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Methyl Methacrylate Polymerization Photoinitiated by Pyrene in the Presence of Triethylamine

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ABSTRACT: The polymerization of methyl methacrylate photosensitized by pyrene and anthracene in the presence of triethylamine has been investigated. Under all conditions employed, anthracene polymerization efficiencies were very low. On the other hand, pyrene is an efficient sensitizer in the presence of triethylamine. The efficiency observed is larger in polar solvents. From the fact that pyrene consumption is prevented by methyl methacrylate and the lack of pyrenyl groups incorporated into the polymer, it is proposed that the active free radicals are produced as a consequence of the interaction of the monomer with the pyrene–triethylamine complex and/or the PyH$^\bullet$ radical.

Introduction

The photopolymerization of vinyl monomers using a photoinitiator and triethylamine as co-initiator has received the attention of many research groups,[1,2] but most of the studies have been carried out using carbonyl compounds as sensitizers.[3–6] For these systems the photoinitiation mechanism is well established, and it proceeds through a charge-transfer complex that decomposes giving free radicals that can initiate the polymerization.[3,5–8] On the other hand, sensitization by aromatic hydrocarbons has been much less studied.[9,10] In particular Kubota and Ogiwara[10] have studied the polymerization of acrylonitrile and methyl methacrylate photoinitiated by aromatic hydrocarbon–amine mixtures. With regard to methyl methacrylate, these authors reported that phenanthrene and naphthalene were efficient photoinitiators in the presence of triethylamine (TEA). However, anthracene was almost completely ineffective. A mechanism was proposed in which radicals are produced from an aromatic–TEA charge-transfer complex. In the present work, we have carried out an analysis of the effect of the solvent polarity and TEA concentration on the photoinitiation efficiency. From these data and an analysis of the effect of the monomer concentration on the sensitizer bleaching rate, further insight is obtained on the initiation mechanism.

Experimental Section

The polycyclic aromatic hydrocarbons (PAH) employed, pyrene (Py) and anthracene (An) (Fluka), were purified by recrystallization from ethanol. Triethylamine (TEA) and methyl methacrylate (MMA) were vacuum distilled prior to their use.

Photopolymerization rates, in arbitrary units (millimeters of contraction/minute) were measured in Pyrex dilatometers under nitrogen at room temperature (20 ± 2 °C). The samples were irradiated with light from a medium-pressure mercury lamp. When An was employed, a glass filter was used to isolate the 366-nm band. Di-*tert*-butyl peroxide and azobis(isobutyronitrile) (AIBN) were employed as reference photoinitiators for Py and An, respectively. Matched solutions of the aromatic polycyclic and the reference compounds were irradiated under identical conditions. TEA addition to the reference initiators did not produce any significant change in the polymerization rates. Low absorbances (below 0.4) were employed to avoid the generation of an inhomogeneous free radical distribution.[11]

Polymer molecular weights were determined viscosimetrically in benzene at 30 °C, $\log \mathrm{MW} = 1.31 \times \log (\eta/5.2 \times 10^{-5})$ with η in g/100 mL.[12]

Quenching experiments of PAH by TEA were carried out in a Perkin-Elmer LS-5 spectrofluorimeter by measuring the fluorescence yield as a function of the TEA concentration. Bleaching experiments were carried out by irradiation of the samples as described for the photopolymerization. The bleaching was evaluated from the change in its near-UV absorption in a Shimadzu-160 spectrophotometer. Carbon tetrachloride was employed as reference.[13] The position and the fine structure of the UV absorption band of pyrene are not altered by the amine addition. Similarly, they were not modified after irradiation of the samples.

Results and Discussion

Polymerization rates photoinitiated by Py were measured as a function of TEA concentration with acetonitrile or benzene as solvent. The results obtained are given in Table I. These data show that Py is a poor initiator both in benzene and in acetonitrile. These results can be explained in terms of the low quenching rate constant ($k_q = 4 \times 10^6$ M^{-1} s^{-1}) reported for the excited singlet pyrene deactivation by MMA.[15] TEA addition notably increases the photopolymerization rate. The effect obtained is more relevant when acetonitrile is employed as solvent. Figure 1 shows that the polymerization rate photoinitiated by Py and TEA changes almost linearly with the percentage of acetonitrile in the solvent mixture. This increase can be

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Table I
Polymerization Rates of Methyl Methacrylate

initiator	solvent[a]	[TEA], mM	R_p (arbitrary units)	f_{exp}
pyrene	acetonitrile		<0.03	
		0.15	0.12	0.021
		0.45	0.20	0.11
		1.5	0.27	0.20
		5.0	0.3	0.24
		10.0	0.3	0.24
		40	0.32	0.28
		50	0.31	0.26
		100	0.33	0.29
	benzene		<0.03	
		0.45	0.05	0.007
		3	0.083	0.018
		10	0.10	0.026
		20	0.12	0.037
		100	0.12	0.037
di-*tert*-butyl peroxide	benzene		0.62	1[b]
	acetonitrile		0.61	1[b]
		60	0.61	1

[a] Monomer:solvent (1:1) v:v. [b] Reference 14.

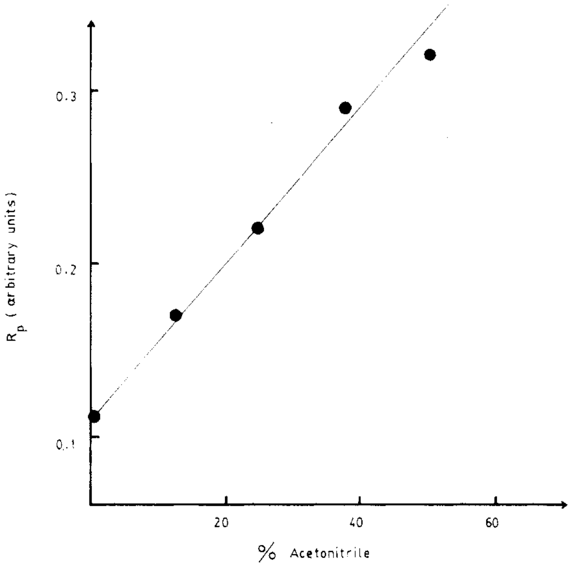


Figure 1. Solvent polarity effect on the polymerization rate. Mixtures comprise equal volumes of solvent (benzene:acetonitrile) and monomer. Photoinitiator system: pyrene–TEA (0.08 M).

related to a change in the initiation efficiency, since the photopolymerization sensitized by di-*tert*-butyl peroxide shows a rate that is nearly independent of the solvent and the TEA concentration (see Table I). This result shows that neither the solvent nor TEA addition significantly modifies the $k_p/k_t^{1/2}$ ratio.

Polymerization sensitized by Py–TEA does occur, even in the more polar solvent, by a free radical mechanism. The relationship obtained between the polymerization rate and the polymer chain length is shown in Figure 2. The data show a linear behavior, with a slope equal to 1, as expected for a simple free radical polymerization. Furthermore, the chain lengths measured are similar to those obtained when the monomer is polymerized at the same rate, under identical conditions, employing di-*tert*-butyl ketone, a typical free radical initiator,[16] as sensitizer.

The initiation efficiency, f_{exp}, can be obtained under matched conditions from

$$f_{exp} = (R_p/R'_p)^2 f' \qquad (1)$$

where R_p is the polymerization rate measured, R'_p is the photopolymerization rate employing a reference initiator, and f' is the reference initiator efficiency. Values obtained by this procedure, employing di-*tert*-butyl peroxide as reference initiator, are also given in Table I.

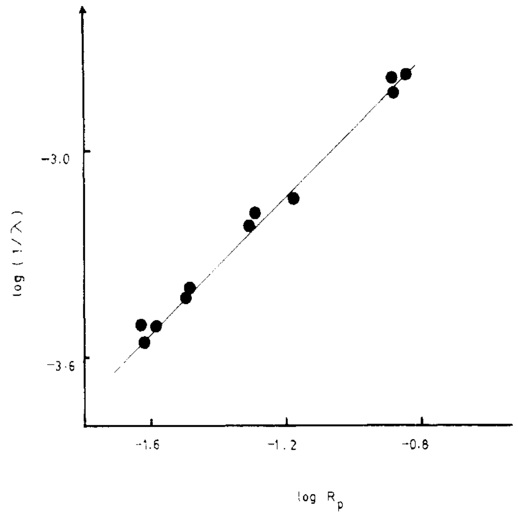


Figure 2. Polymer chain length as a function of polymerization rate in MMA:acetonitrile (1:1); [TEA] = 0.06 M; sensitizer, pyrene.

Table II
Singlet Quenching of Polycyclic Aromatic Hydrocarbons by TEA

PAH	solvent[a]	$k_q\tau_s$[b]	f
pyrene	MMA:benzene	505	0.036
pyrene	MMA:acetonitrile	670	0.29
anthracene	MMA:benzene	13.5	
anthracene	MMA:acetonitrile	18	

[a] 1:1 v:v. [b] Measured under nitrogen.

TEA is an efficient deactivator of Py singlets. Quenching rate constants in the solvent mixtures employed in the polymerization experiments were obtained by measuring the fluorescence decrease as a function of amine addition. The Stern–Volmer plots were linear in all the range of TEA concentrations. The values of the rate constants obtained for Py and An are given in Table II.

From the $k_q\tau_s$ values it is possible to obtain the fraction of Py singlets that are deactivated by the amine according to

$$\alpha = k_q\tau_s[\mathrm{TEA}]/(1 + k_q\tau_s[\mathrm{TEA}]) \qquad (2)$$

If the photoinitiation is due to the interaction PAH*–TEA, the experimental efficiency will be given by

$$f_{exp} = f_0 + (f - f_0)\alpha \qquad (3)$$

where f_0 is the initiation efficiency in absence of TEA, and f is the number of macroradicals produced per PAH*–TEA interaction.

Values the f_{exp} plotted as a function of α for Py are shown in Figure 3. The almost linearity of these plots shows that photoinitiation can be considered an excited singlet process. Values obtained by extrapolation of f_{exp} to $\alpha = 1$ are included in Table II.

Photopolymerization efficiencies by An*–TEA are low both in benzene and in acetonitrile. Even under conditions such that a large proportion of the An singlets are quenched by the amine ($\alpha = 0.64$), the initiation efficiencies (AIBN employed as reference) are smaller than 0.01.

PAH photobleaching is promoted by TEA. The PAH consumption yields obtained in different solvents under conditions of total singlets quenching are given in Table III. PAH singlet states are deactivated by amine through a charge-transfer mechanism that implies an electron transfer from the amine to the aromatic.[16,17] Recent

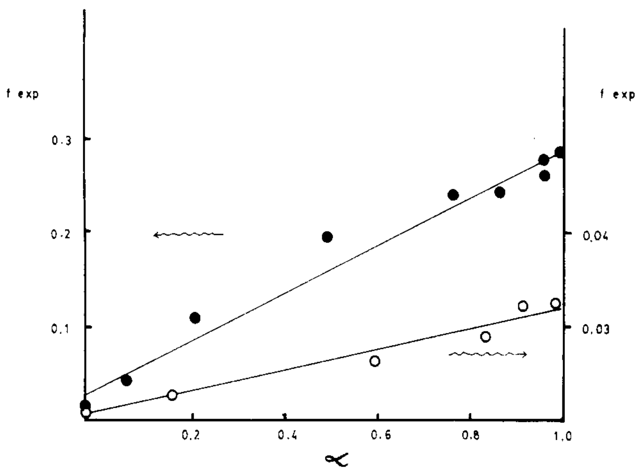


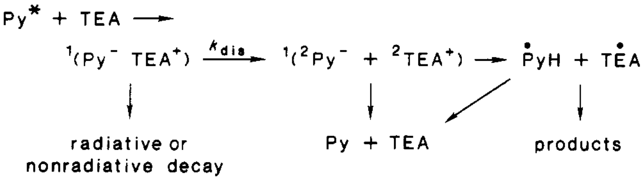
Figure 3. Photoinitiation efficiency (f_{exp}) as a function of the fraction of pyrene singlets quenched by TEA (0.08 M): (●) MMA:acetonitrile (1:1); (○) MMA:benzene (1:1).

Table III
PAH Photobleaching by TEA in Acetonitrile:Benzene Mixtures

PAH	solvent	Φ_{bleach}
pyrene[a]	acetonitrile	0.22
	acetonitrile:benzene (5:1)	0.18
	acetonitrile:benzene (2:1)	0.13
	acetonitrile:benzene (1:1)	0.11
	acetonitrile:benzene (1:2)	0.038
	benzene	0.0007
anthracene[b]	acetonitrile	0.30
	acetonitrile:benzene (1:1)	0.23
	acetonitrile:benzene (1:2)	0.12
	benzene	0.01

[a] TEA = 60 mM. [b] TEA = 36 mM.

Scheme I



studies[18-20] using picosecond laser spectroscopy have suggested that the charge-transfer complex, for the system Py*–TEA, decomposes mainly to a radical ion pair $^1(^2\mathrm{Py}^- + {}^2\mathrm{TEA}^+)$; see Scheme I.

The rate constant of the proton transfer[18,19] and the quantum yield of pyrene radical anion, Φ_{radical},[18,21] depend strongly upon the nature of the amine. Furthermore, Weller[22] has shown that the rate constant of the complex dissociation (k_{dis}) into separated radical ion pairs also depends notably on the dielectric constant of the solvent. For example, for the pair pyrene–dimethylaniline, the value of k_{dis} is equal to 490×10^6 s^{-1} in acetonitrile as solvent and $\ll 10^6$ s^{-1} in diethyl ether.

The dependence of the photobleaching yields with the solvent polarity can be explained in terms of the free energy gain obtained with the decomposition of the complex into radical ions in a polar solvent.[22] This process could be followed by proton transfer from this pair to produce the pyrenyl radical and, from this, the pyrene bleaching.

Kubota and Ogiwara[10] have proposed that photoinitiation is related to the occurrence of process

$$^1(\mathrm{Py^-TEA^+}) \xrightarrow{k_d} \dot{\mathrm{R}} \tag{4}$$

followed by

$$\dot{\mathrm{R}} + \text{monomer} \rightarrow \dot{\mathrm{M}} \tag{5}$$

without discussing the nature of R$^\bullet$. If a mechanism of radical production such as that depicted in Scheme I is considered, the radicals that could lead to initiation will be $\mathrm{Et_2N{-}\dot{C}H{-}CH_3}$ and/or PyH$^\bullet$. To test the participation of PyH$^\bullet$ radicals in the initiation step, we have measured the extent of Py decrease in the solution after precipitation of the produced polymer. Almost total recovery of the Py (evaluated from the UV spectrum) was obtained after producing 1.6×10^{-4} M polymer chain in a process photoinitiated by 6.7×10^{-6} M pyrene. These data conclusively show that Py is not consumed in the initiation step.

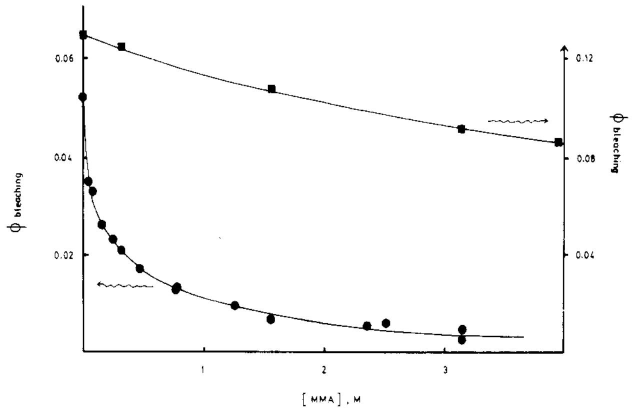


Figure 4. Effect of the MMA addition upon the PAH photobleaching by TEA; initial solvent, acetonitrile:ethyl acetate (1:1): (●) pyrene ([TEA] = 0.06 M); (■) anthracene ([TEA] = 0.4 M).

Further insight on the initiation mechanism can be achieved by evaluating the effect of MMA addition upon Py photobleaching yield. The results obtained are given in Figure 4. These data show that MMA addition markedly decreases the Py photobleaching yield. This decrease cannot be due to a competition in the Py singlets quenching ($k_{\mathrm{TEA}}[\mathrm{TEA}] > k_{\mathrm{MMA}}[\mathrm{MMA}]$) or to a change in the polarity of the medium (which is kept almost constant by keeping constant the amount of MMA plus ethyl acetate). This lack of photobleaching in the presence of MMA is also compatible with the total recovery of Py observed after the polymerization. Two explanations can be given to account for the high polymerization efficiencies and very low Py photobleaching obtained at high MMA concentration. The first one involves the occurrence of

$$\mathrm{PyH^\bullet + MMA \rightarrow MMA(H)^\bullet + Py} \tag{6}$$

a reaction that could be driven by the weakness of the Py–H bond in the pyrenyl radical. The second one involves an interaction of the monomer with the exciplex and/or the geminate ion pair:

$$^1(\mathrm{Py^-TEA^+}) + \mathrm{MMA} \rightarrow \mathrm{Py} + \mathrm{R^\bullet} \tag{7}$$

Deactivation of exciplexes in bimolecular processes has been reported in several systems.[23] This process could lead, when Py is employed, to a pair of MMA(H)$^\bullet$ and $\mathrm{Et_2N\dot{C}HCH_3}$ radicals.

The present data are insufficient to allow a distinction between processes 6 and 7. Transient spectroscopy measurements are in progress to establish the effect of MMA on the quantum yield and lifetime of the PyH$^\bullet$ radical when Py is irradiated in the presence of amines.

Anthracene singlets quenching by TEA is also a diffusion-controlled process, and the energetic of the process (measured by $E^0_{\mathrm{TEA/TEA^+}} - (E_{1/2})_{\mathrm{PAH/PAH^+}} - E_{\mathrm{PHA^*}}$) differs by less than 0.1 V from that of pyrene. Also, extensive An bleaching is observed when this compound is irradiated in the presence of TEA. In spite of this, the pair An*–TEA is considerably less efficient than the Py*–TEA pair as a photoinitiator system. This lack of photoinitiation could be explained in terms of the inefficiency of processes 6 and/or 7. In agreement with this, the data given in Figure 4 show that An photobleaching is considerably less sensitive to MMA addition than Py photobleaching.

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Registry No. Py, 123-00-0; TEA, 121-44-8; MMA, 80-62-6.

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A New Electron-Rich Network Polymer: Poly(1,3,5-triaminobenzene)

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ABSTRACT: In the presence of acid, 1,3,5-triaminobenzene (TAB) polymerizes under mild conditions to form a new network polymer. The mechanism of this unusual, simple polymerization reaction is discussed on the basis of model reactions and the unusual ring protonation of TAB in mild acids. As an example of a model reaction, TAB is reacted with aniline in acetic acid to form 1,3,5-trianilinobenzene. Poly-TAB is a new electron-rich polymer, of special interest as a potential organic ferromagnet or a conducting polymer.

Introduction

In the field of conducting organic solids, polymers have played a critical role.[1] Examples of such polymers include polyacetylene, polypyrrole, polyphenylene, and polyaniline. In the virgin field of ferromagnetic organic solids, polymers are expected to be correspondingly important. The major theories for ferromagnetic interactions in organic solids include orbital degeneracy as the key element.[2–7] In one approach, these degenerate orbitals are nonbonding orbitals.[3,4] Recent work[8] on isolated oligomers of phenylcarbenes has shown ferromagnetic interactions between eight neighboring unpaired spins. In addition, a preliminary Russian report[9] of a ferromagnetic polymer is presumed to involve such types of orbitals. The second approach[2,5–7] involves orbitals whose degeneracy orginates because of high molecular symmetry. Recent work following this approach has involved crystalline charge-transfer salts,[5,10,11] as well as a polymer made from 1,3,5-triaminobenzene, which has been reported[6,12] to be ferromagnetic. These latter two ferromagnetic polymers[6,9] are obtained in extremely poor yield and are very poorly understood in terms of their structure, chemistry, and mechanism of polymerization. For these reasons, there are major problems in reproducibly preparing these organic ferromagnetic materials. More work is clearly necessary to understand these polymers.

In this paper, we report a study of a polymer based on 1,3,5-triaminobenzene (TAB). The initial reports[6,12] described a mterial obtained from a reaction of TAB with iodine in acetic acid and other solvents at room temperature. Chemical analysis of the resulting solids showed a loss of nitrogen and hydrogen. It was speculated that the polymer in Figure 1 (poly-TAB) was produced and was responsible for the ferromagnetic behavior which was found on rare occasions. Note that, in Figure 1, the local structure of these polymeric subunits has the high (three-fold) molecular symmetry necessary to give orbital degeneracy, as required by the appropriate model[6] for organic ferromagnetism. However, if the polymer synthesized from TAB was indeed poly-TAB, its synthesis would have involved a rather unusual reaction: room temperature condensation of two arylamines to form a diarylamine. Although such reactions are known, they normally require very harsh conditions. For instance, aniline can be converted[13] into diphenylamine in moderate yield by heating it with phosphoric acid and zinc chloride for 10 h at 250–270 °C. Previous studies of TAB have focused on the way in which this molecule is protonated (Figure 2): it has been shown[14–16] that the first protonation of TAB occurs not on the amino group but on the ring

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