffective when vinyl acetate is employed as monomer. The trend of photoinitiation efficiencies is then similar to that found for the interaction of Py^- with the monomers and the pyrene photobleaching protection. All these facts would indicate that the interaction pyrene anion–monomer must be the key step in the photoinitiation mechanism.

The 488-nm Py^- transient absorption quenched by the monomer can be due to Py^- present as part of an ion pair (either a charge-transfer complex, a geminate pair, or a secondary pair) or to the free-radical anion. The rather long lifetimes measured in the present work (~1 μs) rule out geminate ion pairs ($\tau < 2$ ns)[6] but can correspond to either the free anion or to nongeminate ion pairs. The fact that the monomer increases the decay rate of the transient absorption of 488 nm without changing its initial intensity would indicate that the monomer interacts with the long-lived, Py^- radical anion, free or in equilibrium with the random ion pair.[6] There are several other examples, in addition to the pyrene system involving of long-lived radical-ion pairs. For example, Jones et al. have reported on systems involving quinones, particularly chloranil.[16,17]

Hirata et al.[6] have proposed the deactivation mechanism of Scheme I

Scheme I

$$\text{products} \leftarrow (\mathrm{Py}^{\cdot-}\cdots\mathrm{TEA}^+) \rightleftharpoons \mathrm{Py}^- + \mathrm{TEA}^+ \rightarrow \text{products}$$

where "products" stands for nonionic species (i.e., Py + TEA or $\mathrm{PyH}^\bullet$ + $\mathrm{TEA}^\bullet$). Secondary reactions of the hydropyrenyl radical probably account for the pyrene consumption observed. Efficient free-radical polymerization has been observed in the presence of MMA.[4] Since MMA is a monomer with rather high electron affinity,[18] the active free radicals may result from the interaction of free pyrene anion and/or the nongeminate radical pair with the monomer;[19] i.e.

$$\mathrm{Py}^- + \mathrm{MMA} \rightarrow \mathrm{Py} + \mathrm{MMA}^- \qquad (1)$$

$$\mathrm{MMA}^- + \mathrm{TEA}^+ \rightarrow \mathrm{MMA(H)}^\bullet + \mathrm{TEA}^\bullet \qquad (2)$$

or

$$(\mathrm{Py}^{\cdot-}\cdots\mathrm{TEA}^+) + \mathrm{MMA} \rightarrow \mathrm{Py} + \mathrm{TEA}^\bullet + \mathrm{MMA(H)}^\bullet \qquad (3)$$

Both, $\mathrm{TEA}^\bullet$ and $\mathrm{MMA(H)}^\bullet$ radicals should be able to initiate the free-radical polymerization chain. This mechanism can explain the effect of the monomer on the 488-nm transient, the decrease in $\mathrm{PyH}^\bullet$ yield, the dependence of the pyrene bleaching rate on the monomer concentration, and the invariance of the $\mathrm{PyH}^\bullet$ decay with the olefin concentration.

In this mechanism the initiation efficiency for a given monomer must be related to its capacity to reduce the pyrene photobleaching rate, since both are determined by the pyrene anion–monomer interaction kinetics. This rate constant will be determined by either the monomer electron affinity (process 1) or the stability of the monomer-derived radical (process 3). The high electron affinity of MMA can explain the faster interaction observed for this monomer. On the other hand, it can be expected that neither reaction 1 nor 3 will be particularly favored when vinyl acetate replaces MMA as monomer.

In conclusion, the photoinitiation of vinyl polymerization by the pyrene–TEA system is due to the reaction of the pyrene radical anion with the monomers; since this process results in the regeneration of pyrene, the monomers effectively prevent the photobleaching of pyrene. Among the monomers examined herein, MMA reacts most efficiently with Py^-.

Acknowledgment. We are grateful to FONDECYT (Grant 1070/88) and DICYT (Universidad de Santiago de Chile) for financial support.

References and Notes

(1) Issued as NRCC-32295.
(2) Universidad de Santiago de Chile.
(3) National Research Council of Canada.
(4) Encinas, M. V.; Majmud, C.; Garrido, J.; Lissi, E. A. *Macromolecules* **1989**, *22*, 563.
(5) Hageman, A. J. *Prog. Org. Coat.* **1985**, *13*, 123.
(6) Hirata, Y.; Saito, T.; Mataga, N. *J. Phys. Chem.* **1987**, *91*, 3119.
(7) Encinas, M. V.; Garrido, J.; Lissi, E. A. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 139.
(8) Schnabel, W. *J. Radiat. Curing* **1986**, *13*, 26.
(9) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.
(10) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.
(11) Okada, T.; Tashita, N.; Mataga, N. *Chem. Phys. Lett.* **1980**, *75*, 220.
(12) Okada, T.; Mori, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3398.
(13) Hirata, Y.; Mataga, N. *J. Phys. Chem.* **1985**, *89*, 2439.
(14) Raisa, W.; Helge, L. *Finn. Chem. Lett.* **1988**, *15*, 71.
(15) Lissi, E. *Can. J. Chem.* **1974**, *52*, 2491.
(16) Jones, G., II; Mouli, N. *J. Phys. Chem.* **1988**, *92*, 7174.
(17) Jones, G., II; Haney, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *110*, 1922.
(18) Schafer, O.; Allan, M.; Haselbach, E.; Davidson, R. S. *Photochem. Photobiol.* **1989**, *50*, 717.
(19) Wayner, D. D. M. In Redox Properties. *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, Chapter 14.

Registry No. TEA, 121-44-8; MMA, 80-62-6; pyrene, 129-00-0; styrene, 100-42-5; vinyl acetate, 108-05-4.