

## PHOTOINITIATION OF POLYMERISATION

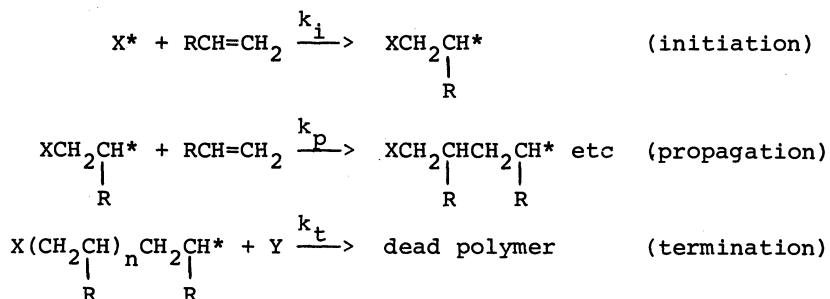
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**Abstract** - General features of photoinitiated free radical polymerisations are outlined with reference to the requirements for useful photocurable films and coatings. Initiation via charge transfer processes, including exciplex formation, is reviewed and details of photoinitiation of methyl methacrylate polymerisation by various amine-fluorenone combinations are presented. Results for polymerisations photoinitiated by small molecule fluorenones and copolymers derived from 2-vinyl fluorenone are compared in an attempt to establish detailed reaction mechanisms.

### INTRODUCTION

Chain reaction polymerisation processes predominate for olefinic monomers (Ref.1). They usually involve propagating intermediates which are free radical, carbocationic, carbanionic or complex organometallic in nature and, in highly simplified form, may be represented as follows:



Mechanisms for termination differ markedly according to the nature of the propagating species as do the variety of chain transfer reactions, deliberately omitted from the simple scheme. However, it is important to remember that the same competing processes control the more complex chain polymerisations leading to formation of insoluble, crosslinked resins from systems comprising multifunctional monomers.

Initiation of chain polymerisation processes is consequent upon generation of the reactive intermediate ( $X^*$ ) by thermal, photochemical or other types of activation or decomposition of a suitable labile molecule. Photochemical methods of activation of labile systems may lead to formation of radicals or ionic species although to date, it is mainly the former which have proved of real value and which will, therefore, occupy the bulk of the following discussion.

### PHOTOINITIATION OF RADICAL CHAIN POLYMERISATION

The photoinitiation of radical chain polymerisations has become increasingly important during the past five to ten years largely because of the ever-increasing requirements for photo-active relief printing plates, printed circuits and a wide variety of photochemically cured surface coatings. Even more recently, there has been an upsurge of interest in development of photochemically curable printing inks for use in applications where environmental or economic considerations demand the use of solvent free systems.

In all these processes the final polymeric product is usually a crosslinked resin produced by photoinitiated polymerisation of mixtures of suitable pre-polymers with mono- and polyfunctional olefins. As we have already noted the basic chain steps are similar irrespective of the degree of functionality of the polymerising components and, for photochemically active free radical systems polymerisation depends upon initial light induced formation of free radicals from a suitable photoinitiator. Assuming the usual radical termination processes, the overall rate of polymerisation ( $R_p$ ) is given by:

$$R_p = \frac{k_p}{k_t^{1/2}} R_i^{1/2} M$$

and the rate of initiation ( $R_i$ ) is approximated by

$$R_i = I_0 \phi \epsilon [\text{initiator}]$$

where  $I_0$  = intensity of incident radiation,  $\phi$  = quantum yield for initiation of radical chains, and  $\epsilon$  = molar extinction coefficient of initiator at the wavelength employed.

Thus, given an appropriate light source, important requirements for efficient photoinitiation include suitable absorption coefficients and wavelength sensitivities for the initiator molecule, together with quantum yields for initiation in the range 0.1-1.0. Another extremely important criterion is that the initiator molecule, or any of its photofragments, should not function as chain transfer or terminating agents. In recent years we have been engaged in a systematic study of a wide range of important photoinitiator systems in an attempt to determine these properties (Ref. 2). Estimates of the chain termination and transfer effects of components and photofragments in any particular polymerising system are readily available from studies of rates of polymerisation and polymer molecular weights, which yield values of the ratio  $k_p/k_t^{1/2}$ . Since  $k_p$  is essentially constant for polymerisation of any given olefin, variations in values of  $k_p/k_t^{1/2}$  arise from termination and transfer processes not apparent in comparable conventional polymerisations initiated (thermally and photochemically) by e.g. AIBN. Molecular weights can only be measured for polymers which are truly soluble and, for convenience, the homopolymerisation of methyl methacrylate in bulk or in various solvents has been chosen as a model system. The majority of commercially applicable photocure systems depend upon formation of insoluble crosslinked resins as products and so caution must be applied when comparing data for relative initiator effects in the model, soluble polymer system and the more viscous, multicomponent, commercially applicable systems.

#### TYPES OF PHOTOINITIATORS FOR FREE RADICAL POLYMERISATION

Free radical initiators are extensively employed as curing agents or promoters in a wide variety of polymerisation processes, especially those required for decorative or protective surface coatings. By definition these initiators are labile molecules unstable to heat or redox catalysts. It is reasonable to ask therefore, why such thermally active initiators are not similarly photochemically active. In reality almost all free radical initiators are photochemically unstable but their light absorption characteristics are frequently unsuitable. Peroxides, azocompounds, and disulphides represent the most important classes of useful (thermal) initiators for radical polymerisation and appropriate light absorption characteristics for common examples are given in Table 1.

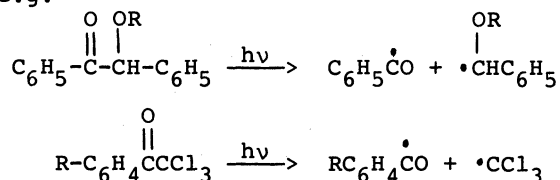
TABLE 1. Light absorption characteristics of initiator molecules

Initiator	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ( $M^{-1} \text{ cm}^{-1}$ )
PhCOOCOPh	275	$2.3 \times 10^3$
Bu <sup>t</sup> -OO-Bu <sup>t</sup>	260	7
$(\text{CH}_3)_2\text{C}=\text{N}=\text{N}-\text{C}(\text{CH}_3)_2$ CN CN	360	11.9
RSSR	260	300

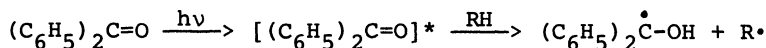
Perhaps a more important disadvantage to the use of thermally labile initiators in photocure systems would be the obvious potential complications of slow decomposition, leading to poor shelf life and unreproducible photoactivity in any given formulation.

A large proportion of the useful range of photoinitiators (Ref. 3) possess, as the light absorbing chromophore, an aromatic carbonyl group (ArCOX). These classes of compound have light absorption characteristics in the 300-400 nm region with high quantum yields for the appropriate radical forming reactions. Aromatic carbonyl compounds may have lowest lying  $\pi, \pi^*$  or  $n, \pi^*$  excited states according to the nature of the aryl group and frequently exhibit highly efficient intersystem crossing to the appropriate lowest energy triplet states. Two genuinely homolytic processes are observed for aromatic carbonyl compounds:

- (i) Photofragmentation of molecules such as benzoin and acetophenone derivatives, e.g.

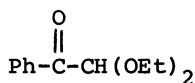


- (ii) Photoinduced hydrogen transfer from substrate, monomer, solvent etc. to an excited (triplet) benzophenone, xanthone or anthraquinone derivative e.g.

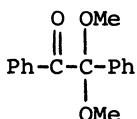


From a technological point of view, photofragmentations of benzoin and acetophenone derivatives are particularly useful because of the availability of the initiators, high quantum efficiencies for their photodecomposition, and high initiating efficiencies of the fragment radicals (Ref. 4). Additionally, the photofragmentation does not appear to be retarded by oxygen although oxygen may exert its normal scavenging effect on the radical fragments or polymerising intermediates. Complicating side reactions (including termination by primary radicals) encountered in photoinitiations via hydrogen abstraction processes of benzophenones and anthraquinones have been reviewed previously (Ref. 5) and a more recent paper (Ref. 6) gives useful information on the excited state quenching behaviour of the coloured species normally observed as by-products.

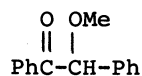
The range of photochemically active acetophenone derivatives has recently been extended (Ref. 7) to include 2,2-diethoxyacetophenone (DEA) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA),



DEA



DMPA



BME

and we have completed a study of their relative efficiencies as photoinitiators for polymerisation of methyl methacrylate in bulk at 30°C. Relevant data (Ref. 8) are given in Table 2. (BME = benzoin methyl ether).

For the model (methyl methacrylate) system DEA is a much less efficient initiator than either DMPA or BME, whereas for related reactive coatings based on 2-ethylhexylacrylate and neopentylglycoldiacrylate DEA is reported (Ref. 7) to be the most efficient, and substantially better than benzoin alkyl ethers. These results serve to illustrate the difficulties in making extrapolations from studies of idealised photoinitiated polymerisations, employing very low concentrations of initiators, to the more commercial systems having higher viscosities and much higher initiator concentrations. It is interesting to speculate that the apparent lower efficiency of DEA in the solution studies might result from increased self quenching compared with BME and DMPA. Steric hindrance will interfere with the close approach of excited and ground state initiator molecules required for quenching and,

of the three initiators listed in Table 2, DEA would offer least hindrance. However, the data in Table 2 show quantum yields for initiation rather than quantum yields for decomposition and hence there could be a variety of other reasons accounting for the differences in activity between the three initiators. It is important to note that values of  $k_p/k_t^{1/2}$  for all three initiators are normal for methyl methacrylate indicating the absence of additional termination or transfer processes.

TABLE 2. Photoinitiated polymerisation of methyl methacrylate in bulk

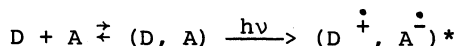
Initiator	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ ( $M^{-1}cm^{-1}$ )	$\phi_{\text{init.}}$ (366 nm)	$k_p/k_t^{1/2}$ ( $M^{-1/2}s^{-1/2}$ )
DMPA	343	242	1.71	0.059
BME	341	215	1.48	0.059
DEA	335	72	0.81	0.058

#### PHOTOINITIATION VIA CHARGE TRANSFER PROCESSES

Photochemically induced electron transfer reactions between neutral organic molecules were initially recognized, and frequently specified, as arising solely from photoactivation of so-called transfer charge complexes. The latter concept arose directly from the Mulliken description (Ref. 9) of the bonding and, more specifically, the electronic transitions observed to occur for combinations of donor molecules (D) - having low ionization potentials ( $I_D$ ), and acceptor molecules (A) - having high electron affinities ( $E_A$ ). A useful generalization arising from the Mulliken theory is that the energy of the charge transfer transitions between organic molecules in solution is given by:

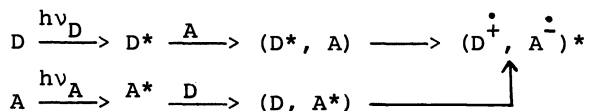
$$h\nu_{CT} = I_D - E_A - C$$

where C is a constant for the particular combination of D and A and represents mainly Coulombic Forces. It follows therefore that the excited states of charge transfer complexes have structures resulting from a considerable degree of electron transfer in comparison to their ground states e.g.



Nevertheless the excited states of a charge transfer complex should not be equated with a thermally equilibrated pair of ion radicals, a point which was first highlighted in the early, but stimulating, review by Kosower (Ref. 10).

More recently, mainly as a result of the pioneering studies of Weller and his associates (Ref. 11), it has become apparent that excited states, having structures equivalent to those of photo-excited charge transfer complexes, may be formed by local excitation of one or other component (i.e. D or A) in systems which do not give evidence of ground state complex formation e.g.

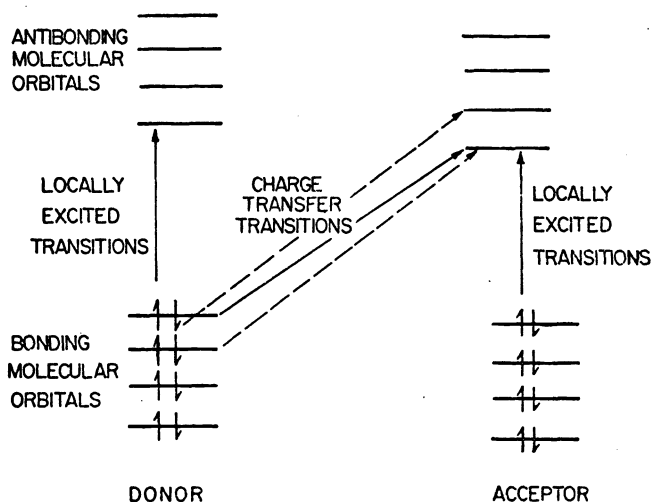


Here the excited state having the most electron transfer character ( $D^{\dot{+}}, A^{\dot{-}})^*$  is termed an exciplex and its formation may be preceded by a variety of collisional complexes (encounter complexes) between an excited donor and ground state acceptor or vice versa, e.g. ( $D^*, A$ ) and ( $D, A^*$ ).

A simplified description of the electronic transitions between donor acceptor pairs is given in Figure 1 and indicates clearly the origins of charge transfer spectra. Exciplex formation in similar systems involves

either donation of electronic charge from a locally excited state of the donor to a low lying unfilled orbital of the acceptor or, donation of electronic charge from a filled highest energy ground state of the donor to the partially filled ground state orbital created by local excitation of the acceptor.

Figure 1.



Utilisation of ground state charge transfer complexes has not yet provided useful systems other than those involving highly reactive olefins such as N-vinylcarbazole, alkyl vinyl ethers, and various cyanoethylenes, for most of which the polymerisations are ionic in nature (Ref. 12). Exciplexes were initially invoked to explain singlet state quenching of many types of luminescing species by additives which for thermodynamic reasons can not participate in energy transfer. Electron transfer via exciplexes was thought to be the operative quenching process. It is now known (Ref. 13) that deactivation of excited states, singlet and triplet, can arise via exciplex or encounter complex formation without the requirements for overall electron transfer. Nevertheless there is, for most systems, a simple correlation between quenching efficiencies and values of  $I_D$  or  $E_A$  as appropriate.

A generalised picture incorporating both ground state charge transfer (CT) complexes and encounter (EC) complexes formed from locally excited components is given in Figure 2. Any distinction between encounter complexes and exciplexes which may be evidenced by their characteristic emission properties) is indicated by the possibility of conversion of the two possible EC complexes to a pair of ion radicals  $[(D^+, A^-)_{REL}]$  having a solvation shell considerably relaxed from the Franck-Condon state  $[(D^+, A^-)_{F-C}]$  formed by direct excitation of a ground state CT complex between the same components. The encounter complexes and the solvent relaxed exciplex could be responsible for formation of the solvent equilibrated pair of ion radicals  $D^+$ ,  $A^-$  responsible for ultimate photochemistry in the system. Reversion back to the neutral starting components will be an important competing process at any stage of the equilibria shown in Figure 2 and, although the diagram uses a common donor D and acceptor A for both ground state CT complexation and exciplex formation, there is no requirement for ground state association prior to EC or exciplex formation. Rather, the scheme is intended to illustrate that photoexcitation of a charge transfer complex does not necessarily lead to the same products as arise from local excitation of donor or acceptor components (Ref. 14). Furthermore, the broad structureless emission observed for exciplexes indicates that the corresponding ground states are repulsive in nature.

There are a large number of useful photoinitiation processes which are most readily interpreted as involving exciplexes prior to overall photoinduced electron transfer. Among these the most obvious redox process involves the photo-oxidation of p-toluenesulphinate ion by excited dyes such as thionine and methylene blue providing the primary step in a commercial

photoimaging process (Ref. 15) for holography in water based systems, e.g.

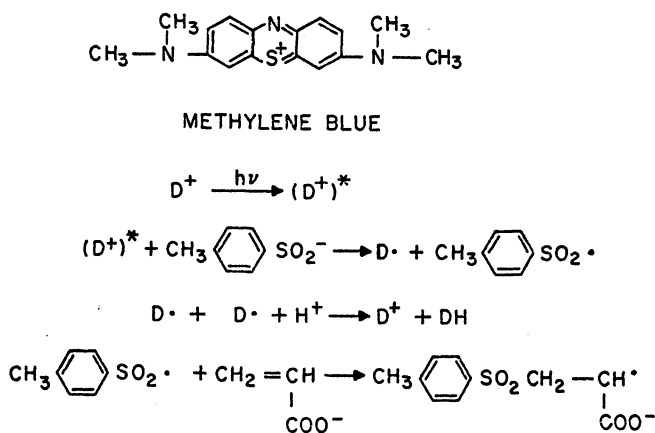
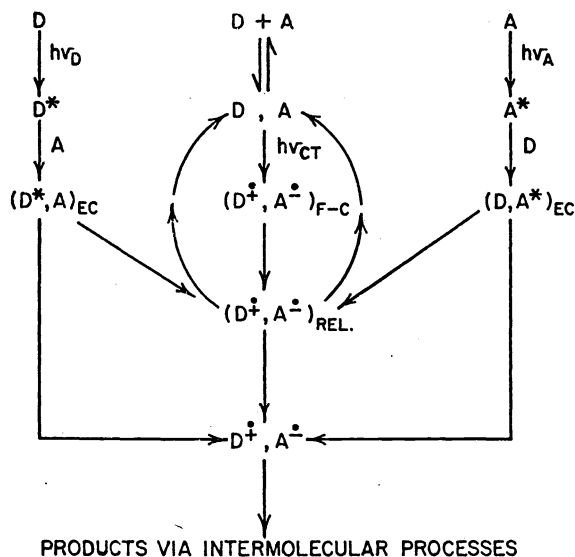
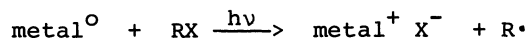


Figure 2

### CHARGE TRANSFER COMPLEX AND ENCOUNTER COMPLEXES

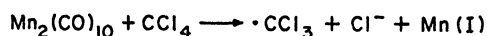
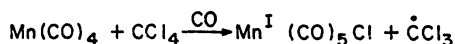
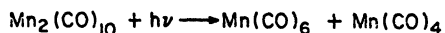


Another type of photoinitiation system involving overall redox processes is that developed by Bamford and collaborators (Ref. 16) in which a transition metal in a low, often zero, valence state is oxidised by exciplex interaction with polyhalomethane derivatives. In outline the reactions may be represented as a simple redox process e.g.



although many systems do not involve the direct reaction indicated. The most active systems involve carbonyl derivatives of Group VIIA metals, particularly manganese  $[\text{Mn}_2(\text{CO})_{10}]$  and rhenium  $[\text{Re}_2(\text{CO})_{10}]$ .

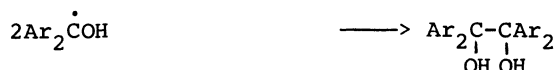
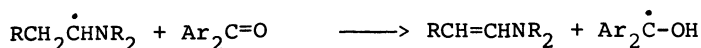
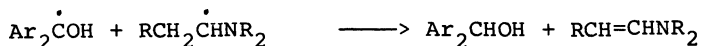
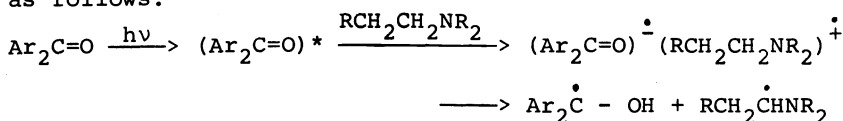
Long wavelength limits of absorption for these sensitizers are approximately 460 and 380 nm, respectively, and photoinitiation with unit quantum efficiency occurs up to these wavelengths in the presence of relatively low halide concentrations e.g.  $[\text{CCl}_4] > 10^{-2} \text{ M}$  for sensitization by  $\text{Mn}_2(\text{CO})_{10}$ . Experimental data support the view that the primary photochemical act is dissociative as indicated below.



#### PHOTOINITIATION VIA EXCIPLEXES OF AROMATIC CARBONYL COMPOUNDS

In contrast to the fully homolytic fragmentation and hydrogen abstraction reactions of aromatic carbonyl compounds referred to above, and which normally involve  $n, \pi^*$  excited states, a very wide range of exciplex interactions involving both  $n, \pi^*$  and  $\pi, \pi^*$  excited states have been observed. Notable among these are the wide variety of photoinduced oxidations of aminocompounds by aromatic carbonyl compounds (Ref. 17,18).

Singlet and triplet states of aromatic ketones are efficiently quenched by a wide variety of aminocompounds and a general correlation exists between quenching efficiency and ionization potential of the amine, for a particular class of amine (Ref. 17). In many cases tertiary amines are more effective than corresponding secondary and primary derivatives although specific solvation phenomena may change this order of reactivity. Reduction of aromatic ketones by amines proceeds at rates which are substantially faster than those observed for corresponding photo-induced hydrogen abstractions from, say, alcohols. Products from photo-oxidation of amines, may be generalized as follows:



In our own work we have preferred to utilize ketones thought to have lowest lying  $\pi, \pi^*$  triplet excited states because, although the point is still uncertain in some cases,  $\pi, \pi^*$  excited triplets do not generally undergo direct hydrogen abstraction reactions with alcohols, alkanes etc. Fluorenone (FLO) is undoubtedly the most useful of the aromatic ketones having lowest lying  $\pi, \pi^*$  triplet excited states and its photophysical characteristics have been extensively studied by several groups of workers (Ref. 19-21).

Photoreduction of fluorenone does not occur in alcohol, ether or alkane solvents but occurs readily in the presence of amines, with tertiary amines being most effective (Ref. 22,23). A rather special feature of the photochemistry of fluorenone is the dramatic effect of solvent on the rates of intersystem crossing from singlet to triplet manifolds. Increasing solvent polarity decreases the facility for intersystem crossing and simultaneously increases the quantum yield for fluorescence. Thus triplet state activity is maximized in solvents such as benzene and cyclohexane, for which values of triplet yields are 0.93 and 1.03 respectively (Ref. 24). In contrast,

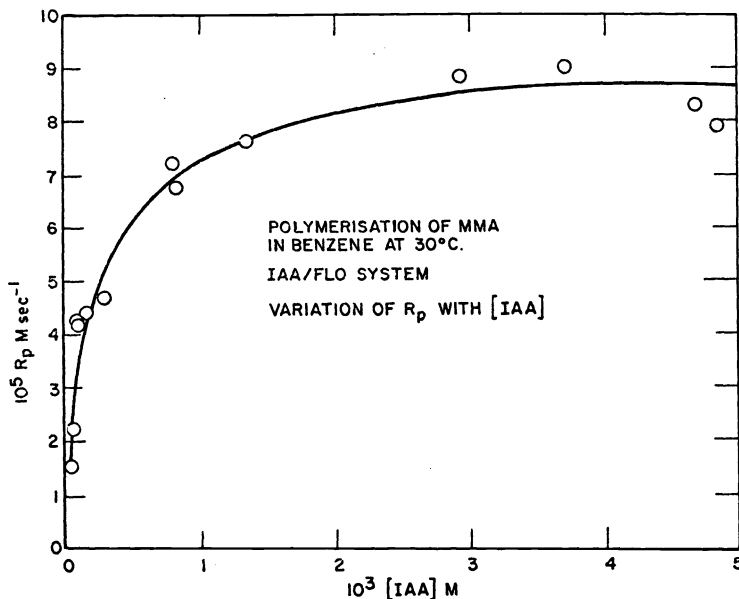
triplet yields in solvents such as alcohols, acetone, acetonitrile are substantially less than unity with a concomitant increase in quantum yields for fluorescence (Ref. 20,21). Ionization potentials of amines are important in determining the quenching ability for both singlet and triplet excited fluorenone but it now appears that photoreduction is consequent upon interaction of triplet excited fluorenone with amine donors (Ref. 17), the main effect of singlet state quenching being to reduce triplet yields. Evidence for the existence of both ion-radical pairs and free radicals is now available from detailed CIDNP studies of photoreduction of benzophenones by several amines (Ref. 25).

We have observed that photoreduction of fluorenone by suitable tertiary amines affords a highly convenient photoinitiation system for free radical polymerisation (Ref. 26). Almost any tertiary amine may be used but the highest efficiencies of radical formation (per mole of amine donor) were observed for comparable reductions using indole-3-yl acetic acid (IAA) as donor although here the reaction mechanism is thought to involve overall photo-decarboxylation (Ref. 27).



Details of the polymerisation of methyl methacrylate in benzene photo-initiated by FLO/ $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$  (DME) combinations have been given previously (Ref. 14) and similar data is now available for FLO/IAA systems (Ref. 28). A major difference between these two amine/FLO combinations is the much greater efficiency of IAA at low concentrations. Typical data for  $R_p$  versus  $[\text{IAA}]$  are given in Figure 3 and it was found that  $R_p$  is linear in  $[\text{FLO}]^{1/2}$  at fixed  $[\text{IAA}]$ .

Figure 3



Quantum yields for initiation by FLO/amine systems fall in the range 0.1-0.3 depending on substrates and conditions and it is important that values of  $k_p/k_t^{1/2}$  may be significantly less than the normal value ( $\sim 0.06$ ). Thus, for IAA/FLO and DME/FLO combinations at 30°C, typical values of  $k_p/k_t^{1/2}$  for polymerisation of methyl methacrylate in benzene are 0.036 and 0.038 respectively. Such low values of  $k_p/k_t^{1/2}$  imply termination or transfer by the initiator components or, more probably, by primary radicals produced on irradiation. In order to gain insight into these effects, a number of substituted fluorenones were evaluated as photoinitiators when

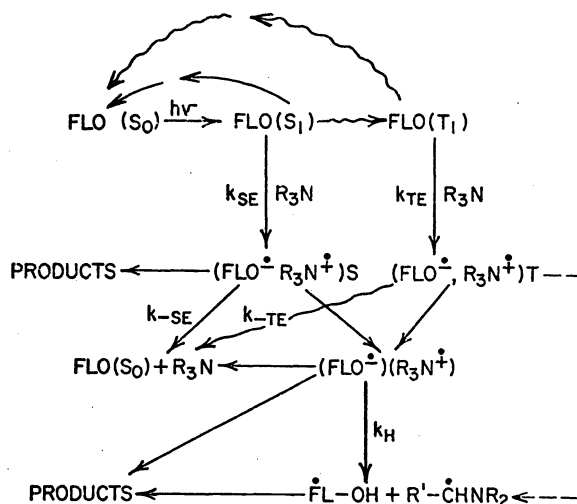


activated by IAA. After correcting for relative light absorption characteristics at the wavelengths employed for activation (366 or 405 nm), relevant data ( $10^4 R_p$ ,  $M \cdot \text{sec}^{-1}$ ,  $k_p/k_t^{1/2}$ ,  $M^{-1/2} \text{sec}^{-1/2}$ ) are as follows: fluorenone (1.04, 0.036); 2-methylfluorenone (0.92, 0.066); 1-methylfluorenone (1.06, 0.042); 2-methoxycarbonylfluorenone (0.73, 0.066); 2-methoxyfluorenone (0.30, 0.042).

These data indicate a great deal of complexity in the various processes competing to deactivate intermediate exciplexes, prior to radical formation and to scavenge radicals once they are formed. Furthermore, the rate data of Figure 3 and that given previously (Ref. 14) for DME/FLO systems indicate clearly that increasing amine concentration is beneficial only up to a certain point after which (presumably) excited fluorenone singlet state quenching by amine becomes a competing process. Quantum yields for reduction of fluorenones are known to vary according to the amine donor (Ref. 17) but an additional complication arises from the presence of methyl methacrylate monomer (MMA). Whereas quantum yields for reduction of fluorenone by IAA in benzene ( $\phi = 0.2$ ) are not affected by addition of MMA, corresponding values for photoreduction of fluorenone by DME ( $\phi = 1.2$ ) and triethylamine ( $\phi = 0.7$ ) are each reduced by a factor of 3-4 in the presence of ca 1.0 M MMA.

A reaction scheme which can be used to account for many of the experimental observations is given in Figure 4.

Figure 4



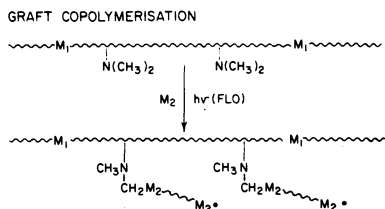
Here the quenching and/or energy wastage mechanisms for excited fluorenone not involving amine are represented, for clarity, by the curved arrows at the top of the diagram. Singlet (S) and triplet (T) exciplexes ( $FLO^{\cdot-} R_3N^{\cdot+}$ ) are produced from the appropriate excited states by collisional encounters with amine molecules ( $k_{SE}$  and  $k_{TE}$  respectively) and may undergo radiationless decay to ground states by the reverse processes ( $k_{-SE}$ ,  $k_{-TE}$ ). Chemical products are seen as arising directly from the triplet exciplex or, via a pair of ion-radicals ( $FLO^{\cdot-}$ ) ( $R_3N^{\cdot+}$ ), formed by further relaxation of either singlet or triplet exciplexes, between which the proton transfer ( $k_H$ ) is kinetically important. Solvent effects previously noted suggest that, for production of radical species, relaxation of singlet exciplexes ( $FLO^{\cdot-} R_3N^{\cdot+}$ )\_S does not compete as favourably with  $k_{-SE}$  as does the comparable relaxation of triplet exciplexes ( $FLO^{\cdot-} R_3N^{\cdot+}$ )\_T with  $k_{-TE}$  or direct formation of the radicals from the triplet exciplex.

Independent studies (Ref. 29,30) indicate that  $\dot{F}LOH$  and related semipinacol radicals are not especially efficient in initiation of polymerisation at ambient temperatures (but see below) and the important initiating species will, therefore, be amine derived radicals such as  $R\dot{C}HNR_2$ . FLO/DME systems have been used successfully to initiate polymerisation of methyl methacrylate, methyl acrylate, acrylonitrile, and styrene and rather similar mechanisms are likely to be involved in the photoinitiation of methyl acrylate

by benzophenone/triethylamine (Ref. 31). Michler's Ketone (4,4'-dimethylaminobenzophenone) and its alkyl homologues possess both a carbonyl group for light activation and an appropriate amino-function for electron transfer. In consequence bimolecular exciplexes involving Michler's Ketone (Ref. 32) with other carbonyl compounds (Ref. 33) may be expected to exhibit free radical initiation capabilities and offer the additional advantage of extending light sensitivity to longer wavelengths. The latter is, of course, particularly important in pigmented systems (Ref. 34).

#### PHOTOCHEMICALLY ACTIVE POLYMERS AS INITIATORS

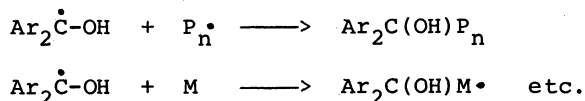
The great variety of substrates participating in exciplex formation may be readily extended to polymer-based systems. Of these, the ketone-amine combinations offer most scope since it is comparatively easy to prepare a range of copolymers containing 2-dimethylaminoethyl methacrylate units as electron donor entities (Ref. 14). Such copolymers when allowed to interact with photoexcited fluorenone are effective in causing rapid cross-linking and gelation as indicated:



More recently we have studied (Ref. 28) the utilisation of copolymers of methyl methacrylate and 2-vinyl-fluorenone (Ref. 35) as photoinitiators. In combination with suitable amine donors, these polymeric carbonyl compounds are effective crosslinking and gelling agents for methyl methacrylate, styrene and acrylonitrile monomers, and in this respect, behave in a manner similar to that of the polymer-based amines. However, detailed examination of rates of polymerisation and molecular weights of products at conversions below the gel-point have indicated new mechanistic features for amine-ketone systems.

Again using methyl methacrylate as the model system in benzene solvent ( $[MMA] = 5.0 M$ ) at  $30^{\circ}C$ , a range of copolymers of 2-vinyl fluorenone with methyl methacrylate (containing from 17-70% 2-vinyl fluorenone) in the presence of IAA or triethylamine, were found to give polymerisation rates and photoreduction characteristics (per mole of ketone) very similar to that given by 2-methylfluorenone. Polymers isolated before gelation were examined by G.P.C. in THF solution and gave clear evidence of both homopolymethyl methacrylate and graft polymethyl methacrylate for reactions co-initiated by IAA. In contrast whereas polymerisations photoinitiated by polymeric ketone and triethylamine (TEA) showed no evidence for graft polymer formation at  $[TEA] = 0.1 M$  and formed gelled systems only after prolonged irradiation, identical polymerisations but keeping  $[TEA] = 0.01 M$  showed slightly higher rates of polymerisation, gave clear (G.P.C.) evidence for grafting and formed gells readily. The conclusion must be that the higher concentrations of TEA retard, or prevent, coupling of the growing chains with polymer based radicals.

Coupling of polymer based radicals to growing chains, or to monomer, would logically involve termination or initiation respectively by the semipinacol radicals produced from the ketone component:



Possible explanations for the effects of amine concentration on rates and products of photoreduction of benzophenone have been discussed independently by Parola et al (Ref. 36) but for the present work an additional process is required whereby triethylamine at 0.1 M suppresses or modifies interaction of polymer based semipinacol radicals with growing chains or monomer. It is tempting to speculate that hydrogen bonding of semipinacol radical to the amine is important, so providing a mechanism for either, amine mediated hydrogen transfer to growing radicals or monomer, e.g.

$\text{Ar}_2\overset{\cdot}{\text{C}}\text{-OH (Amine)} + \text{P}_n^\bullet \longrightarrow \text{Ar}_2\text{C=O (Amine)} + \text{P}_n\text{H}$ , or a diminished capability of  $\text{Ar}_2\overset{\cdot}{\text{C}}\text{OH (Amine)}$  to terminate growing radicals by combination. In any case this result would be extremely important for the design of systems involving polymer based photoinitiators having anticipated rapid cure characteristics.

### References

1. A.D. Jenkins and A. Ledwith (Editors), "Structure, Reactivity and Mechanism in Polymer Chemistry", Wiley, London (1974).
2. H. Block, A. Ledwith and A.R. Taylor, *Polymer*, **12**, 271 (1971); A. Ledwith, G. Ndaalio and A.R. Taylor, *Macromolecules*, **8**, 1 (1975).
3. J. Hutchinson and A. Ledwith, *Adv. Polymer Sci.*, **14**, 49 (1974); S.P. Pappas, *Progr. Org. Coatings*, **2**, 333 (1974).
4. H.G. Heine, H.J. Rosenkranz and H. Rudolph, *Angew. Chem., Int. Edn.*, **11**, 974 (1972); H.G. Heine and H.J. Traenckner, *Progr. Org. Coatings*, **3**, 115 (1975).
5. A. Ledwith, *J. Oil Col. Chem. Assoc.*, **59**, 157 (1976).
6. J. Chilton, L. Giering and C. Steel, *J. Amer. Chem. Soc.*, **98**, 1865 (1976).
7. M.R. Sandner and C.L. Osborn, *Tetrahedron Lett.*, 415 (1974); *idem*, Paper presented at the 167th National Meeting of the American Chemical Society, Los Angeles, April 3, 1974.
8. J.A. Bosley, M. Dale and A. Ledwith, to be published.
9. R.S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).
10. E.M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).
11. A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).
12. P. Hyde and A. Ledwith in "Molecular Complexes (R. Foster, ed.) Vol. II, Elek Science, (1974).
13. M. Gordon and W.R. Ware (Editors), "The Exciplex", Academic Press, London (1975).
14. A. Ledwith, p. 209 in reference 13.
15. J.D. Margerum, A.M. Lackner, M.J. Little and C.T. Petrusis, *J. Phys. Chem.*, **75**, 3066 (1971).
16. C.H. Bamford, p. 52 in reference 1; *Europ. Polymer J.*, (Suppl.) **1** (1969).
17. S.G. Cohen, A. Parola and G.H. Parsons, *Chem. Revs.*, **73**, 141 (1973).
18. R.S. Davidson, in "Molecular Association" (R. Foster, Ed.), Vol. I, Academic Press, London (1975).
19. K. Yoshihara and D.R. Kearns, *J. Chem. Phys.*, **45**, 1991 (1966).
20. L.A. Singer, *Tetrahedron Lett.*, 923 (1969); R.A. Caldwell, *ibid.* 2121, (1969); R.S. Davidson and P.F. Lambeth, *Chem. Commun.*, 1098 (1969).
21. J.B. Guttenplan and S.G. Cohen, *Tetrahedron Lett.*, 2125 (1969).
22. G.A. Davis, P.A. Carapellucci, K. Szoc and J.D. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969).
23. S.G. Cohen and G. Parsons, *J. Amer. Chem. Soc.*, **92**, 7603 (1970).
24. R.S. Davidson, P.F. Lambeth, J.F. McKellar, P.H. Turner and R. Wilson, *Chem. Commun.*, 732 (1969); R.S. Davidson and R. Wilson, *J. Chem. Soc. B* 71 (1970).
25. H.D. Roth and M.L. Manion, *J. Amer. Chem. Soc.*, **97**, 6886 (1975).
26. A. Ledwith and M.D. Purbrick, *Polymer (London)*, **14**, 521 (1973).
27. R.S. Davidson and P.R. Steiner, *J. Chem. Soc., Perkin II*, 1357 (1972).
28. J.A. Bosley, M.D. Purbrick and A. Ledwith, to be published.
29. J. Hutchinson, M.C. Lambert and A. Ledwith, *Polymer (London)*, **14**, 250 (1973).
30. D. Braun and K.H. Becker, *Makromol. Chem.*, **147**, 91 (1971).
31. M.R. Sandner, C.L. Osborne and D.J. Trecker, *J. Polymer Sci.*, A-1, **10**, 3173 (1972).
32. T.H. Koch and A.H. Jones, *J. Amer. Chem. Soc.*, **92**, 7503 (1970); V.D. McGinniss and D.M. Dusek, *Polymer Preprints*, **15**, 480 (1974); V.D. McGinniss, *J. Rad. Curing*, **2**, 3 (1975).
33. D.I. Schuster and M.D. Goldstein, *J. Amer. Chem. Soc.*, **95**, 6484 (1973).
34. V.D. McGinniss, *A.C.S. Symposium Series*, in press.
35. J.F. Yanus and J.M. Pearson, *Macromolecules*, **7**, 716 (1974); D.G. Marsh, J.F. Yanus and J.M. Pearson, *Macromolecules*, **8**, 427 (1975).
36. A.H. Parola, A.W. Rose and S.G. Cohen, *J. Amer. Chem. Soc.*, **97**, 6202 (1975).