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Polymerization of Methyl Methacrylate Photoinitiated by Anthraquinone and 2-*tert*-Butylanthraquinone

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ABSTRACT: Anthraquinone and 2-*tert*-butylanthraquinone are shown to be highly efficient photoinitiators for free-radical polymerization of methyl methacrylate and other monomers under both aerobic and anaerobic conditions in tetrahydrofuran solvent. In the absence of oxygen molecular weights are significantly lower than for comparable reactions thermally initiated by AIBN. On the other hand it is shown that anthraquinone does not have any effect on either rates or molecular weights of AIBN thermally initiated polymerizations of methyl methacrylate. Absorption and fluorescence emission spectroscopy have been used to show that photolysis of the quinones in tetrahydrofuran involves a hydrogen transfer from tetrahydrofuran to the triplet excited quinone with formation of a pair of radicals which subsequently combine to produce an air-sensitive quinone–tetrahydrofuran adduct. Methyl methacrylate intercepts formation of this adduct by reacting with the tetrahydrofuran derived radical to produce polymer. In this case, the quinone derived radical undergoes disproportionation to form the corresponding anthraquinone and anthrahydroquinone with the latter being the effective terminating species accounting for the lower molecular weights observed. Reaction mechanisms and kinetic schemes, consistent with the experimental observations, are presented and discussed.

It has long been known that quinones, and especially *p*-benzoquinonoid compounds, readily undergo reduction when photolyzed in the presence of hydrogen donor solvents such as alcohols.[1] A recent publication by Porter and collaborators[2] details the primary photophysical and photochemical process occurring in a number of *p*-benzoquinones of biological importance. These results supplement earlier reports in the literature[3,4] and confirm that photoinduced hydrogen-atom transfer from donor solvent to triplet excited quinone is an important photochemical process in all cases.

Photoinitiation of free-radical vinyl polymerization is a reaction of considerable technological value, especially when applied to cross linking of polymer-based systems in photoresist printing plates and printed circuits, and, over a period of several years, we have been concerned with quantitative aspects of photoinitiation especially for systems based on aromatic carbonyl compounds.[5]

p-Benzoquinones such as anthraquinone fall into this latter category and it would be anticipated that intermediates involved in photoreduction of anthraquinones might be useful initiating species in free-radical polymerization. There are many reports in the patent literature[6] of the use of anthraquinones as photosensitizers for a variety of cross linking and gelation reaction in polymer-based systems, but few details are available as to the precise reaction mechanisms involved, although one report[7] claims that in polymerization of aqueous methyl acrylate by sodium anthraquinone 2-sulfonate in the presence of chloride ions, the initiating species are chlorine atoms. Since this work was completed, Rabek and Ranby[8] have described efficiencies and mechanisms for the photoinduced oxidative degradation of polystyrene sensitized by several quinones.

It is apparent that while anthraquinone is a perfectly adequate photosensitizer for all of these processes, it has a high lattice energy and, in consequence, exhibits only a low degree of compatibility or solubility in most organic systems. Therefore, for many practical purposes, it is preferable to utilize the much more soluble homolog, 2-*tert*-butylanthraquinone.

In this paper we present details of the kinetics and mechanisms of reactions involved in photoinitiated polymerization of methyl methacrylate in tetrahydrofuran, which is simultaneously a good hydrogen donor and solvent for the reaction components, sensitized by anthraquinone and 2-*tert*-butylanthraquinone.

Experimental Section

Materials. The source and purification procedures for all the monomers, solvents, and AIBN have been described fully.[9] Anthraquinone (Hopkin and Williams, GPR) was recrystallized twice from benzene to yield pale yellow needles, mp 89°. Phenanthraquinone (BDH) was recrystallized from benzene to yield orange plates (mp 210°). 2-*tert*-Butylanthraquinone (Aldrich) was recrystallized twice from aqueous acetone, mp 103°.

Uv–visible spectra were recorded on Unicam SP500 and SP1800 spectrophotometers and fluorescence emmision spectra were recorded on a Perkin-Elmer Model 204 spectrofluorimeter.

Rates of Polymerization. For the most part rates of polymerization were determined by dilatometric measurements in high vacuum degassed reaction mixtures. A full description of the procedures for storage and handling of monomers, filling of dilatometers, irradiation technique, and calibration of light sources has already been given for closely related work with benzophenones as sensitizers.[9]

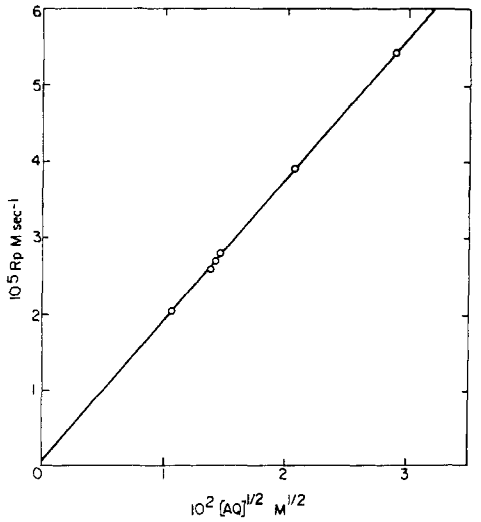


Figure 1. Variation in initial rates of polymerization with concentration of anthraquinone in THF at 30° ([MMA] = 4.68 *M*).

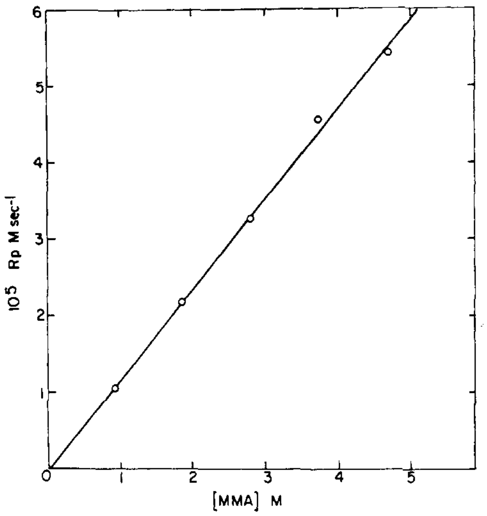


Figure 2. Variation in initial rates of polymerization with concentration of MMA in THF at 30° ([AQ] = 2.91 × 10^{-4} *M*).

Molecular Weights. Intrinsic viscosities $[\eta]$ were determined in benzene at 30° and converted into viscosity average molecular weights ($\overline{M}_v$) and number average molecular weights ($\overline{M}_n$) by the relationships established by Fox, Mason, and Cohn-Ginsberg,[10] *i.e.*

$$\log \overline{M}_v = (\log [\eta] + 4.28)/0.76$$

$$1.05\overline{M}_v/\overline{M}_n = 2.00$$

Results

Preliminary studies of the polymerization of methyl methacrylate (MMA) photoinitiated by anthraquinone (AQ) in tetrahydrofuran (THF) at 30.0° showed that rates of polymerization in air were approximately twice those for corresponding reactions under vacuum. This result is just the opposite of what might have been anticipated since oxygen is frequently an inhibitor or retarder of polymerization and does retard polymerization of MMA photoinitiated by benzophenones. However, the pro-catalytic effects of oxygen are easily understood in terms of the mechanisms to be presented subsequently but, to ensure the required degree of experimental reproducibility, all quantitative studies were made under the usual conditions of high vacuum.

A further effect of dissolved air (oxygen), also noted during preliminary experiments, was that stock solutions of AQ in THF gradually developed a significant thermal initiation capability after standing in daylight. Tests with ferrous thiocyanate reagent established that peroxides were gradually built up during this time, presumably as a result of AQ photosensitized peroxidation of THF, and hence all polymerization solutions were freshly made up from solid anthraquinone. The preliminary experiments also gave a clear indication that 2-*tert*-butylanthraquinone (TBAQ) behaved exactly like AQ in every respect, a result fully born out by the quantitative studies.

Rates of Polymerization and Molecular Weights. As noted above the rates and dependencies of photoinduced polymerization of MMA at 33.0° were very similiar for initiation by AQ and TBAQ. Consequently, for brevity, a description of the kinetic behavior of AQ-containing systems is given fully and representative data for TBAQ are given only in summary form. The effects of varying [AQ] and [MMA] on initial rates of polymerization of MMA at 30° are shown in Figures 1 and 2. Initial rates were mainly used because, as will be shown later, the quinones are consumed steadily during photolysis and this causes a continuous decrease in the instantaneous rates of polymerization. The intensity of incident light was varied by means of wire gauze filters and relative values of the rates of polymerization (R_p) (M sec^{-1} × 10^5) were 14.09, 9.82, and 7.21 for a standard polymerization mixture with relative light intensities of 100, 51, and 26, respectively. These data lead to a light intensity exponent of 0.5.

Because of the steady decrease in rates of polymerization (R_p) with consumption of initiator, correlation of molecular weights with rates was made using values of R_p averaged over the times taken to form the polymer. The effects of changes in [AQ] and [MMA] on molecular weights are indicated by the data of Table I, and the effects of AQ on rates and molecular weight in polymerization of MMA, thermally initiated by AIBN at 50.0°, are indicated by the data of Table II.

Rates and molecular weights observed for polymerization of MMA at 30° photoinitiated by TBAQ were very similiar to those observed for corresponding reactions involving AQ. Representative data are summarized in Table III.

Quinones other than the anthraquinones were also found to be active photoinitiatiators of MMA polymerization and, although the results are not corrected for differing light absorption characteristics of the various sensitizers, a semiquantitative comparison can be made from the data of Table IV, where it is apparent that even well-known inhibitors of radical chain reactions such as *p*-benzoquinone and *p*-chloranil show some activity.

The effects of changing solvent on AQ photoinitiated polymerizations of MMA were investigated in a semiquantitative manner by means of the gravimetric procedure in which standard reaction mixtures were photolyzed for a fixed period and the polymer was recovered by precipitation into methanol. Typical data are given in Table V for mixtures photolyzed for 4 hr at 40.0°, except in the case of ethanol and 2-propanol when the irradiation time was reduced 2 hr so as to prevent precipitation of the polymers.

Related gravimetric experiments were made to investigate the effects of changing monomer. Under conditions such as those described for MMA, anthraquinone was an effective photoinitiator in THF for polymerization of styrene, acrylonitrile, and methyl acrylate, but not for *N*-vinylcarbazole and vinyl acetate. However, photoinduced polymerization of vinyl acetate was observed in toluene solvent and both THF and toluene solvents were useful for AIBN thermally initiated polymerizations. It appears, therefore, as if AQ functions as a retarder of vinyl acetate polymerization.

Table I
Polymerization of MMA Photoinitiated by AQ in Tetrahydrofuran at 30°

[MMA], mol/l.	[Anthraquinone], mol/l.	Av rate of polymerization, mol/l./sec × 10^5	[η] C_6H_6, dl/g (30°)	$\bar{M}_v \times 10^{-5}$
4.68	1.15	1.69	0.866	3.54
4.68	1.15	1.49	0.879	3.61
4.68	1.96	2.00	0.669	2.52
4.68	4.08	3.18	0.568	2.03
4.68	4.15	2.94	0.585	2.11
4.68	4.15	3.07	0.596	2.16
4.68	8.16	3.71	0.486	1.66
4.68	8.45	3.94	0.489	1.67
4.68	8.45	4.08	0.497	1.71
4.68	2.91	3.80	0.461	1.55
3.74	2.91	2.79	0.405	1.31
1.87	2.91	1.26	0.278	0.79
0.94	2.91	0.60	0.190	0.48

Table II
Effect of AQ in the AIBN[a] Thermally Initiated Polymerization of MMA[b] in THF at 50.0°

[Anthraquinone], mol/l. × 10^4	Rate of polymerization, mol/l./sec × 10^5	[η]C_6H_6, dl/g (30°)	$\bar{M}_v \times 10^{-5}$
0.0	6.59	1.26	5.79
0.0	6.63	1.25	5.74
0.0	7.27	1.08	4.73
2.4	6.97	1.23	5.62
4.3	6.78	1.14	5.09
6.7	7.20	1.15	5.15
10.6	6.78	1.23	5.62
14.4	6.95	1.24	5.68

[a] [AIBN] = 7.43 × 10^{-3} *M*. [b] [MMA] = 4.68 *M*.

Table III
Polymerization of MMA Photoinitiated by TBAQ in THF at 30°

[MMA], *M*	[TBAQ], 10^4 *M*	Initial rate, 10^5 *M* sec^{-1}	Av rate, 10^5 *M* sec^{-1}	$\bar{M}_v \times 10^{-5}$
2.69	5.08	7.44	5.82	0.899
3.53	5.08	9.43	7.64	1.080
4.20	5.08	10.99	8.34	1.386
4.71	5.08	13.77	10.45	1.286
5.14	5.08	14.49	10.02	1.696
4.71	3.03	9.36	7.66	1.898
4.71	5.08	13.02	10.45	1.289
4.71	7.08	14.88	10.64	0.983
4.71	9.15	16.34	11.56	0.921
4.71	11.12	18.79	14.13	0.764

Table IV
Relative Efficiencies of Quinones and Benzophenones as Photoinitiators for Polymerization of MMA in THF at 30° [a]

Sensitizer	Relative rate	Sensitizer	Relative rate
Phenanthraquinone	1.93	2-Methylnaphthoquinone	0.38
Naphthoquinone	1.17	Benzophenone	0.27
Anthraquinone	1.00	Benzoquinone	0.23
Acenaphthenequinone	0.92	Chloranil	0.10
BTDA	0.76		

[a] [Sensitizer] = 5.2 × 10^{-4} *M*. [MMA] = 4.68 *M*. BTDA = 3,3′,4,4′-benzophenone tetracarboxylic dianhydride.

Table V
Effect of Solvent on Anthraquinone Photoinitiated Polymerization of MMA at 40° [a]

Solvent	Polymer yield, %	Rate of polymerization, mol/l./sec × 10^5	[η]C_6H_6, dl/g (30°)	$\bar{M}_v \times 10^{-5}$
THF	14.1	4.56	0.260	0.69
THF	15.3	4.96	0.268	0.76
THF	15.1	4.91	0.243	0.67
Ethanol	11.5	7.44	0.316	0.94
Ethanol	12.3	7.87	0.301	0.88
2-Propanol	12.3	7.97	0.278	0.79
Toluene	13.1	4.24	0.333	1.00
Toluene	12.9	4.18	0.308	0.91
Cumene	13.3	4.33	0.306	0.90
Chlorobenzene	7.6	2.46	0.670	2.53
Benzene	6.5	2.10	0.674	2.55

[a] [MMA] = 4.68 *M*. [AQ] = 2.4 × 10^{-3} *M*. Photolysis for 4 hr except for ethanol and 2-propanol in which cases the reaction was stopped after 2 hr to prevent precipitation of the polymers.

Absorption and Emission Spectra of Polymerizing Solutions. In agreement with the rate and molecular weight studies, absorption and emission spectra of photolyzed solutions of the quinones in tetrahydrofuran, with or without added MMA, were essentially identical for equivalent concentrations of AQ and TBAQ. Accordingly the full data for both quinones are not given, but rather, spectra of representative systems involving either quinone are discussed randomly.

Photolysis of the quinones in THF solutions which had been vacuum outgassed was always accompanied by an increased yellowing in color. Furthermore, the photolysis products were intensely luminescent giving rise to a pure blue fluorescence during photolysis of solutions containing only the quinones and a distinct blue-green fluorescence during photolysis of solutions containing quinone and monomer (MMA). While the photoproducts of reactions in the presence and absence of monomer are obviously related, their absorption and emission spectra were sufficiently distinct to permit unambiguous characterization.

Figure 3 shows the fluorescence of irradiated solutions of AQ in THF, AQ + MMA in THF, and the product of reducing TBAQ by Zn–HCl in aqueous THF. Figure 4 gives typical time–conversion absorption spectra for TBAQ in THF with and without MMA. It should be noted that prolonged photolysis of all the systems resulted, after consumption of all quinone, in disappearance of the initial fluorescing species with ultimate formation of a new, and weaker, fluorescing derivative, having a broad structureless emission centered on 375 nm. This product was not identified but has no relevance to the photochemistry discussed below or to the photoinitiated polymerizations. A further point is that photolysis of anthraquinone–THF systems,

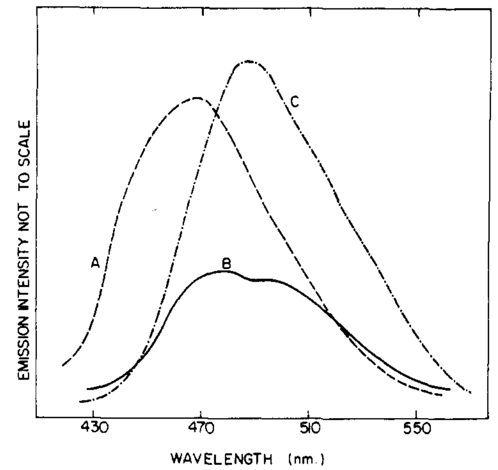


Figure 3. Fluorescence spectra of reduction products of AQ and TBAQ in THF at 30°: (A) photolysis of AQ in THF, (B) photolysis of AQ in 1:1 v/v MMA-THF, (C) emission of product from Zn-HCl reduction of TBAQ.

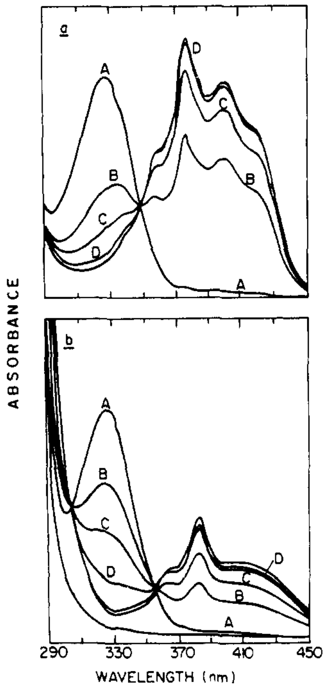


Figure 4. Absorption spectra of irradiated solutions of TBAQ in THF as a function of photolysis time at 30° ([TBAQ] = 2.5 × 10^{-4} *M*). (a) TBAQ in THF, (b) TBAQ in 1:1 v/v MMA-THF. (A) Zero time, (B) after 1 min, (C) after 2 min, (D) after 6 min.

with or without MMA, in the presence of air did not produce any new absorption bands or emission bands. Likewise, admission of air to the vacuum outgassed systems caused immediate disappearance of the absorption and emission spectra of photoreduction products. Quantitative aspects of the conversion of quinone to photoreduction products were studied for the special case of anthraquinone, largely because the spectroscopic characteristics of the fully reduced form of AQ, anthrahydroquinone, were known from related studies of Tickle and Wilkinson.[3] Extinction coefficients for the product of irradiation of anthraquinone in THF were estimated from a full spectrum recorded during an experiment on the variation of the concentration of AQ with time. The concentration of the product was estimated from the known concentrations of AQ initially present and at the time of recording the spectrum. It was assumed that AQ was quantitatively converted to the photoproduct on a mole for mole basis (Figure 4).

Table VI
Absorption Characteristics of Anthraquinone and Its Photoproducts[a]

Compound	λ_{max}, nm (log ε)
Anthraquinone	414 s (1.86); 394 (2.05); 374 (2.15); 322 (3.72)
Anthrahydroquinone	410 (3.67); 383 (3.83); 366 s (3.59).
Anthraquinone-THF photoproduct	420 s (3.65); 400 (3.77); 374 (3.82); 360 s (3.54)

[a] s = shoulder.

On one occasion a solution of the photoproduct in pure THF converted, on standing in the dark for 3 days, into a product having the blue-green fluorescence and absorption spectrum of those normally observed for photoproducts obtained from AQ-MMA-THF systems. The latter gave absorption spectra very similar to that of anthrahydroquinone as reported by Tickle and Wilkinson.[3] Although this experiment could not be repeated it sufficed to permit an estimate of the extinction of anthrahyroquinone, and appropriate data are included in Table VI. Thus irradiation of AQ in pure THF always produced a product absorbing at 374 and 400 nm whereas similiar irradiations of solutions containing MMA gave rise to a characteristic absorption band at 383 nm. That the product formed on irradiation of AQ in a 50% v/v solution of MMA in THF was anthrahydroquinone (λ_{max} 383 nm), and not the same product as formed in pure THF with its absorption maxima shifted due to solvation phenomena, was confirmed by dilution of a sample obtained in pure THF with an equal volume of MMA. The resulting solution showed absorption maxima at 374 and 400 nm with optical densities of 1.33 and 1.27, respectively, the latter being in good agreement with values of 1.27 and 1.15 obtained on dilution of a second sample with an equal volume of THF.

Several experiments were performed in which the decay of anthraquinone absorbance at 322 nm was followed simultaneously with the appearance of absorption at 374 and 400 nm (pure THF) and 383 nm (THF-MMA) and representative data are indicated by the plots in Figure 5. With or without MMA, the absorbance of AQ at 322 nm fell to a small residual constant value caused by the short wavelength absorption tail of the respective photoproducts. Furthermore, it is evident that MMA does not affect the rate of photoconsumption of AQ. On the other hand, Figure 5 shows clearly that the limiting optical densities at 374 and 400 nm for photolysis of AQ in pure THF were much greater than that observed at 383 nm for a comparable photolysis in the presence of MMA. The extinction coefficients of the two photoproducts at these wavelengths are rather similiar and it would appear that, in the presence of monomer, some of the anthraquinone was converted into products which did not absorb appreciably in the near-ultraviolet region.

After correcting for residual absorbance by AQ at 374 nm, and by the photoproduct at 322 nm, it was shown that, for photolysis in pure THF, decay of AQ and appearance of the photoproduct were both apparent first-order processes with specific rates of 8.4 × 10^{-2} and 9.4 × 10^{-2} min^{-1}, respectively. Considering the errors involved in estimating optical densities of reactants and products at the two wavelengths, these data must be regarded as being in good agreement. For photolysis of AQ in THF-MMA solutions, while the rate of decay of AQ was essentially identical with

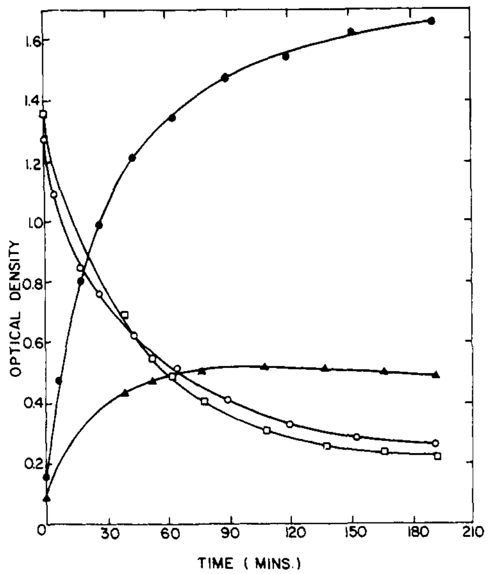
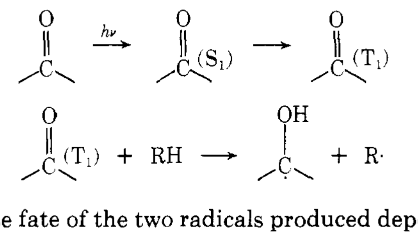


Figure 5. Optical densities of characteristic absorption bands for anthraquinone and its photoproducts as a function of irradiation time ($[\mathrm{AQ}]_0 = \sim 2 \times 10^{-4}$): (●) AQ in THF, optical density of adduct at 374 nm; (▲) AQ in 1:1 v/v MMA–THF, optical density of anthrahydroquinone at 383 nm; (□) AQ in THF, optical density of AQ at 323 nm; (○) AQ in 1:1 v/v MMA–THF, optical density of AQ at 323 nm.

that noted above for photolysis in pure THF, the rate of appearance of anthrahydroquinone was much lower and leveled at a much lower steady value. It was not possible to isolate the product of photolysis in THF in a pure state because of its air sensitivity. However, as noted earlier, anthraquinone was reformed on admission of air to the system. On the other hand, if the initial photoproduct was subjected to prolonged irradiation (75% reduction in absorption at 374 nm), no appreciable amount of AQ was formed on admission of air.

Discussion

The behavior of AQ and TBAQ as photoinitiators for free radical polymerization of MMA in THF shows many similiarities to that, previously reported in detail,[9] for photoinitiation of related polymerizations by benzophenone and its derivatives. Generally, the mechanisms established for photoreduction of quinones by a variety of hydrogen donors may be represented as involving an initial hydrogen abstraction by triplet excited quinone; the excited state being n,π* in character, *e.g.*



The precise fate of the two radicals produced depends upon the particular reaction conditions and will be discussed later for the special case of THF and anthraquinones.

Polymerization of methyl methacrylate in THF photoinitiated by anthraquinone and 2-*tert*-butylanthraquinone was highly efficient under both high vacuum and aerobic conditions. 2-*tert*-Butylanthraquinone is much more soluble in organic media than anthraquinone but there was no significant difference between the two sensitizers with respect to rates, molecular weights, or photoreduction products. Consequently although the remaining part of this discussion will be applied to anthraquinone (AQ), for simplicity, the behavior of TBAQ is assumed identical in all significant aspects.

Rates of polymerization of MMA photoinitiated by AQ under standard high vacuum conditions decreased with apparent ease of hydrogen abstraction from solvent in the sequence: 2-propanol > ethanol > THF > toluene > benzene (see Table V). These results indicate clearly that hydrogen abstraction by a triplet n,π* excited anthraquinone is the important primary photochemical process (benzene is here assumed to be a very poor hydrogen donor). Reaction rates, determined dilatometrically, were reproducible to better than ±10% and the kinetic data presented in Tables I and III and Figures 1 and 2 may be summarized by the rate expression

$$-\mathrm{d}[\mathrm{MMA}]/\mathrm{d}t = R_\mathrm{p} = K[\mathrm{MMA}][\mathrm{AQ}]^{0.5}[I_0]^{0.5}$$

where R_p is the initial rate of polymerization and I_0 is the incident light intensity. Viscosity average molecular weights of the polymers produced were found to vary inversely as the average rates of polymerization and yielded values of 0.043 (AQ) and 0.044 $M^{-1/2}$ $\mathrm{sec}^{-1/2}$ (TBAQ), respectively, for the ratio $k_\mathrm{p}/k_\mathrm{t}^{1/2}$ (see below). These values are significantly less than that (0.0658 $M^{1/2}$ $\mathrm{sec}^{1/2}$) previously determined[9] for polymerization of MMA in THF photoinitiated by AIBN at the same temperature (30°).

The differences in values of $k_\mathrm{p}/k_\mathrm{t}^{1/2}$ for the two systems indicate that termination processes (represented by k_t) are more important for AQ-initiated systems than for corresponding AIBN systems. On the other hand, the data of Table II show clearly that, in the concentration range employed, anthraquinone does not affect either rates or molecular weights in polymerization of MMA in THF thermally initiated by AIBN at 50°. Since AQ does not retard free-radical polymerization of MMA, the species responsible for reduction of molecular weights must be either an intermediate or product of the photochemical reaction involved in initiation of polymerization. In spite of the fact that the value of $k_\mathrm{p}/k_\mathrm{t}^{1/2}$ is much less for AQ than for AIBN photoinitiated polymerizations, the actual rate of polymerization at equal concentrations is much greater for AQ than for AIBN. From the gradients of plots of [MMA] *vs.* [photoinitiator]$^{1/2}$ a relative efficiency factor of 5.4 was determined for anthraquinone. Since the values of $k_\mathrm{p}/k_\mathrm{t}^{1/2}$ differ by a factor of about 1.5 for the two sensitizers, the relative efficiency of initiation by AQ may be estimated as about 50 times greater than that of AIBN. This factor does not, of course, take account of the differing light absorption characteristics of AQ and AIBN in the wavelength region 310–450 nm but serves, nonetheless, to indicate the potential usefulness of anthraquinones as photoinitiators for free-radical polymerization.

We have noted that the instantaneous rate of polymerization fell continuously during a kinetic run, as the sensitizer was consumed, and conversion–time (t) data gave a good fit to an expression of the form

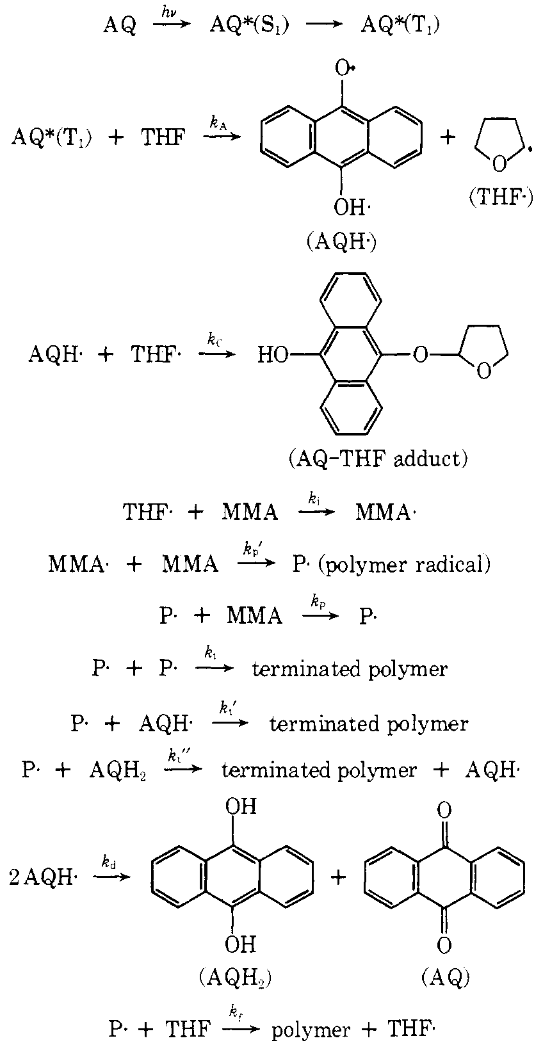
$$([\mathrm{MMA}]_0 - [\mathrm{MMA}]_t)/[\mathrm{MMA}]_0 = C_2(1 - e^{-C_3 t}) + C_1 t$$

where C_1, C_2, and C_3 are constants. This expression is essentially the same as that previously used[9] to describe the fall in rate of polymerization with time for polymerization of MMA photoinitiated by benzophenones.

A simplified reaction mechanism consistent with the experimental observations is shown in Scheme I.

The initiation reactions are equivalent to those well enough established in quinone photochemistry, and propagation is that normally encountered for polymerization of

Scheme I



MMA. Reactions of growing radicals with AQ are excluded by the experimental results (Table II), but those represented by k_t' and k_t'' are included to explain the lower molecular weights obtained when anthraquinone is used as sensitizer (see below).

Assuming a steady state for all radicals and excited states, and that $k_p' = k_p$, it may be adduced that for initial rates

$$[\mathrm{P}\cdot] = (I_0\phi\epsilon)^{1/2}[\mathrm{AQ}]^{1/2}/k_t^{1/2}(1 + \alpha)^{1/2}$$

where I_0 = intensity of incident irradiation, ϕ = quantum yield for production of radicals, ϵ = molar extinction coefficient of anthraquinone at the wavelength employed, and $\alpha = k_t'/(k_t k_d)^{1/2}$. Monomer is consumed mainly in the propagation process and for long chains

$$R_p = -\mathrm{d}[\mathrm{MMA}]/\mathrm{d}t = k_p[\mathrm{MMA}][\mathrm{P}\cdot]$$

$$R_p = \frac{k_p}{k_t^{1/2}(1 + \alpha)^{1/2}}(I_0\phi\epsilon)^{1/2}[\mathrm{AQ}]^{1/2}[\mathrm{MMA}]$$

This expression is in excellent agreement with the overall rate equation established from measurements of initial rates, and, from the values of $k_p/k_t^{1/2}$ for AQ and AIBN ($\alpha = 0$) sensitized reactions, it can be shown that $\alpha = 1.35$ for anthraquinone, indicating that additional transfer and termination reactions in AQ sensitized systems are not as significant as those observed in corresponding reactions sensitized by benzophenone,[9] for which $\alpha = 3.6$.

Emission and absorption spectra of photolysis products from anthraquinone in THF provide confirmation of the reaction mechanisms invoked above in the kinetic analysis. Physically the most obvious difference between anaerobic photolysis of AQ in THF and of AQ in THF containing MMA is the immediate appearance of a blue fluorescence in the former case, and a characteristic blue green fluorescence in the latter case. The blue-green fluorescence is now known to arise, at least in part, from anthrahydroquinone. Irradiation of phenanthraquinone in tetrahydrofuran gives a product with spectral features similar to those of the photoproduct from AQ in THF and, although these photoproducts were too unstable for characterization, it seems reasonable to assume that a similiar photoadduct is formed in each case.[11,12] Emission spectra of the photoadduct of THF with AQ and the Zn–HCl reduction products of AQ in aqueous THF (see Figure 3) suggest that the blue-green fluorescence observed after photolysis of AQ in MMA–THF arises from the presence of a mixture of anthrahydroquinone and AQ–THF photoadduct.

The extinction coefficients, estimated for the photoproducts of anthraquinone (Table VI), are based on complete conversion of anthraquinone to AQ-THF adduct, and the assumption that for the sample, which was converted to anthrahydroquinone on standing in the dark, one adduct molecule produced one anthrahydroquinone molecule. The assumption appears reasonable, since the logarithmic extinction coefficient of 3.83 estimated at 383 nm for anthrahydroquinone agrees well with the value of Tickle and Wilkinson.[3]

The increase in the intensity of the absorption bands in the near-ultraviolet region on forming the photoproducts of anthraquinone presumably arises from the conversion of the quinoid structure into a true aromatic structure.

A large number of experiments were carried out on the irradiation of anthraquinone in tetrahydrofuran and the results obtained may be summarized as follows (Figure 5). (i) The rate of decay of anthraquinone was approximately the same in tetrahydrofuran and a 50% v/v solution of methyl methacrylate in tetrahydrofuran. (ii) The limiting concentration of adduct formed in pure tetrahydrofuran was greater than the limiting concentration of anthrahydroquinone formed in the presence of methyl methacrylate. (iii) The maximum anthrahydroquinone concentration was reached well before the limiting adduct concentration. (iv) On prolonged irradiation of an adduct solution, the optical density at 374 nm began to decrease again. These observations may be rationalized by the kinetic and mechanistic scheme, already proposed.

The structure of the AQ–THF photoadduct is analogous to those formed from phenanthraquinone with a variety of ether molecules.[1,11,12] Although the nature of the product formed on further irradiation of this adduct is not known, the fact that it does not absorb appreciably in the near ultraviolet suggests that it may be an anthrone derivative.

Competition for the THF radical by AQH· and MMA will dominate the kinetic picture and, while collapse to THF–AQ adduct is the only process in pure THF (*i.e.*, reaction 2), scavenging of THF radicals by MMA (reaction 3) is a highly efficient process leading to radical polymerization. Formation of the THF–AQ adduct will affect spectroscopic studies of these systems but will not affect the kinetics of polymerization during the initial rate period.

It has already been postulated, in connection with the kinetics of polymerization, that the reduced molecular weights found for anthraquinone as compared with azodiisobutyronitrile are caused by termination of growing polymer radicals by semiquinone radicals. Thus if, in the presence of MMA

$$k_i[\mathrm{MMA}] >> k_c[\mathrm{THF}\cdot][\mathrm{AQH}\cdot]$$

no adduct will be formed. This must be true for appreciable polymerization to occur. The semiquinone radicals will now decay by disproportionation (k_d) or termination of polymer radicals (k_t'). If appreciable termination by semiquinone radicals occurs, as has been shown to be the case, the rate of formation of anthrahydroquinone will be small and the rate of decay of anthraquinone in the presence of monomer will be approximately the same as in pure tetrahydrofuran as found experimentally.

Since AQ–THF adduct and anthrahydroquinone have similiar extinction coefficients, removal of semiquinone radicals by growing polymer radicals accounts for the observation that the limiting absorbance of adduct in pure tetrahydrofuran is greater than that of anthrahydroquinone in polymerizing systems.

The observation that the maximum anthrahydroquinone concentration is reached well before the limiting concentration of THF–AQ adduct can be explained by postulating termination of growing polymer radicals by anthrahydroquinone. In terms of the scheme proposed for the mechanism of polymerization

$$d[AQH_2]/dt = \frac{1}{2}k_d[AQH\cdot]^2 - k_t''[P\cdot][AQH_2]$$

As polymerization proceeds, $[AQH\cdot]$ and $[P\cdot]$ will decrease, while $[AQH_2]$ increases. Eventually the two rates will balance and $[AQH_2]$ will reach a maximum value. This will occur before complete consumption of anthraquinone, and hence before the limiting concentration of THF–AQ adduct would have been reached.

Further Scope of Quinone–THF Photoinitiation Systems. We have seen that the AQ–THF combination provides a useful photoinitiating system for polymerization of MMA, methyl acrylate, styrene, and acrylonitrile but not for vinyl acetate and vinyl carbazole. For the latter monomer it is known[14] that photolysis in the presence of AQ leads to formation of the cyclodimer of *N*-vinyl carbazole. The case of vinyl acetate in THF is instructive because these systems always give rise to the blue fluorescence of simple THF–AQ combinations indicating that the monomer does not compete effectively for the THF · radicals. Thus for vinyl acetate it may be assumed that

$$k_c[AQH\cdot][THF\cdot] > k_i[THF\cdot][VA]$$

This is quite possible, since vinyl acetate is much less reactive than methyl methacrylate toward free radicals, with the two monomers differing in reactivity toward methyl radicals by a factor of 40 at 65°.[15] With the less reactive tetrahydrofuran radical at 30° this factor may be much larger, certainly sufficient to cause the observed differences in initiation. The tetrahydrofuran radical is similar in structure to those obtained on addition of radicals to alkyl vinyl ethers and would not be expected to react with vinyl acetate because of the known difficulty of copolymerizing alkyl vinyl ethers with vinyl acetate.[16]

In addition to the two anthraquinones, photosensitization of the polymerization of methyl methacrylate in tetrahydrofuran was shown to occur with other quinones. The relative efficiencies observed for a series of quinones, and also two benzophenones, were in the order: phenanthraquinone > naphthoquinone > anthraquinone > acenaphthenequinone > $3,3^1,4,4^1$-benzophenonetetracarboxylic dianhydride > 2-methylnaphthoquinone > benzophenone > chloranil. The molecular weights of the polymers produced indicate that much of the differences in reactivity are due to differences in rates of initiation, *i.e.*, more efficient sensitizers give lower molecular weights.

Finally it is worth noting that the enhanced rates of polymerization observed for photoinitiation by anthraquinones, under aerobic conditions, probably arise because of the very rapid reactions of dissolved oxygen with photoreduction products of anthraquinones, simultaneously regenerating quinone sensitizer and possibly forming initiating peroxy radicals

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