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Nonketonic Perester Photoinitiators

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ABSTRACT: *tert*-Butyl peresters based on aromatic hydrocarbons have been synthesized and tested as photoinitiators in free radical processes. The relative efficiencies of these initiators are compared for the photoinitiation of the polymerizations of methyl methacrylate and styrene. Experimental data for variations in the polymerization rate (R_p) with perester structure, concentration, and monomer concentration are reported. The effect of these variations on the molecular weight of the polymers produced was also studied. The experiments were carried out at 30 °C by using degassed solutions sealed under high vacuum and employing a mercury arc source equipped with appropriate wavelength filters to isolate the 366-nm region.

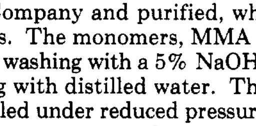
Introduction

As part of our continuing effort to design new photoinitiators for free radical processes and specifically as catalysts for vinyl polymerization, we have reported several examples of photoinitiators whose photochemical reactivity derives from light absorption by an aromatic carbonyl chromophore.[1,2] The translation of the energy derived from that absorption process into the dissociation of a conjugated, or in some cases remote, *tert*-butyl perester functionality has been shown to be an efficient photochemical source of a free radical pair.[1-3]

In view of the efficiency of the photochemical processes deriving from carbonyl chromophores coupled, via conjugation, to perester functionalities, we determined that *tert*-butyl peresters coupled with chromophores which were $\pi-\pi^*$ would be of interest. Our rationale was that the excited states of these systems would not be as susceptible to energy-transfer quenching since they themselves were of lower energy. Hence monomer quenching would cause fewer problems.[4]

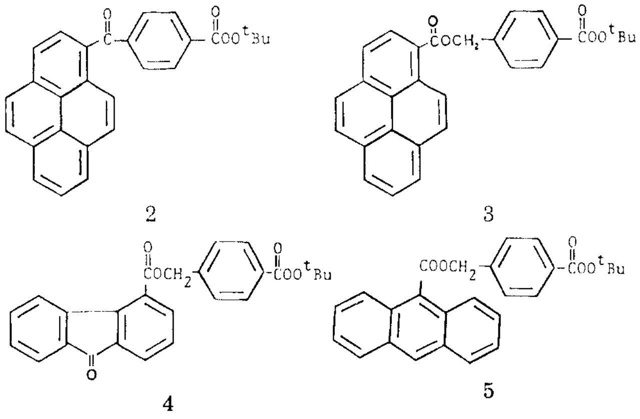
In addition, and in view of the potential utility of initiators which absorbed in regions of the spectrum other than where aromatic carbonyl compounds absorb, aromatic hydrocarbon residues provided the potential for strong absorption over a wide spectral range.

The initiators reported herein derive from three general chromophores: pyrene, anthracene, and fluorenone. All of these systems have $\pi-\pi^*$ lowest lying singlet or triplet states, and the perester unit is thereby coupled—not to an $\eta-\pi^*$ triplet absorption but to either a $\pi-\pi^*$ singlet or triplet or, possibly, an $\eta-\pi^*$ singlet. We based our syntheses on a general perester, 1. The initiators of interest are, with the exception of 2, nonconjugated peresters based on pyrene, anthracene, and fluorenone as indicated in Chart I.


$BrCH_2-C_6H_4-\overset{O}{\overset{\|}{C}}OO^tBu$

1

Chart I



Experimental Section

Starting materials and other reagents were obtained from Aldrich Chemical Company and purified, where necessary, by standard procedures. The monomers, MMA and styrene, were freed of inhibitor by washing with a 5% NaOH solution followed by repeated washing with distilled water. The monomers were then dried and distilled under reduced pressure just prior to use. All melting points are uncorrected. Ultraviolet spectra were obtained on a Varian Model 219 spectrometer. The intensity of the radiation was monitored constantly by benzophenone/benzhydrol actinometry[2] at 30 °C and observed to be 9.15×10^{17} quanta/min.

4-(Bromomethyl)benzoyl Chloride and 4-(Bromomethyl)peroxybenzoic Acid *tert*-Butyl Ester (Crucial Perester Intermediate 1). 4-(Bromomethyl)benzoic acid (18.53 g, 0.086 mol) which had been prepared by the Tuleen method[5] and finely powdered was refluxed for 1 h with an excess of thionyl chloride and a few drops of pyridine. A rapid evolution of hydrogen chloride took place for a few minutes and then stopped. Excess thionyl chloride was distilled off under vacuum and the oily residue dissolved in hexane. Crystallization occurred soon in the refrigerator. Filtration gave 14.32 g (71% yield) of the acid chloride.

Preparation of Perester 1. To an ice–salt cooled solution of 13.22 g (56 mmol) of 4-(bromomethyl)benzoyl chloride in 125 mL of dry ether was added dropwise over 30 min under magnetic stirring a solution of 5.45 g (60 mmol) of *tert*-butyl hydroperoxide and 6.56 g (65 mmol) of triethylamine in 50 mL of ether. After the addition the mixture was stirred for another hour. Filtration and evaporation left a solid. This was dissolved in dichloromethane and chromatographed over silica gel with dichloromethane as eluent. This gave 16.46 g of a colorless perester (90% yield) which was further purified by vacuum sublimation: mp (pure sample) 93–94 °C; IR (KBr) 1760 cm^{-1} ($\nu_{C=O}$ perester); NMR ($CDCl_3$) δ 1.44 (s, 9 H, CH_3), 4.52 (s, 2 H, CH_2), 7.44–8.00 (9 H, aromatic).

Synthesis of 4-[(1-Pyrenyl)carbonyl]peroxybenzoic Acid *tert*-Butyl Ester (2). Pyrene (6.75 g, 0.033 mol) was dissolved in 75 mL of dry benzene. 4-Carbomethoxybenzoyl chloride (6.0 g, 0.030 mol) was added. To this solution 6.75 g (0.050 mol) of aluminum chloride was gradually added. A dark color developed. After the addition of $AlCl_3$ the temperature increased slightly, and then the temperature of the mixture was increased to 40 °C with a water bath and gradually recooled to room temperature. The reaction mixture was then poured into an ice bath to which 5 mL of HCl had been added. The benzene was removed by steam distillation. The organic mixture was extracted with benzene and dried over magnesium sulfate. The solvent was evaporated and the residue chromatographed on silical gel with hexane. Elution with carbon tetrachloride gave pyrene, 3.2 g. Elution with carbon tetrachloride/chloroform (1:2) gave a yellow solid in two fractions (1.62 g; 3.25 g). The former fraction contained some pyrene. The latter fraction was extracted with hot ethanol to give 2.55 g of a yellow solid (mp 141–144 °C), identified as 4-[(1-pyrenyl)carbonyl]benzoic acid methyl ester. From the 1.62 g in fraction

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one of the eluted ketone, 1.01 g was obtained.

4-[(1-Pyrenyl)carbonyl]benzoic acid methyl ester (2.55 g, 7 mmol) was dissolved in 25 mL of benzene. A solution of 354 mg (6.4 mmol) of KOH in 5 mL MeOH was added, and the mixture was boiled. Precipitation of the potassium salt occurred. The mixture was extracted with water to give a yellow water layer, which was acidified with dilute HCl to give a light yellow precipitate. Filtration gave 1.73 g (5 mmol) of 4-[(1-pyrenyl)carbonyl]benzoic acid: IR 3600–3350, 1710, 1665 cm^{-1}.

4-[(1-Pyrenyl)carbonyl]benzoic acid (1.73 g, 5 mmol) was refluxed with 10 mL of $SOCl_2$ and 3 drops of pyridine for 3 h. A yellow/brown solution resulted. The excess thionyl chloride was evaporated, and the residue was triturated with ether/hexane and filtered to give the yellow acid chloride: IR 1652, 1770 cm^{-1}.

The acid chloride was dissolved in 60 mL of a benzene/chloroform mixture (50/10), and a mixture of *tert*-butyl hydroperoxide (5.2 mmol) and triethylamine (606 mg, 6 mmol) was added. After the addition the mixture was stirred for 2 h at room temperature and then heated to 50 °C for a few minutes.

The solvent was evaporated, and the residue was dissolved in dichloromethane and chromatographed over silica gel. Elution with CH_2Cl_2 gave a yellow band, which oiled when the solvent contained no perester. Elution was continued in the dark to give 1.50 g of a dark yellow oil which, when heated with cyclohexane/benzene, dissolved. After several days in the refrigerator, light yellow crystals formed which analyzed as perester 2: IR 1660 ($\nu_{C=O}$ ketone), 1770 ($\nu_{C=O}$ adjacent to perester) cm^{-1}; NMR ($CDCl_3$) δ 1.43 (s, 9 H, CH_3), 7.9–8.4 (m, 13 H, aromatic). Anal. Calcd for $C_{28}H_{22}O_4$: C, 79.55; H 5.25. Found: C, 79.40; H, 5.32.

4-[(((1-Pyrenyl)carbonyl)oxy)methyl]peroxybenzoic Acid *tert*-Butyl Ester. Pyrene-1-carboxylic acid (1 g, 4 mmol) was converted into the dry potassium salt as previously described. A suspension of the potassium salt, 0.65 g of bromomethyl perester 1 (2 mmol), and 60 mg of 18-crown-6 (0.23 mmol) was stirred for 60 h in the dark. Evaporation and chromatography of the residue over silica gel with carbon tetrachloride/chloroform (1:1) as eluent gave 1.0 g of yellow oil. Recrystallization from cyclohexane gave 0.82 g of crystals, mp = 105–108 °C. Another recrystallization raised the melting point 2 °C: IR (KBr) 1750 ($\nu_{C=O}$ adjacent to perester), 1720 ($\nu_{C=O}$ ester) cm^{-1}; NMR ($CDCl_3$) δ 1.41 (s, 9 H, CH_3), 5.56 (s, 2 H, CH_2), 7.55–9.32 (m, 13 H, aromatic protons with a doublet for one proton at δ 9.26, a doublet for another proton at δ 8.64, and a doublet for 2 protons at δ 7.61, apparently as part of an AB system). Anal. Calcd: C, 76.99; H, 5.31. Found: C, 76.81; H, 5.39.

Preparation of 4-[(((9*H*-Fluoren-9-on-4-yl)carbonyl)oxy)methyl]peroxybenzoic Acid *tert*-Butyl Ester (4). 4-Carboxyfluorenone (896 mg, 4 mmol) was treated as a suspension in 50 mL of water with an equivalent amount of KOH solution (224 mg KOH, approximately 4 mmol; pH of the solution close to 7.0). Filtration removed the small amount of undissolved solid, and the obtained filtrate was evaporated to dryness. The so-obtained potassium salt of the acid was thoroughly dried in an Abderhalen drying apparatus. A suspension was made of the potassium salt in 10 mL of dry acetonitrile, and 0.65 g of 4-bromomethyl perester 1 (2 mmol) and 60 mg of 18-crown-6 (0.23 mmoles) were added. The mixtures was stirred for 16 h in the dark while the progress of the reaction was followed by TLC. Evaporation and chromatography, on silica gel with 1:1 carbon tetrachloride/chloroform as the eluting solvent, gave 0.85 g of the perester as a yellow oil. Recrystallization from cyclohexane gave yellow crystals: mp 102–104 °C; IR (KBr) 1750 ($\nu_{C=O}$ adjacent to perester), 1725 ($\nu_{C=O}$ ester), 1710 ($\nu_{C=O}$ ketone); NMR ($CDCl_3$) δ 1.4 (s 9 H, methyl), 5.4 (s, 2 H, methylene), 7.49–8.03 (m, 11 H, aromatic). Anal. Calcd: C, 72.56; H, 5.11. Found: C, 72.65; H, 5.15.

4-[(((9-Anthryl)carbonyl)oxy)methyl]peroxybenzoic Acid *tert*-Butyl Ester (5). Anthracene-9-carboxylic acid (888 mg, 4 mmol) was converted to the dry potassium salt by the same procedure as above. A suspension of the potassium salt in 10 mL of dry acetonitrile was stirred over the weekend with 0.65 g (2 mmol) of bromomethyl perester 1 and 60 mg (10.23 mmol) of 18-crown-6. Evaporation and chromatography of the residue as before with carbon tetrachloride/chloroform (1:1) gave a yellow oil (0.82 g). Recrystallization from cyclohexane gave 0.58 g of yellow crystals: mp 118–119 °C; IR (KBr) 1750 ($\nu_{C=O}$ adjacent to perester), 1720 ($\nu_{C=O}$ ester) cm^{-1}; NMR (benzene-*d*) δ 1.70 (s, 9 H, CH_3), 5.28 (s, 2 H, CH_2), 7.18–8.09 (m, 13 H, aromatic).

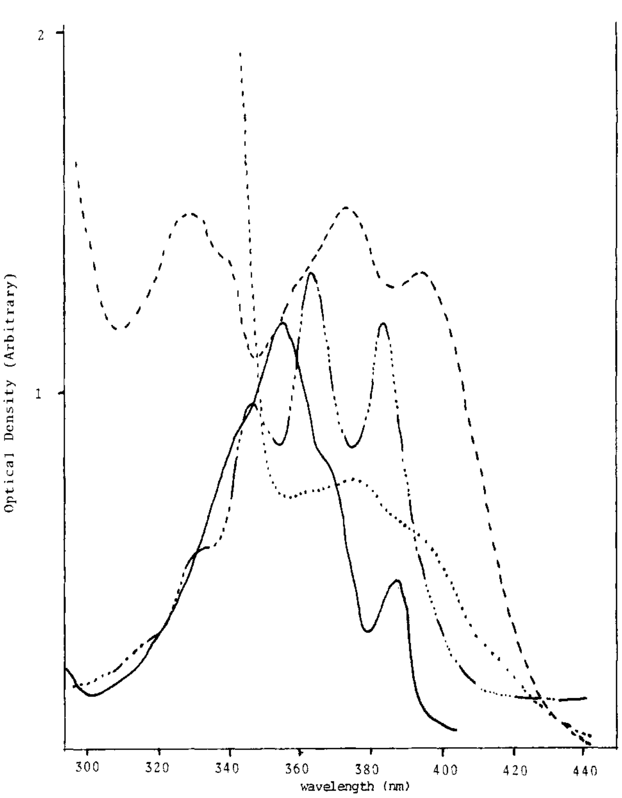


Figure 1. UV spectra in dichloromethane: (···) fluorenone perester 4; (– – –) pyrene ketone perester 2; (—···—) anthracene perester 5; (—) pyrene ester perester 3.

Photopolymerizations. Photopolymerizations were carried out in sealed, degassed tubes (12-mm diameter) by irradiation at 366 nm with a high-pressure mercury arc. All irradiation techniques were identical with those previously reported.[3] After the irradiation period, the polymers obtained were precipitated in methanol and analyzed gravimetrically.

Initiator concentrations for the bulk polymerizations were 2.4 × 10^{-3} mol/L and in the case of solution polymerizations varied as specified in the particular experiment.

Polymer molecular weights were determined in dichloromethane with a Waters Associates Model 440 GPC and were calculated from elution volumes with reference to polystyrene standards. These standards were used for calibration at a solvent flow rate of 1.5 mL/min and a polymer concentration of 1 mg/mL.

Results

A series of peresters based on aromatic chromophores which absorb radiation at about 366 nm but which do not produce η–π* excited triplet states upon absorption are reported. Three of the peresters were synthesized from crucial intermediate bromomethyl perester 1, by nucleophilic displacement of bromide ion. One of the peresters, 2, was synthesized directly from the appropriate carboxylic acid by a Friedel–Crafts process. Important generally is that we have discovered a series of routine nucleophilic displacement reactions which can be carried out on perester containing an appropriate leaving group without disturbing the –O–O– bond of the perester unit.[6] The physical and spectroscopic parameters of the peresters designed are reported in Table I. UV spectra for the peresters synthesized herein are shown in Figure 1.

In every respect, the compounds reflect the photochemistry and the spectroscopy of the parent chromophore except that they are coupled to a *tert*-butyl perester functionality, either conjugated directly or insulated by at least one methylene group included in the molecule. For these peresters to be useful photoinitiators they must

Table I
Characteristics of Peresters 2-5

perester structure	ϵ,[a] L mol^{-1} cm^{-1}	mp, °C	yield, %
fluorenone, 4	2.73×10^2	102-104	79
anthracene, 5	8.3×10^3	118-119	68
pyrene ketone, 2	1.0×10^4	122	65
pyrene ester, 3	1.82×10^4	107-109	80

[a] Extinction coefficient at 366 nm in CH_2Cl_2.

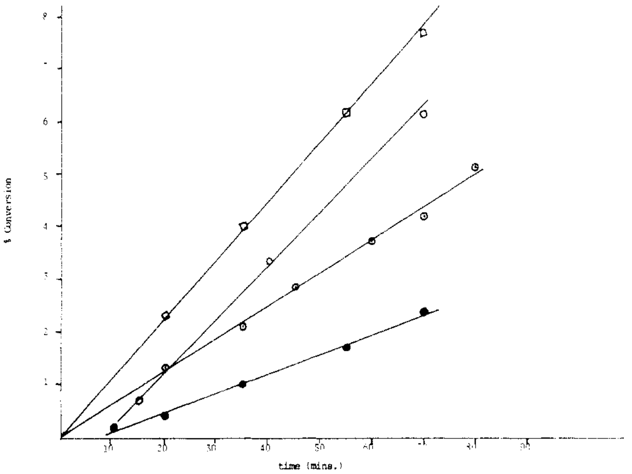


Figure 2. Photopolymerization of MMA (bulk) initiated by various peresters, ([perester] = 2.4×10^{-3} mol/L): (□) fluorenone perester 4; (○) pyrene ketone perester 2; (⊙) pyrene ester perester 3; (•) anthracene perester 5.

absorb a light quantum and convert the derived energy to a bond homolysis reaction producing a *tert*-butoxy and an aryloxy free radical pair.[7,8] This they all do.

$$\text{chromophore–(spacer)–C(O)OO-}t\text{-Bu} \xrightarrow{h\nu} \text{chromophore–(spacer)–C(O)O}\cdot + t\text{-BuO}\cdot$$

We have studied the ability of the photoinitiators in Table I to produce free radicals which initiate vinyl polymerization by measuring the rate of polymerization of methyl methacrylate and styrene under identical conditions of light intensity, initiator concentration, monomer concentration, and temperature. The conversion vs. time curves for the photopolymerization of methyl methacrylate using these initiators are given in Figure 2. As shown there, the rate of MMA photopolymerization decreases in the following sequence of perester structure: fluorenone 4 > pyrene ketone 2 > pyrene ester 3 > anthracene 5 >.

The photoinitiation of styrene initiated by each of these peresters was carried out similarly and is shown in Figure 3. The rate of styrene photopolymerization decreased in the following order: pyrene ketone 2 > pyrene ester 3 > anthracene 5 > fluorenone 4.

It is clear from Figures 2 and 3 that the reactivity order of these aromatic peresters depends on the type of monomer being polymerized. Thus in the polymerization of MMA, the fluorenone perester is the fastest, whereas in the polymerization styrene, it is the slowest. The rates of polymerization, at identical times for the two monomers MMA and styrene, are compared in Table II.

Effects of Monomer and Perester Concentration on the Polymerization Rate. The relationship between the rate of polymerization, R_p, and the concentration of the monomer is function of the structure of both the initiator and the monomer being polymerized. Thus the R_p of MMA with fluorenone perester 4 as the initiator increases to a maximum as the monomer concentration is increased (to about 3.5 M in benzene) and then levels off (Figure 4).

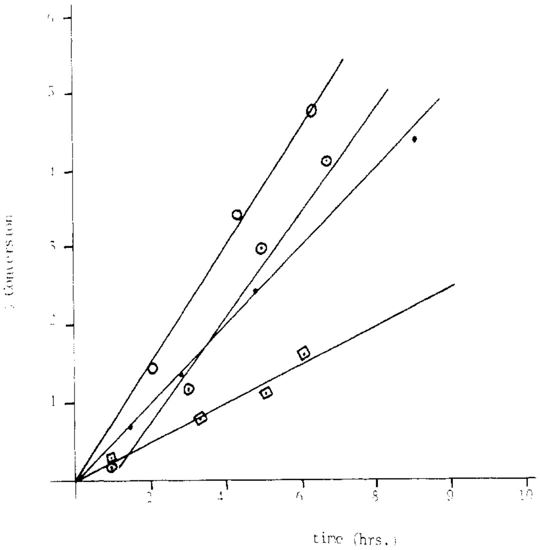


Figure 3. Photopolymerization of styrene (bulk) initiated by various peresters ([perester] = 2.4×10^{-3} mol/L): (○) pyrene ketone perester 2, (⊙) pyrene ester perester 3; (•) anthracene perester 5; (□) fluorenone perester 4.

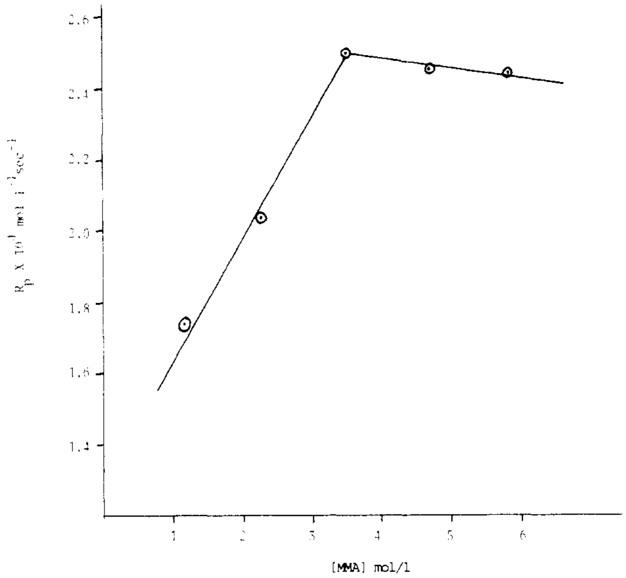


Figure 4. Photopolymerization of MMA initiated by fluorenone perester 4 ([perester] = 3×10^{-3} mol/L; time = 65 min; solvent = benzene).

Table II
Photopolymerization (Bulk) of Vinyl Monomers Initiated by Various Peresters

initiator	R_p, mol L^{-1} s^{-1} MMA[a]	R_p, mol L^{-1} s^{-1} styrene[b]
pyrene ester perester 3	1.1×10^{-4}	1.95×10^{-5}
pyrene ketone perester 2	1.54×10^{-4}	2.44×10^{-5}
fluorenone perester 4	1.92×10^{-4}	9.8×10^{-6}
anthracene perester 5	5.63×10^{-5}	1.22×10^{-5}

[a] After 60 min. [b] After 3 h.

For styrene photopolymerization utilizing the same initiator, we found as the concentration of styrene increases, the rate of polymerization decreases (Figure 5). In this instance either the excited state of the initiator is quenched by the monomer or the monomer reacts with the initiator before bond homolysis occurs.

Peresters 2 and 3 present interesting test cases by means of which the localization of energy in the excited state can be assessed. The keto pyrene perester, 2, is quenched by

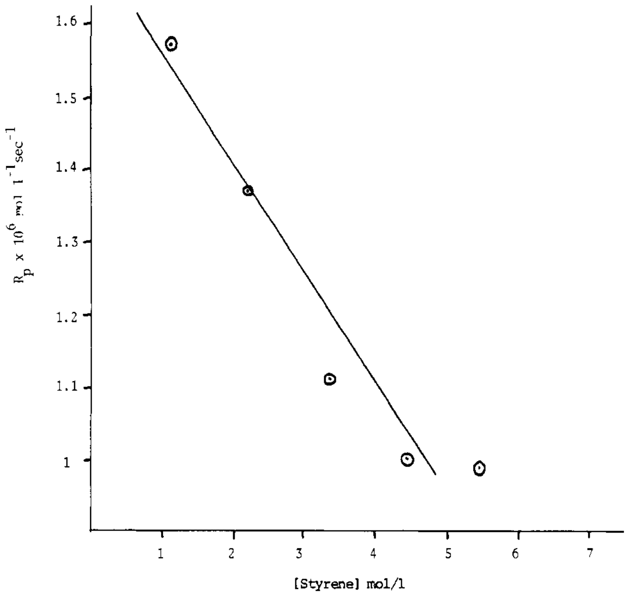


Figure 5. Photopolymerization of styrene initiated by fluorenone perester 4 (solvent = benzene; [initiator] = 3 × 10^{-3} mol/L; time = 4.45 h).

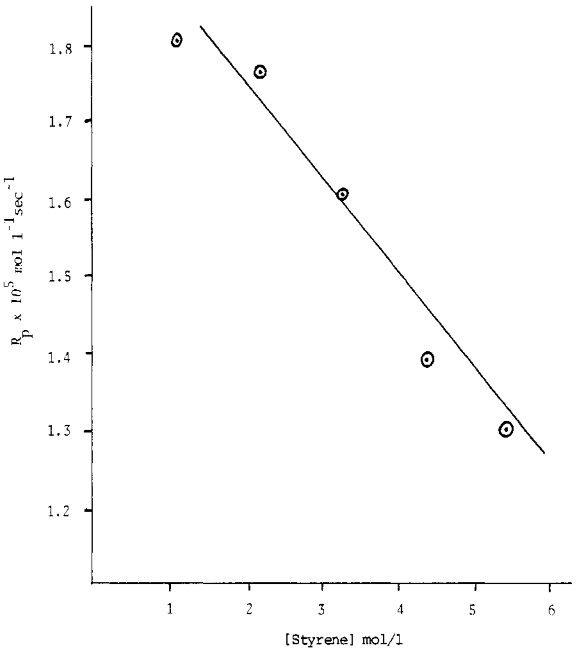


Figure 6. Photopolymerization of styrene initiated by pyrene ketone perester 2 (solvent = benzene; [initiator] = 3.3 × 10^{-3} mol/L; time = 5.30 h).

styrene—or at least the rate of polymerization decreases as the styrene concentration is increased (Figure 6).

The nonketonic pyrene photoinitiator, 3, behaves more normally, with the rate of styrene polymerization actually increasing with concentration of monomer when it is used (Figure 7).

Parenthetically, styrene solutions of nonketonic pyrene initiator 3 fluoresce while being irradiated in the monomer (styrene or MMA) for the purpose of studying them as photoinitiators, while ketonic pyrene systems 2 are nonemitting under identical conditions.

Figure 8 shows the rate of photopolymerization of styrene as a function of styrene concentration initiated by another π–π^* photoinitiator, the anthracene derivative 5. As in the case of pyrene perester 3, the anthracene system is not quenched by styrene and the R_p increases with increasing styrene concentration.

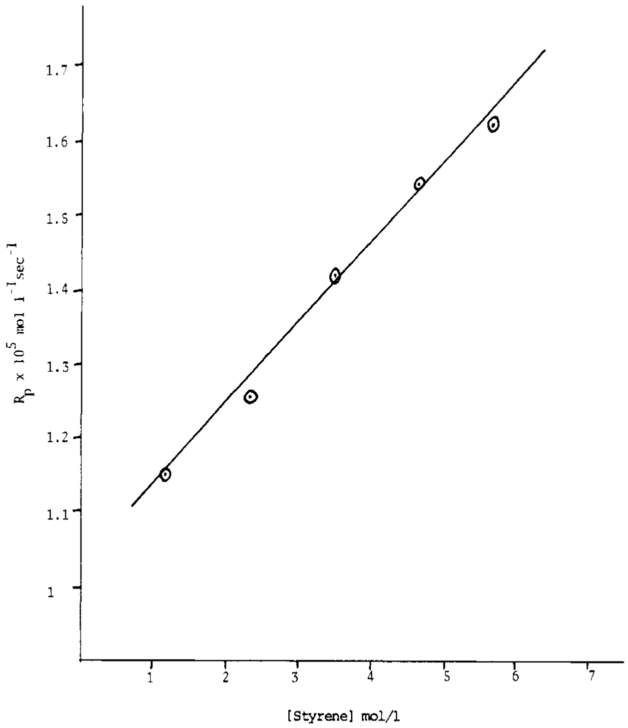


Figure 7. Dependence of the photopolymerization rate R_p of styrene on the monomer concentration in benzene (initiator is pyrene ester perester 3; [initiator] = 1.84 × 10^{-3} mol/L; time = 7 h).

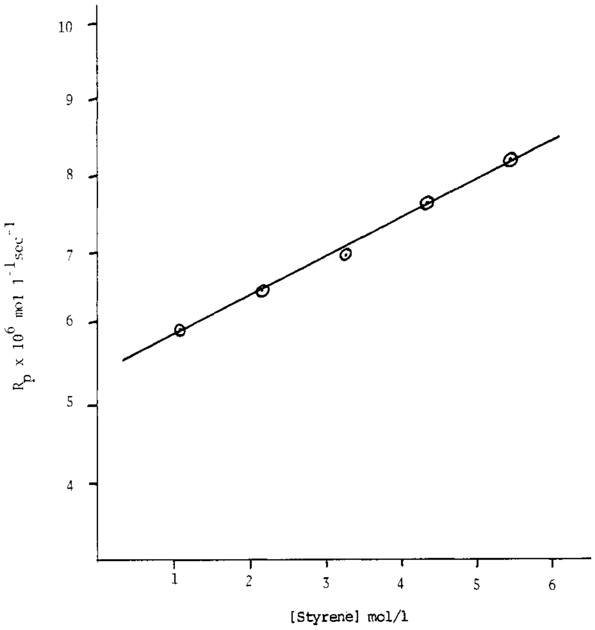


Figure 8. Dependence of the photopolymerization rate R_p of styrene on the monomer concentration (initiator is anthracene perester 5; [initiator] = 2.7 × 10^{-3} mol/L; time = 16 h).

The effect of initiator concentration on the rate of polymerization is determined by the termination step of the radical chain[9] and is half order in initiator when termination is bimolecular in chain fragments. The rate, as a function of initiator concentration, also is a function of self-quenching of initiator excited states. Thus, the only way the rate of polymerization of MMA could decrease as a function of pyrene perester concentration (Figure 9) is if the excited state of the perester were quenched either by another perester ground state or by a perester residue present in a polymer chain. In other words, increasing the initiator fragments in the system increases the possibility

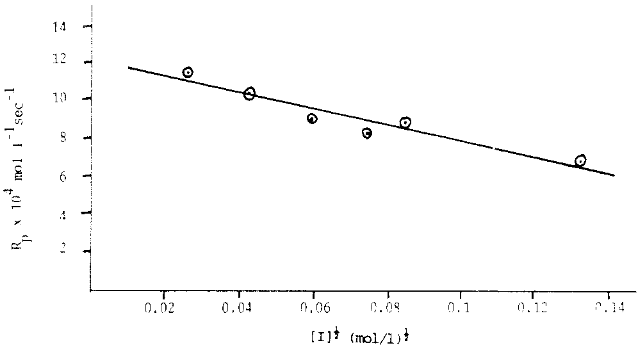


Figure 9. Dependence of the photopolymerization rate R_p of MMA on the initiator concentration (initiator is pyrene ester perester **3**; time = 90 min).

Table III
Molecular Weight Dependence on Initiator Structure and Polymerization Time for Photopolymerization of MMA (Bulk) Initiated by Various Peresters

initiator	t_p,[a] min	$\overline{M}_n$ (average)
pyrene ketone perester 2	40	1.7×10^4
	70	2.23×10^4
fluorenone perester 4	10	3.15×10^4
	25	3.87×10^4
	40	4.15×10^4
	70	5.0×10^4
anthracene perester 5	20	1.0×10^5
	35	1.3×10^5
	70	7.9×10^5
pyrene ester perester 3	35	5.8×10^4
	45	7.0×10^4
	60	7.9×10^4
	100	1.58×10^5

[a] Polymerization time.

Table IV
Photopolymerization of Styrene (Bulk) Initiated by Various Peresters

initiator	t_p,[a] h	$\overline{M}_n$
pyrene ester perester 3	1	2.5×10^4
	3.15	5.6×10^4
	5	6.3×10^4
fluorenone perester 4	3	1.17×10^5
	6	1.12×10^5
	10.15	1.05×10^5
pyrene ketone perester 2	4.20	2.5×10^4
	6.15	3.1×10^4
	10.30	1.4×10^5
anthracene perester 5	1.30	1.78×10^5
	3	2.3×10^5
	4.50	2.8×10^5

[a] Photopolymerization time.

of chromophore self-quenching and decreases the rate of initiation at higher concentrations of photoinitiator.

Effect of Monomer and Perester Concentration on the Molecular Weight of the Polymer. Tables III and IV show the effect of polymerization time and the structure of the aromatic perester photoinitiator on the molecular weight of the derived polymer, in the case of both methyl methacrylate and styrene. Figure 10 shows that the molecular weight of the MMA formed from one of the aromatic photoinitiators is inversely proportional to the square root of the initiator concentration.

Figure 11 shows that the molecular weight of polystyrene formed from the anthracene perester photoinitiation increases as the monomer concentration increases. Figure 12 shows the same relationship between styrene concentration and its polymer molecular weight where the ini-

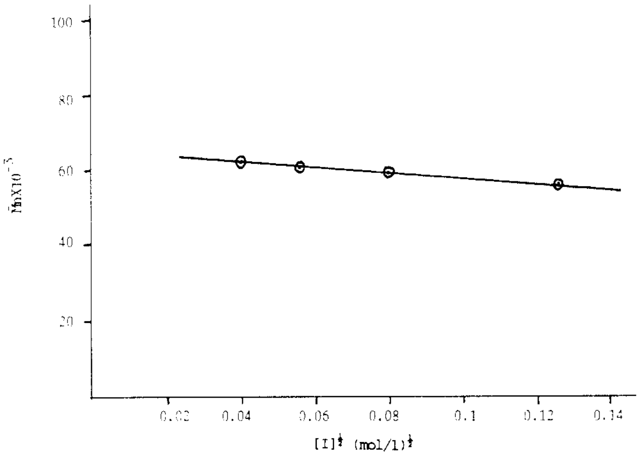


Figure 10. Dependence of the molecular weight of the polymer on the initiator concentration for photopolymerization of MMA (bulk) initiated by pyrene ester perester **3** (time = 90 min).

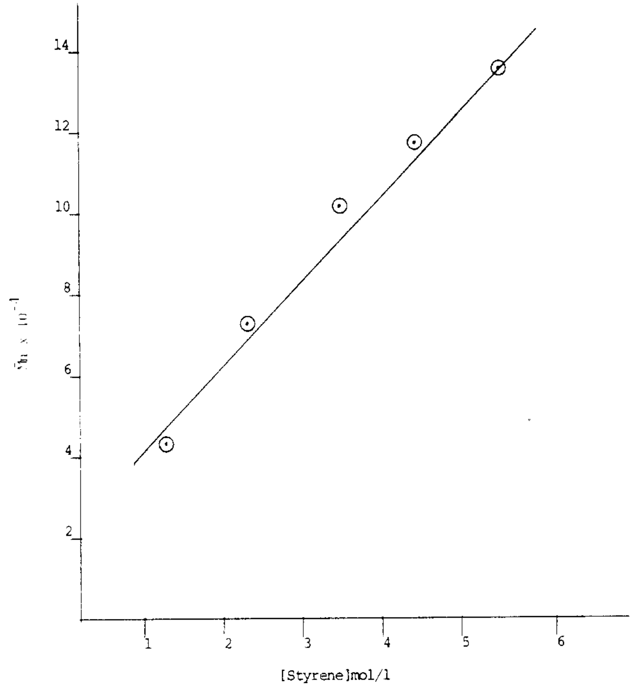


Figure 11. Dependence of the molecular weight of the polymer on the monomer concentration for photopolymerization of styrene initiated by anthracene perester 5 ([initiator] = 2.7×10^{-3} mol/L).

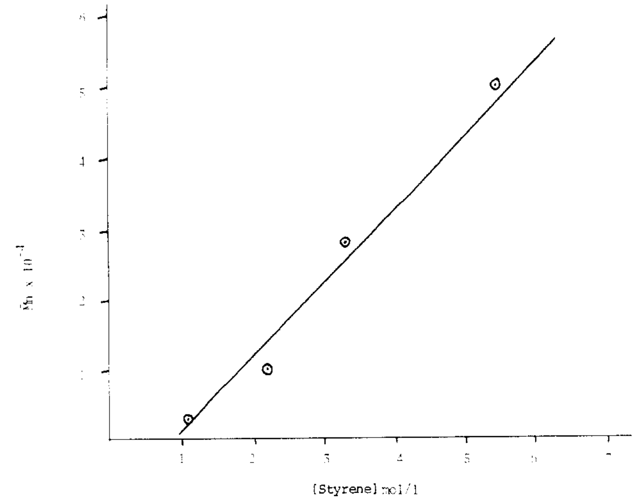


Figure 12. Photopolymerization of styrene (bulk) initiated by pyrene ester perester **3** (time = 7 h).

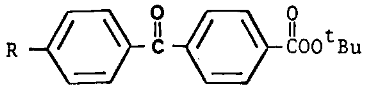
tiator is pyrene ester system **3**.

It is an anomaly that though the rate of polymerization of styrene with initiator **5** is 1–2 orders of magnitude larger than for **3**, the $\bar{M}_n$ of polymers deriving from **5** are higher than with **3**. The reason for this is that polycyclic aromatic hydrocarbons also serve as radical inhibitors. Thus, these peresters also participate in noninitiating reactions with growing radical chains. This can be demonstrated by polymerization of the appropriate monomer thermally with AIBN in the presence of initiators **2–5**. All monomers except **4** terminate radical chains sufficiently to decrease the rate of polymerization by as much as 10%, when present in concentrations equivalent to those of the AIBN initiator at 70 °C.

Discussion

Peresters **2–5** represent new examples of unimolecular photoinitiators. They decompose homolytically upon the absorption of a light quantum. The rationale for their design is like that we have previously reported for 4-benzoylperoxybenzoic acid *tert*-butyl ester, **6**, and some of its analogs (1–3) except that we have taken a more general approach for synthesizing the chromophore-containing photoinitiators. Thus 4-(bromomethyl)peroxybenzoic acid *tert*-butyl ester, **1**, is the crucial reaction intermediate in the synthesis of several of the chromophore-bearing peresters we have studied in this work.

At the outset the thought was that one could control the efficiency of free radical formation from a photoinitiator by controlling the chromophore absorbing the radiation. As we have indicated above, and as we have demonstrated previously, nucleophilic displacement reactions, if carefully controlled, can be carried out routinely on perester **1**. Thus perester **1** provides a general route to chromophore-bearing peresters **2–5**. Studies of analogous peresters, **6**, have been previously reported.[1–3]



6, R = CH_3, OCH_3, $t\text{-BuOO}\overset{O}{\overset{\|}{C}}$—

Though the perester function in peresters **2–5** is not conjugated with the light-absorbing chromophore, and in intramolecular photoinitiator design one might think that feature not only important but almost necessary, such does not turn out to be the case. However, and this will be the subject of a later report, certain chromophore-specific quenching reactions occur more efficiently in systems where the perester function is conjugated to the absorbing chromophores, and these reactions also affect the relative efficiency of the photoinitiator. Some of these disadvantages can be avoided with nonconjugated photoinitiators where through-space energy transfer provides the energy for -O–O- bond cleavages.

Whatever, and this is important, chromophore peresters of the general type **2–5** decompose photochemically and initiate the polymerization of monomer by so doing. The initiation rate is generally first order in monomer concentration.

Excited states of different general characteristics and lifetimes are apparently responsible for the decomposition of our new initiators. As we have previously shown, the photodecomposition of peroxybenzoic acid *tert*-butyl ester, **6**, is quenched by styrene. This is clearly indicated by a R_p that decreases as the monomer concentration increases. We have suggested that styrene monomer quenches the excited triplet state of the initiator since the triplet energy of styrene is about 62 kcal/mol and that of the perester is about 67.5 kcal/mol.

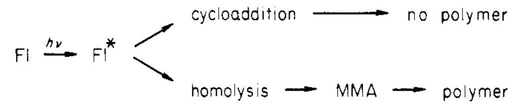
All of the peresters, **2–5**, emit at 77 K in a glass (EtOH/MeOH , 4/1). Pyrene ketone perester **2** and anthracene perester **5** phosphoresce with the 0–0 bond of the former at 45.8 kcal/mol and that of the latter (a very weak phosphorescence) at 53.0 kcal/mol. The fluorescence λ_{max} are as follows: **2**, very weak; **3**, 420 nm; **4**, 395 nm; **5**, 480 nm. The emission spectra of the peresters are wholly similar to those of nonperester analogs; therefore the statement is valid that the photochemical behavior of the attached perester functions should reflect the behavior of model excited states derived from nonperester analogs.

The R_p of two of the four peresters studied herein, **2** and **4**, decreases for styrene polymerization as the monomer concentration increases while the R_p for the other two initiators, **3** and **5**, increases as the styrene concentration increases. We suggest, therefore, that excited states of peresters **2** and **4** either react with styrene or are quenched by it. The other two photoinitators, **3** and **5**, are π–π* initiators with low intersystem crossing rates. The singlet states of these systems are responsible for bond homolysis, and the reactions competitive with decompositions in these systems are fluorescence and other reactions of the singlet state. The excited states of **3** and **5** are not quenched competively by styrene, and R_p increases—normally—with initiator concentration.

Methyl methacrylate, typical of acrylate monomers, behaves normally in the photoinitiated reactions. Its triplet energy is substantially higher than the triplet energy of any of the chromophores in the photoinitiators reported herein, therefore R_p increases with initiator concentration in the general case.

One perester does not behave normally with MMA, that being fluorenone perester **2**. Thus R_p increases with MMA concentration until the monomer concentration reaches about 3.5 M and then levels off. We suggest in the case that two processes compete—bond homolysis and another reaction of the excited state that requires MMA but consumes the excited state and therefore inhibits perester decomposition to radicals. Since the excited state energies of both the triplet and the singlet of fluorenone are well below that of MMA, there can be no energy transfer.

Such a reaction is cycloaddition. Cycloaddition is a reaction of the triplet excited state of a carbonyl function that is biomolecular and which can consume the excited state of the fluorenone function prior to decomposition. Kinetically this might compete with perester decomposition as follows:



Thus at 3.5 M MMA, the bimolecular term becomes greater than the unimolecular term.

Like the general case of initiated vinyl polymerization, R_p depends on initiator concentration, with there being a $^1/_2$-order dependence at low concentration of initiator. Rates of initiation are also subject to bimolecular quenching and—in the pyrene case (Figure 9)—decrease with increasing concentrations of the initiator. This suggests that the excited state of one pyrene residue is quenched by another pyrene in the ground state.

The same thing appears to be true in the anthracene case: thus, we suggest here the photodecomposition of the perester competes with anthracene dimerization, a known process for anthracene derivatives at high concentration of anthracene.[10–12]

Summary

tert-Butyl peresters based on aromatic hydrocarbon and aryl ketone chromophores with lowest lying $\pi-\pi^*$ transitions have been synthesized and tested as photoinitiators in radical processes. The systems designed are of varying efficacy, with the nonketonic systems serving as better initiators with higher concentrations of aromatic monomers such as styrene.

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Registry No. **1**, 88475-85-8; **2**, 88475-86-9; **3**, 88475-87-0; **4**, 88475-88-1; **5**, 88475-89-2; 4-(bromomethyl)benzoyl chloride, 52780-16-2; pyrene, 129-00-0; 4-carbomethoxybenzoyl chloride, 7377-26-6; 4-[(1-pyrenyl)carbonyl]benzoic acid, methyl ester, 88475-90-5; 4-[(1-pyrenyl)carbonyl]benzoic acid, 88475-91-6; pyrene-1-carboxylic acid, 19694-02-1; 4-carboxyfluorenone, 6223-83-2; anthracene-9-carboxylic acid, 723-62-6; styrene, 100-42-5; polystyrene, 9003-53-6; MMA, 80-62-6; poly(MMA), 9011-14-7.

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Photolysis of Poly(acrylic acid) Containing an Aryl Ketone Chromophore

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ABSTRACT: The synthesis of a copolymer of phenyl isopropenyl ketone and acrylic acid gives a water-soluble photodegradable polyelectrolyte. The ultraviolet spectra are different in dioxane and water solutions. The quantum yields ϕ of the Norrish type II photoreaction at 313 nm are determined in dioxane and in water solution at different degrees of ionization and ionic strengths, where the polyelectrolyte is in a more or less expanded random coil or in a stretched conformation. The value of ϕ is 0.13 in dioxane solution and 0.07 in water solutions, in spite of the different conformations. This behavior is explained by identical local conformation of the dyad acid–ketone, which differs from the overall conformation of the macromolecule.

The photochemistry of polymeric carboxylic acids has been studied mainly on poly(methacrylic acid) at a wavelength of 254 nm[1-3] in aqueous solution. The first step of the photochemical reaction is a carboxylic group abstraction followed by a scission of the chain.[1] The quantum yields of chain scission seem dependent both on the pH and on the tacticity.[2,3]

The photochemistry of poly(acrylic acid) (PAA) has not been investigated at short wavelengths, but poly(alkyl acrylates)[4,5] and poly(naphthyl acrylates)[6] underwent simultaneous photolysis and cross-linking, probably due to the recombination of radicals formed by tertiary hydrogen abstraction.[6]

The introduction in the polymer chain of a ketone chromophore can induce photolysis at wavelengths where the remainder of the polymer does not absorb. The Norrish type II reaction is responsible for the chain scission.

Amerik and Guillet have reported the photolysis of a methyl methacrylate–methyl vinyl ketone copolymer at 313 nm,[7] and similar studies have been made with styrene–phenyl vinyl ketone copolymers.[8] In both cases, a low ketone content (2.3 mol %) in the copolymer was sufficient to induce extensive photodegradation. The photolysis of such copolymers makes possible the investigation of the mechanism of main-chain scission in polymeric ketones,[9] which has been the subject of a great number of papers.

Nevertheless, the problem of the dependence of the quantum yield of the chain scission process on polymer configuration is not yet clear. Tanaka and Otsu[10] found greater quantum yields for atactic poly(*tert*-butyl vinyl ketone) than for the isotactic configuration. However, Kilp et al. found no difference in the quantum yield of main-chain scission between isotactic and atactic poly(phenyl vinyl ketones).[11] This was explained on the basis of identical local conformations of the biradical intermediate.

Determination of Quantum Yields of Main-Chain Scission

In polyelectrolytes, changes in chain conformation can be easily obtained without changing the solvent or the temperature since the conformation of a polyelectrolyte is dependent both on the pH and on the ionic strength. A polyelectrolyte such as PAA, which is a weak flexible polyacid, is in a Θ condition in dioxane at 30 °C,[12] in a

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