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POLYMERIZABLE & POLYMERIC

TYPE I & TYPE II PHOTOINITIATORS

by

SANDRALEE PATRICIA LEWIS

A thesis submitted for the degree of Doctor of Philosophy (PhD) in the Chemistry Department of the City University, London.

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ABSTRACT

A number of monomeric and polymeric benzil and benzoin derivatives were prepared and were evaluated as photoinitiators for the polymerization of vinyl monomers. Some of the benzoin derivatives were designed such as to exhibit water compatibility, and were evaluated in aqueous media.

The mode of photodecomposition of the polymeric photoinitiators was determined by radical trapping experiments, and a chain transfer agent was employed to control their molecular weights. In all cases, the performance of the polymeric photoinitiators was compared to that of a monomeric analogue, in order to determine the effects on efficiency of incorporation of the photoreactive groups into a polymeric system. For all of the photoinitiators evaluated in this manner, it was observed that incorporation into a polymeric network - whether as pendant groups or as a part of the polymer backbone - led to an enhancement of efficiency. Reasons for this observation are suggested in the text.

All of the monomeric photoinitiators prepared carried substituents at the 4 and 4' positions, which would enable them to be built into a polymer chain. Comparisons were made between the efficiencies of the various monomeric systems, in order to observe any effect which the substituents may have had on performance. In all cases, evaluations were carried out in both the presence and absence of a tertiary amine synergist. It was generally observed that the presence of electron-donating substituents at the 4 and 4' positions led to an increase in photoinitiating efficiency.

The relative efficiencies of the photoinitiators in the initiation of vinyl polymerizations were evaluated by two or more of the following methods: solution polymerization, thin film UV curing and real-time infrared spectroscopy.

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CHAPTER I:

INTRODUCTION TO PHOTOINITIATION & PHOTOINITIATORS

1.1 BACKGROUND PHOTOCHEMISTRY

A molecule possesses its minimum electronic energy when in the ground state which, for most molecules, is a singlet state, characterized by an even number of spin-paired electrons. Absorption of light by the molecule results in an electron being promoted from the highest occupied molecular orbital in the ground state, to a molecular orbital in a higher energy state; if promotion takes place to the lowest unoccupied molecular orbital, the state produced is known as the first excited state and the transition giving rise to the first excited state is the transition of lowest energy which can result in change in electronic configuration.

Electrons from a spin-paired ground state remain spin-paired in excited states directly populated by light absorption but, following promotion from the ground state to an excited state of the same multiplicity, spin-unpairing may occur. The spin multiplicity (i.e.singlet state, triplet state etc.) of a given energy state is determined by the number of spin-unpaired electrons associated with that state; the terms 'singlet', 'doublet' and 'triplet' are given to represent states in which the number of spin-unpaired electrons is zero, one and two, respectively.

Light absorption by ground state singlets gives rise to excited state singlets, which may subsequently undergo spin-unpairing to yield excited state triplets. In the case of such singlet to triplet state conversion, or conversion from any state to another of different spin-multiplicity, the process which takes place is referred to as 'intersystem crossing'.

The Pauli exclusion principle states that electrons with parallel spins cannot occupy the same molecular orbital and must, therefore, exist in different spatial regions. Thus inter-electronic repulsions will be reduced relative to a corresponding spin-paired state. It follows from this that triplet states (spin-unpaired) will be of lower energy than their corresponding singlet states (spin-paired). This is in accordance with Hundt's rule, which stipulates that, all other things being equal, the electronic configuration with the higher spin multiplicity is more stable.

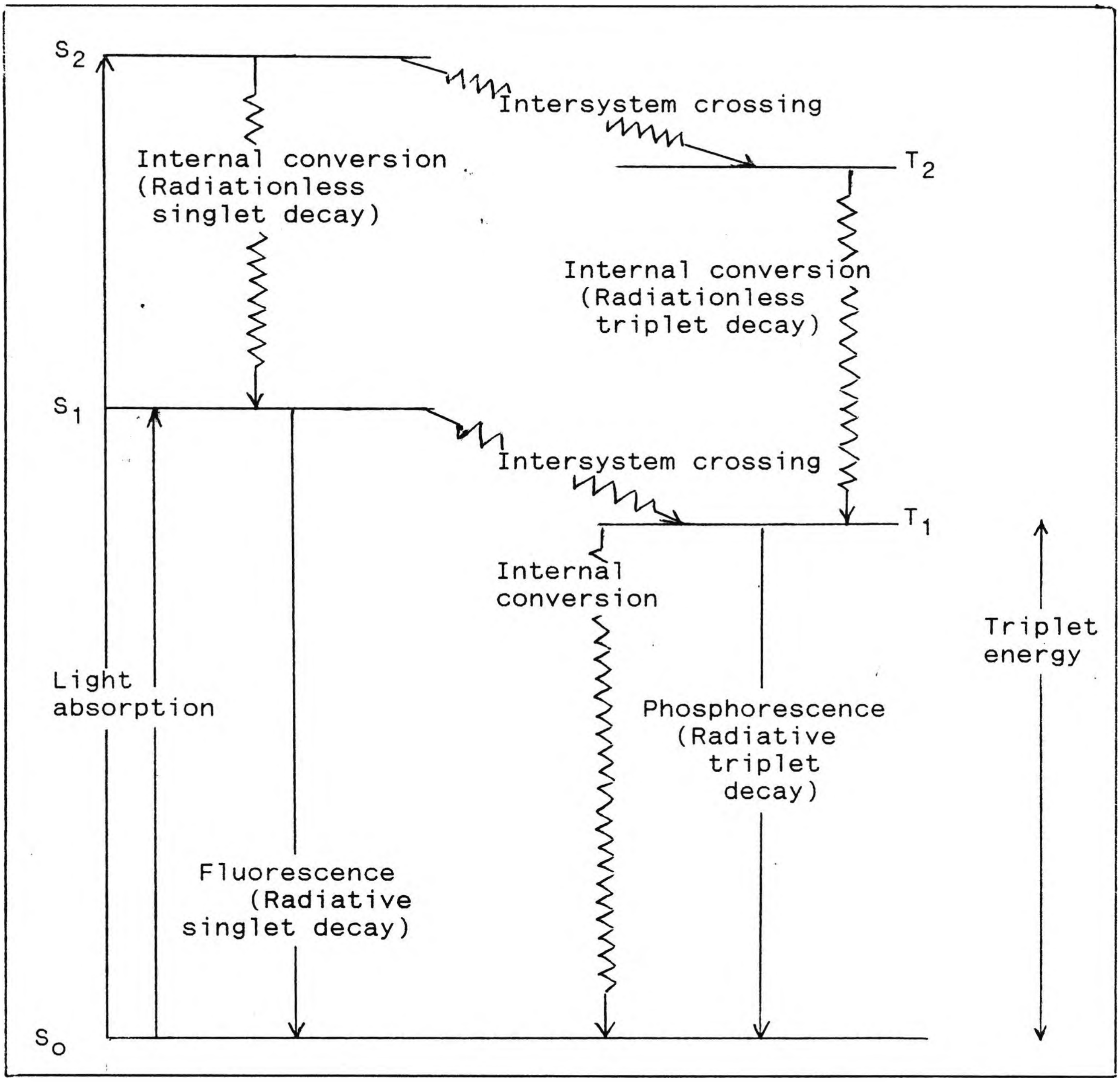
It is generally accepted that photochemical reactions occur from both singlet and triplet excited states, usually from the lowest excited singlet and triplet states, S_1 and T_1 respectively. However, since the lifetime of T_1 states is often of the order of one hundred times or more that of S_1 states (the lifetime of T_1 states is generally greater than 10^{-6} sec, compared to a lifetime of less than 10^{-8} sec. for S_1 states) many photochemical reactions - especially those which occur intermolecularly - occur via T_1 states. Once formed, the excited states may lose their excitation energy by any of four main alternatives:

(i) Radiationless conversion back to the ground state (internal conversion).

(ii) Radiative conversion back to the ground state (referred to as fluorescence in the case of conversion from a singlet excited state and phosphorescence when the excited state is a triplet).

(iii) Quenching of the excited state by interactions with other components of the system e.g. solvent molecules.

(iv) Intersystem crossing

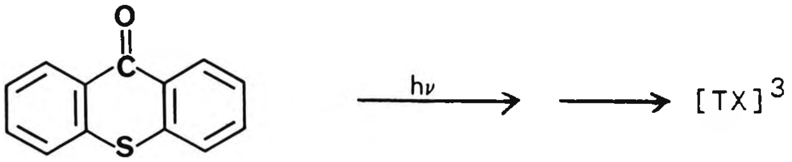


1.2 PHOTOCHEMISTRY OF PHOTOINITIATORS & PHOTOINITIATION

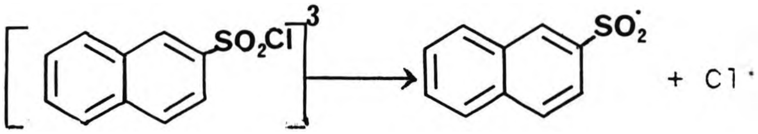
Before a photoinitiator can be active in the initiation of polymerization, population of its chemically-reactive excited state must first take place. From this state the initiator radicals are formed which proceed to interact with reactive monomers or oligomers and thus initiate polymerization.

As stated previously, many photochemical reactions occur exclusively via T_1 states and, hence, population of the chemically-reactive excited state may involve intersystem crossing. Consequently, the efficiency with which intersystem crossing occurs is often an important factor in determining the overall efficiency of photoinitiation. The benzoin ethers and their derivatives are known to undergo intersystem crossing with high efficiency and probably react via the T_1 state, although it has been suggested by Heine[1] that the photocleavage of benzoin alkyl ethers may occur via the singlet state.

In some cases it is not possible for direct interaction to occur between the photoinitiator molecule and light of a particular wavelength, and an alternative process is then required for population of the chemically-reactive excited state; this process is known as photosensitization. In the event of photosensitization taking place, the light energy is absorbed by the photosensitizer, which is consequently promoted to its singlet excited state. Intersystem crossing then affords the corresponding triplet excited state. Energy transfer from the triplet excited state of the photosensitizer to the compound of interest results in the latter being elevated to its chemically-reactive excited state. Compounds such as thioxanthones have been used as triplet sensitizers for the decomposition of aryl sulphonyl chlorides.



Thioxanthone TX



An obvious requirement for any molecule to be used as a photosensitizer is that it should absorb light of the required wavelength, whilst a high efficiency of intersystem crossing is also desirable. Moreover, if the transfer of energy from the photosensitizer to the co-initiator is to occur with a reasonable level of efficiency, it is essential that the triplet excited state of the photosensitizer be of higher energy than that of the co-initiator, since the latter state must be created by the energy provided by the former.

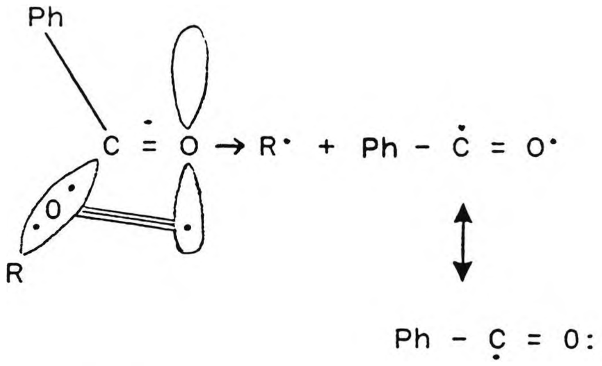
The formation of initiator radicals by the reactive excited state of the initiator molecule may occur by either intramolecular photocleavage of the excited state or by the abstraction of hydrogen from a suitable hydrogen donor. Being an intermolecular process, the production of radicals by H-abstraction may be limited by diffusion and competition from other, destructive, bimolecular reactions, whilst photocleavage requires the reactive state to be sufficiently energetic for bond dissociation to be efficient. If the chemically-reactive excited state from which radicals are produced is a singlet state, the radical formation process must compete with intersystem crossing to the triplet state and decay (radiative and radiationless) to the ground state. In the case of initiator radicals being formed via the T_1 state, triplet decay to the ground state competes with the radical formation process, but since the lifetime of the triplet state is considerably greater than that of singlets, there is the additional problem of a greater probability of the excited state being quenched by various bimolecular processes.

The term 'photoinitiator' is generally used to describe compounds which absorb light and undergo efficient dissociation to produce initiating species. Photoinitiators for free radical polymerization are used to initiate the polymerization of unsaturated compounds, such as vinyl and acrylic monomers. The radical species formed are initially contained within a 'cage' of substrate molecules and are able to undergo combination or disproportionation reactions whilst still inside the cage. On escaping from the substrate cage the primary radicals are able to interact with the monomers, thus initiating the chain reaction to produce a polymeric system.

Photoinitiators for the UV curing of thin films can generally be divided into two main groups: free radical photoinitiators and cationic photoinitiators. The free radical photoinitiator group can be further divided into those photoinitiators which generate radicals via unimolecular cleavage and those which follow a bimolecular cleavage mechanism (i.e. intermolecular H-abstraction). These two sub-divisions have several common features, the most important being the presence of at least one carbonyl function conjugated to an aromatic ring. The popularity of these aromatic carbonyl compounds is largely due to their absorption characteristics in the 300-400nm range and the wide variety of photoreactions which they undergo. Since carbonyl compounds possess two electrons in each of the non-bonding orbitals of the carbonyl oxygen atom, the absorption of light can result in one of these electrons being promoted into either an anti-bonding sigma orbital (σ^*) or an anti-bonding pi orbital (π^*), i.e. either $n \rightarrow \sigma^*$ or $n \rightarrow \pi^*$ transitions result. In the majority of cases the order of energies for molecular bonding and anti-bonding orbitals is as follows:-

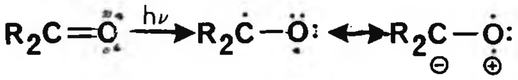
$$\sigma^* > \pi^* > n > \pi > \sigma$$

This order of orbital energies means that $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ are the most readily observed transitions, $n \rightarrow \pi^*$ usually being of lower energy than corresponding $\pi \rightarrow \pi^*$ transitions. In the case of conjugated, unsaturated carbonyl compounds, however, the π orbital is usually of higher energy than the n orbital, so that less energy is required to promote an electron from a π to a π^* orbital than to promote from an n to a π^* orbital. The (n, π^*) and (π, π^*) excited states possess very different chemical reactivities, as illustrated by the photoreduction and α-cleavage reactions of aryl alkyl ketones performed by Lewis and Magyar[2], which led them to conclude that α-cleavage occurs more efficiently from (n,π^*) than from (π,π^*) triplet states. They attributed this difference in reactivities to an overlap between the half-vacant non-bonding orbital of the oxygen atom in the (n,π^*) excited state of the carbonyl and the bond undergoing homolytic fission.



For the (π,π^*) excited state such overlap is not possible, hence its lower reactivity relative to the (n,π^*) state of aryl alkyl ketones.

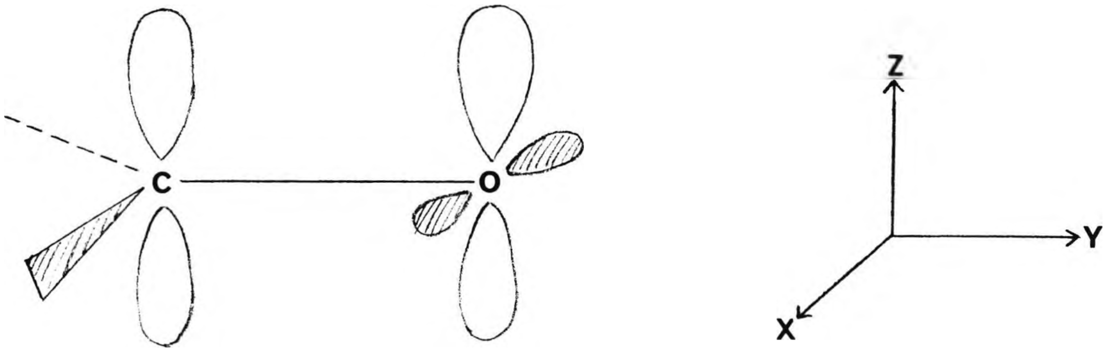
Walling and Gibian[3] studied the competitive consumption of several hydrocarbon substrates in the photoreduction of benzophenone and other ketones and found that the reactivity series observed was very similar to that followed by tertiary-butoxy radicals. This similarity between ketone triplets and alkoxy radicals they explained, electronically, as follows: In an n→π^* transition an electron is promoted from one of the oxygen lone pairs to the carbon-oxygen π^* orbital and can be represented in valence bond terms as:



$$R_2C{=}\ddot{O}: \xrightarrow{h\nu} R_2\dot{C}-\dot{\ddot{O}}: \longleftrightarrow R_2\underset{\ominus}{C}-\underset{\oplus}{\dot{O}}:$$

The left-hand resonance structure is the major contributor, which means that the triplet approximates to a species with seven electrons on single-bonded oxygen. (Contributions from the right-hand structure, however, contribute a positive charge to the oxygen, which could increase its capacity as an electron-acceptor). Thus, the promotion of an electron from an n orbital to a π^*-antibonding orbital effectively removes electron density from the oxygen atom, resulting in a similarity between the reactivities of (n,π^*) excited states and alkoxy radicals. On the other hand, when an electron is promoted from a π-bonding orbital to a π^*-antibonding orbital the effect is to increase electron density at the oxygen atom and, consequently, increase the polarity of the C=O bond also.

As can be seen from the orbital diagram, spatial overlap between the n and π^* orbitals is poor and, according to the selection rule for electronic transitions, (n, π^*) excited states are classified as being partially forbidden, whilst (π,π^*) excited states are allowed. As a consequence, the



Molecular orbitals of the C=O group

molar extinction coefficients for $\pi \rightarrow \pi^*$ transitions are in the region of 10 - $10^4 M^{-1} cm^{-1}$ larger than for $n \rightarrow \pi^*$ transitions.

The most significant difference between the (n, π^*) and (π, π^*) excited states of aromatic carbonyl compounds, however, is the much higher efficiency with which intersystem crossing occurs in the former. The greater efficiency of intersystem crossing in (n, π^*) excited states can be attributed to two major factors:

(a) Since the $n - \pi^*$ transition is partly forbidden by the electronic transition selection rules, the reverse transition is also partly forbidden. Consequently, S_1 (n,π^*) states generally have longer lifetimes than S_1 (π,π^*) states and, hence, the probability of conversion to the T_1 state is accordingly higher for the (n,π^*) state.

(b) The difference in energies between the S_1 and T_1 states is much greater for (π,π^*) states than for (n,π^*) states.

1.3 PHOTOINITIATOR TYPES

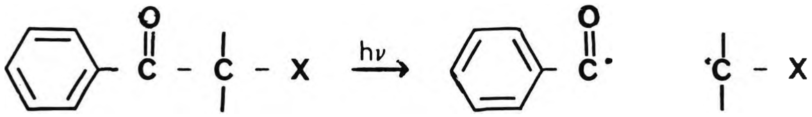
1.3.1 Intramolecular Bond Cleavage Photoinitiators

It is important for photoinitiators of this type to possess a bond for which the dissociation energy is lower than the excitation energy of the chemically-reactive excited state, whilst still being sufficiently high to give a reasonable degree of heat stability. A high rate of photocleavage and the efficient initiation of polymer chains by the free radicals produced are further desirable characteristics. Photoinitiators which produce radicals by direct fragmentation include many aromatic carbonyl compounds, of which benzoin and its alkyl ethers have been the most widely used as photoinitiators for the polymerization of vinyl monomers. In fact benzoin ethers were probably the first of this type of photoinitiator to be used commercially, and many remain in use at present.

There are generally two mechanisms by which initiating radicals can be produced by direct photofragmentation of aromatic carbonyl compounds:

1.3.1.1 *α*- Cleavage (Norrish Type I Cleavage)

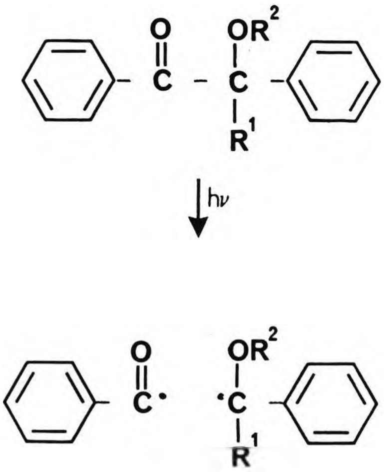
Norrish Type I cleavage involves cleavage of the carbon-carbon bond in the α- position to the carbonyl group



Many of the commercial photoinitiators currently in use undergo photocleavage according to this mechanism.

1.3.1.1.1 Benzoin Derivatives

The usefulness of benzoin in photopolymerization reactions was first suggested in the chemical literature by Chinmayanandam and Melville[4] in 1953, who provided evidence (from kinetics) for its photocleavage into radicals. Proof for the α- cleavage of benzoin and its ethers on irradiation has since been provided in a variety of ways, the most notable being the CIDNP studies of Closs and Paulson[5] on solutions of aromatic carbonyl compounds; Ledwith and Sutcliffe's[6] combination of the radical scavenging and ESR techniques to characterize the radicals produced on the photocleavage of benzoin and benzoin methyl ether; and the structure-reactivity studies on benzoin and several of its derivatives performed by Lewis et al.[7], amongst others.



R^1=H, alkyl aryl or substituted alkyl;

R^2=H, alkyl,aryl, substituted alkyl,

$-COR^3$ or $-SO_2R^3$;

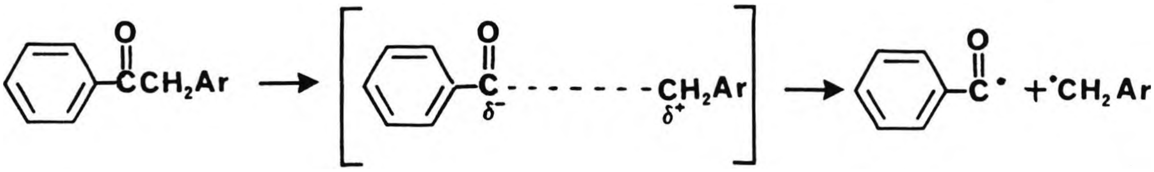
R^3=alkyl or aryl

α-Cleavage of Benzoin and its Derivatives

Studies of polymerization reactions with C^{14}-labelled benzoin methyl ethers performed by Pappas together with Chattopadhyay[8] and Carlblom[9] further supported the α-cleavage mechanism of benzoin ethers to produce a benzoyl and α-substituted benzyl radical pair.

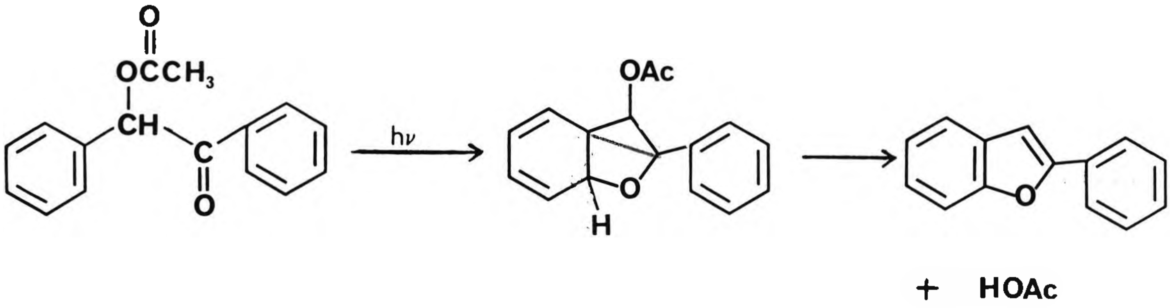
Irradiation of benzoin derivatives with light in the 300-360nm range results in excitation to a higher singlet state, from which efficient intersystem crossing to the chemically-reactive T_1 state occurs. At this point the difference in lifetimes of the triplet excited states of the various benzoin derivatives becomes apparent. The fact that it is not possible to quench the photocleavage of the benzoin ethers with usual triplet quenchers led Heine[1] to suggest that reaction may be taking place via the singlet state, but photosensitization studies performed with benzoin isopropyl ether by Pappas and Chattopadhyay[10] seemed to suggest photocleavage via an excited triplet, rather than a singlet state. An (n, π^*) triplet state energy of 73kcal mol^{-1} for benzoin ethers is more than sufficient to allow bond dissociation (63kcal mol^{-1} required) to occur via this state, whilst the inability of the usual triplet quenchers to affect photocleavage indicates that reaction occurs with a rate constant in excess of $10^{10}sec^{-1}$ (i.e. triplet lifetime $\leqslant 10^{10}sec$). The photocleavage of benzoin esters, on the other hand, is quenchable by the usual triplet quenching agents, and the corresponding lifetime for the triplet excited states of benzoin acetate and desoxybenzoin are in the order of 10^{-6} - 10^{-8} sec. The difference in triplet excited state lifetimes can be used to rationalize the greater effectiveness of benzoin ethers, relative to other benzoin derivatives and benzoin itself, as photoinitiators, since the shorter triplet lifetime corresponds to a higher rate constant for α-cleavage. Since initiator radical production must compete with triplet quenching reactions, the greater rate constant for photocleavage leads to a greater efficiency of radical formation.

From their studies of substituent effects on the photochemical α-cleavage of benzoin derivatives, Lewis et al.[7] concluded that α-cleavage for these compounds proceeded via a polar transition state, and attributed the difference in rate constants / triplet lifetimes to polar contributions in the intermediate activated complex.



Activated complex

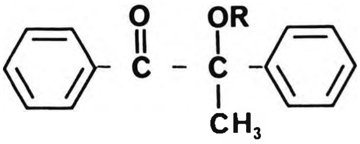
A further difference between benzoin and the ethers, and the benzoin esters, is the fact that the latter group of compounds does not undergo α-cleavage as the sole major reaction on irradiation, intramolecular cyclization followed by the elimination of acid also taking place in competition.



Solly and Benson[11] have provided evidence to suggest that the unpaired electron of the benzoyl radical produced on the photochemical α-cleavage of benzoin and its derivatives is not delocalized into the nucleus of the aromatic system, which means that benzoyl radicals should be efficient initiators with high reactivity. The previously mentioned studies of Pappas with Chattopadhyay[8] and Carlblom,[9] using C^{14}-labelled benzoin methyl ethers, indicated that the benzoyl and benzyl ether radicals produced on α-cleavage are both effective in initiating the polymerization of methyl acrylate and methyl methacrylate, although the work of Heine and Traencker[12] suggests that the benzoyl radical may be more reactive in the case of styrene being used as the monomer.

Confirmation for the initiating ability of the benzoyl radical and the terminating tendency of the α-substituted benzyl radical would seem to be forthcoming from the work carried out by Hageman and co-workers[13,14], but it is still possible that the α-substituted benzyl radical does add to the olefinic double bond.

One major disadvantage with benzoin ether photoinitiators is their apparent instability in the presence of monomers, which results in the premature polymerization of monomers whilst stored in the dark. This instability has been rationalized in terms of the presence of the readily abstractable benzylic H-atom, since substitution of this H-atom, as in systems such as α-methyl benzoin methyl ether or ester derivatives, leads to a dramatic increase in shelf-life relative to unsubstituted ethers.

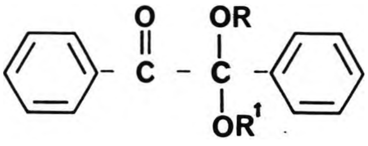


α- Methyl Benzoin Methyl Ether

Furthermore, the increasing stability in the alkyl substituent series methyl through to tertiary-butyl can be attributed to an increase in shielding of the benzylic H-atom.

In the next group of photoinitiators undergoing α-cleavage to produce radicals, the problem of storage instability as a result of the presence of the benzylic H-atom is eliminated.

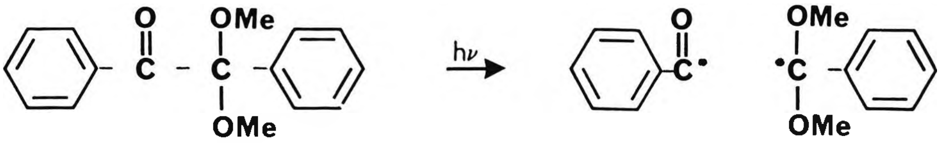
1.3.1.1.2 Benzilketals



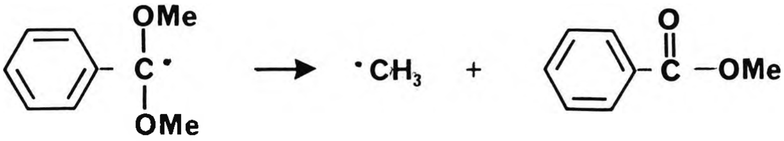
R,R^1=alkyl or substituted alkyl

The benzilketals have been found to possess high thermal stability as well as a high efficiency of initiation and, thus, find use in a wide range of commercial applications.

Benzildimethylketal (α,α-dimethoxy- α- phenylacetophenone, DMPA) has been shown to undergo α-cleavage with high efficiency to yield the benzoyl and α,α-dimethoxybenzyl radicals.



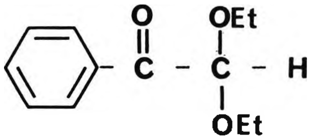
Methyl benzoate and a methyl radical are formed on subsequent fragmentation of the disubstituted benzyl radical.



Using 1,1-diphenylethylene as a model substrate, Hageman et al.[14] showed that the benzoyl radical is active in the initiation process; the α,α-dimethoxybenzyl radical, whilst being involved in termination to some extent, undergoes sequential fragmentation - as shown above - as the major reaction, the methyl radical thus formed making a small contribution to the initiation process.

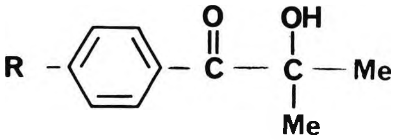
1.3.1.1.3 Acetophenone Derivatives

α,α-Diethoxyacetophenone (DEAP) is representative of the acetophenone-type photoinitiators and has been shown to approximately equal benzil dimethylketal for effectiveness in initiating the photopolymerization of vinyl monomers.



The fact that the α-hydrogen atom in this system is not benzylic leads to a stability greater than that found with the benzoin ethers, but the absence of any α-phenyl group causes a substantial reduction in the rate constant for photocleavage so that, whilst α-cleavage does take place, β-cleavage (Norrish Type II) occurs also. However, the CIDNP studies of Borer, Kirchmayer and Rist[15] indicate that the radicals primarily involved in the initiation process are those generated by α-cleavage, results which have been confirmed by radical trapping experiments[16].

1.3.1.1.4 α-Hydroxyalkylphenones



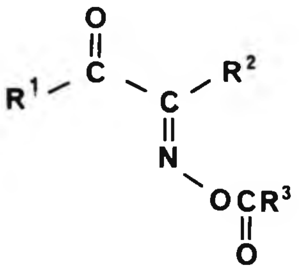
It has been claimed that this class of compounds exhibits comparable efficiencies to benzil dimethylketal with respect to initiating the photopolymerization of vinyl monomers.

The α-hydroxyalkylphenones have the additional advantages of good solubility and high storage stability. α-cleavage to form benzoyl and 2-hydroxy-2-propyl radicals has been confirmed by both CIDNP and radical trapping studies to be the predominant mechanism for deactivation of the chemically reactive excited triplet state.

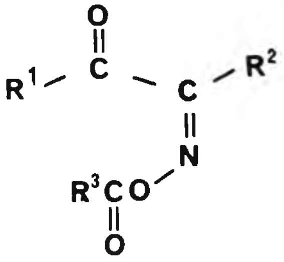
1.3.1.1.5 O-Acyl-α-Oximinoketones

In the photoinitiated polymerization of certain vinyl monomers, such as acrylamide[17] and various acrylate esters[17,18], O-acyloximinoketones have been reported to exhibit higher efficiences than the benzoin alkyl ethers.

Although this group of compounds can, in principle, exist in either of two geometrical isomeric forms, the synthetic routes by which they are usually produced lead almost exclusively to the (E), rather than (Z), isomers.



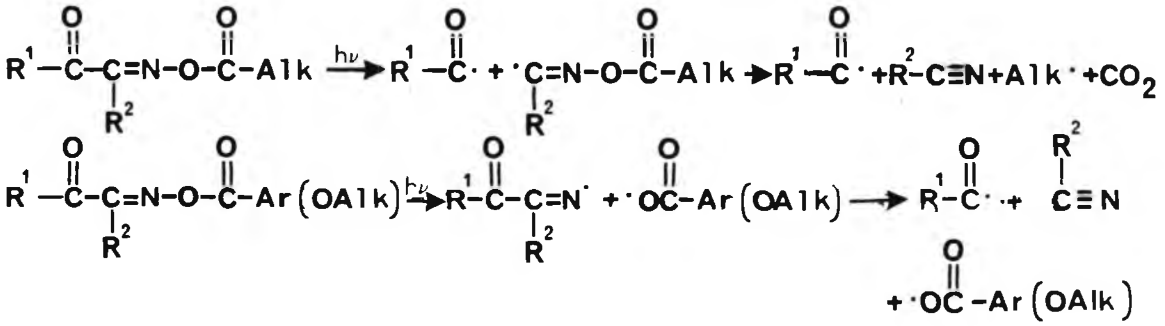
(E)



(Z)

R^1=aryl , R^2=alkyl or aryl, R^3=alkyl,substituted alkyl,aryl or alkoxy

Based on results obtained from laser flash photolysis studies[19], it has been assumed that α-cleavage occurs when R^3 is either alkyl or substituted alkyl but, in the case of this substituent being an aryl or alkoxy group, cleavage of the N-O bond occurs instead.



Thus the enhanced efficiency of certain O-acylaminoketones relative to benzoin alkyl ethers can be partially attributed to the generation of two reactive radicals (the acetoxy as well as the benzoyl radical) by each photoinitiator molecule.

The major disadvantage with this type of photoinitiator is the low stability displayed on storage in a variety of UV-curable formulations.

1.3.1.1.6 Acylphosphine Oxides

This group of compounds was first introduced as photoinitiators for polymerization in 1983. Laser flash photolysis experiments carried out by Sumiyoshi and co-workers[20,21,22] led to the deduction that acylphosphine oxides and related compounds produce radicals via the cleavage of excited triplet states with an estimatedlifetime of less than one nanosecond. Recent CIDEP studies[23] have provided conclusive evidence for the α-cleavage of acylphosphine oxides, whilst chemical evidence for such solvent-independent α-cleavage to give acyl and phosphinyl radicals has been afforded by the radical trapping experiments of Baxter and Davidson in co-operation with Hageman and Overeem[24].

Considering the rapidity of the photocleavage process, the observed effect that the addition of tertiary amine to UV-curing formulations containing acylphosphine oxide photoinitiators results in a considerable enhancement of curing efficiency has led to the conclusion that the added amine adopts the rôle of oxygen scavenger, thus dramatically reducing the susceptibility of the system to the effect of O_2-inhibition[25]. Whilst enhancing polymerization and cure rates in most cases, it was reported, in the same publication, that the addition of tertiary amine caused a reduction in the shelf-life of one of the formulations tested, thus highlighting the need for care when using amines as synergists with acylphosphine oxides.

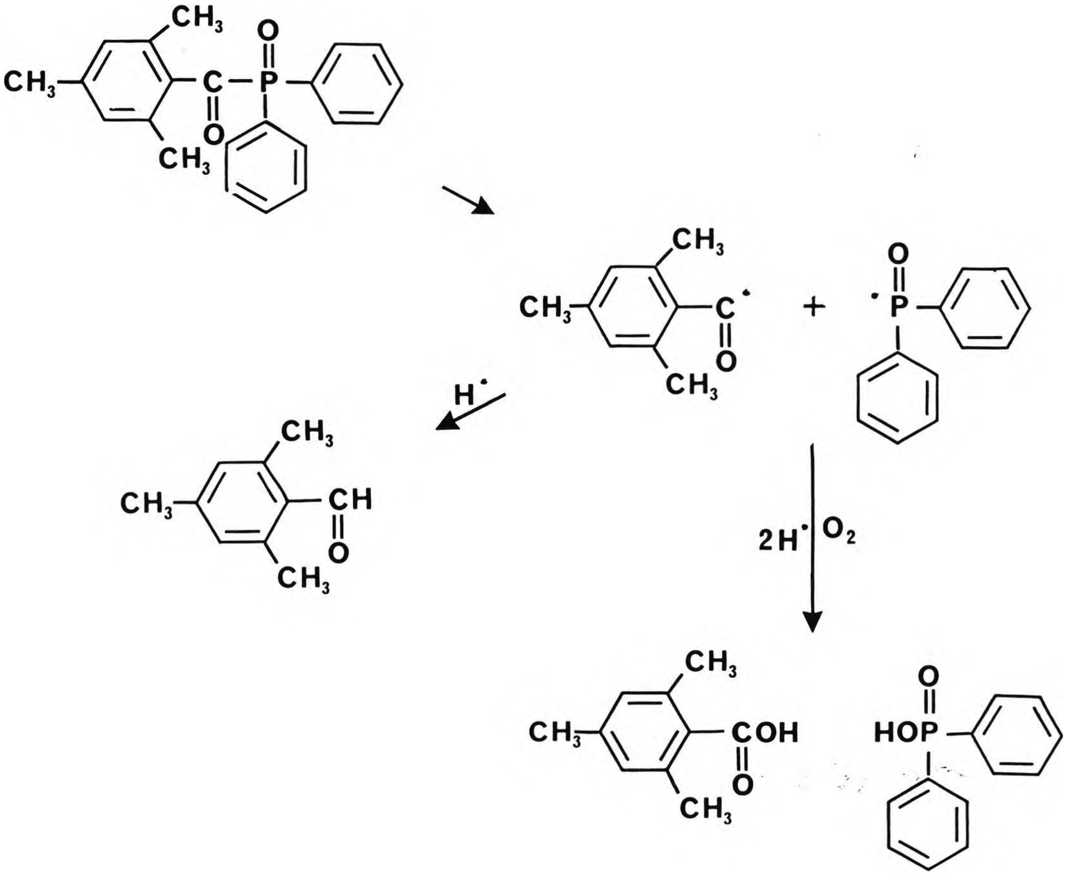
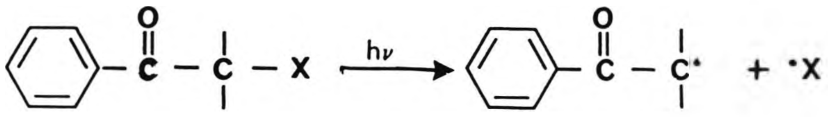


Illustration of the decomposition of the acylphosphine oxide TMBPO under UV curing conditions in the presence of oxygen

1.3.1.2 β-Cleavage (Norrish Type II)

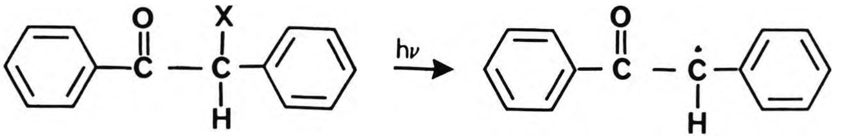
β- or Norrish Type II-cleavage involves fragmentation of the bond α-β to the carbonyl group on the abstraction of a γ-hydrogen atom by an excited carbonyl group.



1.3.1.2.1 Benzoin Derivatives

Benzoin aryl ethers have been observed, on separate occasions, to undergo β-cleavage to a limited extent. As for α-cleavage, it has been shown that reaction occurs from a triplet excited state, the lifetime of which, in this case, is of sufficient duration to allow quenching by triplet quenchers such as naphthalene. Lower initiating efficiencies have been reported for these compounds than for corresponding benzoin alkyl ethers with unsaturated polyester systems, and this has been partially attributed to some quenching by styrene as well as lower reaction rate constants.

The benzoin derivatives known as desyl halides and desyl aryl sulphides have been reported to undergo β-cleavage exclusively. Whilst claims have been made that some desyl aryl sulphides are capable of functioning as photoinitiators for the polymerization of acrylate esters[26] and unsaturated polyesters, it has yet to be determined which of the radicals produced by β-cleavage is responsible for the initiation.

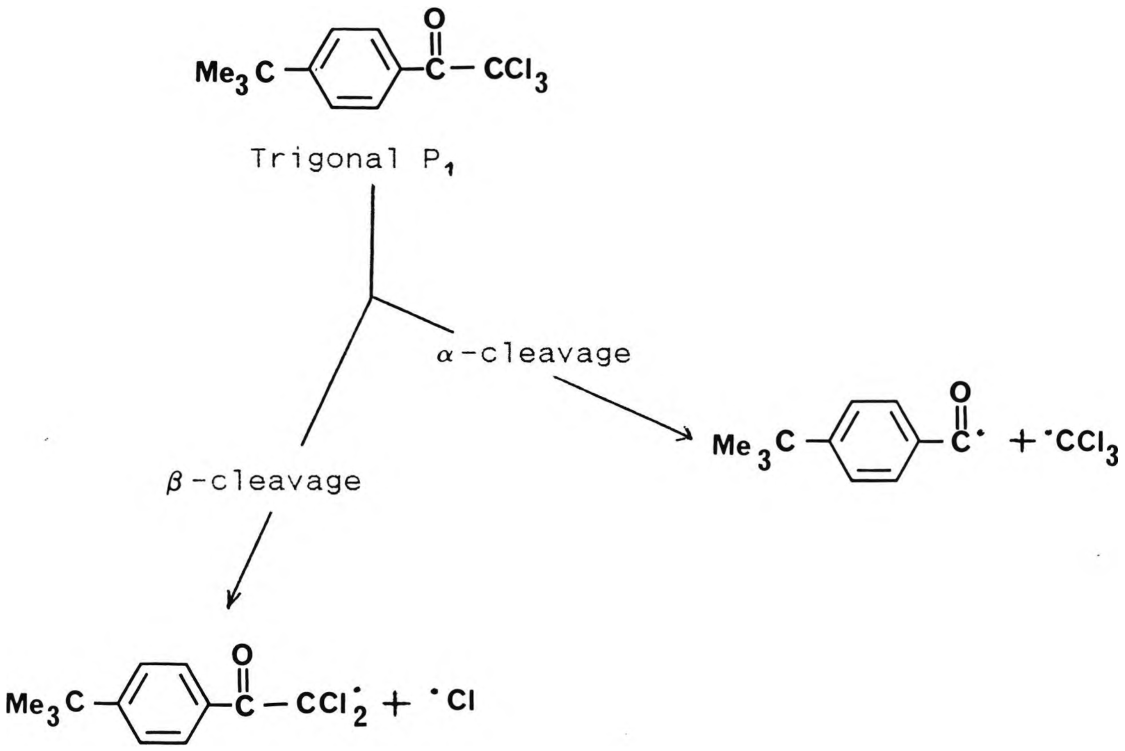


+ ˙X ; X=S-Ar or halogen

1.3.1.2.2 Acetophenone Derivatives

Those acetophenone derivatives which undergo β-cleavage all belong to the α-halogeno acetophenone group. One derivative in particular, namely Trigonal P_1 (trade name), has been studied in some detail, and CIDNP experiments reveal that photofragmentation via α-cleavage is also a minor reaction.

In terms of photoinitiating ability and storage stability, Trigonal P_1 is reported to be comparable to benzil dimethylketal and α,α-diethoxyacetophenone.



1.3.2 Intermolecular Hydrogen-Abstracting Photoinitiators

Certain aromatic ketones, on UV-excitation to their chemically reactive states, do not undergo photofragmentation but produce radicals via hydrogen abstraction from a hydrogen-donating molecule instead. The efficiency of the hydrogen abstraction process is determined by three major factors, as follows:

(i) the electronic configuration of the triplet state from which reaction occurs;

(ii) the strength of the bond undergoing fission in the hydrogen donor;

(iii) the relevant triplet energy of the carbonyl compound.

It has been found that vinyl monomers with triplet energies lower than that of the aromatic ketone cannot be polymerized by H-abstrating photoinitiators because of quenching. In such cases the excitation energy of the triplet excited photoinitiator is transferred to the vinyl monomer, resulting in de-excitation of the photoinitiator before hydrogen-abstraction from a suitable donor can take place. It should also be noted that photoinitiator triplet lifetimes are reduced considerably by the presence of oxygen.

Photoinitiators which operate via an intermolecular H-abstraction mechanism are generally benzophenone derivatives, although benzil and the quinones also initiate photopolymerization by abstracting hydrogen from an appropriate donor.

If PI and R-H represent the photoinitiator and hydrogen-donor respectively, then the following can be used to illustrate the reactions of importance to photoinitiation by an H-abstraction mechanism.

$PI \rightarrow PI^*$	Generation of the singlet excited state by the absorption of light.	
$^1PI^* \rightarrow {}^3PI^*$	Intersystem crossing from the excited singlet to the corresponding excited triplet state.	
$^1PI^* \rightarrow PI$	Radiative and non-radiative singlet decay back to the ground state compete with the intersystem crossing.	
$^3PI^* + R\text{-}H \longrightarrow P\dot{I}\text{-}H + R^{\bullet}$	Generation of initiator radicals via H- abstraction from the donor molecule.	
$^3PI \rightarrow PI$	Triplet decay	Compete with the H-abstraction processes.
$^3PI^* + Q \rightarrow PI$	Bimolecular quenching	

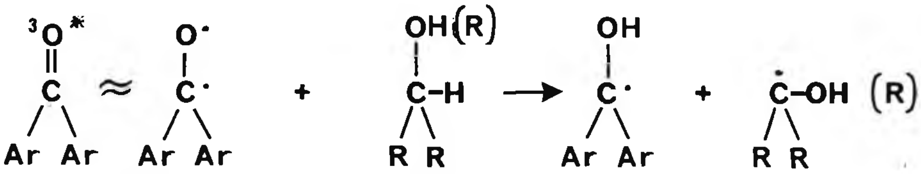
1.3.2.1 Reactivities of Hydrogen Donors

The most reactive types of H-donors in these reactions have been found to be those in which the active hydrogen atom is in the α-position to an oxygen or nitrogen atom, or in which it is connected directly to a sulphur atom; representative examples of each of these types of hydrogen-donor are given by the alcohols, tertiary amines and thiols, respectively.

As explained by Cohen, Parola and Parsons[27], triplet ketones abstract hydrogen more readily from tertiary amines than from alcohols, ethers or thiols, the greater reactivity leading to less competition by triplet deactivation processes (.i.e. triplet decay and bimolecular quenching) when a tertiary amine is the hydrogen donor.

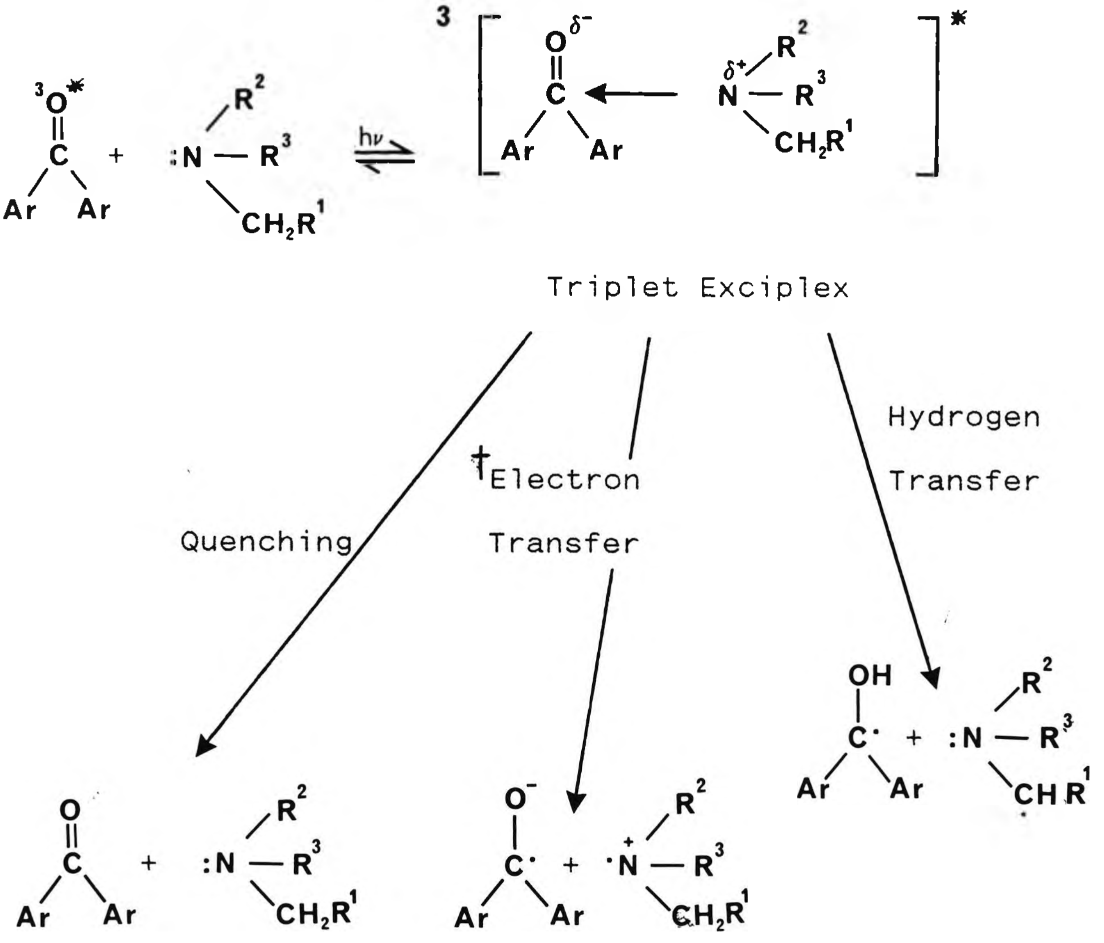
It was stated earlier that the reactivity of ketones is dependent upon the nature and energy of the excited triplet state. Alcohols and ethers have been found to undergo efficient reaction with ketones only with (n,π^*) triplet states, whereas amines exhibit general reactivity with both (n,π^*) and (π,π^*) triplet excited states. This difference in reactivities of the potential hydrogen donors is of particular importance when using aryl ketones in which their high absorptivity is attributable to the presence of electron-donating substituents (e.g. thioxanthone) since, in such cases, the (π,π^*)triplet tends to be of lower energy than the (n,π^*) state.

It would seem that the abstraction of hydrogen from alcohols and ethers is a direct hydrogen transfer from the donor to the (n,π^*) triplet ketone.



The rate of this hydrogen transfer reaction is generally lower than the rate at which the (n,π^*) triplet state of the ketone is quenched by oxygen, hence alcohol and ether hydrogen donors do not find widespread application.

The hydrogen abstraction reaction which takes place with amines, on the other hand, is not a simple hydrogen transfer, various spectroscopic methods providing evidence for the formation of an excited state complex (exiplex) between the amine and triplet ketone prior to the actual hydrogen transfer.



†Only important in polar media and with aromatic amines[28,29].

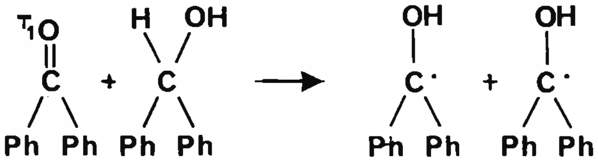
On the absorption of energy, electron transfer from the nitrogen lone pair to the oxygen atom of the carbonyl function results in the formation of an exciplex, which can either revert to the starting materials via back electron transfer, or form a ketyl and an α-amino alkyl radical by transfer of a hydrogen atom.

The formation of the exciplex may be attributed to charge transfer stabilization arising from the relatively low ionization potential of amines. A rough correlation actually exists between the ionization potential of the hydrogen donor and the rate constant for quenching of the carbonyl triplet state, in the case of the donor having an ionization potential of less than $\sim$9eV. The rate of formation of the exciplex increases with decreasing ionization potential of the amine and increasing electron affinity of the triplet ketone.

In those cases in which both quenching and hydrogen transfer may occur, several factors need to be considered before attempting to predict what will determine whether H-transfer will take place. Firstly, the rate of amine complexation must be taken into account and, as stated above, this is favoured by a low ionization potential of the amine. Secondly, there is the partitioning of the exciplex between hydrogen transfer and quenching, and it should be noted that quenching may also be favoured by a low amine ionization potential. The efficiency with which the amine radical initiates polymerization and the possibility of a neighbouring group participating in the hydrogen transfer process are further factors for consideration.

With regard to the abstraction of hydrogen from thiols, it is unlikely that complex formation will be a significant factor, since thiols have ionization potentials which are only slightly less than those of alcohols and ethers. Accordingly, experimental results indicate that the hydrogen donors are most reactive with (n, π^*) triplet ketones.

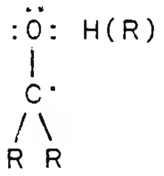
The hydrogen abstraction process produces two radicals potentially capable of initiating free radical polymerization. Considering the relatively high stability and bulkiness of aromatic ketyl radicals, together with the fact that they have a notable tendency towards pinacol formation via radical coupling, it seems unlikely that they would be particularly effective as initiators. In experiments performed by Ledwith et al.[30], benzhydrol was used as the hydrogen donor for triplet excited benzophenone, so that both reactants produced the same ketyl radical.

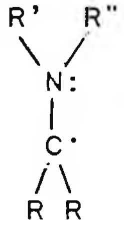


Using this photoinitiating system for the polymerization of methyl methacrylate, it was found that the addition of benzhydrol led to a retardation of the rate of polymerization and a drastic reduction in the molecular weight of the polymer formed. Thus, it can be concluded that the hydrogen donor radical must be that which induces the initiation of polymerization.

Later experiments by Kinstle and Watson[31], using benzophenone with N,N-diethylaniline as the hydrogen donor, showed the α-amino radical produced by the hydrogen donor to be 2-3 times more effective than the ketyl radical as an initiator for photopolymerization. Further supporting evidence for the higher initiating activity of the radical derived from the hydrogen donor comes from the work of Hutchinson, Lambert and Ledwith[32], in which kinetic studies on the photopolymerization of methyl methacrylate initiated by benzophenone with tetrahydrofuran (THF) as the hydrogen donor showed the ketyl radical to function primarily in a chain terminating capacity in this particular reaction.

The above, and other, results lead to the conclusion that the efficiency of photoinitiation in hydrogen abstracting photoinitiator/hydrogen donor systems depends heavily on the co-initiator radicals derived from the hydrogen donors. In the case of alcohol, ether and amine hydrogen donors the α-hydroxy, α-alkoxy and α-amino radicals formed are electron rich due to resonance effects on the adjacent heteroatom.

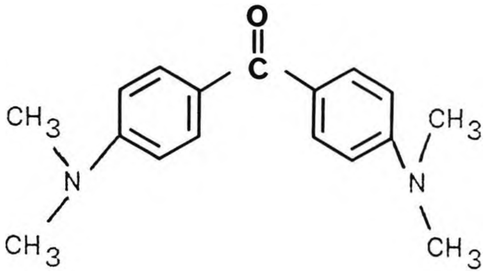




Thus, with these hydrogen donors a high efficiency of initiation is expected with electron deficient monomers such as acrylates. On the other hand, the thiyl radical formed on the abstraction of hydrogen from thiol hydrogen donors is relatively electron deficient due to the electronegativity of the sulphur atom, hence it would be expected that hydrogen donors of this type exhibit higher efficiency with electron rich monomers, such as vinyl ethers. Some form of support for these predictions is afforded by experimental evidence in the case of thiols[33], and indirect evidence in the case of amine co-initiators[34,35].

1.3.2.2 Michler's Ketone

Some mention should be made of a particular hydrogen abstracting diaryl ketone, known as Michler's ketone (bis(4,4'-dimethylamino)benzophenone). Michler's ketone (MK) possesses both diaryl ketone and tertiary amine groups, which enable photoinduced hydrogen abstraction to occur by triplet state MK from ground state MK. Excited state MK also undergoes hydrogen transfer with benzophenone, and such a combination is reported to exhibit synergism when applied to the UV curing of printing inks. In the case of two MK molecules reacting, interaction occurs between the triplet state molecule and one of the N-methyls of the ground state system to form an initiating species[36]; the reaction with benzophenone (BP) probably takes place via an exciplex formed between triplet state MK and ground state BP, followed by the abstraction of hydrogen by BP from MK.



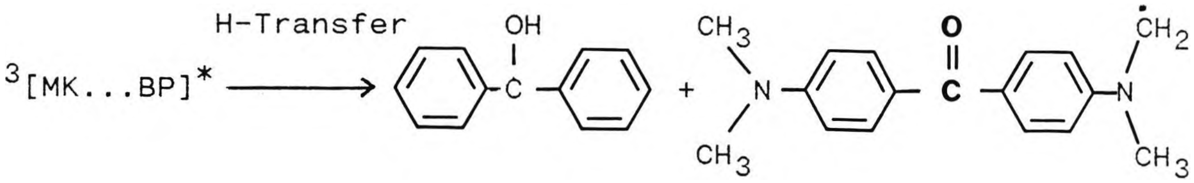
Michler's Ketone

Bis(4,4'-Dimethylamino)Benzophenone

$$MK \xrightarrow{h\nu} {}^1MK^* \xrightarrow{ISC} {}^3MK^*$$

$$^3MK^* + BP \longrightarrow {}^3[MK....BP]^*$$

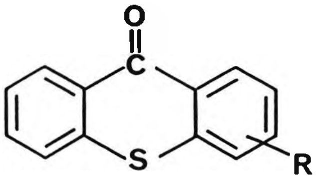
Triplet complex



The presence of the electron donating dimethylamino groups on the phenyl rings of Michler's ketone leads to a high absorptivity ($\varepsilon_{250nm} \sim 15{,}000; \varepsilon_{350nm} \sim 40{,}000$) in the near UV region of the electromagnetic spectrum - a desirable characteristic for photoinitiators for pigmented UV-curable systems, since the photoinitiator must compete with the pigment in order to absorb light in this region.

1.3.2.3 Thioxanthones

The thioxanthones are another group of hydrogen abstracting photoinitiators which exhibit high absorptivity in the near UV region of the spectrum, the electron donating substituents again being a major factor. One advantage which they have over Michler's ketone, however, is that the thioxanthone analogues combine high absorptivity with low coloration, which makes them very attractive as photoinitiating systems for clear thin films and white pigmented films. Used in combination with amine hydrogen donors, the thioxanthone derivatives operate via a mechanism similar to that of benzophenone with amines.

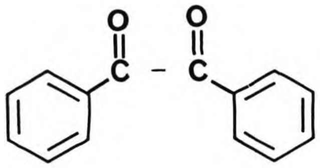


R=Cl,dodecyl or i-Pr

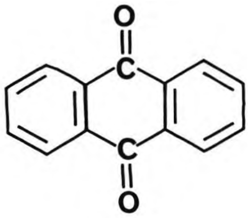
Substituted Thioxanthone

1.3.2.4 Benzil & Quinones

As was mentioned earlier, benzil and quinones also function as hydrogen abstracting photoinitiators with tertiary amine donors. The effectiveness of benzil as an intermolecular hydrogen abstracting photoinitiator has been demonstrated by Sengupta and Modak[37], whilst substantial evidence against the possibility of it undergoing cleavage has been afforded by radical scavenging experiments[6]. Claims have been made regarding the ability of anthraquinones to function as efficient photoinitiators for the polymerization of methyl methacrylate in THF, the solvent functioning as the hydrogen donor.



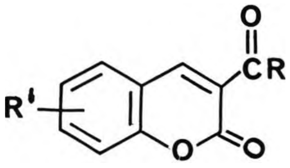
Benzil



Anthraquinone

1.3.2.5 3-Ketocoumarins

Finally, 3-ketocoumarins, which were initially developed as photosensitizers for imaging applications, have also been found to function as hydrogen abstracting photoinitiators, the optimal photocuring performance being obtained with certain tertiary amines - N-phenylglycine or indolacetic acid derivatives - in the rôle of hydrogen donor.



General Structure of 3-Ketocoumarins

Careful selection of the R and R' substituents allows the absorptivity of these systems to be varied across the UV/visible spectral region. As with Michler's ketone, 3-ketocoumarins exhibit high absorptivity, and it has been claimed that, combined with a suitable hydrogen donor, the 3-ketocoumarins demonstrate photoinitiating efficiencies comparable to that of the Michler's ketone/benzophenone system.

1.3.3 Combinations of Intra- and Inter-molecular Reaction Photoinitiators

In practise it is quite common for both hydrogen abstracting photoinitiators and photoinitiators which undergo intramolecular cleavage to be used simultaneously, the H-abstracting species being fed by donor sites on reactive monomers and oligomers in the system. By combining photoinitiator types in this manner, the problems caused by air-inhibition of UV-curing can be reduced, and a possible mechanism for the reactions taking place is as follows:

$PI_1 \rightarrow R^{\cdot}$

$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$

$RO_2^{\cdot} + RH \rightarrow RO_2H + R$

PI_1 = Photoinitiator which undergoes photoinduced unimolecular cleavage

$PI_2 - PI_2^{*}$

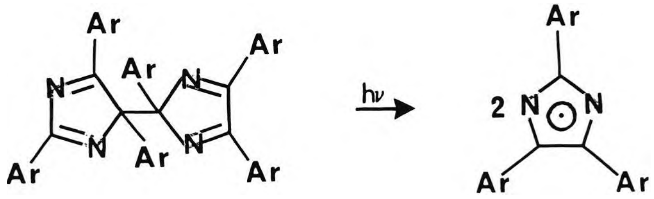
$PI_2^{*} + RO_2H - PI_2 + RO^{\cdot} + {}^{\cdot}OH$

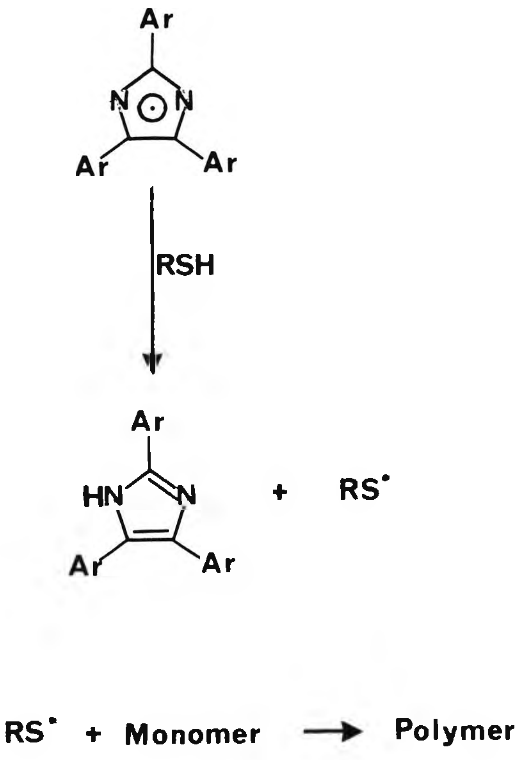
$RO^{\cdot}({}^{\cdot}OH) + \text{Monomer} - \text{Polymer}$

PI_2 = Photoinitiator which reacts via H-abstraction

The radicals produced on photocleavage of PI_1 react with O_2 to give peroxy radicals. These peroxy radicals may then abstract hydrogen atoms from monomers and oligomers in the system, thus regenerating reactive radicals. This chain process leads to the concurrent formation of hydroperoxides and depletion of oxygen, the latter increasing the lifetime of PI_2^* and, hence, the efficiency in decomposing the hydroperoxides formed to yield hydroxy and alkoxy radicals. Whereas peroxy radicals are generally inactive species, the hydroxy and alkyl radicals formed are effective initiators for the polymerization of acrylates.

The bis-triarylimidazoyl system, combined with hydrogen donors such as thiols, undergoes photoinduced intramolecular bond cleavage to yield non-initiating imidazoyl radicals, which then abstract hydrogen from the donor to produce initiating radicals. Thus, the combination of an H-abstracting photoinitiator with one which undergoes intramolecular photocleavage is achieved within one molecular system.





1.3.4 Cationic Photoinitiators

Unlike photoinduced free radical polymerizations, which have been known of, and researched into, for some considerable time, photoinduced ionic polymerization reactions have received relatively little attention. The main reason for this has been a lack of suitable photoinitiators but, in recent years, considerable progress has been made in the area of development of new photoinitiating systems for cationic polymerizations. Whilst the majority of current research is still directed towards radical photopolymerizations, it is widely acknowledged that cationic photopolymerizations possess great potential in many areas of application.

The major attraction which cationic polymerizations hold is that, potentially, at least, an extremely wide range of chemical and physical properties can be attained through the polymerization of such monomers as epoxides, lactones, olefins and many others. One very important advantage which cationic photopolymerization systems afford over free radical polymerizations is that they are not susceptible to oxygen inhibition, which means that complete, rapid polymerization can be achieved in air.

Before the development of aryldiazonium salts as general photoinitiators for cationic polymerization, only limited success had been realized in isolated systems using various organometallic and donor-acceptor complexes as photoinitiators. Aryldiazonium salts have now largely been replaced by diaryliodonium and triarylsulphonium salts since, although being efficient initiators for the photopolymerization of epoxy monomers, the aryldiazonium salts exhibited poor thermal stability and caused bubbles in UV-cured films through the evolution of nitrogen gas.

$$Ar - N^{+}\equiv NBF^{-}_{4} \xrightarrow{h\nu} Ar\text{-}F + N_2 + BF_3$$

1.3.4.1 Diaryliodonium Salts

Crivello and Lam[38,39] reported in the 1970's that diaryliodonium salts with complex metal halide counterions functioned as efficient photoinitiators for the cationic polymerization of a variety of monomers. Molecular oxygen has been found to have no quenching effect on the photolysis of diaryliodonium salts, and the usual singlet and triplet quenchers are also ineffective. Clearly, a radical chain process cannot be involved in the mechanistic pathway followed by these salt systems, since their photolysis is totally unaffected by molecular oxygen and other radical traps. Crivello, Lam and Volante[40] suggested a scheme for the cationic photopolymerization of monomers, initiated by diaryliodonium salts, in which the protonic acid HX, generated on photolysis of the diaryliodonium salt, protonates the monomer.

$$Ar_2I^+X^- \xrightarrow[SH]{h\nu} ArI + Ar^{\bullet} + S^{\bullet} + HX$$

$$HX + M \rightarrow HM^+X^-$$

$$HM^+X^- + M \rightarrow HMM^+X^-$$

$$nM + HMM^+X^- \rightarrow HM(M)^+_{n+1}X^-$$

Cationic polymerizations can be terminated in a number of ways, including the interaction of growing cationic chains with basic or nucleophilic impurities in the monomer, or with the counterion X^- in the absence of such impurities. Any interaction with X^- is very slow, however, and gives rise to 'living' polymers, i.e., systems in which propagation, once initiated, will continue until essentially all of the available monomer has been consumed.

1.3.4.2 Triarylsulphonium Salts

The triarylsulphonium salts represent a class of highly stable crystalline materials, first reported in the literature in 1891[41]. Crivello and Lam[42,43] claimed in the late 1970's that triarylsulphonium salts with non-nucleophilic anions of the type $X^- = ClO_4^-, PF_6^-$ etc. were highly efficient photoinitiators for cationic polymerizations. Whilst radical inhibitors have no effect on the polymerization rates with these photoinitiators - indicating either no radical chain involvement or a very short kinetic length - it has also been found that molecular oxygen and common singlet and triplet quenching agents fail to quench the photolysis. Nevertheless, a number of observations seem to substantiate the following photodecomposition mechanism, proposed by Crivello and Lam.

$$Ar_3S^+X^- \overset{h\nu}{\rightleftharpoons} (Ar_2S^{\dot{+}}, Ar\cdot)X^- \longrightarrow Ar_2S^{\dot{+}} + Ar\cdot + X^-$$

$$Ar_2S^{\dot{+}} + RH \longrightarrow Ar_2S^+\text{-}H + R\cdot$$

$$Ar_2S^+\text{-}H \longrightarrow Ar_2S + H^+$$

The above mechanism has radical fragments being produced in addition to Bronsted acids, and these radical fragments should be capable of initiating radical polymerizations. Such has been observed to be the case, with certain vinyl monomers readily undergoing polymerization when exposed to UV light in the presence of triarylsulphonium salts. Simultaneous radical and cationic polymerizations have been effected also. Further supporting evidence for the proposed mechanism is afforded by the fact that the initiation of cationic polymerizations is consistent with the formation of a long-lived species such as HX, since rapid polymerization is observed when a triarylsulphonium salt is pre-irradiated alone prior to the introduction of a polymerizable monomer into the environment[42].

Experiments performed by Crivello[44] show that the structure of the anion has no effect whatsoever on the photolysis rates obtained with these triarylsulphonium salt photoinitiators. The mechanism by which these salts initiate the photopolymerization of olefinic monomers involves the generation of HX in the photolysis step, and this acid subsequently protonates the monomer to form a carbonium species.

$Ar_3S^+X^- \xrightarrow[\text{Solvent-H}]{h\nu} Ar_2S + Ar\cdot + HX_{(s)}$ Photolysis

$M + HX_{(s)} \rightleftharpoons \underset{\text{Carbonium Species}}{HM^+X^-}$ Initiation

$HM^+X^- + nM \rightarrow H(M)_nM^+X^-$ Propagation

Dektar and Hacker[45] have shown that the Bronsted acid can be formed by a mechanism involving homolysis, heterolysis or molecular rearrangement of the photoexcited state of the triphenylphosphonium salt.

$$Ph_3S^+X^- \xrightarrow{h\nu} [Ph_3S^+X^-]^*$$

$$[Ph_3S^+X^-]^* \longrightarrow Ph_2S^{+\cdot} + Ph^\cdot + X^-$$

$$Ph_2S^{+\cdot} + RH \longrightarrow Ph_2S^+ - H + R^\cdot$$

$$Ph_2S^+\text{-}H \longrightarrow Ph_2S + H^+$$

$$Ph^\cdot + RH \longrightarrow PhH + R^\cdot$$

$$Ph^\cdot + Ph^\cdot \longrightarrow Ph - Ph$$

$$Ph^\cdot + R^\cdot \longrightarrow Ph - R$$

$$R^\cdot + R^\cdot \longrightarrow R - R$$

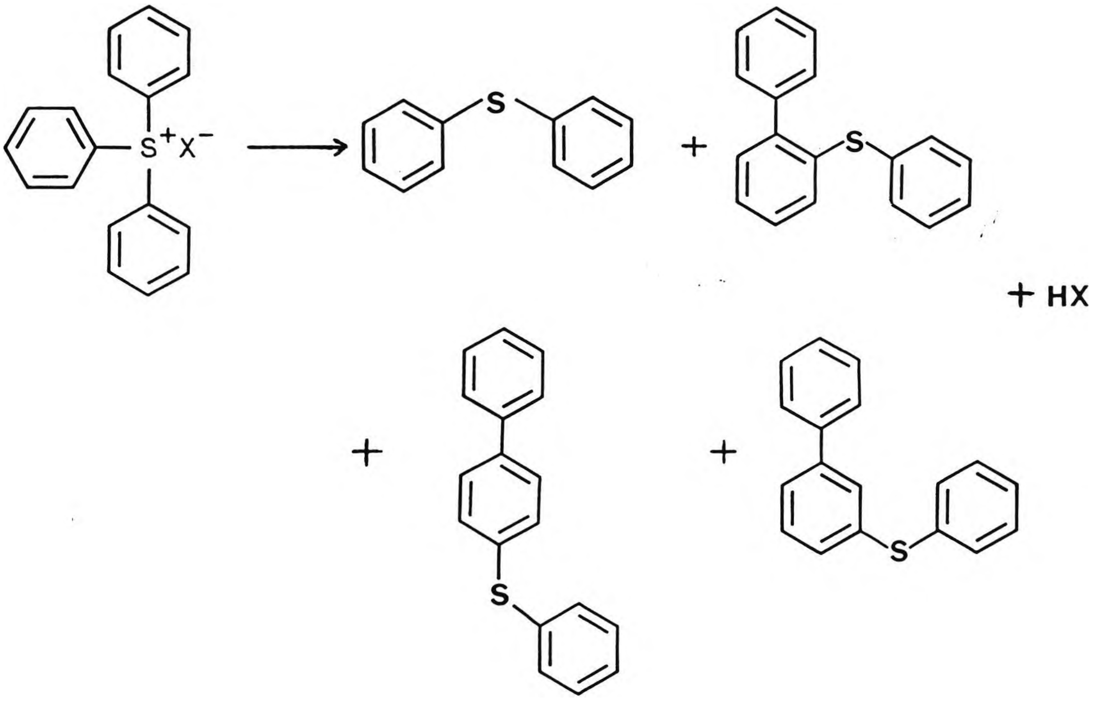
Homolytic Decomposition Pathway

$$Ph_3S^+X^- \xrightarrow{h\nu} [Ph_3S^+X^-]^*$$

$$[Ph_3S^+X^-]^* \longrightarrow Ph_2S + Ph^+ + X^-$$

$$Ph^+ + RH \longrightarrow PhR + H^+$$

Heterolytic Decomposition Pathway



$X = Br^-, CF_3SO_3^-, SbF_6^-, PF_6^-, BF_4^-$

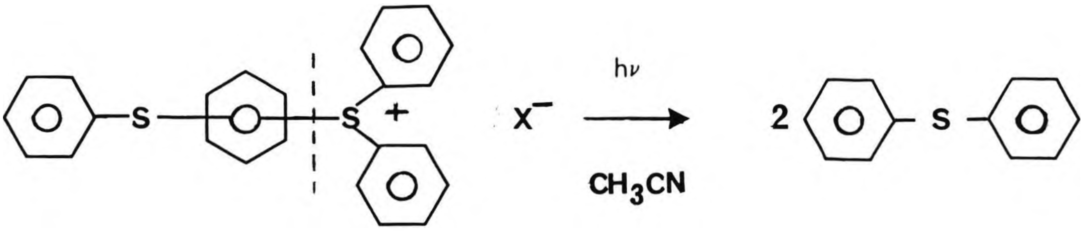
Products from Irradiation of Triphenylsulphonium Salts

The excited state produced on photolysis of the triphenylsulphonium salt can undergo homolysis to yield the phenyl radical and diphenylsulphinyl radical cation, or it can undergo heterolytic cleavage to give the diphenyl cation and diphenyl sulphide. In the case of homolysis taking place, the triphenylsulphinyl radical cation will abstract a hydrogen atom from the solvent and consequently decompose to yield a Bronsted acid and diphenyl sulphide. With the heterolytic process, acid is formed via diphenyl sulphide and the phenyl cation. These mechanisms can be followed if the phenyl radical or phenyl cation escapes from the solvent cage. If escape does not take place, then recombination can occur either directly - in which case the triphenylsulphonium salt is formed - or by molecular rearrangement to yield the three phenylthiobiphenyl isomers illustrated. The rearrangement products also yield acid.

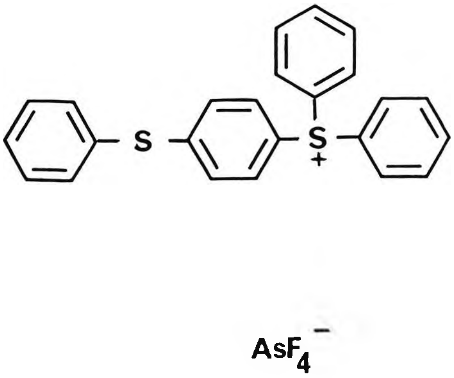
1.3.4.3 Complex Triarylsulphonium Salts

As well as simple triarylsulphonium salts, complex triarylsulphoniums can also be used as cationic photoinitiators, the complex salts affording an enhanced efficiency.

When complex triarylsulphonium salts in which the thiophenoxy chromophoric group is situated ortho, meta or para to the positively charged sulphur atom undergo photolysis, the major reaction product is found to be diphenyl sulphide, indicating specific cleavage at one carbon-sulphur bond.



The enhanced photolysis rates obtained with the complex triarylsulphonium salts are largely attributable to resonance interaction between the thiophenoxy chromophore and the positively charged sulphur atom. In those instances in which the chromophore group is situated either ortho or meta to the sulphur atom, the resonance interaction is interfered with by either steric hindrance or the position of the chromophore relative to the positively charged sulphur atom. If the thiophenoxy group is oxidized to the sulphone a reduction in the resonance interaction results also, as indicated by a generally reduced photolysis rate.

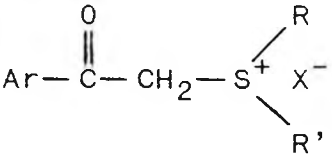


The complex diphenyl-4-thiophenoxyphenysulphonium hexafluoroarsenate salt.

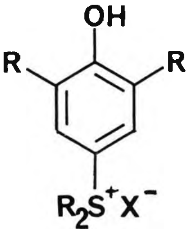
Complex triarylsulphonium salts initiate cationic photopolymerizations via a mechanism directly analogous to that proposed for the simple triarylsulphonium salts, which involves the generation of a strong protonic acid.

1.3.4.4 Other Sulphonium Salt Photoinitiators

Fairly recent additions to the class of sulphonium salts which can be used as photoinitiators of cationic polymerization include dialkylphenacylsulphonium salts and dialkyl-4-hydroxyphenylsulphonium salts.

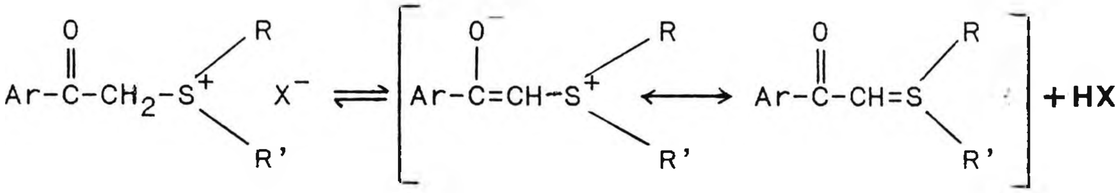


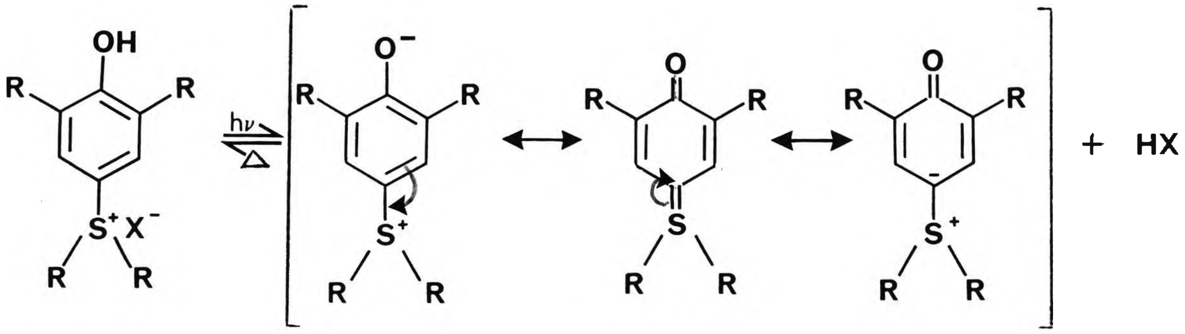
Dialkylphenacylsulphonium Salts



Dialkyl-4-hydroxysulphonium Salts

The photochemistry of these compounds has been found to differ considerably from that of triarylsulphonium salts. Whereas the latter group of photoinitiators undergo irreversible photocleavage of a carbon-sulphur bond, the former type undergo reversible dissociation, yielding resonance stabilized ylids and protonic acids.

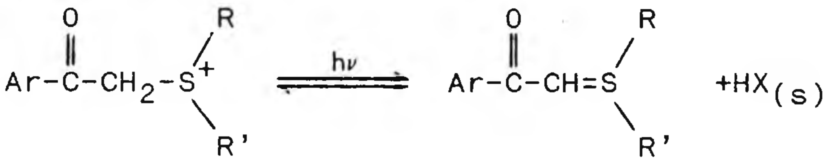




In both cases competition arises between the thermal back reaction and the forward photolysis, giving rise to a steady state concentration of ylid and acid. Only those sulphonium salts which give resonance stabilized ylids have been found to be of any use as photoinitiators.

The following mechanisms for photoinitiated cationic polymerization by dialkylphenacysulphonium salts was proposed by Cowan, Field and Barton[46].

Photolysis



$$\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}\overset{R}{\underset{R'}{S^+}}} \xrightleftharpoons{h\nu} \mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}CH{=}\overset{R}{\underset{R'}{S}}} \quad +HX_{(s)}$$

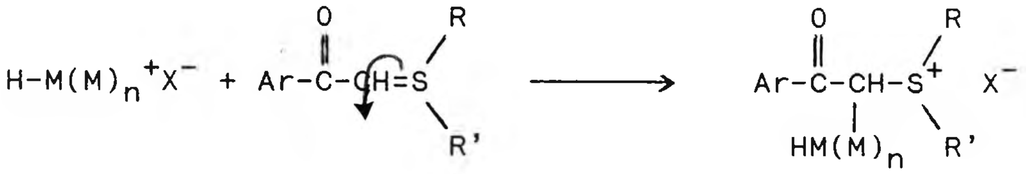
Initiation

$$M + HX_{(s)} \longrightarrow HM^+X^-.$$

Propagation

$$nM + HM^{+}X^{-} \longrightarrow H{-}M(M)_n{}^{+}X^{-}.$$

Termination



$$H{-}M(M)_n{}^{+}X^{-} + Ar{-}\overset{\overset{O}{\|}}{C}{-}CH{=}S\begin{smallmatrix}R\\R'\end{smallmatrix} \longrightarrow Ar{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{HM(M)_n}{|}}{CH}{-}S^{+}\begin{smallmatrix}R\\R'\end{smallmatrix}\ X^{-}$$

Due to the reversibility of ylid formation by the dialkylphenacysulphonium salts and dialkyl-4-hydroxyphenylsulphonium salts, competition for the acid HX occurs between the ylids and the monomer. The relative nucleophilicities of the two compounds will determine whether polymerization occurs, and the ylids themselves are able to terminate the growing cationic chain by the termination step shown above.

Oxiranes, vinyl ethers and cyclic acetals are readily polymerized using dialkylphenacylsulphonium and dialkyl-4-hydroxyphenylsulphonium salts as photoinitiators, unlike THF,

ε-caprolactone and α-methylstyrene, which are not polymerized under similar conditions. Two possible reasons for the failure of these monomers to undergo polymerization are that:

(a) initiation occurs at a slower rate than recombination of the ylids and acid; and

(b) efficient termination of the growing chains by the ylids may remove the active cationic species completely from the polymerization mixture.

1.3.4.5 Triarylselenonium Salt Photoinitiators

Triarylselenonium salts, like triarylsulphonium salts, are highly efficient photoinitiators for cationic polymerization and appear to decompose in an analogous manner.

$$Ar_3Se^+MX_n^- \longrightarrow [Ar_3Se^+MX_n^-]^*$$

$$[Ar_3Se^+MX_n^-]^* \longrightarrow Ar_2Se^{+\cdot} + Ar^\cdot + MX_n^-$$

$$Ar_2Se^{+\cdot} \longrightarrow Ar_2Se^+\text{-}H + S^\cdot$$

$$Ar_2Se^+\text{-}H \longrightarrow Ar_2Se + H^+$$

The efficiency of triarylselenonium salts has been found to be close to that of triarylsulphonium salts in the polymerization of various olefinic and heterocyclic monomers.

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CHAPTER II:

INTRODUCTION
TO
UV CURING

One of the first recorded examples of a light induced polymerization dates back over 4,000 years to the preparation of mummies. The Ancient Egyptians are said to have dipped linen into bitumen found in Judea prior to exposing the mummies, wrapped in the strips, to the sunlight for hardening. The bitumen used in this process is known to contain unsaturated compounds, which underwent cross-linking to form a cured, protective coating on the linen on exposure to UV radiation.

It was not until the 1940's that any real scientific interest in UV curable systems developed,with the granting of the first patent for unsaturated polyester-styrene printing inks which underwent facile polymerization when exposed to UV irradiation. In the 1960's such UV curable systems were introduced to the wood finishing industry, and this remains one of the major commercial uses for UV curable resins today.

The past twenty years have seen a rapid increase in the extent of application of UV curing technology. Its popularity over traditional methods of polymerization to obtain highly crosslinked systems arises from a number of factors:

(i) An obvious advantage of the UV curing technique is the rapidity with which the formulations dry.

(ii) The absence of by-products leads to a reduction in resulting pollution relative to conventional methods of curing.

(iii) Since no solvent is required (as in other methods which involve drying via solvent evaporation) the cost efficiency of UV curing is much higher than that of other curing methods.

(iv) The fact that all the energy involved in the polymerization process is concentrated in the actual surface coating or thin film itself means that incidental heating of this substrate is minimal and the total energy consumption is less than in other, conventional curing methods.

(v) The UV curing process can be effected at relatively low temperatures, allowing heat sensitive substrates to be used.

(vi) UV curing equipment is quite compact compared to the apparatus required to cure by other methods, hence conservation of space is another factor in favour of the UV initiated technique. This is particularly true when considering the huge ovens used for drying in the metal decorating process. Furthermore, the compactness of the UV lamps available allows the use of interstation drying on multi-unit processes.

(vii) Due to the high molecular weight of the crosslinked films produced, UV curing leads to an improvement in product quality, particularly with regard to solvent, chemical, abrasion and scratch resistance.

(viii) The extensive variety of monomers and oligomers now commercially available allows the production of well defined, crosslinked polymeric systems with the exact characteristics desired for the particular end-use for which the polymer was designed.

In spite of its many advantages over the other curing methods, the UV curing technique is not without disadvantages of its own and, in certain applications, these actually outweigh the advantages. The major disadvantages associated with the UV curing and UV curable systems can be summarized as follows:

(i) In the printing industry, the major reason for the use of UV curing not being more widespread is that UV inks are significantly more expensive than conventional inks. However, in those cases in which UV inks are employed, their use is justified by the overall economics of the printing process.

(ii) There is the possibility of toxicological problems arising, especially with UV curable formulations based on acrylates.

(iii) The handling of UV components requires considerable care, since the materials in question are reactive chemicals.

(iv) UV cured systems may have less gloss than their conventional counterparts. Furthermore, since the UV curing process freezes the coating or ink in the surface configuration adopted at the time of exposure to the radiation, any surface imperfections arising from substrate irregularity will remain in the finished product.

(v) The UV curing of highly pigmented systems is often difficult to achieve, and pure metallic pigmented inks are resistant to UV curing as a result of their ability to reflect UV radiation.

(vi) The UV curing of substrates with non-flat surfaces can give rise to problems, and is a major limitation on occasions.

(vii) UV curable formulations are essentially for interior use and are not ideal for exterior applications.

The increased application of photoinitiated polymerization over recent years can almost certainly be largely attributed to the increase in basic knowledge and understanding of the photochemical process. A polymer network can be formed by either bridging together existing polymer chains or by promoting the polymerization of a monomer containing two or more reactive double bonds. Since this latter process is a chain reaction rapid, extensive development can take place, especially when the initiating species are produced by the application of intense UV radiations. The end product of the UV curing reaction is ultimately a three-dimensional polymer network with a crosslink concentration which depends on the length of the monomer used, but can be as high as 10 mol l^{-1}.[1]

One of the most fascinating aspects of UV curing is the fact that polymerization of a monomer can take place extensively within a fraction of a second. In conventional polymerization reactions, in which termination of polymer chains occurs by combination of radicals, a large increase in initiation rate will lead to a corresponding drop in the efficiency of polymerization; this effect is caused by the fact that, when radicals are present in high concentrations, the problem of radical-radical reactions automatically becomes a possibility and a shortening of polymer chain lengths may result from primary radical termination. Consequently, when exposed to the intense irradiations characteristic of the equipment employed for the UV curing technique, polymerization in thin films should, theoretically, hardly proceed at all, with both the kinetic chain length and quantum yield for polymerization decreasing as the light intensity increases. Whilst this situation was found to be true for UV curable systems containing monofunctional monomers, it is not valid for multifunctional monomers for which, according to the observations of Decker[1], the relationship between the rate of polymerization and the intensity of irradiation is close to first order; this means that the quantum yield for polymerization and kinetic chain length is, in fact, virtually unaffected by any dramatic increase in light intensity for curing formulations containing monofunctional monomers. A natural conclusion from this result is that the polymerization of monofunctional monomers occurs by a different mechanism in the condensed phase, at least with regard to the termination process.

When multifunctional monomers are exposed to UV irradiation, a linear polymer chain with pendant double bonds is formed initially. As soon as polymerization of any one of the pendant double bonds begins, the radical becomes attached to the network and loses mobility. Provided that monomer molecules are able to approach the radical sites closely enough to be scavenged, the radical chain will continue to grow, but the chances of it encountering another radical attached to a growing polymer chain are very small, i.e. the probability of bimolecular chain termination is low. Eventually a point is reached at which the bulk of the polymer is such that free access to the radical site is prevented by steric factors, hence further growth of the polymer chain is no longer possible. The radical centre, however, remains alive, but is trapped within the polymer network and unable to react with other species. Thus, the termination process by which growth of a polymer chain is halted is a first order process, and it is this which enables such extensive polymerization at even very high initiation rates. As a consequence of this, it is feasible for lasers, which produce a very intense, concentrated beam of light, to be used as the irradiation source, giving rise to extremely high rates of cure in polymerizable systems.

Due to the high crosslink density, certain specific properties are associated with the products of UV curing. First of all, coatings cured by the UV initiated process are, essentially, insoluble in organic solvents - a property which is exploited in the lithographic industries. Secondly, UV cured materials show good thermal resistance, and also exhibit low sensitivity, in general, to natural weathering - a direct result of their high crosslink density, by which cage recombination of primary radicals is favoured over chain propagation, since mobility of the polymer segments is severely limited.

Whereas the above properties can be applied to UV cured materials in general, the mechanical behaviour of polymers produced by UV curing depends upon the functionality and structure of the species which undergoes polymerization.

2.1 Composition of Formulations for UV Curing

UV curable formulations are generally composed of the following constituents:

(i) Prepolymer - this is the species which actually undergoes further polymerization or crosslinking to form the final three-dimensional network.

(ii) Monomer - a reactive diluent or solvent used for the purpose of reducing the viscosity of the prepolymer.

(iii) Photoinitiating system - this can be either a photoinitiator which operates via a unimolecular mechanism, or a hydrogen-abstracting photoinitiator with a suitable hydrogen donor.

(iv) Additives - minor components of the UV curable formulation which come in many varieties and produce numerous effects, e.g. driers, pigments, etc.

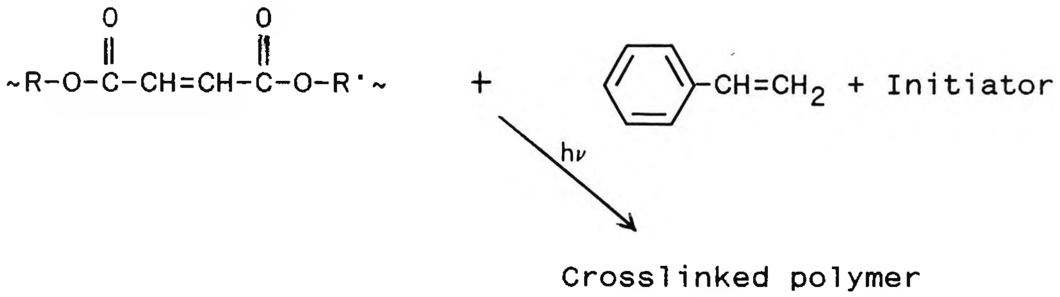
2.1.1 Prepolymers

For obvious reasons, the prepolymer is often referred to as the film-forming component of surface coatings. In industrial applications it is usual for two or more prepolymers to be used together to obtain the desired combinaion of properties in the finished product.

A few more widely used prepolymers are discussed below.

2.1.1.1 Unsaturated Polyester Resins

The simplest and most common polyesters are prepared from maleic anhydride/phthalic anhydride mixtures esterified with glycols; resins thus formed are dissolved in styrene. The maleic unsaturation in the polyester undergoes free radical copolymerization with the vinyl monomer, the copolymerization usually being initiated by a transition metal/organic hydroperoxide system.



Both pigmented and unpigmented unsaturated polyesters find extensive use in the wood finishing industry as a result of their low cost.

The cured materials are very hard and solvent resistant, but curing occurs at a relatively slow rate and the volatility of the styrene diluent may give rise to practical problems.

2.1.1.2 <u>Amino Resins</u>

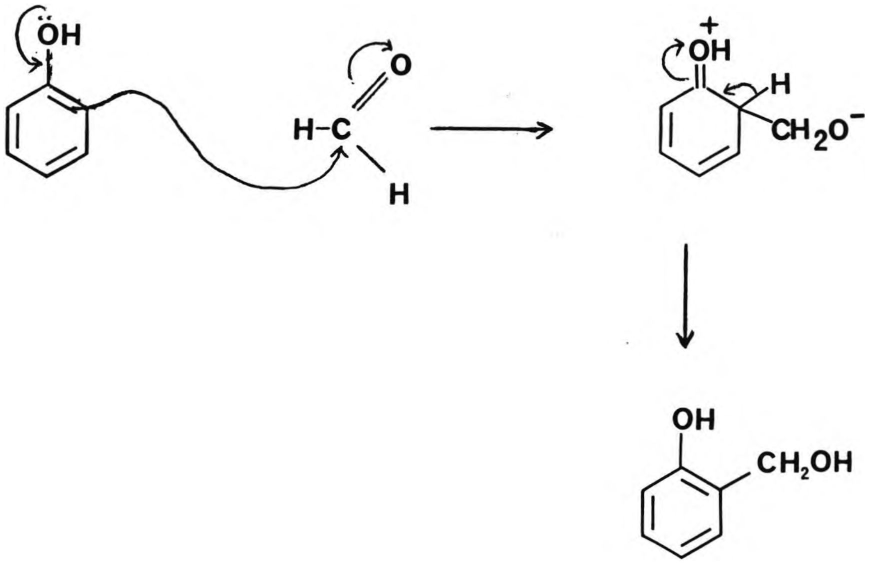
The most common amino resins are reaction products of urea or melamine with formaldehyde. Preparation of the resins in alcoholic media enables control of the molecular weight and degree of branching according to the end use to which the resin is to be put. Subseqeunt addition, condensation and etherification reactions of the polymers produced lead to complex, highly branched polymeric systems.

Amino resins are able to cure or crosslink to solid films, an ability which can be used as a means of curing acrylic resins. In prepolymers of this type a small quantity of monomer, such as N-butoxymethylacrylamide, is incorporated into the polymer. The presence of the solvent provides reactive sites which enable crosslinking of the acrylic copolymer.

Apart from the urea and melamine resins, a number of other amino resins, made from various alkyl and aryl substituted amines, are used in surface coatings. The resins available cover a wide range of performance characteristics and solution viscosities. Amino resins, in general, tend to be hard and brittle and lacking in adhesive ability when used alone, hence they are almost invariably blended with other, softer resins for use as surface coatings. One example of this is the alkyd-amino resin mixture, which is used for many high grade finishes because of its hardening, easy pigmentation and reasonable cost, in addition to its retention of gloss and resistance to colour change and weathering. Alkyd resins are based on non-drying oils such as castor oil, coconut oil etc. and are forumulated to contain free hydroxyl groups, which act as sites for crosslinking. Also, the alkyd resins retain acidity, the acid groups acting as catalysts for the curing process.

2.1.1.3 Phenolic Resins

Phenolic resins were among the first synthetic resins to be developed, and are made principally by the reaction of phenol with formaldehyde. Electrophilic substitution of the phenol ring results in the formation of a phenol alcohol, as illustrated below.

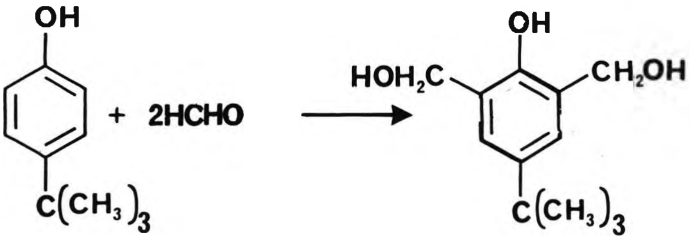


(Reaction occurs at the para position also)

Whilst methylol phenols are stable at temperatures below 50^{o}C and at high pH, when exposed to elevated temperatures or acidic media reaction will take place between the methylol groups of neighbouring molecules. These condensation reactions result in the formation of polymeric products. The relative rates of the methylolation and polymerization reactions are largely dependent upon the formaldehyde/phenol ratio and the reaction conditions. Alkaline conditions combined with a formaldehyde/phenol ratio greater than unity will favour the methylolation reaction, the resins formed in this case being termed 'resoles'. Condensation is favoured by formaldehyde/phenol ratios less than one and acidic conditions, and results in the formation of 'novolacs'.

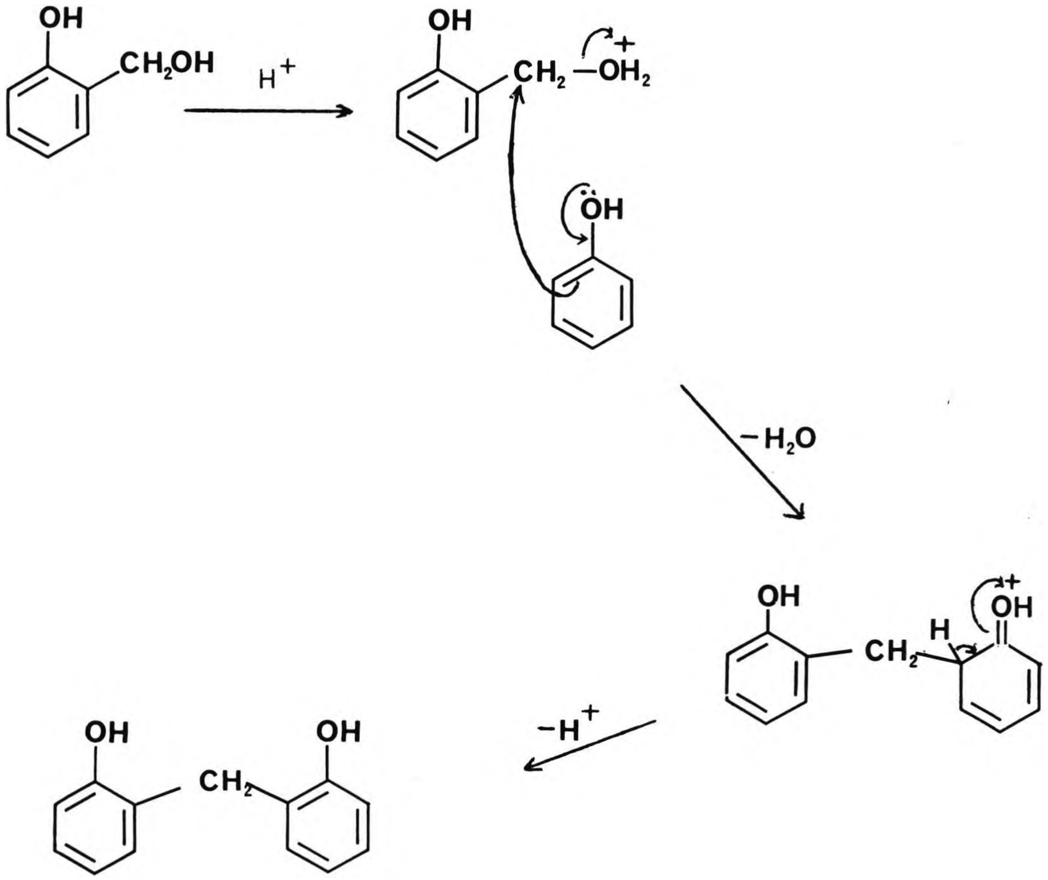
When methylolation occurs, the introduction of the first methylol group onto the benzene ring activates the phenol to further methylolation. Consequently, some trimethylol phenols will be formed and, if dimethylol phenols are required, a phenol derivative with a blocked para-position is often used,

e.g.



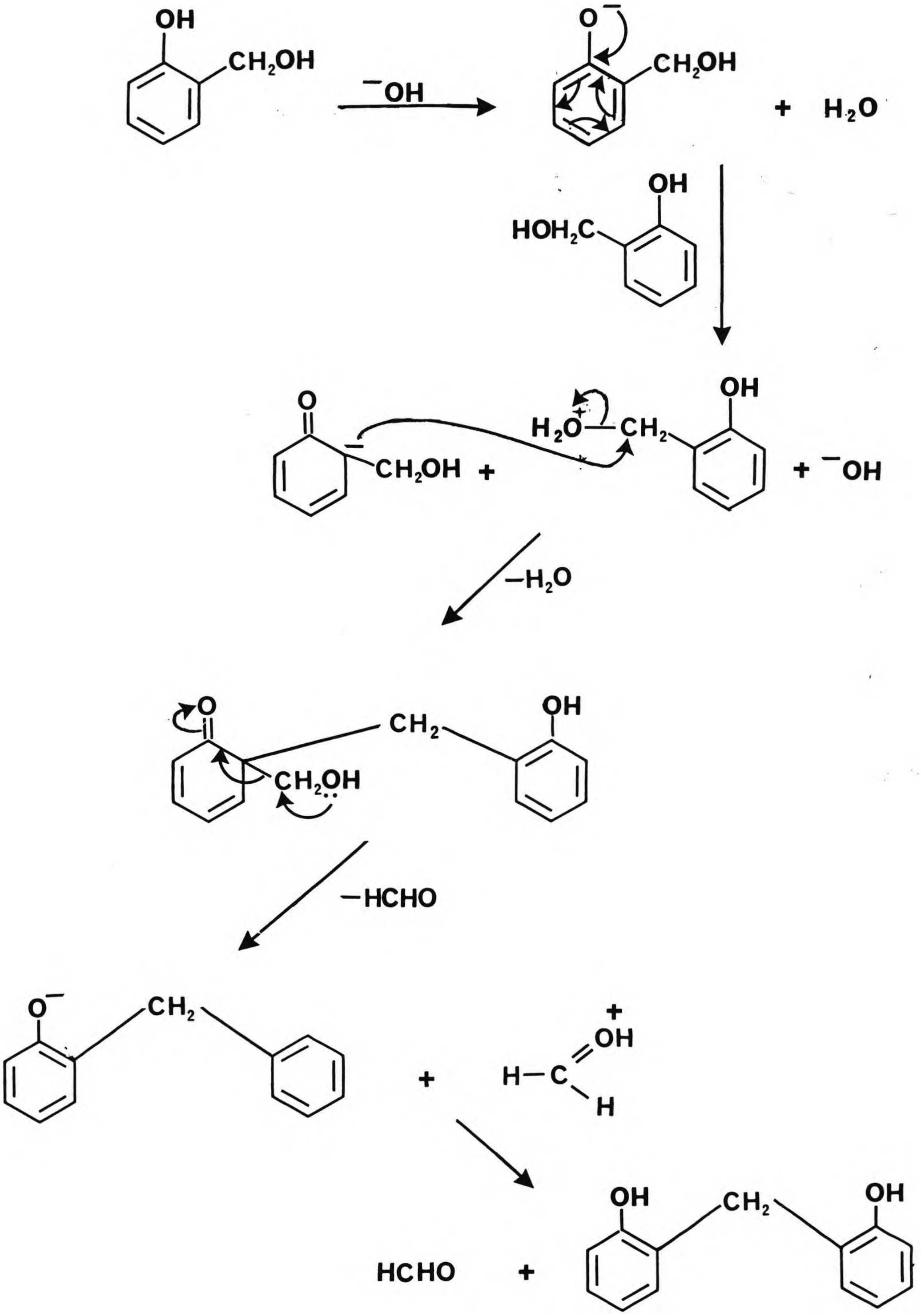
Polymerization of the methylol phenol to yield a low molecular weight polymer occurs via a condensation reaction, which can take place under either acidic or alkaline conditions.

Acidic Conditions:

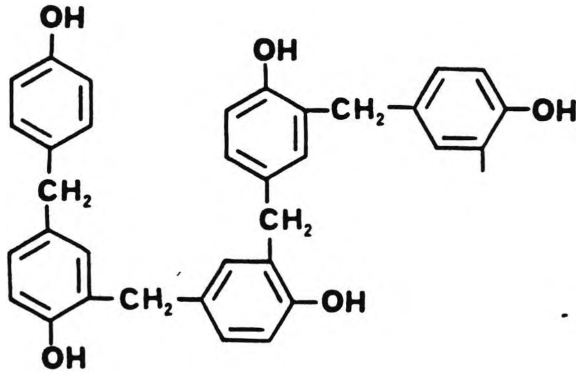


Residual methylol groups ——> further reaction and polynuclear products

Alkaline Conditions:



Unlike resoles, novolacs contain no residual methylol groups, and the addition of formaldehyde is therefore required for crosslinking to take place. For most commercial formulations a formaldehyde/phenol ratio of 0.75-0.85 is used, reaction occurring under acidic conditions.

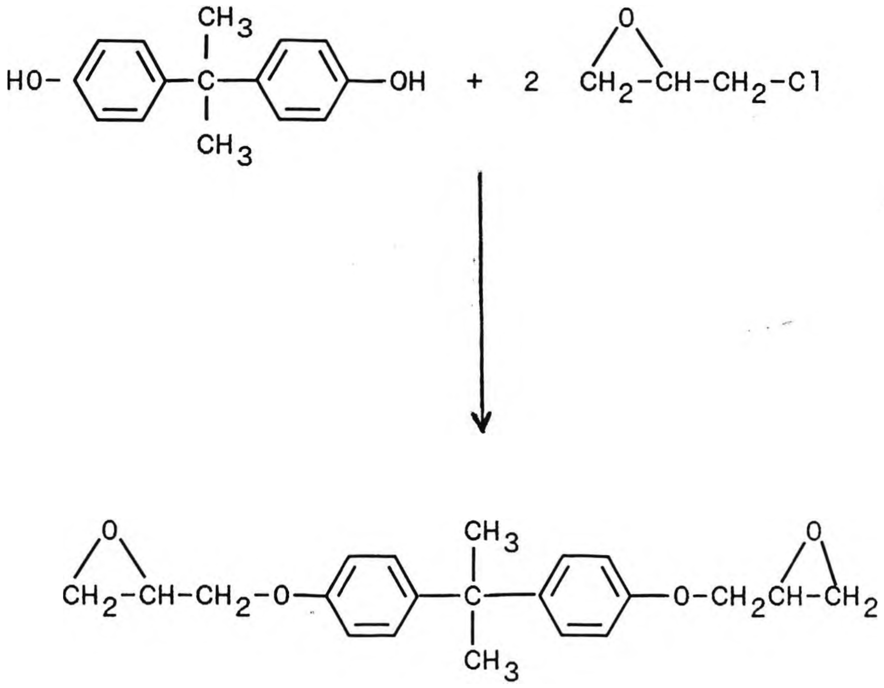


Typical novolac structure

Phenolic resins are always used in combination with other prepolymers and tend to confer chemical resistance to the composition in which they are used.

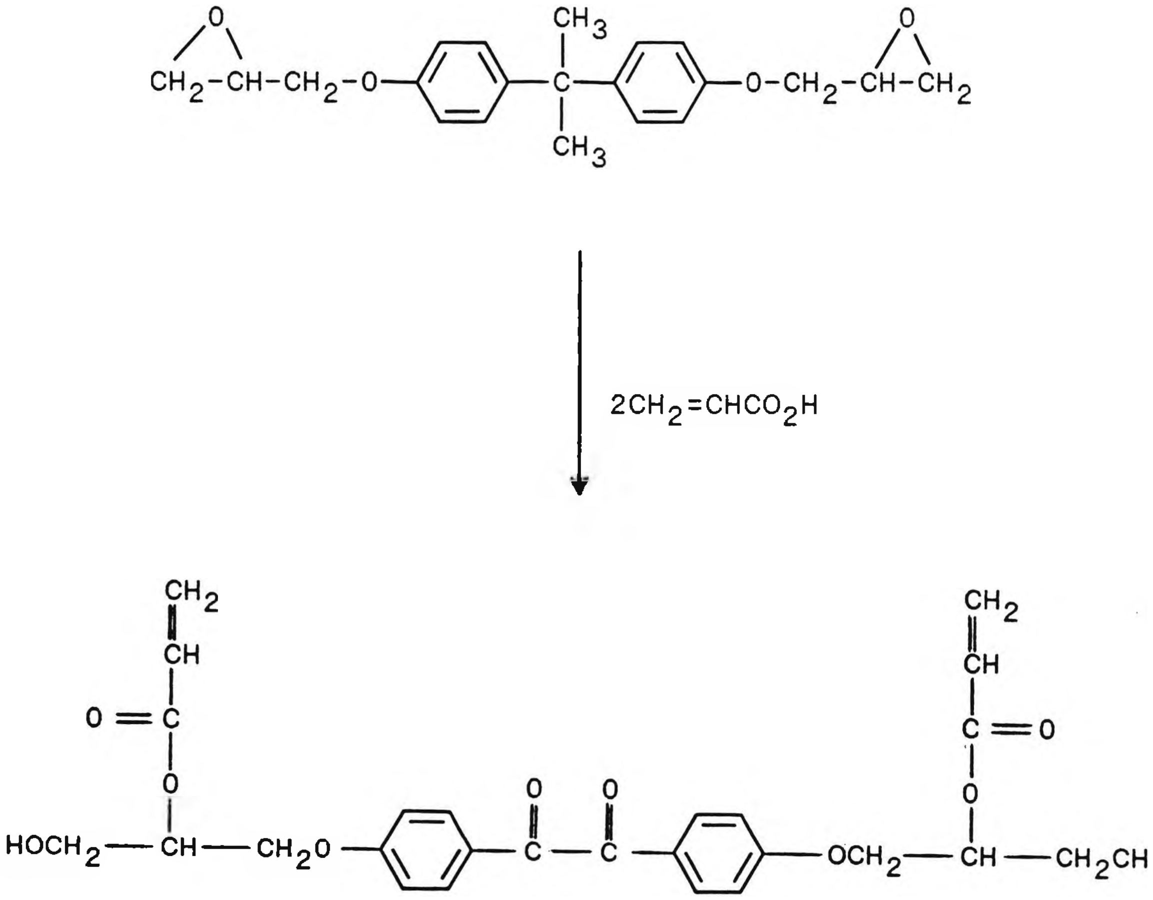
2.1.1.4 Epoxy Resins

The majority of epoxy resins used in the area of surface coatings are prepared from bisphenol A and epichlorohydrin, the proportions of the respective reactants being determined by the properties required in the finished product.



Basic Epoxy Unit

Epoxy resins are of little practical use in surface coatings when used alone, since they are unable to polymerize by themselves. A popular method of converting the pure epoxy resins to usable surface coatings is by esterification of the epoxide and hydroxyl groups, the epoxide rings being opened in the process. One such esterification reaction is achieved by the addition of acrylic acid to yield epoxy acrylates.

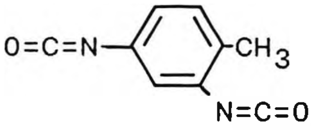


Acrylated Epoxy Resin

Epoxy acrylates offer good adhesion to a variety of substrates, as well as flexibility. One disadvantage associated with this type of resin, however, arises from the fact that it is extremely viscous and, hence, requires the addition of large volumes of monomer before a practicable consistency is achieved. Nevertheless, the versatility of epoxy acrylate resins has led to their employment in a considerable range of UV curing applications.

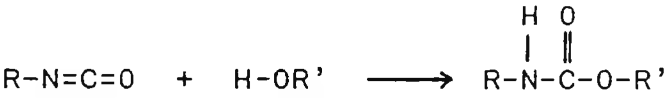
2.1.1.5 Polyurethane Resins

Polyurethane prepolymers may be formulated in a range of film properties from highly flexible coatings for rubber, leather, plastic sheets etc., to hard, tough finishes for metal and masonry. The resins are made from isocyanates - toluene diisocyanate, TDI, in particular. TDI exists in several isomeric forms, but almost exclusive use is made of a 1:4 mixture of the 2,6 and 2,4 isomers respectively, for purely economic reasons.



2,4 Isomer of TDI

The prepolymers are formed by reaction of TDI with polyols in such proportions that the products contain major amounts of unreacted -NCO groups. The viscosity of the prepolymers thus formed is sufficiently low to permit direct application, after which further reaction at the -NCO functionalities results in the production of dry, polymerized films. The polyols used to form polyurethane prepolymers are special moisture-free urethane grades of polyethers, polyesters, glycols and castor oil derivatives, the hydroxyl groups of which form urethane linkages by reacting with the isocyanate groups of TDI.



$$R{-}N{=}C{=}O \quad + \quad H{-}OR' \longrightarrow R{-}\overset{\overset{H}{|}}{N}{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'$$

Urethane

Due to their low cost and high resistance to abrasion, polyethers find the widest use. Whilst giving high chemical and solvent resistance, polyesters tend to result in lower resistance to abrasion than polyethers, and are more expensive. Glycols are often used in combination with polyethers or polyesters to add flexibility to the resin, whilst blending with castor oil and its derivatives improves weather and water resistance.

2.1.2 Monomers

With the exception of water, all monomers used in surface coatings are low molecular weight organic compounds. These organic materials can be divided into two basic types : hydrocarbons and oxygenated compounds. In chemical terms, the range of oxygenated compounds is much greater than the range of hydrocarbons, and includes ketones, ethers, esters and alcohols. The choice of monomer for any particular application is determined by a number of factors, most notably solvency, viscosity, boiling point, toxicity, odour and cost. Flashpoints and rates of solvent evaporation must also be taken into account.

2.1.2.1 Hydrocarbons

The individual hydrocarbons usually present in commercially available hydrocarbon solvents can generally be divided into three classes : aromatics, naphthenes and aliphatics. Aromatics tend to exhibit the best solvency of the three, whilst the aliphatics show the least solvency.

Many hydrocarbon solvents occur in nature and need to be only separated and purified before use. Of the pure aromatics available, toluene and xylene are the main ones used in the surface coatings industry. Toluene is an excellent solvent for many natural and synthetic resins, and the solvency of xylene is only slightly less. In addition to good solvency, however, xylene has a higher boiling range and slower evaporation rate than toluene.

The most widely used hydrocarbon solvent is commonly referred to as 'mineral spirits' and is composed predominantly of paraffins and naphthenes with a small quantity of aromatics. Because of its good volatility range, clean evaporation and good brushability, mineral spirits is a suitable solvent in house paints, enamels etc.

2.1.2.2 Oxygenated Solvents

In general, oxygenated solvents possess a more powerful solvent action than hydrocarbons, especially for synthetic resins and high polymers.

2.1.2.2.1 Alcohols

Only the relatively low molecular weight alcohols (C_1-C_6) are generally applied directly as solvents in the coatings industries. Alcohols are used as solvents for natural resins and gums, and for synthetic resins. When mixed with aromatic hydrocarbons they find use as solvents for ethyl cellulose, alkyd, phenolic, urea and melamine formaldehyde resins.

2.1.2.2.2 Esters

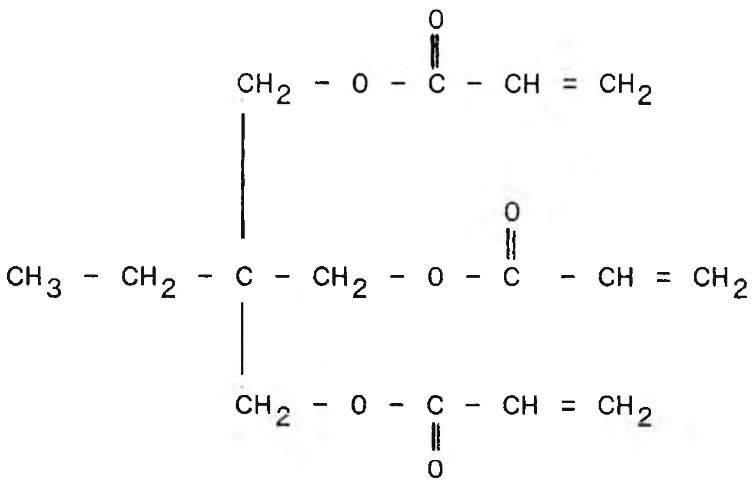
Esters of principal use in the surface coatings industry are acetates and acrylates. Perhaps the most common acetate is vinyl acetate - a highly reactive monomer, but one which is volatile and flammable. Formulations containing this solvent tend to show low resistance to weathering when cured.

Because of their high reactivity, moderate cost and low volatility, acrylate monomers are amongst the most widely used in UV curing systems at present. These monomers come in a variety of functionalities :

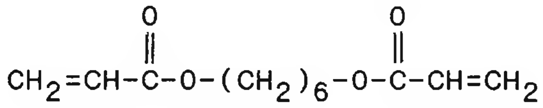
Monofunctional acrylates can be straight chain, branched or attached to a cyclic group. Straight chain alkyl acrylates find limited use in UV curable formulations as a result of their characteristic strong odour, volatility (in the case of short chain alkyl acrylates) and tendency to produce soft films (long chain alkyl acrylates). Branched acrylates, with their plasticizing properties and relatively low volatility, are potentially useful materials, but their use is limited by very pungent odours. Attachment of the acrylate functionality to a cyclic system also results in strong odours, but these are less volatile than other monofunctional monomers and have low toxicity.

Difunctional acrylates are produced by the reaction of acrylic acid and diols in a 2:1 molar ratio. Those most common in industrial applications include tetraethylene glycol diacrylate (TEGDA) and 1,6-hexanediol diacrylate (HDDA). TEGDA is usually employed in formulations for low viscosity coatings requiring good adhesion and flexibility, whereas HDDA finds extensive use in floor coverings, wood coatings etc.

The trifunctional acrylates include the widely used trimethylol propane triacrylate (TMPTA), and possess considerably higher viscosities and reactivities than the difunctional compounds. The use of trifunctional monomers, however, is limited because the polymers they produce tend to possess high crosslink densities, which may cause brittleness and shrinkage of the coatings, and eventually result in adhesion failure.

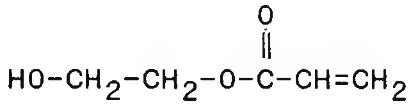


Trimethylolpropane Triacrylate, TMPTA



$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}(CH_2)_6{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2$$

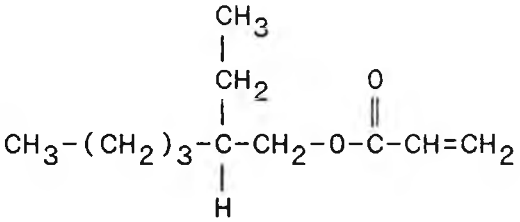
1,6-Hexanediol Diacrylate, HDDA



$$HO{-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2$$

2-Hydroxyethyl Acrylate, HEA

(Straight chain monofunctional acrylate)



$$CH_3-(CH_2)_3-\underset{\underset{H}{|}}{\overset{\overset{\overset{CH_3}{|}}{CH_2}}{\overset{|}{C}}}-CH_2-O-\overset{\overset{O}{\|}}{C}-CH=CH_2$$

2-Ethylhexyl Acrylate, EHA

(Branched monofunctional acrylate)

2.1.3 Photoinitiators

The various photoinitiator types available have been described in some detail in the previous section and will only be mentioned briefly here.

The choice of photoinitiator for any UV curable formulation is largely dependent upon the nature of prepolymer/solvent system being used. For unsaturated polyester resins containing maleic or fumaric double bonds and dissolved in styrene, unimolecular fragmentation type photoinitiators such as benzoin ethers and benzil dimethylketal are those principally used. Benzophenone and similar photoinitiators cannot be employed with these systems, since their reactive excited states are rapidly quenched by styrene. UV-curable formulations containing unsaturated polyester resins with unimolecular photocleavage-type initiators are mainly used in wood primers, finishing lacquers for furniture and cork (mixtures of benzoin ether and benzildimethylketal are often used for such products), gel coats, and in the preparation of high thickness finished products (e.g. corrugated materials, tubes etc.).

The presence of acrylic double bonds in the prepolymer greatly increases the variety of photoinitiators suitable to be used with it, as does use in conjunction with a thiol. With such systems it is possible to use either unimolecular cleavage or hydrogen-abstracting photoinitiators. Transport fomulations for a wide range of applications generally make use of benzil dimethylketal and/or benzophenone - trialkylamine combinations; for transparent systems which are required to form products resistant to yellowing and the effects of age, α-hydroxyalkylphenones or slightly less efficient photoinitiators, such as diethoxyacetophenone or methylphenylglyoxylate, are used; pigmented systems and inks require photoinitiators for which the absorption spectrum possesses bands at wavelengths at which light is able to penetrate most deeply into the system. Since it is not always possible to satisfy this criterion, spectrum sensitizers are often used in combination with the photoinitiator. 2-isopropylthioxanthone is often used together with aromatic dialkylamines if the curing formulation contains titanium dioxide, whilst the Michler's ketone - benzophenone combination has been found to be highly effective for inks of various pigmentations used for graphic purposes.

In the case of aliphatic or aromatic prepolymers with epoxidic monomers, cycloaliphatic photoinitiators with triphenylsulphonium salts are most commonly used. Applications of such systems include paints for metallic supports, sealants, resists, and masks for printed and integrated circuits.

2.1.4 Additives

A number of materials used in surface coatings are added in small percentages to perform certain specific functions which are not fulfilled by the major components of the formulations. Before being used, each additive must be carefully tested to determine its effect on curing and stability.

An extensive range of additives is used for surface coatings and includes fungicides, agents which increase gloss, drying agents and, of course, pigments. The addition of pigments to any UV curable formulation can have a number of highly significant effects. Although most of these effects relate to the actual curing process, it is possible for storage stability, gloss and flow properties to be severely affected also. There are two major mechanisms by which pigmentation can affect the curing process:

(i) by scattering and/or absorbing radiation so that absorption by the photoinitiator or photosensitizer is reduced;

(ii) by being involved photochemically in the curing process.

In the case of a pigment absorbing radiation in competition with the photoinitiator, the extinction coefficient of the two compounds will change differently with wavelength, and the fraction of light absorbed by the photoinitiator will vary with wavelength. This can result in the photoinitiator absorbing so strongly in the upper layers of the film that very little radiation is able to reach the bottom layers, and only a fraction of the radiation will be available for absorption by the photoinitiator. Since many pigments absorb radiation in the UV range, their presence will reduce the absorption of photoinitiators particularly in the lower layers of films, thus making thorough curing in these regions difficult.

If the pigment scatters radiation, the degree to which scattering occurs is dependent upon the differences in the refractive indices of the pigment and the rest of the formulation, the concentration of the pigment and the wavelength of the radiation. Scattering has three main effects on the radiation entering a film:

(a) reflectance can be increased;

(b) the effective path in the film is increased;

(c) scattering diffuses radiation in the film so that reflection back into the film from the underside of the top surface increases.

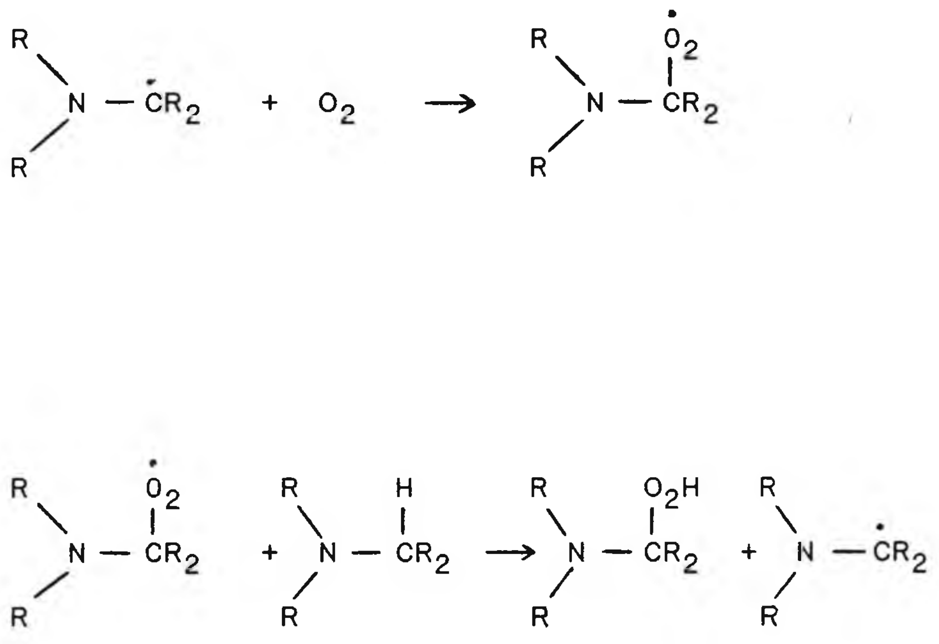
UV curable coatings containing pigments which scatter and absorb UV radiation are particularly susceptible to surface wrinkling, caused by the surface of the film polymerizing before the lower layers. Some pigments are also known to have an adverse effect on the storage stability of coatings.

2.2 Oxygen Inhibition

One phenomenon which causes considerable complications when photoinitiated radical polymerizations are carried out in the air is inhibition by atmospheric oxygen. The paramagnetic character of oxygen means that it is able to intercept the initiating radicals and growing polymer chains, reducing the rate of polymerization and ultimately quenching the reaction. Oxygen inhibition is particularly problematic in the UV curing of surface coatings, due to the unfavourable surface/volume ratio which allows optimal diffusion of oxygen into the film. Since the rate constant of quenching by oxygen is so large, only a small concentration of oxygen is required to prevent polymerization. Reaction of oxygen with the initiating radicals yields peroxy radicals, which are inefficient as initiators of polymerization reactions and, thus, reduce the efficiency of initiation. Peroxy radicals are also formed in the reaction of oxygen with the growing polymer radicals and, in this case, lead to a reduction in the efficiency of propagation.

These inhibiting reactions with oxygen occur primarily at the interface between the coating and the atmosphere, resulting in the selective retardation of photoinitiated polymerization at the surface. Consequently, a high concentration of initiator radicals is required at the surface of a film to counteract oxygen inhibition when curing in air; alternatively, increasing the intensity of irradiation so that the intensity absorbed at the surface is higher, could also be used as a means of minimizing oxygen inhibition. Either of these approaches will mean that the number of initiating radicals is sufficiently high that, whilst some of the growing polymer chains initiated will be terminated by oxygen, a number of them will survive and propagate the initial stages of polymerization. Adding high concentrations of multifunctional acrylates also serves to minimize the effects of atmospheric oxygen; as before, some quenching by oxygen will occur but, if a few of the unsaturation sites of an oligomeric species of high molecular weight are able to react, polymerization to give a cured product can still be achieved.

Employment of a photoinitiating system composed of an hydrogen abstracting aromatic ketone and a tertiary amine hydrogen donor is one of the most efficient methods of counteracting the effects of oxygen. Hydrogen abstraction by benzophenone results in the formation of an alkyl amino radical, which interacts preferentially with oxygen, yielding a peroxy radical. The peroxy radical thus formed will then abstract hydrogen from another amine to yield another alkyl amino radical and a hydroperoxide, i.e. the oxygen present is consumed by a chain process. It has been reported that the formation of one alkyl amino radical may result in the consumption of as many as twelve molecules of oxygen.[2]



Mechanism of Oxygen Consumption by Tertiary Amines

Several new methods of dealing with oxygen inhibition have recently emerged, one of which attempts to completely consume all the oxygen prior to the initiation of polymerization. This is done by the use of a dye sensitizer which, on irradiation, will sensitize the conversion of ground state triplet oxygen to the singlet state. Compounds such as 1,3-diphenylisobenzofuran, which reacts readily with singlet oxygen to form carbonyl compounds, are then used as scavengers for singlet oxygen, thus effectively removing the quencher triplet oxygen from the system. In the case of 1,3-diphenylisobenzofuran, the orthodibenzoyl benzene formed by the oxidation of the acceptor molecule also initiates polymerization efficiently when irradiated at a different wavelength.

Hult and Ranby[3] have demonstrated the use of unimolecular fragmentation type photoinitiators in conjunction with interfacial action fluorinated compounds as an alternative method for overcoming oxygen inhibition. Migration of the surface active material allows sufficient reaction to occur at the surface to result in a compact layer of cured polymer at the interface, preventing further diffusion of oxygen into the system.

References

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2. R.F. Bartholomew and R.S. Davidson, J. Chem. Soc.(C) 2342 (1975)

3. A Hult and B. Ranby, 'Polym. Prepr.', Am. Chem. Soc., Div. Polym. Chem. (1984)

CHAPTER III:

POLYMERIC TYPE I PHOTOINITIATORS

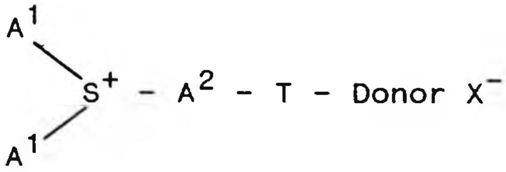
3.1 INTRODUCTION TO POLYMERIC PHOTOINITATORS

It is to be expected that polymeric photoinitiators for UV-curable coatings would offer a number of advantages over similar monomeric systems[1]. First of all, the possibility exists for energy migration along the polymer chain, which would give rise to high efficiencies of initiation. Intramolecular reactions in the polymer molecule could produce high yields of free radicals. This, in addition to synergistic effects arising from the attachment of various photoreactive groups to the same macromolecule, would again lead to high initiation efficiencies. By means of copolymerization, photoinitiators with photoreactive moieties in different chemical environments and at varying separations from each other could be achieved. In this way the efficiency of the photoinitiating system could be modulated. Finally, the problems associated with unreacted photoinitiator fragments migrating to the surface would be reduced if low molecular weight photoinitators were replaced by polymeric systems.

All of the above-mentioned advantages have, in fact,been realized. In 1981 Neckers et al.[2] reported the preparation of a novel vinyl monomer, which contained a carbonyl triplet sensitizer group, and a perester group as radical source.

Homopolymerization and copolymerization of the monomer with styrene were effected without loss of perester activity. In the photoinitiated polymerization of styrene, much higher rates were obtained with the homopolymer than with the parent monomer. This was attributed to gel formation, the high molecular weight of the polymer and energy migration. The first two factors would shield the propagating free radical site from termination, allowing chain growth for a much longer time than would be allowed for the radical chains initiated by the monomeric ester. As polymerization proceeds the conformational rigidity of successive perester groups will increase, facilitating energy migration between them. A later publication by Carlini et al.[3] cited photo-excitation energy migration in addition to intramolecular hydrogen abstraction as the major factors in the enhanced photoinitiating activity displayed by benzophenone-containing polymers, compared to their low molecular weight analogues.

Wright and DeVoe[4] claimed synergistic effects when an electron donor and/or sensitizer was tethered to a triarylsulphonium salt photoinitiator in free radical polymerizable compositions. The tethered sulphonium salt-containing compositions were reported as curing more rapidly than compositions using even larger amounts of untethered sulphonium salt initiator. Furthermore, the tethered compositions possessed greater thermal stability. The tethered sulphonium salts can be represented by two general formulae:



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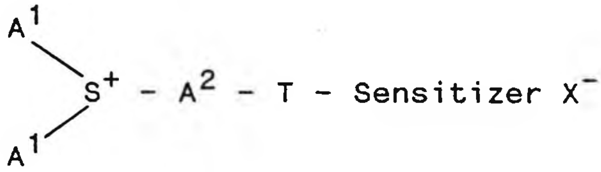


II

where S^+ is a positively-charged sulphur atom; A^1 is an aryl group with between six and fifty carbon atoms; A^2 is an arylene group of between six and fifty carbon atoms; T is the tether linking the triarylsulphonium salt moiety to the electron donor or photosensitizer; and X^- is the counter ion.

Another notable effect which has been observed with some polymeric photoinitiators is hyperchromism. Optically active copolymers of (-) menthyl acrylate with racemic α-methylolbenzoin methyl ether acrylate (MBA) showed a marked increase in the molar absorptivity for the $\pi \rightarrow \pi^*$ transition, per MBA unit, on decreasing the MBA content[5]. This behaviour was attributed to interactions between adjacent aromatic chromophores[6,7].

On exposure to UV irradiation, benzophenone will abstract hydrogen from a suitable donor to produce two radicals[8]. If the hydrogen donor is a tertiary amine, an exciplex is formed between the amine and the excited triplet ketone:

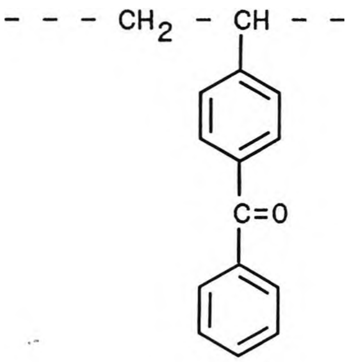
$$(Ar_2C{=}O)^*_T + :NR_2{-}CR'_2H \longrightarrow (Ar_2C{=}O^{\delta-} \longleftarrow N^{\delta+} R_2CR'_2H)^*_T$$

Exciplex

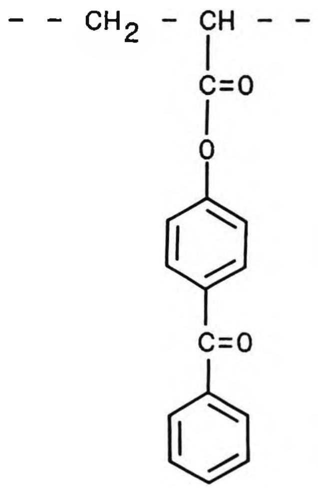
$$\downarrow$$

$$Ar_2\dot{C}{-}OH + :NR_2 - \dot{C}R'_2$$

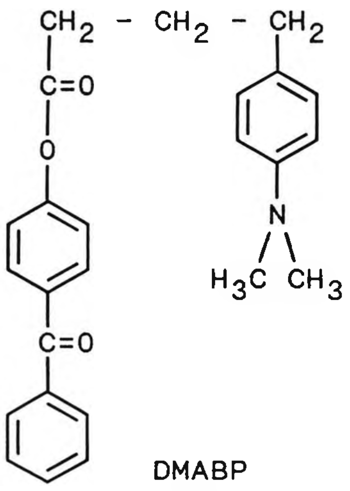
Hydrogen transfer then affords the ketyl and α-aminoalkyl radicals, the latter of which has been shown to be active in the initiation of polymerization[9,10]. Benzophenone/tertiary amine combinations are very active in the UV-initiated polymerization of unsaturated monomers[11,12]. Consequently, Carlini et al.[3] prepared polymeric photoinitiators containing both side-chain benzophenone and tertiary amine moieties, in the expectation that very high photoinitiation rates would result. Copolymers of 4-vinylbenzophenone (VBP) with 4-(N,N-dimethylamino) styrene (DMAS) and with 2-(N,N-dimethylamino) ethyl acrylate (DEAA), and of 4-acryloxybenzophenone (ABP) with DMAS and DEAA, were prepared. The copolymers, referred to as poly(VBP-co-DMAS), poly(VBP-co-DEAA), poly(ABP-co-DMAS) and poly(ABP-co-DEAA), respectively, were used as photoinitiators for the polymerization of an equimolar 1,6-hexanedioldiacrylate (HDDA)/n-butyl acrylate (BA) mixture. Comparisons were made with the homopolymers poly(ABP) and poly(VBP), with the mixtures poly(ABP)/DMA and poly(ABP)/poly(DMAS), and with the low molecular weight compound DMABP.



Poly (VBP)

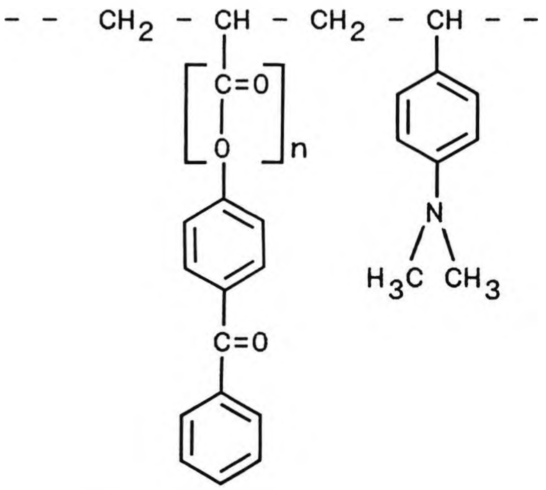


Poly (ABP)



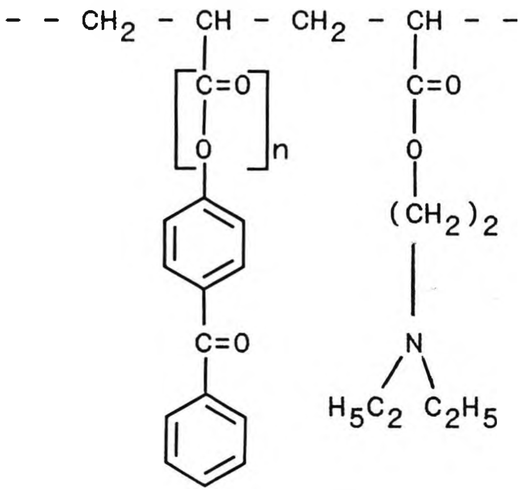
DMABP

Low molecular weight model



n=0 : Poly(VBP-co-DMAS)

n=1 : Poly(ABP-co-DMAS)



n=0 : Poly(VBP-co-DEAA)

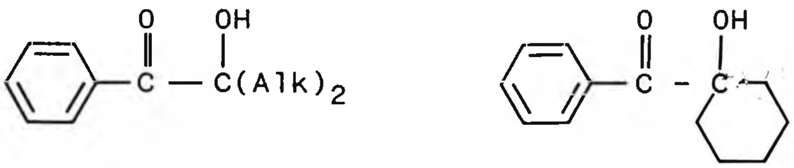
n=1 : Poly(ABP-co-DEAA)

It was found that poly(VBP-co-DMAS) and poly(ABP-co-DMAS) exhibited considerably lower activities than the corresponding benzophenone-containing homopolymers. The highest activity of all was found with poly(ABP)/DMA, where DMA = N,N-dimethyl aniline, the observed order being poly(ABP)/DMA > poly(ABP-co-DEAA) > DMABP ~ poly(ABP)/ poly(DMAS) > poly(ABP) > poly(VBP-co-DEAA) ~ poly(VBP) >> poly(ABP-co-DMAS) > poly(VBP-co-DMAS).

The absorption spectra of mixtures of poly(VBP) and poly(DMAS), and of mixtures of the corresponding low molecular weight model compounds, show no intermolecular gound state donor-acceptor complex formation[13]. No evidence of ground state complex formation was found by Carlini in the UV-spectra of poly (VBP-co-DEAA) or poly (ABP-co-DEAA), and it was expected that similar results would occur for poly(VBP-co-DEAA) and poly(ABP-co-DEAA). The unexpectedly low activity of poly(VBP-co-DMAS) and poly(ABP-co-DMAS) was, therefore, rationalized in terms of in-cage radical recombination. The high local concentration of amine-derived radicals in these latter two copolymers facilitates recombination of the radicals. In DMABP, despite the high probability of exciplex formation, the local concentration of the amine-derived radicals should be relatively low. Thus, the initiation of polymerization is favoured over radical recombination and DMABP accordingly shows a higher photoinitiating activity. In poly(ABP-co-DEAA) and poly(VBP-co-DEAA) also, the concentration of exciplexes was found to be low, and this led to the conclusion that little or no cage recombination of amine-derived radicals would probably occur; hence the much higher activities than with poly(ABP-co-DMAS) and poly(VBP-co-DMAS). It is also expected that the flexibility of the spacers between the amine groups and polymer backbone will reduce polymer coil shielding of the amine-derived radicals. Consequently, the efficiency of the radicals in initiating polymerization will be greatly increased in the DEAA copolymers.

Finally, the highest activity observed for poly(ABP)/DMA was attributed to energy migration between adjacent benzophenone moieties and to exciplex formation[14]. The amine-derived radicals in this photoinitiating system are free to diffuse in the polymerization medium, unlike the poly(ABP)/poly(DMAS) system, which accordingly shows much lower activity.

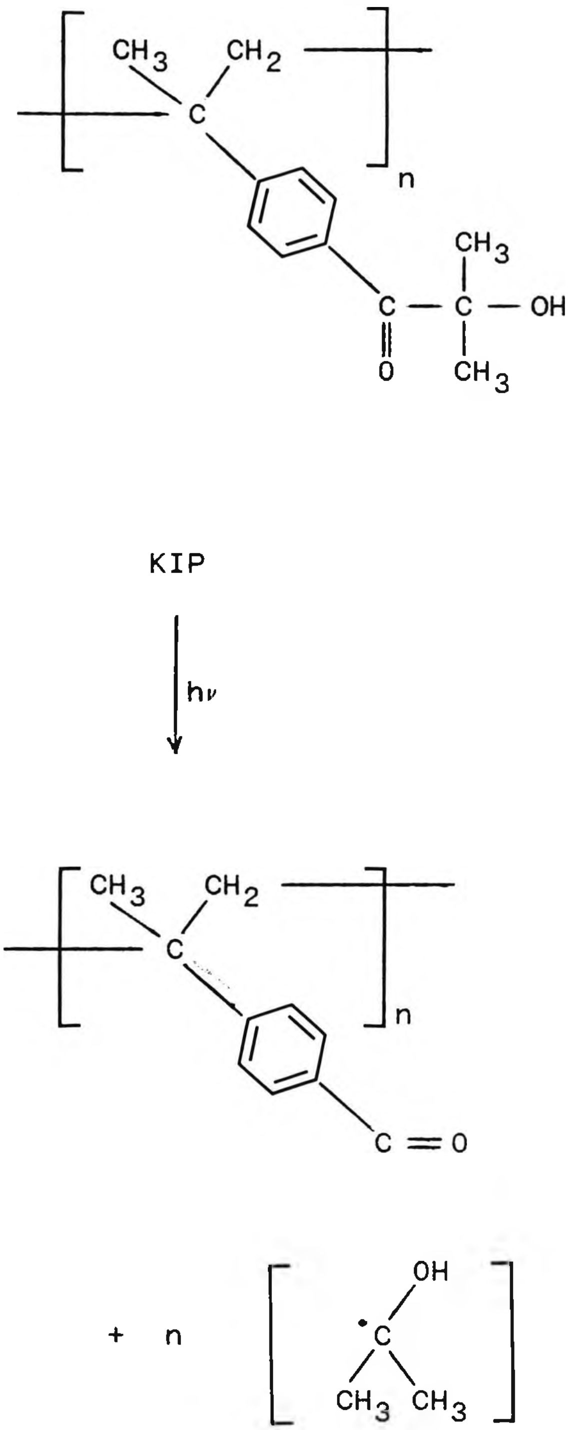
Thus it can be seen that photoinitiating efficiency can indeed be modulated by copolymerizing with different comonomers. With regard to the problems derived from the migration of unreacted, low molecular weight fragments, these have been a major concern in the production of clear coatings. In the early 1980's a new class of photoinitiators, known as α-hydroxyalkylphenones, became commercially available[15]. It was claimed that these compounds initiate the photopolymerization of vinyl monomers with efficiencies comparable to that of benzildimethylketal[16]



α-Hydroxyalkylphenones

The absence of aromatic substituents in the hydroxyalkyl moieties prevents the formation of chromophoric compounds, so that clear, non-yellowing acrylic coatings can be achieved[17]. Proton NMR and C.I.D.N.P. experiments have shown α-cleavage to take place, yielding a benzoyl and ketyl radical[18,19].

In spite of the achievement of clear coatings, two major problems still remained with the α-hydroxyalkylphenones. Firstly, the photoinitiators themselves were of low molecular weight and high volatility, or were readily solvent-extractable from cured compositions. Secondly, the photolysis products obtained from rearrangements of unconsumed radical pairs were generally volatile and odorous substances. A possible solution to these problems would be to use copolymerizable or polymeric photoinitiators. Consequently, Li Bassi et al. prepared a number of polymeric α-hydroxyalkylphenone photoinitiators[17]. For the polymers which they prepared, the best results were obtained with an oligomeric molecule derived from α-methylstyrene, and referred to as KIP.

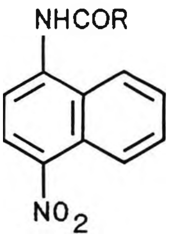


This was found to undergo α-cleavage to yield 2-hydroxypropyl and polymeric benzoyl radicals, as illustrated above.

KIP was demonstrated to be a highly reactive photoinitiator, particularly suitable for clear, non-yellowing, UV-curable coatings. Furthermore, due to the low volatility of KIP and its photolysis fragments, practically odourless coatings could be produced if purified monomers and oligomers were used.

Whilst the many advantages associated with the use of polymeric photoinitiators have been described in the preceding pages, binding a photoinitiator to a polymeric system can result in diminished efficiency. One such case has already been described in relation to the copolymers containing both benzophenone and tertiary amine moieties[3]. Another example of diminished photoinitiating activity was reported by Allen et al.[20] Copolymerization of 2-acryloylthioxanthone with monomers such as methyl methacrylate yielded products which were lipophilic and highly compatible with commercial acrylic resins. Other polymeric thioxanthone photoinitiators were prepared by binding the chromophore to functionalized polystyrene. The photoinitiating efficiencies of the polymers and the monomer were compared for a commercial triacrylate resin. It was found that the cure rate with 2-acryloylthioxanthone was greatly accelerated by the addition of triethylamine. This can be explained by the formation of a triplet exciplex between the thioxanthone molecule and the amine[21]. The highest rate of all was achieved with the methylmethacrylate copolymer and added amine, whilst the thioxanthone bound to polystyrene was found to be less effective than the monomeric analogue, 2-benzoylthioxanthone. This reduction in efficiency was attributed to a loss of absorbed light energy caused by energy migration, and quenching by the phenyl units on the polymer backbone.

Another case of polymer binding leading to a reduction in activity was reported by Diaz[22]. Tsuda had claimed that aromatic nitro-carbonyl compounds functioned as efficient photosensitizers for the dimerization of cinnamoyl groups[23]. It had also been shown that N-acetyl-4-nitro-1-naphthylamine could initiate photopolymerizations[24]. Combining these two observations, Diaz et al. synthesized a number of monomers, homopolymers and copolymers containing the 4-nitro-1-naphthylcarbamoyl photosensitizer group[22].



R = CH_3/C_6H_5 - Model compounds

R = $CH{=}CH_2/C_6H_4CH{=}CH_2$ - Monomers prepared as starting materials

Monomers and model compounds containing the 4-nitro-1- naphthylcarbamoyl group

One of the polymeric photosensitizers and the model compound were tested as triplet sensitizers, their efficiences being compared with that of trans-stilbene. Whilst good efficiencies were obtained with the 4-nitro-1-naphthylcarbamoyl sensitizer group, the efficiency was found to decrease upon binding the chromophore to the polymer. The authors claimed that diffusional effects were responsible for the observed decrease in the energy transfer constant and corresponding loss of efficiency. Despite the fact that the polymeric sensitizer exhibited lower efficiency than the free sensitizer model, the former was, nevertheless, still an efficient energy donor.

In general, the examples discussed in this introductory section demonstrate that polymeric photoinitiators can offer a number of advantages over similar monomeric counterparts. Interest in this field is growing continuously and the number of polymeric systems of both commercial and academic value is rising accordingly. The advantages afforded by these new discoveries extend to areas including photoresists for electrodeposition[25,26]; positive-type resists sensitive to deep UV[27]; non-silver materials for reprography[28]; light-sensitive materials for packaging[29]; and UV-curable printing inks and surface coatings.

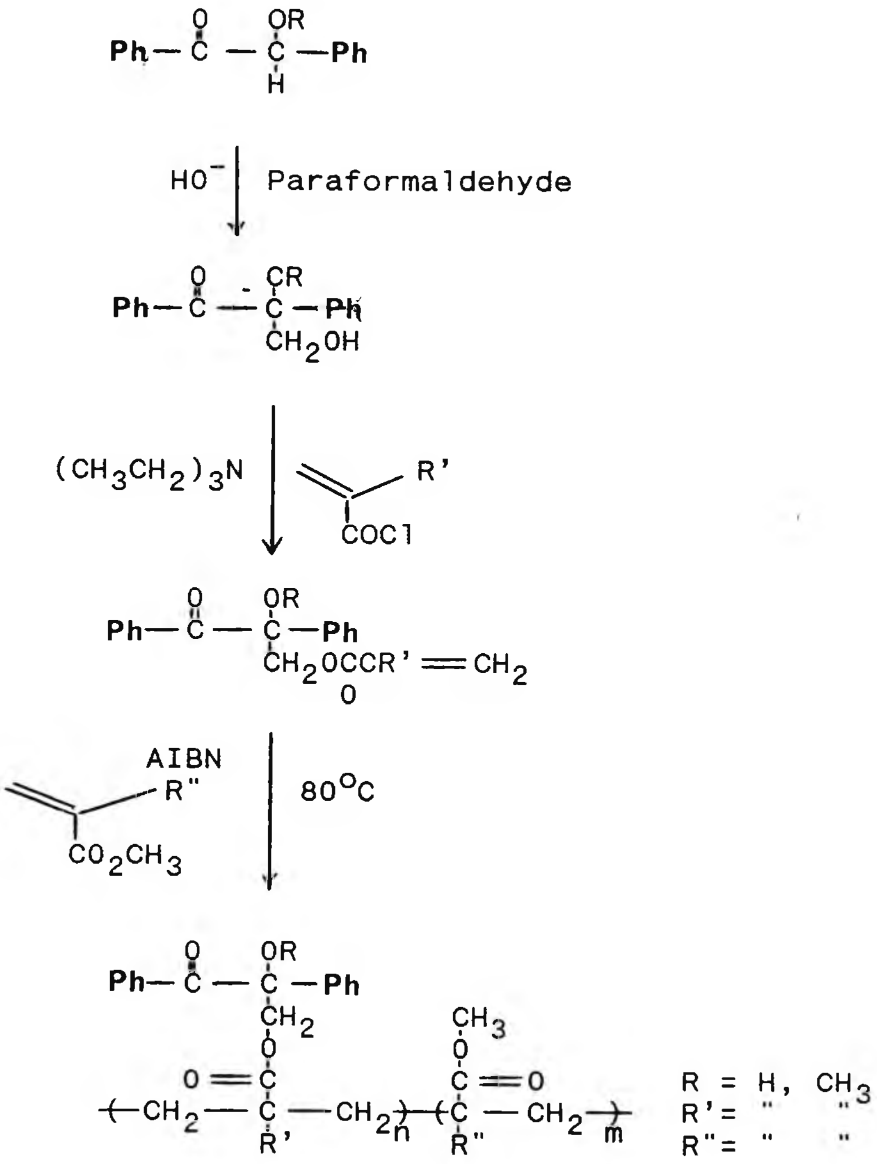
In 1986 it was reported that photosensitive polymers with benzoin methyl ether side chains showed greater photoinitiating efficiency than monomeric benzoin derivatives[30]. This enhancement of efficiency was attributed to protection of the propagating radicals by the polymer coils, allowing the formation of longer chains.

α-Methylolbenzoin can be readily obtained from the reaction of formaldehyde with benzoin[31], and has been claimed to be a high-activity photoinitiator[32]. In the light of the claims made by Ahn et al.[30], it was decided to esterify the primary hydroxyl function of α-methylolbenzoin, and subsequently attach it to a polymer backbone as a photoreactive pendant group. The experimental work presented in this chapter relates to the preparation of such polymeric photoinitiators and subsequent investigations into their photoactivity.

3.2 EXPERIMENTAL

3.2.1 PREPARATION OF PHOTOINITIATORS

General Scheme

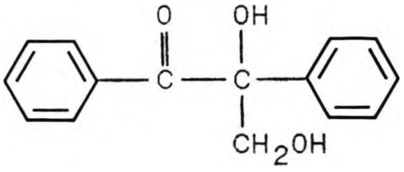


All reagents were supplied by Aldrich Chemical Company and were used without further purification. Methyl acrylate and methyl methacrylate contained 200 p.p.m. and 10 p.p.m. hydroquinone methyl ether, respectively. Melting points were determined with a Griffin melting point apparatus, serial number P.1158.

NMR spectra were recorded on a Jeol JNM-PMX 60SI spectrometer, using tetramethylsilane as internal standard. UV spectra were recorded on a Perkin-Elmer Lambda 5 UV/visible spectrophotometer. IR spectra were recorded on a Perkin-Elmer 983G infra-red spectrophotometer.

3.2.1.1 Preparation of Alcohols

α-Methylolbenzoin



I

Compound I was prepared according to the procedures of Hageman[31].

Procedure 1

0.5ml of a methanolic solution of potassium hydroxide (consisting of 1.5g potassium hydroxide in 10ml methanol) was added to 10.6g (0.050 mol) benzoin and 1.67g (0.056 mol) paraformaldehyde in 16ml benzene. Tlc analysis (silica gel, methanol) showed complete conversion of starting material to product after heating to 60°C for 1.1/2 hrs. The resulting solution was neutralized with acetic acid, washed with water and dried over anhydrous sodium sulphate. The solid residue afforded by solvent evaporation was recrystallized from toluene in 78% yield with a melting point of 83.5-84.0°C (literature value[31] 84.8-85.6°C).

<u>NMR</u> ($CDCl_3$) : δ 7.8-7.6 (m,2H,benzoyl); 7.3-7.0 (m,8H,phenyl); 4.3-3.4 (2d,2H J=12Hz,$-CH_2O-$); 1.9 (s,1H,-OH);

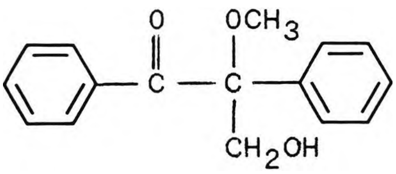
<u>IR</u> (KBrDisc) : 3489 (-O-H str. of $-CH_2OH$), 3342 (O-H str. of $\underset{/}{\overset{\backslash}{-C}}$-OH); 3029 (aryl C-H str.); 1664 (carbonyl C=O str.), 1594, 1576 & 1495 (aryl C-C str.); 1445 (C-H def. of $-CH_2$); 1188 (tertiary alcohol C-O str/O-H def.); 1045 (primary alcohol C-O str./O-H def.), 761 & 701 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

<u>Procedure 2</u>

1.0ml of a methanolic potassium hydroxide solution (as above) was added to 10.6g (0.05 mol) benzoin and 1.7g (0.06

mol) paraformaldehyde in 25ml toluene. The mixture was heated to 80°C for 8 hrs, 0.25g quantities of paraformaldehyde being added at 2 hr intervals. Solvent evaporation in vacuo yielded a yellow, syrupy residue which was crystallized twice from toluene, to give colourless crystals in 35% yield. Melting point = 84.5-85.0°C. Spectral analyses previously mentioned.

α-Methylolbenzoin Methyl Ether



II

Compound II was prepared according to the procedure of Ahn et al.[30]

Procedure

2.5g Paraformaldehyde were added to a stirred solution of 15g benzoin methyl ether (0.065 mol) in 100ml dimethyl sulphoxide containing 0.2g potassium hydroxide in 2.5ml ethanol. The mixture was heated under nitrogen for 3 hrs. at 40°C, cooled to room temperature and neutralized with dilute hydrochloric acid. The neutralized solution was diluted to a volume of

600ml with a saturated sodium chloride solution and extracted with ethyl acetate. The organic extract was washed three times with saturated sodium chloride solution and dried over anhydrous sodium sulphate. The yellow oil afforded by solvent evaporation crystallized slowly on refrigeration and was recrystallized twice from toluene/hexane in 53% yield, melting point 72.5-73.5°C (literature value[33] 72-73°C).

NMR ($CDCl_2$): δ 8.0-7.8 (m,2H,benzoyl); 7.5-7.0 (m,8H,phenyl); 4.5-4.1 (2d,2H,$-CH_2O$ -, J=13Hz); 3.3(s,3H,$-OCH_3$);

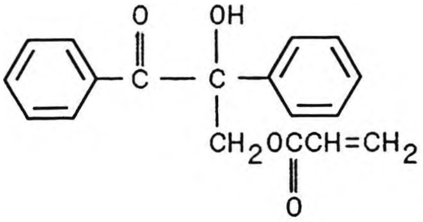
IR (KBr Disc); 3374 (O-H str.), 3029 (aryl C-H str.); 2959, 2936 & 2886 (alkyl C-H str.); 2830 & 2061 (C-H str. of CH_3-O-C-); 1670 (ketone C=O str.); 1602, 1583 & 1489 (aryl C-C str.), 1448 (alkyl C-H def.); 1337 (primary alcohol O-H def./C-O str.), 1072 & 1059 (primary alcohol C-O str./O-H def. & ether C-O str.); 760 & 733 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

C.H.N. Analysis : Found 75.00% C; 6.42% H;
Theory 74.98% C; 6.29% H;

3.2.1.2 Preparation of Esters

The acrylate and methacrylate esters were prepared by reaction of the methylolbenzoin alcohols with the appropriate acid chlorides. Both the acrylate and methacrylate esters of α-methylolbenzoin were formed in reasonable yields. All attempts to obtain the methacrylate of α-methylolbenzoin methyl ether proved unsuccessful.

α-Methylolbenzoin Acrylate



III

Procedure

30.04g (0.332 mol) acryloyl chloride were added dropwise to a stirred solution of 11.62g (0.048 mol) α-methylolbenzoin, 6.86g (0.068 mol) triethylamine and 50ml chloroform below 5°C. T.L.C. analysis (dichlormethane/methanol) showed the reaction to have reached completion after heating to 30°C for 90 mins. Conventional work-up (i.e. ether extraction, washing and drying of organic layer, solvent evaporation) yielded a yellow oil, which formed a white solid on refrigeration.

The product was recrystallized from ethanol in 48% yield, melting point 80.0-81.0^{o}C.

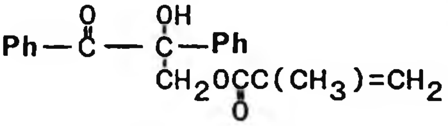
<u>NMR</u> ($CDCl_3$):δ 7.9-7.7 (m,2H,benzoyl); 7.6-7.1 (m,8H, phenyl); 6.5-5.9 (m,3H,$-CH=CH_2$); 5.2-4.5(2d,2H,J=12Hz,OCH_2);

<u>IR</u> (KBr Disc): 3431(O-H str.), 3067 (C-H str. of $CH_2=CH-$), 1715 (ester C=O str.), 1673 (ketone C=O str.); 1635 (C=C str. of $CH_2=CH-$); 1596 (aryl C-C str.); 1447 (C-H def. of $>CH_2$); 1414 (C-H def. of $CH_2=CH-$); 1302 (C-O str./O-H def. of $-\overset{\backslash}{\underset{/}{C}}-$OH); 1221 (C-O str. of α,β-unsaturated ester); 1163 & 1152 (C-O str. of α,β-unsaturated ester & C-O str./O-H def. of $-\overset{\backslash}{\underset{/}{C}}-$OH); 760 & 699 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

<u>C.H.N Analysis</u> : Found 72.66% C; 5.44% H;
Theory 72.96%,C; 5.44% H;

<u>UV</u> ($CHCl_3$) : $n-\pi^*$ λ_{max}= 318nm; ε= 202

<u>α-Methylolbenzoin Methacrylate</u>



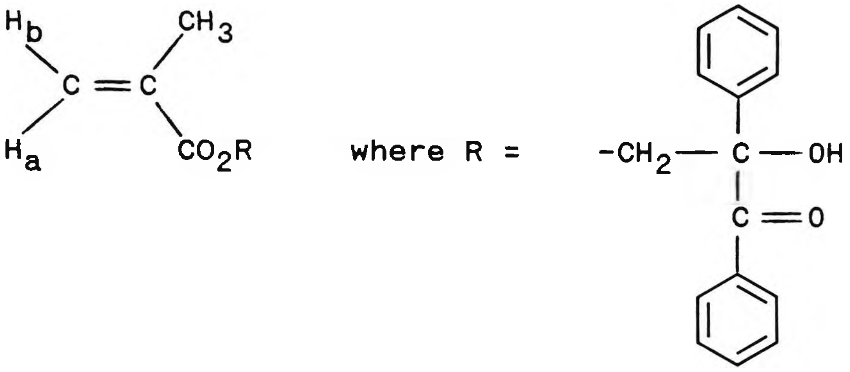
$$Ph-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{\underset{CH_2O\underset{O}{\underset{\|}{C}}C(CH_3)=CH_2}{\underset{|}{C}}}}-Ph$$

IV

Procedure

21.40g (0.205 mol) methacryloylchloride were added dropwise to a stirred solution of 11.62g (0.048 mol) α-methylolbenzoin, 6.86g (0.068 mol) triethylamine and 50ml chloroform below 5°C. Tlc analysis showed the reaction to be complete after heating to 30°C for 2.1/2 hrs. Conventional work-up yielded an orange-coloured oily liquid. Crystallization from toluene gave a 39% yield with melting point 87.0-87.5°C.

NMR ($CDCl_3$): δ 7.9-7.7 (m,2H,benzoyl); 7.6-7.2 (m,8H, phenyl); 6.0-5.9 (m,1H,H_a); 5.6-5.4 (m,1H,H_b); 5.2-4.5 (2d,2H,J=12Hz;$-CH_2O-$); 1.8 (s,3H,$-CH_3$);



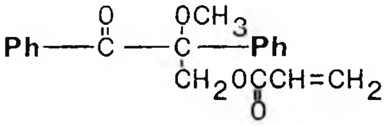
IR (KBr Disc): 3446(O-H str.), 3072 & 3011 (aryl C-H str.); 1699 (ester C=O str.), 1673 (ketone C=O str.); 1633 (olefinic C-H str.) 1597, 1576 & 1491 (aryl C-C str.); 1448 (alkyl C-H def.); 1401 (olefinic C-H def.) 1382 (alkyl C-H def.) 1174 (tertiary hydroxyl C-O str./O-H def.); 762 & 700 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

C,H,N Analysis : Found 73.47% C; 5.94% H;

Theory 73.53%,C; 5.84% H;

UV $(CHCl_3)$ $n-\pi^*$ λ_{max}= 320nm; ε = 206

α-Methylolbenzoin Methyl Ether Acrylate



$$Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{\|}{\overset{}{C}}CH=CH_2}{\overset{OCH_3}{C}}-Ph$$

V

Procedure

18.75g (0.208 mol) acryloyl chloride were added dropwise to a stirred solution of 7.50g (0.029 mol) α-methylolbenzoin methyl ether and 2.90g (0.029 mol) triethylamine in 30ml chloroform below 5°C. Tlc analysis indicated that the reaction was complete after heating to 40°C for 2 hrs.

Conventional work-up yielded an oily liquid which formed a crystalline solid on refrigeration. Recrystallization from ethanol afforded 47% product with a melting point of 56.0-57.0^oC (literature value[30] 56^oC).

NMR ($CDCl_3$):δ 7.8-7.6 (m,2H,benzoyl); 7.3-6.8 (m,8H, phenyl); 6.0-5.3(m,3H,$-CH=CH_2$); 4.9-4.3(2d,2H,J=12Hz, $-CH_2O-$); 3.0 (s,3H,$-OCH_3$).

IR (KBr Disc): 3068 (C-H str. of $CH_2=CH-$); 2940 & 2897 (alkyl C-H str.); 2831 (C-H str. of CH_3-O-); 1735 (ester C=0 str.), 1673 (ketone C=0 str.); 1635 (C=C str. of $CH_2=CH-$); 1594 & 1575 (aryl C-C str.); 1447 (alkyl C-H def.) 1218 & 1145 (C-0 str. α,β-unsaturated ester); 1089 (ether C-0 str.); 761 & 720 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

C.H.N Analysis : Found 73.50% C; 5.80% H;
Theory 73.55% C; 5.81% H;

3.2.1.3 Advancement of Esters to Copolymeric Systems

Copolymers were prepared by reacting the acrylate and methacrylate esters with either methyl acrylate or methyl methacrylate. The thermal reactions were initiated by azobisisobutyronitrile (AIBN), with methyl isobutyl ketone being used as the reaction solvent.

An example of the procedure used to produce the copolymers follows:

Copolymerization of α-Methylolbenzoin Acrylate with Methyl Acrylate

Procedure

0.60g (2.0×10^{-3} mol) α-methylolbenzoin acrylate, 0.52g (6.0×10^{-3} mol) methyl acrylate and 0.04g (4.2×10^{-4} mol) AIBN were dissolved in MIBK and made up to a volume of 8ml in a test tube. The solution was degassed by bubbling argon gas through it for approximately ten minutes, and the test tube was then sealed. The sealed test tube was place in an oil bath at 80^{o}C and 2ml aliquots of solution were removed after 120, 150, 180 and 210 mins. Pouring the aliquots into excess pet. ether (60-80^{o}C fraction) resulted in precipitation of the copolymers, which were isolated by reduced pressure filtration and analyzed by UV and NMR spectroscopy.

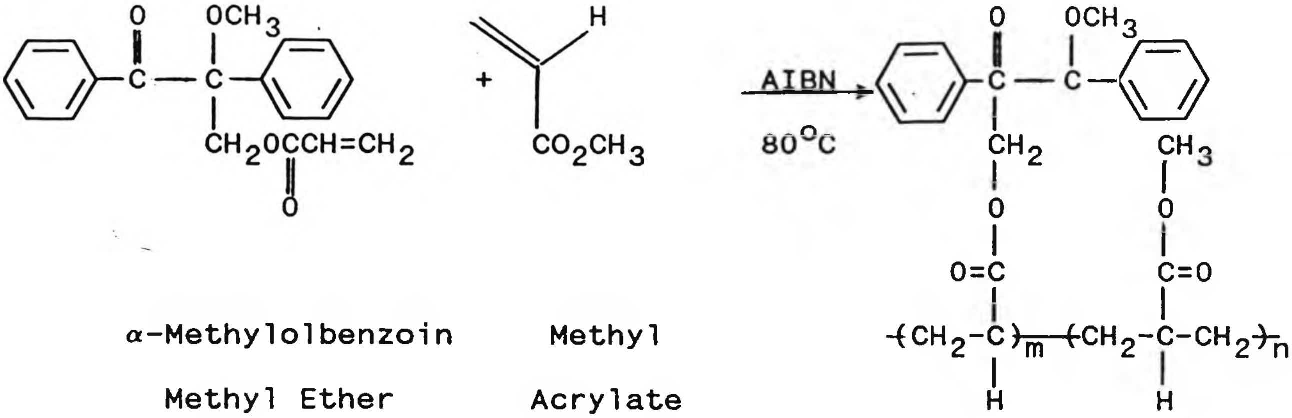
All copolymers were prepared by a similar method to that outlined on the previous page. The reactant and thermal initiator ratios were kept constant in all cases except in the preparation of copolymers MB 1:1, MB 2:1 and MB 1:2 (see below).

Copolymerization of α-Methylolbenzoin Methyl Ether with Methyl Acrylate: Preparation of MB 1:1

Procedure

0.31g (1.00×10^{-3}mol) α-methylolbenzoin methyl ether, 0.09g (1.00×10^{-3}mol) methyl acrylate and 0.02g (2.10×10^{-4} mol) AIBN were dissolved in MIBK and made up to 4ml. After degassing with argon for approximately 5 mins. the solution was heated to 80°C for 2 hrs. Precipitation of the copolymer was effected by pouring the hot solution into pet. ether (60-80°C fraction).

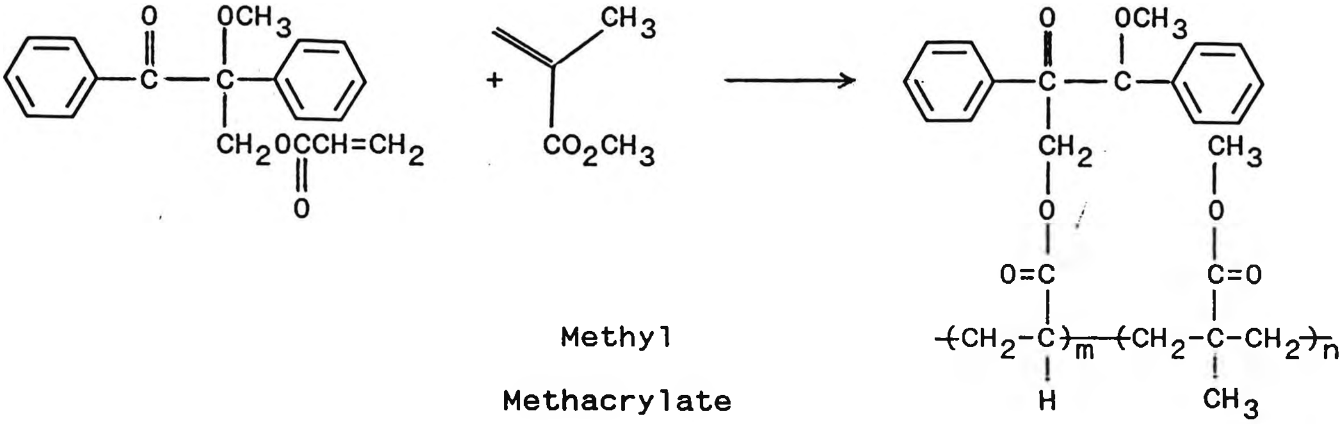
Copolymers MB 1:2 and MB 2:1 were prepared similarly but with 0.31g α-methylolbenzoin methyl ether to 0.18g methyl acrylate, and 0.62g α-methylolbenzoin methyl ether to 0.09g methylacrylate, respectively.



α-Methylolbenzoin Methyl Ether Acrylate

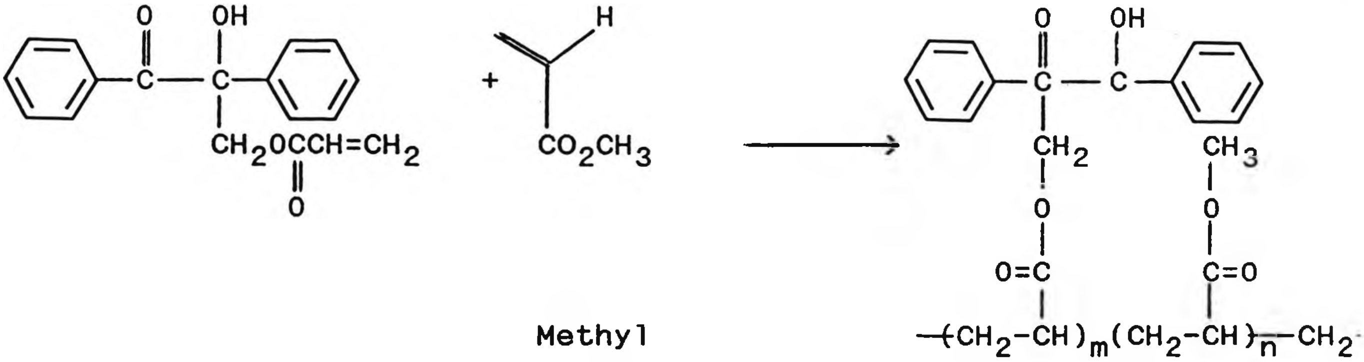
Methyl Acrylate

MB Copolymers



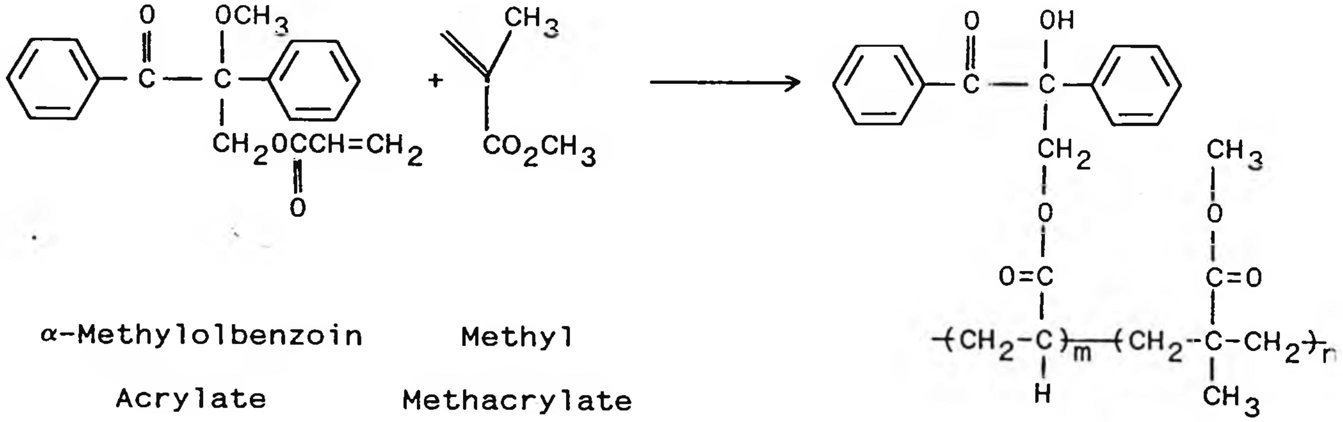
Methyl Methacrylate

MB/MMA Copolymers



Methyl Acrylate

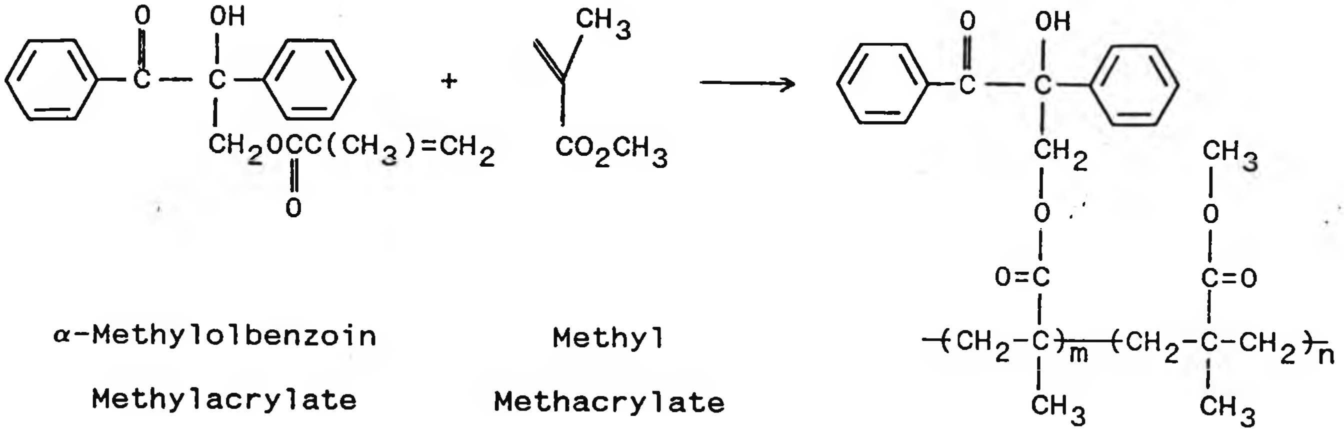
MA Copolymers



α-Methylolbenzoin Acrylate

Methyl Methacrylate

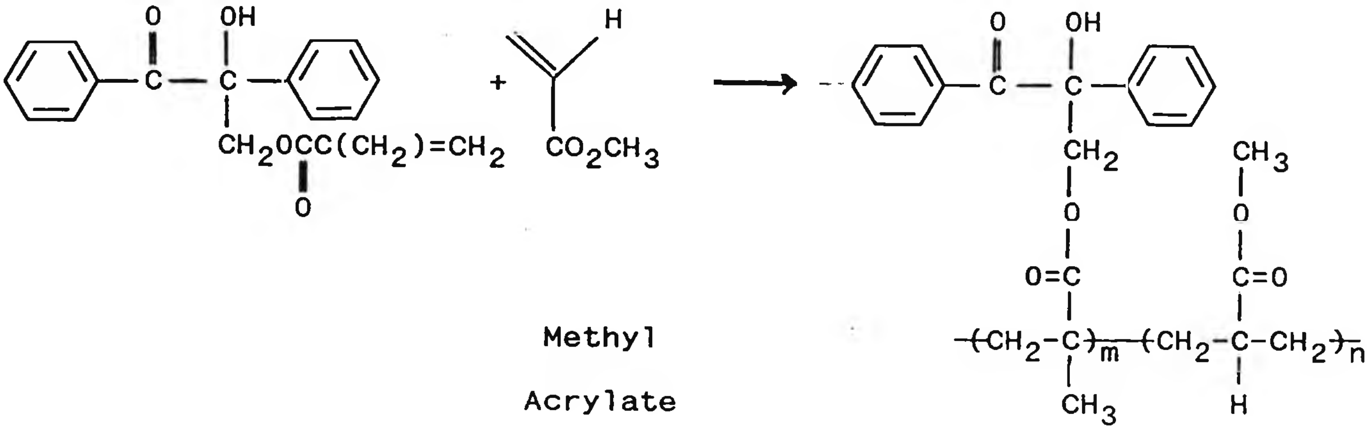
KIII/MMA Copolymers



α-Methylolbenzoin Methylacrylate

Methyl Methacrylate

MMA Copolymers

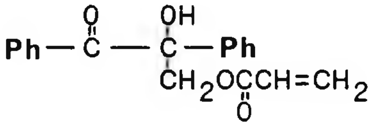
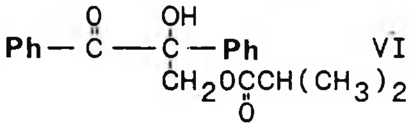
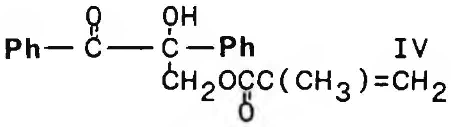
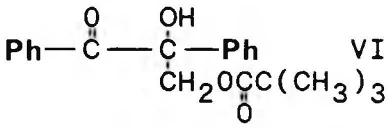
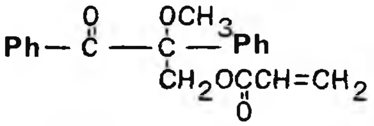
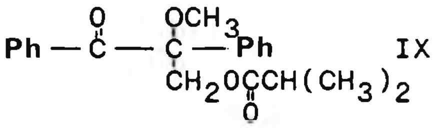
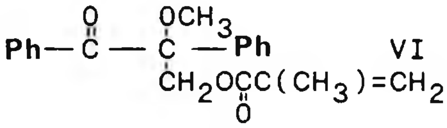
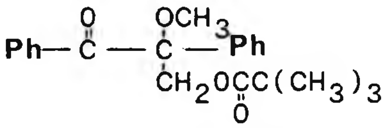


Methyl Acrylate

KM/MA Copolymers

3.2.2 MONOMERIC MODEL COMPOUNDS

Incorporation of the acrylate and methacrylate esters into a polymeric network requires saturation of the carbon-carbon double bonds. Thus the original esters are no longer representative of the structures of the photoinitiating groups, once copolymerization has taken place. In order to obtain a more accurate comparison of the difference in photoinitiating efficiency between the photoinitiating groups when in monomeric and polymeric form, model compounds were synthesized to mimic the units of structure adopted by the esters once copolymerized.

Acrylate/Methacrylate Ester	Monomeric Model Compound
 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}CH=CH_2}{\overset{OH}{C}}-Ph}$ III α-Methylolbenzoin Acrylate	 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}CH(CH_3)_2}{\overset{OH}{C}}-Ph}$ VII α-Methylolbenzoin Isobutyrate
 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}C(CH_3)=CH_2}{\overset{OH}{C}}-Ph}$ IV α-Methylolbenzoin Methacrylate	 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}C(CH_3)_3}{\overset{OH}{C}}-Ph}$ VIII α-Methylolbenzoin Pivalate
 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}CH=CH_2}{\overset{OCH_3}{C}}-Ph}$ V α-Methylolbenzoin Methyl Ether Acrylate	 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}CH(CH_3)_2}{\overset{OCH_3}{C}}-Ph}$ IX α-Methylolbenzoin Methyl Ether Isobutyrate
 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}C(CH_3)=CH_2}{\overset{OCH_3}{C}}-Ph}$ VI α-Methylolbenzoin Methyl Ether Methacrylate (not obtained)	 $\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\underset{CH_2O\underset{O}{\underset{\|}{C}}C(CH_3)_3}{\overset{OCH_3}{C}}-Ph}$ X α-Methylolbenzoin Methyl Ether Pivalate

3.2.2.1 Preparation of Model Compounds

α-Methylolbenzoin Isobutyrate (VIII)

Procedure

1.07g (0.01 mol) isobutyryl chloride were added dropwise to a stirred solution of 2.42g (0.01 mol) α-methylolbenzoin in 100ml ether and 1.01g (0.01 mol) triethylamine. Tlc analysis ($CHCl_3$/MeOH 99:1) showed the reaction to be complete after stirring at room temperature overnight. The amine salt was removed by filtration and the ethereal solution was washed with water and dried over anhydrous sodium sulphate. The oily liquid afforded by solvent evaporation was crystallized from toluene in 72% yield with a melting point of 85.0-86.0°C.

NMR ($CDCl_3$):δ 7.9-7.7 (m,2H,benzoyl); 7.6-7.1 (m,8H, phenyl); 4.9-4.3 (2d,2H,J=12Hz; $-CH_2O-$); 2.7-2.1(m,1H,-CH-); 1.2-0.9 (d,6H,J=7Hz; $-(CH_3)_2$);

IR (KBr Disc): 3454(O-H str.), 3058 (aromatic C-H str.); 2957 (alkyl C-H str.), 1734 (ester C=O str.); 1667 (ketone C=O str.); 1594, 1575 & 1491 (aryl C-C str.); 1385 & 1350 ($>C(CH_3)_2$ C-H def.); 757 & 699 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

C,H,N Analysis : Found 72.86% C; 6.73% H;

Theory 73.05%,C; 6.45% H;

UV (CHCl$_3$) n-π^* λ_{max}= 320nm; ε = 208

α-Methylolbenzoin Pivalate (VIII)

It was found that a small quantity of 4-dimethylaminopyridine as catalyst was required to give reasonable yields for this preparation.

Procedure

2.42g (0.02 mol) pivaloyl chloride were added dropwise to a stirred solution of 2.42g (0.01 mol) α-methylolbenzoin, 2.02g (0.02 mol) triethylamine and 0.12g (1.00×10^{-3} mol) 4-dimethylaminopyridine in 50ml tetrahydrofuran. Tlc analysis (CHCl$_3$/MeOH 99:1) showed the reaction to be complete after stirring at room temperature for 30 mins. The solution was then stirred with 50ml water to hydrolyze any unreacted acid chloride to the corresponding acid. Solvent evaporation was followed by extraction into ether. The ether extract was neutralized with 5M sodium hydroxide,and conventional work-up yielded a solid white product. Recrystallization from ethanol afforded a 30% yield, melting point 97.0-97.5^{o}C.

NMR (CDCl$_3$):δ 7.9-7.7 (m,2H,benzoyl); 7.6-7.2 (m,8H, phenyl); 5.1-4.5 (2d,2H,J=12Hz,-CH$_2$O-); 1.1 (s,9H,(CH$_3$)$_3$);

IR (KBr Disc): 3440(O-H str.), 3043 (aryl C-H str.), 2961 & 2905 (alkyl C-H str.), 1740 (ester C=O str.); 1674 (ketone C=O str.); 1597, 1565 & 1501 (aryl C-C str.); 1389 & 1365 (C(CH$_3$)$_3$ C-H str.); 747 & 659 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

C,H,N Analysis : Found 73.56% C; 6.82% H;
Theory 73.59% C; 6.79% H;

α-Methylolbenzoin Methyl Ether Isobutyrate (IX)

Procedure

2.14g (0.02 mol) isobutyryl chloride were added dropwise to a stirred solution of 2.56g (0.01 mol)α-methylolbenzoin, 2.02g (0.02 mol) triethylamine and 0.12g (1.00 x 10^{-3} mol) 4-dimethylaminopyridine in 50ml tetrahydrofuran. Tlc analysis (CHCl$_3$/MeOH 99:1) showed the reaction to be complete after stirring overnight at room temperature. The mixture was stirred with an excess of water prior to solvent evaporation *in vacuo*. The product was extracted into ether and the ethereal solution was neutralized with 5M sodium hydroxide solution. Conventional work-up yielded an oil, which crystallized from ethanol in 38% yield with a melting point of 49.0-50.0°C.

NMR (CDCl$_3$):δ 8.0-7.6 (m,2H,benzoyl); 7.5-7.2 (m,8H, phenyl); 5.1-4.5 (2d,2H,J=12Hz; -CH$_2$O-); 3.3 (s,3H,-OCH$_3$); 2.6-2.1 (m,1H,C$\underline{H}$(CH$_3$)$_3$); 1.1-0.9 (q,6H,(CH$_3$)$_2$);

IR (KBr Disc): 3027(aryl C-H str.), 2950 & 2853 (ethyl C-H str.) 2818 (CH$_3$O C-H str.); 1736 (ester C=O str.); 1670 (ketone C=O str.) 1601, 1572 & 1508 (aryl C-C str.); 1473, 1395 & 1356 (isobutyryl C-H def.); 1441 (alkyl C-H def.); 1088 (ether C-O str.); 760 & 708 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

C,H,N Analysis :		
	Found	73.39% C; 6.89% H;
	Theory	73.59% C; 6.79% H;

α-Methylolbenzoin Methyl Ether Pivalate (X)

Procedure

2.42g (0.02 mol) pivaloyl chloride were added dropwise to a stirred solution of 2.56g (0.01 mol)α-methylolbenzoin methyl ether, 2.02g (0.02 mol) triethylamine and 0.12g (1.00 x 10^{-3} mol) 4-dimethylaminopyridine in 50ml tetrahydrofuran. Following the procedure outlined above afforded an oily product, which solidified on refrigeration. Recrystallization from ethanol gave a 46% yield, product melting point 86.0-87.0^{o}C.

NMR ($CDCl_3$): δ 8.0-7.8 (m,2H,benzoyl); 7.6-7.0 (m,8H, phenyl); 5.1-4.5 (2d,2H,J=12Hz; $-CH_2O-$); 3.3 (s,3H,$-OCH_3$); 1.0 (s,9H,$-(CH_3)_3$);

IR (KBr Disc): 3033(aryl C-H str.), 2954,2910 & 2876 (alkyl C-H str.); 2819 (methoxy C-H str.); 1738 (ester C=0 str.); 1678 (ketone C=0 str.); 1451, 1387 & 1364 (pivaloyl C-H def.) 1091 (ether C-0 str.); 749 & 689 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

C,H,N Analysis : Found 74.26% C; 7.37% H;

Theory 74.09% C; 7.10% H;

3.2.3 CHARACTERIZATION OF COPOLYMERIC PHOTOINITIATORS

3.2.3.1 Determination of Photoreactive Group Contents

Both UV and NMR spectral analyses were used to determine the photoinitiating group contents of the various copolymers.

The NMR spectra of the copolymeric samples possess an aromatic signal which is uniquely associated with the benzoin moiety, and a methanoate signal which is similarly associated with the methyl acrylate or methacrylate. It follows that a comparison of the integrals of these two signals will enable the determination of the photoreactive benzoin group content of the copolymers. All NMR spectra were recorded in deuterated chloroform ($CDCl_3$) on a Jeol JNM-PMX 60 SI spectrometer.

In the case of UV spectral analysis the benzoin carbonyl $n \rightarrow \pi^*$ absorption (located in the 320nm region) was used as the basis for characterization. Having determined the value of the molar absorptivity for the relevant monomeric model compound, the Beer-Lambert law was then applied to solutions of the copolymers, in order to evaluate the benzoin group contents. It was assumed that the $n \rightarrow \pi^*$ absorption in the copolymers would be proportional to the benzoin moiety content. According to the Beer-Lambert law $c=A/_{l\varepsilon}$ [34], where c is the molar concentration of the solution, A is the absorbance at a given wavelength, l is the path length (cm) and ε is the molar absorptivity ($l mol^{-1} cm^{-1}$). Thus, by using copolymer solutions of known weight/volume concentration, and assuming that ε would be the same for the copolymerized benzoin moieties as for the corresponding model compounds, photoreactive group contents were calculated.

Chloroform was used as the solvent for all UV spectra, which were recorded on a Perkin-Elmer Lambda 5 UV/visible spectrophotometer.

3.2.3.2 **Molecular Weight Determination by G.P.C. Analysis**

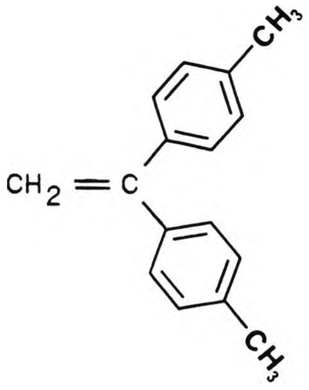
Gel permeation chromatography (G.P.C.) was first introduced in 1959[35]. The earliest use of the technique was in the analysis of water-soluble polymers, using cross-linked dextran gels. The development in the 1960's of a rigid gel, suitable for use with organic solvents, permitted the extension of G.P.C. to the analysis of commercially important synthetic gels[36].

The technique of G.P.C. is based upon the separation of molecules in solution according to their size. A dilute solution of the sample is injected into a stream of solvent flowing through a set of chromatographic columns. The columns are packed with porous gels of various pore sizes so that, as the solution passes through, the size of the largest molecules prevents them from entering the gel pores. These molecules will, therefore, pass through the columns at the same speed as the solvent. The smallest molecules, however, are able to penetrate the pores of the gel and their progress through the columns is thus retarded. The extent of retardation of molecules of intermediate size will be determined by the size of the molecules and the distribution of pore sizes within the gel.

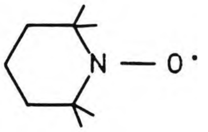
The retention volume for a molecule of given weight is defined as the total volume of solvent passing through the column in the time between the sample being injected into the column and the molecule being eluted. By relating molecular size to retention volume a chromatogram can be produced. This chromatogram affords information on the molecular weight averages and molecular weight distribution of the sample.

Gel permeation chromatograms were recorded for solutions of the copolymeric photoinitiators in toluene. Polystyrene - divinylbenzene columns of pore size 1000Å (supplied by Poly Labs. U.K.) were eluted with tetrahydrofuran at a flow rate of 1ml min^{-1}. A UV detection system was used (254 nm) and molecular weights were determined using a narrow standard calibration curve.

3.2.4 Determination of Photodecomposition Mechanisms by Radical Trapping Experiments



1,1-Ditolylethylene (DTE)



2,2,6,6-Tetramethylpiperidinoxyl Radical (T.M.P.O.)

Benzoin ethers have been shown to undergo α-cleavage on photolysis[37,38]. The benzoyl and ketyl radicals thus produced can, theoretically, add to D.T.E. as follows:

$$Ar-\overset{\overset{O}{\|}}{C}\cdot + H_2C=C\begin{matrix}C_6H_4CH_3\\ C_6H_4CH_3\end{matrix} \longrightarrow Ar-\overset{\overset{O}{\|}}{C}-CH_2-\underset{C_6H_4CH_3}{\overset{C_6H_4CH_3}{C}}\cdot$$

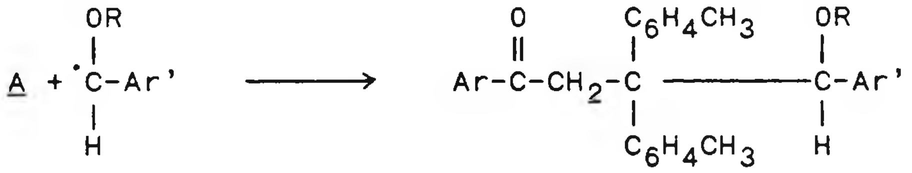
A

$$\mathrm{Ar'{-}\overset{OR}{\underset{H}{C}}{}^{\bullet} + H_2C{=}C(C_6H_4CH_3)_2 \longrightarrow Ar'\overset{OR}{\underset{H}{C}}{-}CH_2{-}\overset{C_6H_4CH_3}{\underset{C_6H_4CH_3}{C}}{}^{\bullet}}$$

B

Thus, radical polymerization would be initiated.

The experimental work of Hageman et al.[39] has shown, however, that the β-acyloxyketyl radical is unlikely to play a part in the initiation of polymerization (i.e. the second reaction scheme above does not occur) but is active in the termination of A.

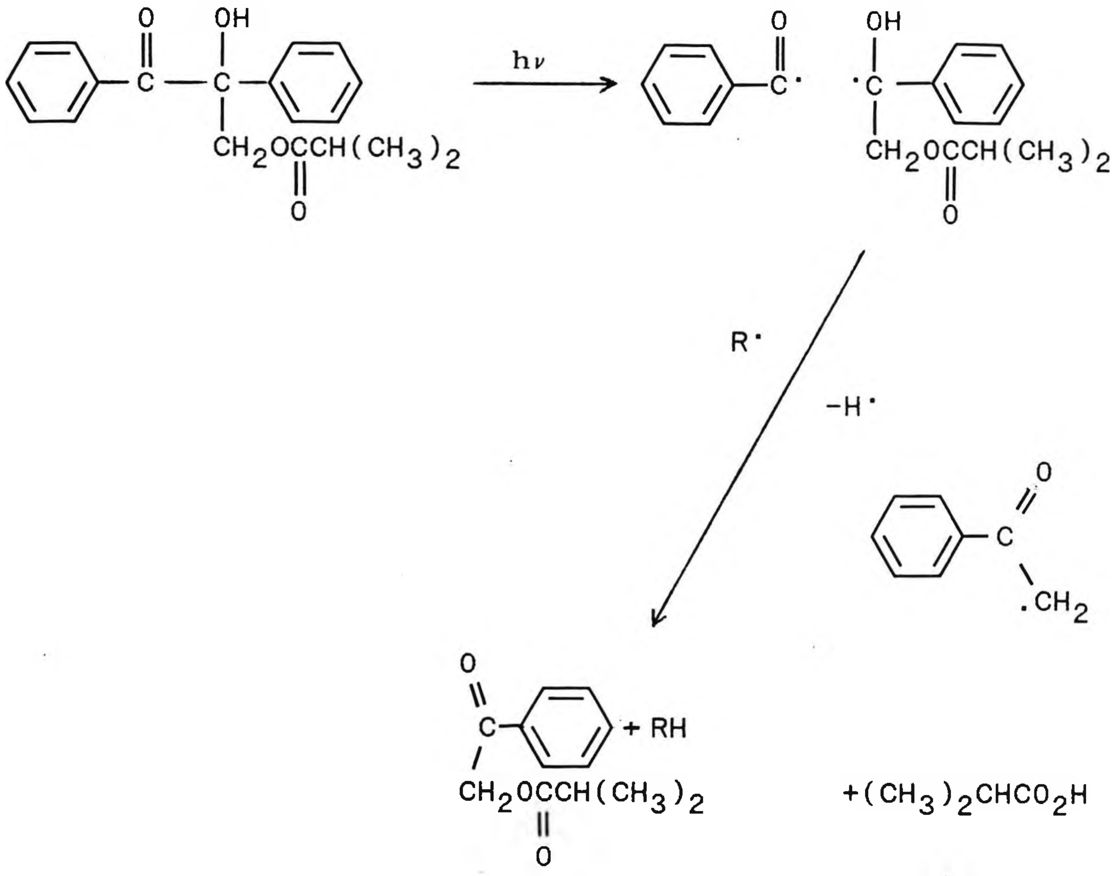


$$\mathrm{\underline{A} + {}^{\bullet}\overset{OR}{\underset{H}{C}}{-}Ar' \longrightarrow Ar{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{C_6H_4CH_3}{\underset{C_6H_4CH_3}{C}}{-}\overset{OR}{\underset{H}{C}}{-}Ar'}$$

These findings are demonstrative of the strong tendency of β-acyloxyketyl radicals to undergo radical-radical recombination in preference to addition to alkenyl double bonds.

Rizzardo and Solomon[40] have shown TMPO to undergo rapid reaction with carbon-centred radicals to yield stable products. Hageman and Overeem[41] used TMPO as a trapping agent for primary radicals generated by photoinitiators. Since the rate of radical-radical recombinations is diffusion-controlled, TMPO traps the primary radicals at a rate in the region of $10^9 s^{-1}$. The addition of radicals to double bonds, on the other hand, occurs at a rate in the order of $10^5 s^{-1}$. Thus, the benzoyl radicals would be trapped immediately by TMPO and it would be expected that very little benzil (formed by the combination of two benzoyl radicals) would be detected. The much lower rate of addition to DTE favours benzil formation with this trapping agent.

In addition to the primary radicals produced directly upon irradiation of benzoin and the ethers, radicals can also be produced by secondary cleavage.



Phenacyl ester

In order to ascertain whether secondary cleavages of this kind were taking place,the phenacyl esters of model compounds VII and VIII were prepared for comparison with the product mixtures following irradiation.10^{-2}M solutions of the various photoinitiating units in benzene were irradiated in the presence of the radical trapping agents. Molar ratios of 2TMPO/1 photoinitiating unit and 4 DTE/1 photoinitiating unit were employed. The solutions were placed in stoppered Pyrex glass tubes and irradiated in a revolving photolysis apparatus fitted with 350nm mercury lamps. A small amount of each sample was removed before and after irradiation for analysis.

Note: An excess of DTE was used to compensate for the rates of radical addition to the model substrate being considerably less than that for radical-radical combination.

3.2.4.1 Preparation of Phenacyl Esters

The relevant phenacyl esters were prepared according to the procedure described by Sheehan and Umezawa[42].

Phenacyl Isobutyrate

Procedure

8.8g (0.1 mol) isobutyric acid, 10.1g (0.1 mol) triethylamine and 19.9g (0.1 mol) phenacyl bromide were combined with 200ml dimethylformamide. The resulting solution was refrigerated for 24 hrs, then triturated with 1.4ml ice water. The precipitate thus formed was isolated by filtration and suspended in 800ml pet. ether (40-60°C) whilst stirring. Reduced pressure filtration and recrystallization from isopropanol afforded the phenacyl ester in 58% yield with a melting point of 28.3-30.1°C (literature boiling point 101°C at 0.1mm Hg[43])

NMR ($CDCl_3$): δ 7.93(d,2H,J=8Hz; benzoyl); 7.65-7.29 (m,3H,phenyl);5.32(s,2H,$-CH_2O-$); 2.79-2.73 (q,1H,J=7Hz;-CH-); 1.25 (d,6H,J=8Hz; $-(CH_3)_2$);

IR (KBr Disc) 3029 (aryl C-H str.); 2946 & 2815 (alkyl C-H str.), 1738 (ester C=O str.); 1651 (ketone C=O str.), 1608, 1577 & 1510 (aryl C-C str.); 1439, 1399 & 1380 (isobutyryl C-H def.); 742 & 689 (mono - substituted aromatic out-of-plane C-H def.) cm^{-1}.

Phenacyl Pivalate

Procedure

A similar procedure to that described above was used, with the isobutyric acid being replaced by 10.2g (0.1 mol) pivalic acid. The product was recrystallized from isopropanol in 69% yield, with a melting point of 59.2-59.8°C (literature melting point 61-62°C)[43].

NMR ($CDCl_3$): δ 7.92(d,2H,J=8Hz; benzoyl); 7.64-7.42 (m,3H,phenyl); 5.32 (s,2H,$-CH_2-$); 1.30 (s,9H,$(CH_3)_3$);

IR (KBr Disc): 3030 (aryl C-H str.); 2951 & 2816 (alkyl C-H str.); 1734 (ester C=0 str.); 1652 (ketone C=0 str.), 1605, 1580 & 1511 (aryl C-C str.); 1459, 1390 & 1372 (puraloyl C-H def.); 745 & 692 (mono – substituted aromatic out-of-plane C-H def.) cm^{-1}.

3.2.5 CONTROL OF COPOLYMERIC SYSTEM MOLECULAR WEIGHTS

In 1957 Flory[44] proposed a four-step mechanism to explain the observed behaviour of vinyl polymerizations.

$M_1 + M_1 \longrightarrow 2M^*$ (1) Initiation

$M^*_n + M_1 \longrightarrow M^*_{n+1}$ (2) Propagation

$M^*_n + M \longrightarrow M_n + M^*$ (3) Chain Transfer

$M^*_n + M^*_m \longrightarrow M_n + M_m$ or M_{n+m} (4) Termination

A chain transfer reaction was introduced in step 3 and represented transfer of the active centre from the growing polymer molecule to a species denoted M. Having obtained an active centre this second species would then be able to initiate the growth of a different polymer molecule. Chain termination was represented in step 4.

Mayo[45] used the concept of chain transfer to explain the observation that lower product molecular weights were obtained when styrene was polymerized in a solvent than when no solvent was used. Swain, Stockmayer and Clarke[46] also showed that radical-induced reactions can be repressed by the use of reactive solvents or polymerization inhibitors.

As can be seen from the afore-mentioned mechanism, although the original molecular chain is terminated by chain transfer, the radical centre is preserved. Therefore, the kinetic chain is continued and the overall rate of polymerization remains essentially unchanged[45,47]. A number of compounds possess a labile atom which is readily abstracted by a growing polymer chain. Such compounds can be represented by M in step (3) of Flory's mechanism, and are generally referred to as chain transfer agents. The efficiency of a transfer agent is measured by the ease with which the agent terminates polymer chain growth and initiates the formation of a second chain. Chain transfer efficiency is dependent upon the type of monomer being used.

Making several assumptions, Mayo[44] derived the following equation relating to the polymerization of styrene:

$${}^{1}/_{\bar{P}} = {}^{c(s)}/_{(M)} + {}^{1}/_{\bar{P}_o}$$

where $\bar{P}$ is the degree of polymerization, (s) is the concentration of solvent, c is the transfer constant, (M) is the concentration of monomer and P_o is the degree of polymerization in the absence of a solvent. It was assumed that all of the steps involved in this uncatalyzed polymerization of styrene are second order reactions; that all growing polymer radicals possess the same reactivity and that the radicals formed by chain transfer are of similar reactivity; and that the conventional steady state approximation can be applied to initial free radical concentrations.

The value of the chain transfer constant for a given system can be easily found by plotting $^{1}/_{\bar{P}}$ against $^{(s)}/_{(M)}$ and is dependent upon the nature of the solvent and monomer, and upon the temperature. The degree of polymerization is defined as the ratio of the number average molecular weight of the polymer to the molecular weight of the monomer. Thus, for a system for which the chain transfer constant is known, the Mayo equation can be used to determine polymer molecular weights.

The Mayo equation was originally derived for a system in which chain transfer occurs only to a solvent. However, it is equally applicable to cases in which transfer occurs to a specific chain transfer agent, added to the system for molecular weight control. Thus, the term (s) in the Mayo equation is then replaced by the concentration of the transfer agent.

3.2.5.1 Determination of a Chain Transfer Constant for the MA Copolymeric System with 1-Dodecanethiol as Transfer Agent

Long-chain aliphatic thiols are widely-used for molecular weight control when performing polymerizationswith vinyl monomers. Dodecanethiol was chosen as the chain transfer agent in the following procedures, since it affords reasonable transfer efficiency without the pungent odour associated with longer-chain thiols.

Procedure

0.296g (1.00 x 10^{-3} mol) α-methylolbenzoin, 0.258g (3.00 x 10^{-3} mol) methyl acrylate and 1.60 x 10^{-3}g (1.00 x 10^{-5} mol) azobisisobutyronitrile were combined with 0.00 , 2.02 x 10^{-3}, 4.04 x 10^{-3}, 6.06 x 10^{-3}, 8.08 x 10^{-3} and 1.01 x 10^{-2}g dodecanethiol. When dissolved in methylisobutyl ketone and made up to a volume of 3ml, these gave a series of solutions with a transfer agent concentration of 0, 1, 2, 3, 4 and 5%, respectively. 1ml aliquots of each solution were degassed on a vacuum line using the freeze-thaw technique. The sample tubes were then sealed and heated to 80°C for 60 mins. Once cooled,the solutions were analyzed by G.P.C.,and a Mayo plot was constructed. From the Mayo plot the chain transfer constant for the MA system could be evaluated and, by extrapolation, the concentration of chain transfer agent required to produce a copolymer with a number average molecular weight between two and three thousand determined.

3.2.5.2 Preparation of MA Copolymers in the Presence of 1-Dodecanethiol

Procedure

A solution of 14.8g (0.05 mol) α-methylolbenzoin, 12.9g (0.15 mol) methyl acrylate, 8.2×10^{-2}g (5.00×10^{-4} mol) azobisisobutyronitrile (AIBN) and 1.4g (6.92×10^{-3} mol) 1-dodecanethiol in 148ml methylisobutyl ketone was deaerated with nitrogen for approximately 39 mins. The flask was then sealed and heated to 80°C in an oil bath for 60 mins. The hot solution was poured into excess petroleum ether 60-80°C fraction, resulting in the formation of a waxy, white solid. Repeatedly triturating with petroleum ether and centrifuging for 15 minute-periods at 3000 revs. min^{-1} enabled the product to be isolated. After drying for 48 hrs in a vacuum oven at

35^oC,a yield of 17.5g of product was obtained.
G.P.C. gave $\bar{Mn}$ = 2593, $\bar{Mw}$ = 3796
The copolymer thus prepared is hereafter referred to as MA 060.

NMR ($CDCl_3$): δ 7.95-7.80 (m,2H,benzyl protons), 7.63-7.48 (m,2H,benzoyl); 7.47-7.17 (m,6H,aryl); 3.72-3.38 (s,7H, $-OCH_3$); 2.41-2.20 (m,2.5H,-CH-); 1.80-1.54 (s,5H,$-CH_2-$).
- The peaks recorded above are those which identify the copolymer. The ratio of methoxy to aromatic integrals gives a photoreactive group content of 59%. Simultaneously with the preparation of MA 060, a further quantity of MA copolymer was being prepared as previously described, in the absence of a chain transfer agent. This would allow comparison of the photoinitiating efficiencies of MA-type copolymers of significantly different molecular weights.

3.2.5.3 Preparation of MA Copolymer in the Absence of a Chain Transfer Agent

Procedure

8.88g (0.03 mol) α-methylolbenzoin acrylate, 7.74g (0.09 mol) methyl acrylate and 0.60g (3.75×10^{-3} mol) AIBN were dissolved in methyl isobutylketone and made up to a volume of 100ml. The solution was degassed with argon and the reaction vessel sealed. After heating to 80^{O}C in an oil bath for 45 mins the hot solution was poured into excess petroleum ether 60-80^{O}C fraction. Standing at room temperature resulted in the formation of a gummy white solid. The product was isolated by repeatedly pouring off the solvent and triturating with petroleum ether. This procedure yielded a more crystalline product, which was dried for ~60 hrs in a vacuum oven at 35^{O}C. The copolymer thus formed is referred to as MA P45. G.P.C. analysis gave $M\bar{n}$ = 7960, $M\bar{w}$ 26588. A similar NMR spectrum to that of MA 060 was obtained. Comparison of aromatic and methoxy signal integrals gave a photoreactive group content of 54%.

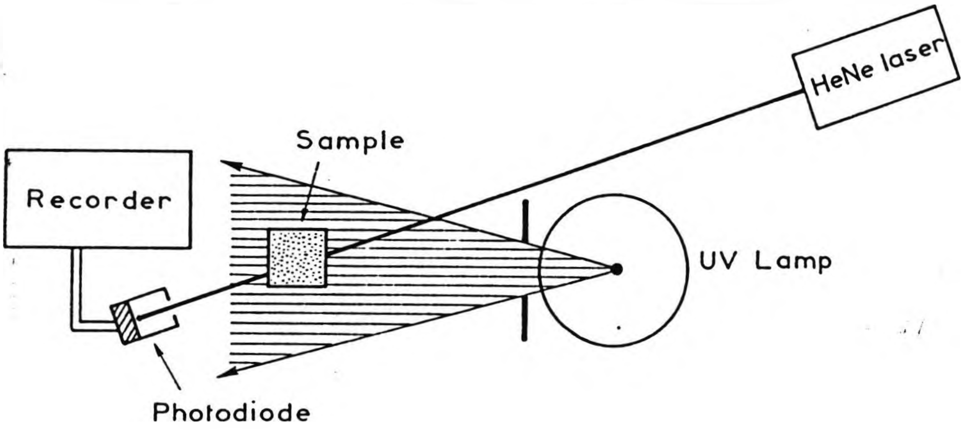
α-Methylolbenzoin was prepared as previously described. Methyl acrylate and methylisobutylketone were supplied by Baker and were used without further purification. 1-Dodecanethiol (Aldrich) and AIBN (Merck) were also used without further purification. NMR spectra were recorded on a Bruker W H 270 spectrometer using tetramethylsilane as internal standard. G.P.C. analyses were carried out using a Waters Associates' instrument with a 254nm UV detector. The P.L. 1000 polystyrene-divinylbenzene column (supplied by Poly Labs. U.K.) was eluted with tetrahydrofuran at a flow rate of 1ml min^{-1}. Molecular weights were determined by means of a narrow standards calibration curve.

3.2.6 SCREENING OF PHOTOINITIATORS

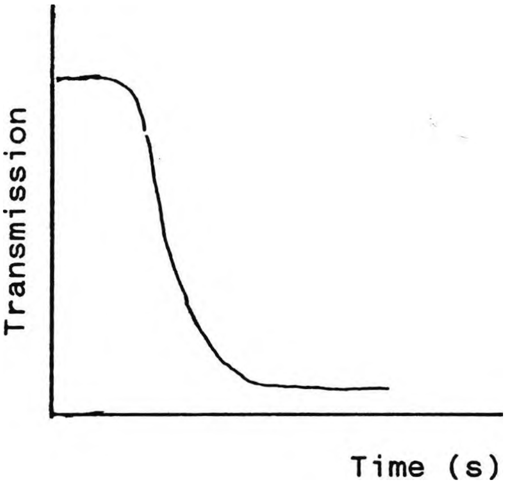
3.2.6.1 Laser Nephelometry

The technique of laser nephelometric analysis of photopolymerizations was developed in 1980 as a means of continuously following the kinetics of these high-speed reactions[48].

Laser-nephelometric analysis of photopolymerizations



Propan-2-ol is generally used as the reaction solvent, since it is a non-solvent for the crosslinked polymers formed on exposure of the sample solution to UV light. The sample solution consists of the photoinitiator and trimethylolpropane triacrylate (TMPTA), as monomer, in propan-2-ol. As the polymeric product is formed,the turbidity of the sample increases. Consequently, absorption of the laser beam increases also and the amount of light transmitted to the diode rapidly decreases. The curves produced are, therefore, a direct reflection of the polymerization kinetics.



Illustrated above is a typical plot of laser beam transmission against irradiation time for a photopolymerization performed in the presence of air. The induction period results from oxygen inhibition[48].

The apparatus was previously calibrated by plotting the weight of polymer formed against irradiation time for a standard photoinitiator system[49]. This enabled the estimation of polymerization rates from the slopes of the curves produced by the chart recorder.

10^{-2}M solutions of the photoinitiators in a propan-2-

ol/TMPTA solution were irradiated in polystyrene cuvettes produced by Witeg. The propan-2-ol/TMPTA solution consisted of 10g TMPTA per litre of propan-2-ol. A 632.8nm helium-neon laser was used, the power of which was adjusted such that a linear photodiode response was obtained on reduction of the laser beam intensity by means of neutral density filters. The UV source was a high pressure 90W mercury lamp, supplied by Ealing. Propan-2-ol was supplied by Baker and was used without further purification.

3.2.6.2 Photoinitiated Solution Polymerization of Methyl Methacrylate

With solution polymerizations, the sample remains in solution in a suitable solvent both before and throughout the irradiation process. Following photolysis, the sample solution can be added to a non-solvent to effect precipitation of the product.

10^{-2}M solutions of photoreactive benzoin moieties in a 5:1 benzene/methyl methacrylate mixture were irradiated with UV light for 2 hrs. The irradiated solutions were then added to a five-fold excess of methanol with vigorous stirring. The precipitated poly(methyl methacrylate) samples were isolated by filtration and dried overnight in a vacuum oven at 30^{o}C. Solution photolyses were performed in duplicate for each photoinitiator, and mean polymer yields recorded. The solutions were irradiated in stoppered Pyrex glass cylindrical tubes, which were placed in a Rayonet RPR-208 photoreactor fitted with 350nm mercury lamps. Benzene and methyl methacrylate were both supplied by Baker and were used without further purification.

3.2.6.3 UV Curing of Thin Films

Thin film curing is the most widely-used industrial method for measuring rates of cure. The sample solution is spread as a thin layer on a suitable substrate and is passed beneath a UV source until completely cured. The UV source usually consists of a set of medium-pressure mercury lamps, but microwave-excited lamps can also be used.

The UV curing technique, which requires a thin,uniform coating of the photoinitiator solution on a suitable substrate, produces a large sample surface area/volume ratio. Susceptibility to the inhibitory effects of atmospheric oxygen is very high under these conditions. In solution polymerization experiments, on the other hand, the sample solution is irradiated in a sealed narrow cylinder, so that the ratio of surface area exposed to atmospheric oxygen/volume is relatively small. Consequently, discrepancies often occur between relative photoinitiator efficiencies indicated by the two methods[50].

0.1M solutions of photoreactive groups in either tetraethyleneglycol diacrylate (TEGDA) or a 73.4% TEGDA/26.6% UVE 74 mixture were used. (UVE 74 is the tradename of the epoxydiacrylate of Setacure AP570). The solutions were coated onto strips of satinized paper or G.N.T. paper obtained from Wiggins Teape, U.K. Films of uniform thickness were produced by means of K-bars manufactured by Erichsen (20 and 50 m films) and R.K. Print-Coat Instruments Ltd. (6 m films). The coated paper was passed beneath the UV source by means of a moving belt system. UV sources were either a high pressure Philips HOK-6 mercury lamp or a medium pressure 80 W cm^{-1} mercury lamp manufactured by ColorDry. TEGDA was used as supplied by Aldrich Chemical Company without further purification. UVE 74 was obtained from Synthese and is the epoxydiacrylate of Setacure AP-570. When films were cured in the presence of N-methyl diethanolamine as a tertiary amine synergist, a 6:1 molar ratio of N-methyl diethanolamine/photoreactive groups was used.

Films were defined as being cured when a rubber teat drawn heavily along the surface ceased to leave a visible track. This method of testing only provides a measure of surface cure, failing to differentiate between films which were cured throughout and those which were cured at the surface but not at the lower layers.

The benzoin $\pi \rightarrow \pi^*$ absorption occurs in the 250nm region, whilst the $n \rightarrow \pi^*$ absorption is in the region of 330nm. For photoinitiators which absorb radiation in these two areas it appears that the shorter wavelength radiation is largely responsible for surface curing and the longer wavelength is predominant in determining through cure[51]. Film thickness is also an important factor in determining rates of cure, since thin films (<5 μm) often display reduced scratch and solvent resistance. Thick films, on the other hand, often suffer from undercure at the interface between the coating and the substrate, depending upon the molar absorptivity of the photoinitiator. Using a benzoin butyl ether photoinitiator with a 12μm film thickness, Roffey quoted relative energy requirements of 20:1 to cure the surface 1μm layer and bottom 1μm layer, respectively[51]. The additional energy for cure of the surface layer is to allow the formation of a sufficient excess of initiating radicals to overcome oxygen inhibition.

The rate R_i at which initiator species are formed is given by the following equation: $R_i = I_A \emptyset$[52]. I_A represents the intensity of light absorbed by the photoinitiator and $\emptyset$ is the fraction of excited-state photoinitiator which produces initiator species. I_A is related to the absorbed light intensity, I_o, by the Beer-Lambert law: $\mathrm{Log}\left(I_o/I_A\right) = \varepsilon cl$ and the quantity $\log\left(I_o/I_A\right)$ is equal to the photoinitiator absorbance. It can thus be seen that I_A and R_i will increase as both I_o and the photoinitiator concentration increase.

From the above considerations it would be expected that an optimum photoinitiator concentration exists for UV curing, and would decrease with increasing film thickness. This has been verified experimentally[53].

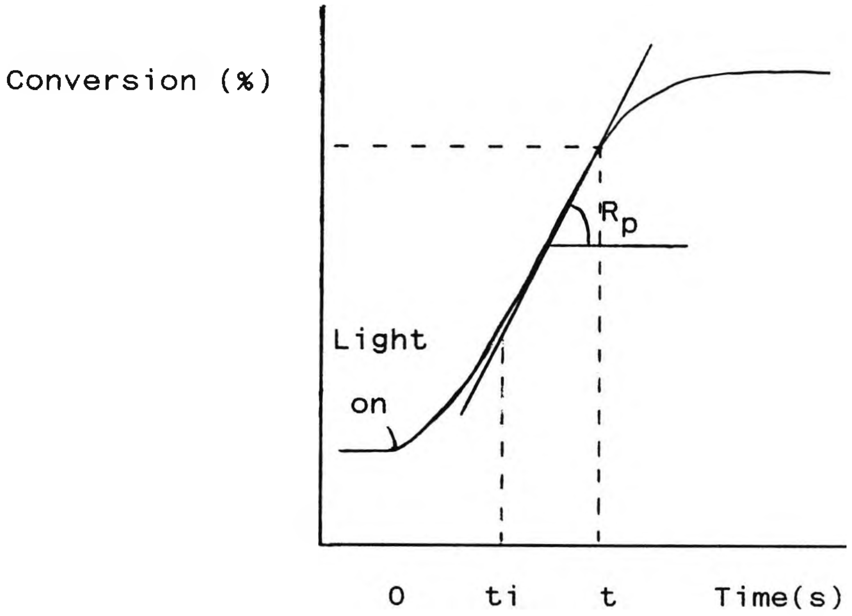
Through-cure is retarded by photoinitiator and other absorbing species, such as pigments, which effectively screen the film from the radiation. High rates of radical formation are required for surface cure in air to compete with new oxygen diffusing to the surface, as well as to consume oxygen already at the surface. This can be achieved by the use of high intensity lamps, resulting in a large value for I_o. I_o is dependent upon lamp intensity and, even more significantly, upon lamp focus. A combination of high

I_o and low photoinitiator concentration would be expected to enhance depth of cure for polymerization initiated by either free radical or cationic means.

The dependence of curing efficiency of the copolymeric photoinitiators on concentration was investigated and was compared to that of the monomeric model and of the commercial type I photoinitiator Irgacure 651. The number of passes required to cure TEGDA films on GNT paper were recorded for various photoinitiator concentrations at a set belt speed and film thickness. From these measurements, graphs of irradiation time required to cure the films against photoinitiator concentration were constructed. A 0.6M N-methyl diethanolamine concentration was used for each photoinitiator concentration, and the films were cured at a belt speed of 30m min^{-1}. The UV curing apparatus consisted of an 80W cm^{-1} medium pressure mercury lamp over a moving belt arrangement, supplied by ColorDry

3.2.6.4 Real-Time Infra-red Spectroscopy

UV radiation curing is noted for the speed with which a liquid film is transformed into a solid coating[54]. This has led to problems in quantitative, real-time monitoring of the curing process. Infrared spectrometry was first used to monitor polymerization reactions in a UV curing context in 1976[55], and the following year the use of a real-time infrared analytical technique was described[56]. Real-time infrared spectroscopy is based on the simultaneous exposure of the sample to both the polymerizing UV beam and the analyzing infra-red (IR) beam. Changes taking place in the intensity of the functionality undergoing polymerization are recorded as a function of time by operating the IR spectrophotometer in a time drive mode (i.e. chart moving without scanning), whilst being set at the wavenumber corresponding to the reactive group.

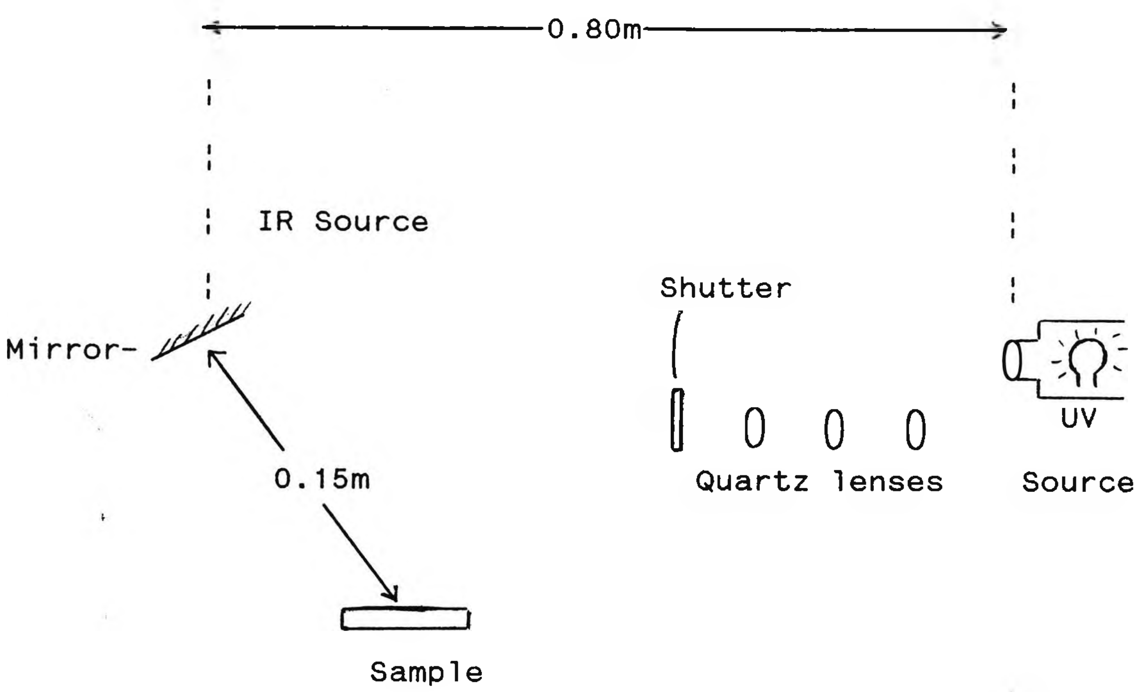


Typical cure profile for an acrylic coating

The cure profile generally adopts a characteristic S-shape[54]. The initial plateau is caused by oxygen inhibition, and the final progressive deceleration results from gellification of the resin. Thus, the length of the induction period is indicative of the extent to which oxygen inhibition is a problem under the experimental conditions. The rate of polymerization (R_p) can be evaluated at any time during the reaction from the slope of the reaction profile.

0.1M solutions of photoreactive groups in TEGDA, with a 0.6M concentration of N-methyl diethanolamine, were coated on strips of acetate sheets. Since the samples were to be placed vertically in the spectrophotometer, a small strip of sheet polythene was used to prevent run-off. After recording the initial IR spectrum, the spectrophotometer was switched to time drive mode at maximum speed and locked onto the 810cm^{-1} acrylate absorption peak. The sample was then exposed to the UV beam and the cure profile recorded simultaneously. From the kinetics curves obtained,relative ratesof polymerization of the acrylate double bonds were measured at 0, 3, 6 and 30 secs. after exposure of the samples to UV radiation.

A high-pressure 100W mercury lamp (Osram HBO 100 W/2) was used as the UV source and was focussed through three quartz lenses. The spectrophotometer was a Perkin-Elmer 599 infra-



Schematic Representation of Real-Time Infrared Apparatus

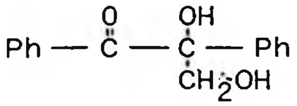
red spectrophotometer.

Tetraethyleneglycol diacrylate (TEGDA) and N-methyl diethanolamine were both obtained from Aldrich Chemical Company and were used without further purification. The acetate sheets were supplied by Staedtler, West Germany; polythene strips were taken from food bags produced by Alcan, U.K.

3.3 RESULTS & DISCUSSION

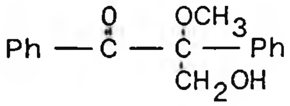
Monomeric and Polymeric Photoinitiator Structures with Corresponding Codes

Monomers



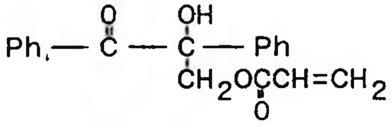
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{CH_2OH}{C}}-Ph}$

α-Methylolbenzoin, I



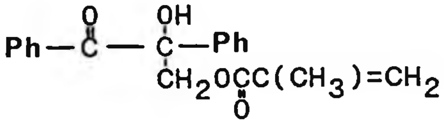
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{\underset{CH_2OH}{C}}-Ph}$

α-Methylolbenzoin Methyl Ether, II



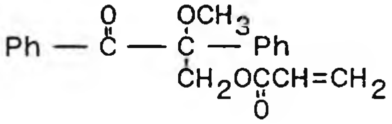
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{CH_2O\underset{\underset{O}{\|}}{C}CH=CH_2}{C}}-Ph}$

α-Methylolbenzoin Acrylate, III



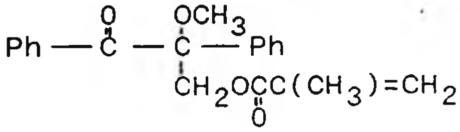
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{CH_2O\underset{\underset{O}{\|}}{C}C(CH_3)=CH_2}{C}}-Ph}$

α-Methylolbenzoin Methylacrylate, IV



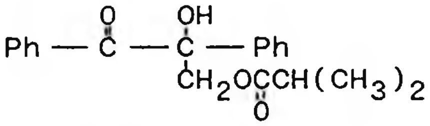
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{\underset{CH_2O\underset{\underset{O}{\|}}{C}CH=CH_2}{C}}-Ph}$

α-Methylolbenzoin Methyl Ether Acrylate, V



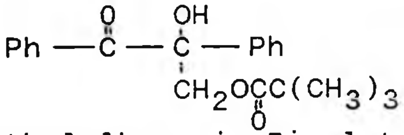
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{\underset{CH_2O\underset{\underset{O}{\|}}{C}C(CH_3)=CH_2}{C}}-Ph}$

α-Methylolbenzoin Methyl Ether Methacrylate, VI



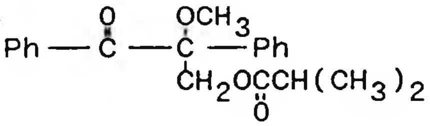
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{CH_2O\underset{\underset{O}{\|}}{C}CH(CH_3)_2}{C}}-Ph}$

α-Methylolbenzoin Isobutyrate, VII



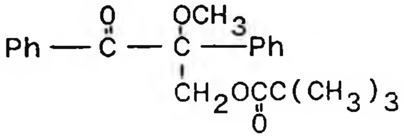
$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{CH_2O\underset{\underset{O}{\|}}{C}C(CH_3)_3}{C}}-Ph}$

α-Methylolbenzoin Pivalate, VIII



$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{\underset{CH_2O\underset{\underset{O}{\|}}{C}CH(CH_3)_2}{C}}-Ph}$

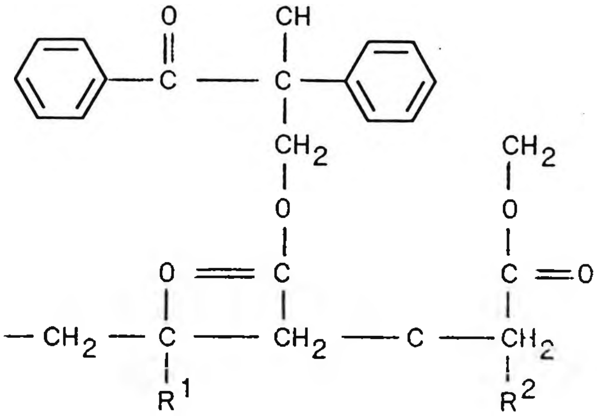
α-Methylolbenzoin Methyl Ether Isobutyrate, IX



$\mathrm{Ph-\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{\underset{CH_2O\underset{\underset{O}{\|}}{C}C(CH_3)_3}{C}}-Ph}$

α-Methylolbenzoin Methyl Ether Pivalate, X

Polymers



MA Copolymers : R = H; R^1 = H; R^2 = H

MMA Copolymers : R = H; R^1 = CH_3; R^2 = CH_3

MB Copolymers : R = CH_3; R^1 = H; R^2 = H

KIII/MMA Copolymers : R = H; R^1 = H; R^2 = $-CH_3$

KM/MA Copolymers : R = H; R^1 = CH_3; R^2 = H

MB/MMA Copolymers : R = CH_3; R^1 = H; R^2 = CH_3

Numbers following the codes represent copolymerization times, except in the case of MB 1:2 and MB 2:1. For MB 1:2 a reagent molar ratio of 1 α-methylolbenzoin methyl ether acrylate/2 methyl acrylate was used, and the reverse for MB 2:1. A 1:1 molar ratio was used in the preparation of MB 1:1. For all MB copolymers a 2 hr. reaction time was used.

MA 060 was prepared in the presence of 1-dodecanethiol and was found to have a number average molecular weight of 2593. MA P45, similarly to the earlier copolymers, was prepared in the absence of a chain transfer agent and was found to have a number average molecular weight of 7960.

In the following pages the numbers associated with the copolymer types relate to reaction times, in minutes.

3.3.1 CHARACTERIZATION OF COPOLYMERIC PHOTOINITIATORS

3.3.1.1 Determination of Photoreactive Group Contents

3.3.1.1.1 UV Spectral Analayses

Model Compound	$n \rightarrow \pi^* \ \varepsilon$ in Chloroform
VII	198
VIII	202
IX	200

Copolymer	Photoreactive Group Content By Weight (%)
MA 20	64
MA 45	57
MA 90	57
MA 120	60
MA 140	60
MA 150	48
MA 180	53
MA 210	60
KIII/MMA 20	40
KIII/MMA 70	50
KIII/MMA 120	51

/Contd.

Copolymer	Photoreactive Group Content By Weight (%)
MMA 20	79
MMA 70	58
MMA 120	57
MMA 150	58
MMA 180	54
MMA 200	55
MMA 240	55
KM/MA 20	76
KM/MA 70	65
KM/MA 120	54
MB 20	61
MB 70	60
MB 120	58
MB 150	54
MB 180	50
MB 210	59
MB 240	63
MB/MMA 20	32
MB/MMA 120	41
MB 2:1	74
MB 1:2	63

3.3.1.1.2 NMR Spectral Analyses (Spectra recorded in $CDCl_3$)

Copolymer	Photoreactive Group Content By Weight (%)
MA 20	51
MA 45	46
MA 90	44
MA 120	48
MA 140	49
MA 150	40
MA 180	44
MA 210	49

/Contd.

Copolymer	Photoreactive Group Content By Weight (%)
MMA 20	60
MMA 70	49
MMA 120	51
MMA 150	49
MMA 180	52
MMA 200	44
MMA 240	49
KM/MA 70	64
KM/MA 120	51
MB 20	54
MB 70	59
MB 120	55
MB 150	55
MB 180	57
MB 210	58
MB 240	58
MB/MMA 120	37
MB 2:1	68
MB 1:2	59

The UV method used to determine the photoreactive group contents was based upon the assumption that the molar absorptivity per photoreactive group is dependent only on the total concentration of that group. Thus, the value of ε for a monomeric system should remain unchanged when the monomer is (co)polymerized. UV analysis, however, led to values for photoreactive group contents of the copolymers which were consistently in the region of 10-20% higher than those values obtained by the NMR method. Amongst other things, molar absorptivity depends on solvent, temperature[57], tacticity and the sequential arrangement of monomeric units[58]. These factors could account for some slight variation in ε and, consequently, in the calculated photoreactive group contents, but would not explain the discrepancy observed with the two methods of calculation. Since the NMR method involves a simple comparison of the integrals of specific signals, it is justifiable to consider the results to be more reliable than those afforded by UV spectroscopy. The implication is, therefore, that the aforementioned assumption, relating to molar absorptivities, is incorrect.

The results show that, for the $n-\pi^*$ transition, the molar absorptivity per benzoin-derived unit increases when going from monomer to polymer. Similar effects have been reported by Carlini et al. when working with copolymers of methyl acrylate with styrene[59] and with α-methylolbenzoin methyl ether acrylate[60], and by Stützel et al.[57] for copolymers of methyl methacrylate with styrene. It has been known for some time that biological macromolecules, such as proteins, exhibit different spectral properties to those of the monomeric chromophores. In 1959 Tinoco[6] noted that the UV absorption of a polynucleotide is considerably less than would be expected from the sum of the absorptions of its constituent nucleotides. He attributed this phenomenon -

known as hypochromism - to coulombic interactions. Tinoco hypothesized that, if the constituent groups within a polynucleotide (and, therefore, their transition moments also) are arranged randomly, there will be no overall effect on the UV spectral properties. If, however, the transition moments adopt a colinear arrangement, an increase in the absorption will result (hyperchromism). Conversely, a decrease in absorption (hypochromism) will result from a parallel stacking of transition moments.

Hypochromism - up to 40% - occurs commonly with both nucleic acids and synthetic polynucleotides, the conformations of which have undergone a transition from a random coil to a helical structure[61]. This hypochromism is associated with the $\pi \rightarrow \pi^*$ transition component of the 260nm bond[61]. In addition to this, however, a small but significant hypochromic shift, associated with the $n \rightarrow \pi^*$ component, has been observed[62].

Whilst the above observations and explanations regarding hypochromism and hyperchromism were originally related to polynucleotides, they are equally applicable to any system consisting of an ordered molecular arrangement[61]. Thus it would seem that the observed discrepancy in the results obtained by the NMR and UV analytical methods can be attributed to dipole-dipole interactions between neighbouring chromophoric groups. This in itself is evidence that the copolymers prepared adopt ordered structures in solution. Furthermore, the observation of such effects suggest that the chromophoric groups are able to approach each other closely.

In addition to the flexibility of the polymer chain and spacer groups, the presence of hydrogen bonding between the chromophoric carbonyl and hydroxyl groups is probably a factor. The absence of such hydrogen bonding in the MB copolymers,in which the hydroxyl is replaced by a methyl group , could explain the lower hyperchromicity observed with these copolymers, relative to the other copolymer types.

3.3.1.2 Molecular Weight Determinations

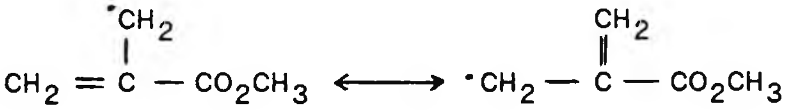
The number average molecular weight is defined by the following equation: $\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$[63] where n_i is the number of moles of molecular weight M_i present in the sample.

Number average molecular weights for the copolymeric samples are recorded in the following table. (Due to the time-consuming nature of the G.P.C. technique, chromatograms were not recorded for all the samples prepared)

Copolymer	$\bar{M}_n$	Copolymer	$\bar{M}_n$
MA 20	17039	MMA 200	6746
MA 120	10876	KM/MA 20	22248
MA 180	9169	KM/MA 70	17717
KIII/MMA 70	9629		
KIII/MMA 120	8583	MB 70	7170
		MB 180	6422
MMA 20	8785	MB 240	6001
MMA 70	8421	MB 1:2	6008
MMA 120	8149	MB 2:1	6284
MMA 180	7095	MB/MMA 120	6769

It can be seen from the results table above that, for each type of copolymer, $\bar{M}_n$ has the maximum value at the shortest reaction time and decreases with increasing reaction time throughout the series. This observation is consistent with a mechanism in which primary radical termination plays a significant part. Primary radical termination is known to take place if the primary radicals are produced at too high a concentration, or if the monomer concentration is too low for the monomer to react efficiently and rapidly with the primary radicals. Under such conditions a deviation from the common radical chain polymerization rate expression is observed[64]. Clearly, as the polymerization process proceeds monomer levels will be depleted, increasing the possibility of primary radical termination. Furthermore, the viscosity of the solution will increase as reaction time is increased and more polymer is formed. This increased viscosity will lead to greater restriction of movement of the chain radicals, so that the probability of bimolecular termination between propagating chain radicals will fall. The primary radicals, on the other hand, being of far smaller size, are considerably less restricted by the increase in viscosity and will be able to interact much more freely with the chain radicals. Thus the observed molecular weight/polymerization time trends are not totally unexpected.

A further observation which can be made is that, for the MA and MMA copolymers prepared with similar reaction times, much higher number average molecular weights were obtained with methyl acrylate as comonomer in place of methyl methacrylate. This suggests that transfer occurs to a greater degree when methyl methacrylate is the monomer. (In the absence of transfer to solvent, initiator or polymer it is transfer to monomer which determines the maximum molecular weight of polymer formed[65].) Monomer chain transfer constants are generally very low (typically in the range 10^{-5} - 10^{-4})[66]. The reason for this is that transfer to monomer involves cleavage of vinylic C-H bonds. In the case of methyl methacrylate, which has an α-methyl group in place of an α-hydrogen atom, the possibility of resonance stabilization exists for the radical formed by hydrogen abstraction.



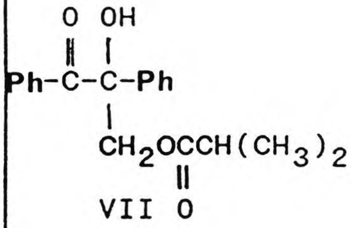
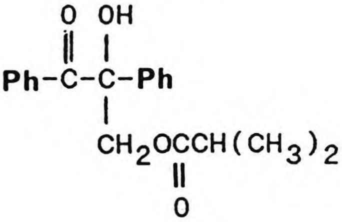
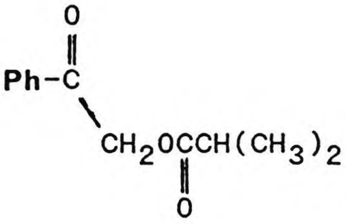
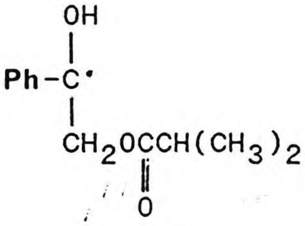
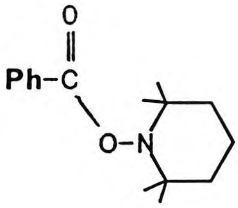
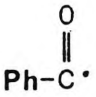
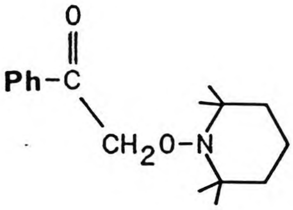
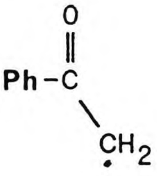
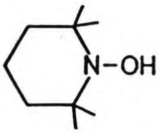
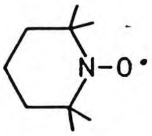
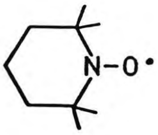
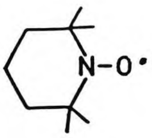
$$CH_2{=}\overset{\cdot CH_2}{\overset{|}{C}}-CO_2CH_3 \longleftrightarrow {}^{\cdot}CH_2-\overset{CH_2}{\overset{\|}{C}}-CO_2CH_3$$

This could result in retardation of polymerization, as has been observed with propenyl acetate[67].

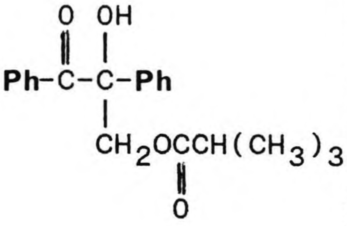
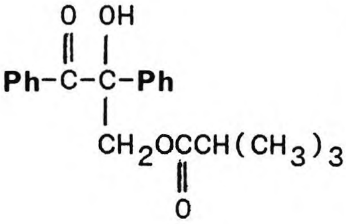
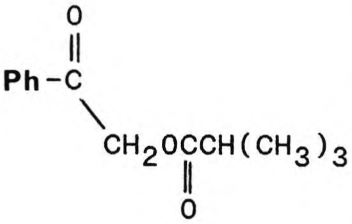
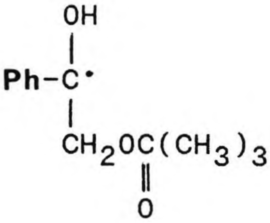
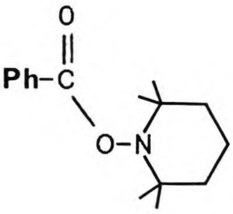
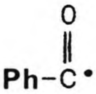
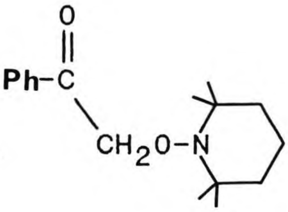
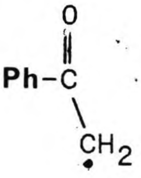
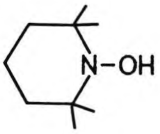
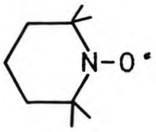
In addition to this, acrylates are known to be generally more reactive than similar methacrylates. In the AIBN-initiated polymerization of methyl acrylate and methyl methacrylate, reactivity rates of 250 and 27, respectively, have been determined for the two monomers[68]. It is to be expected, therefore, that this greater reactivity would lead to the formation of longer polymer chains within a given reaction time.

3.3.2 DETERMINATION OF PHOTODECOMPOSITION MECHANISMS BY RADICAL TRAPPING EXPERIMENTS

Photolyses Performed in the Presence of TMPO

Photoinitiator	Products Identified	Radical Species Implicated
 $PhCOC(OH)(Ph)CH_2OCOCH(CH_3)_2$ VII	 $PhCOC(OH)(Ph)CH_2OCOCH(CH_3)_2$	-
	 $PhCOCH_2OCOCH(CH_3)_2$	 $Ph\dot{C}(OH)CH_2OCOCH(CH_3)_2$
		 $PhC^{\bullet}O$
		 $PhCO\dot{C}H_2$
		
		

/Contd.

Photoinitiator	Products	Radical Species
	Identified	Implicated
 $\mathrm{Ph{-}C(=O){-}C(OH)(Ph){-}CH_2OC(=O)CH(CH_3)_3}$ VIII	 $\mathrm{Ph{-}C(=O){-}C(OH)(Ph){-}CH_2OC(=O)CH(CH_3)_3}$	–
	 $\mathrm{Ph{-}C(=O){-}CH_2OC(=O)CH(CH_3)_3}$	 $\mathrm{Ph{-}\dot{C}(OH){-}CH_2OC(=O)C(CH_3)_3}$
		 $\mathrm{Ph{-}\dot{C}{=}O}$
		 $\mathrm{Ph{-}C(=O){-}\dot{C}H_2}$
		

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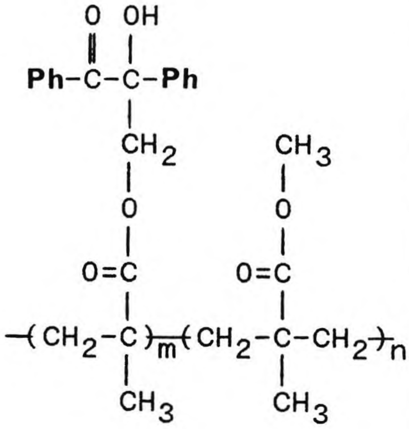
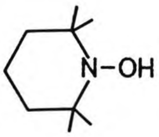
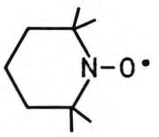
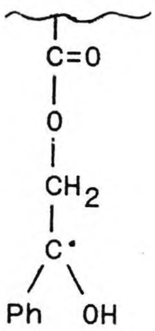
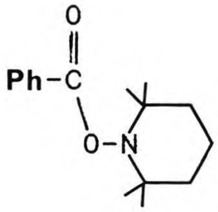
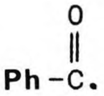
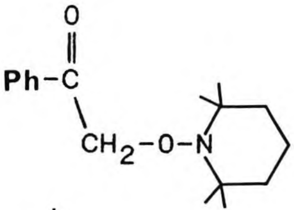
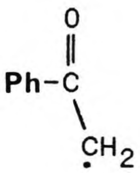
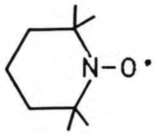
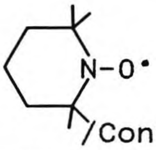
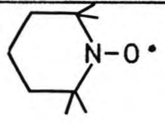
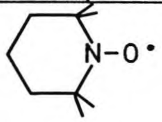
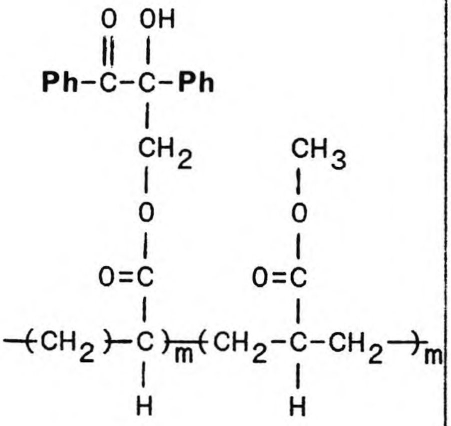
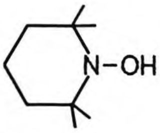
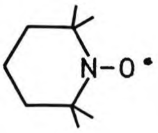
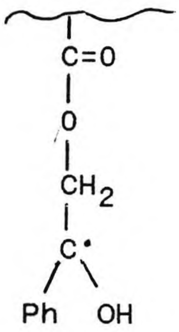
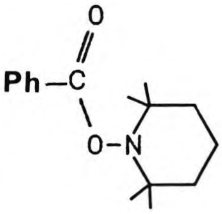
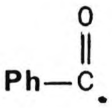
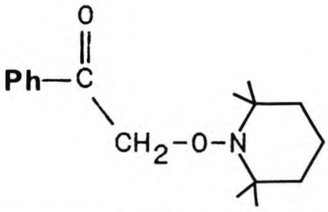
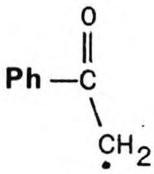
 MMA Copolymers	Unreacted copolymer	-
		 & 
		
		
		 /Contd.

Photoinitiator	Products Identified	Radical Species Implicated
		
 MA Copolymers	Unreacted copolymer	-
		 & 
		
		

The results obtained when using TMPO as radical trapping agent clearly indicate that both monomeric and polymeric photoinitiators produce initiating radicals by Type I cleavage. This is as expected for benzoin-based photoinitiators. The presence of TMPO in the product mixture is readily explained by the ease with which the reduced form is re-oxidized to the radical. (This can be seen from the characteristic orange coloration which rapidly returns to a solution of reduced TMPO when exposed to oxygen).

3.3.3 MOLECULAR WEIGHT CONTROL OF COPOLYMERIC SYSTEMS

3.3.3.1 Determination of a Chain Transfer Constant for the MA Copolymeric System with 1-Dodecanethiol as Transfer Agent

The Mayo equation[45] can be represented by $1/\bar{P} = C(S)/(M) + 1/\bar{P}_o$.

$\bar{P}$ is the degree of polymerization for the polymer formed and equates to $\bar{M}_n/M$, where $\bar{M}_n$ is the number average molecular weight of the polymer and M is the molecular weight of the monomer; S is the chain transfer agent, in this case 1-dodecanethiol ;C and $\bar{P}_o$ represent the chain transfer constant for the system and the degree of polymerization in the absence of a chain transfer agent, respectively.

Plotting $^{M}/\overline{M_n}$ against $^{(S)}/_{(M)}$ (i.e. construction of a 'Mayo plot') should produce a straight line graph, the gradient of which is equal to the value of the chain transfer constant for the given polymerization system.

Sample No.	M	$\overline{M}_n$	(S)/mol l^{-1}	(M)/mol l^{-1}	$^{M}/\overline{M_n}$	$^{(S)}/_{(M)}$
0	296	23767	0.00	3.33×10^{-7}	0.012	0.00
1	296	17012	3.33×10^{-9}	3.33×10^{-7}	0.017	0.01
2	296	11241	6.66×10^{-9}	3.33×10^{-7}	0.026	0.02
3	296	8206	9.99×10^{-9}	3.33×10^{-7}	0.036	0.03
4	296	7315	1.33×10^{-8}	3.33×10^{-7}	0.040	0.04
5	296	4940	1.67×10^{-8}	3.33×10^{-7}	0.060	0.05

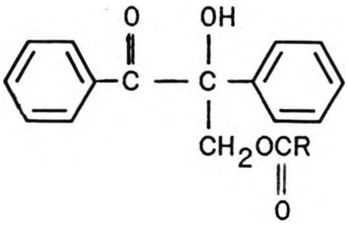
The Mayo plot gives a chain transfer constant of ~ 1.13 for the MA copolymerization system. In general, chain transfer constants greater than ten lead to high yields of simple 1:1 addition products, whilst chain transfer constants less than unity give rise to predominantly telomeric products under the same conditions[69].

A chain transfer constant of 1.13 is consistent with the NMR (and UV) measurements, which were indicative of photoreactive group contents in the region of 50%, by weight. This corresponds to the incorporation into the copolymeric structure of approximately three methyl acrylate units per α-methylolbenzoin acrylate unit, i.e. telomer formation rather than the formation of a 1:1 copolymeric product.

In addition to allowing evaluation of the chain transfer constant, a Mayo plot can be used as a calibration curve for a given polymerization system. For the MA copolymers,a value of $\overline{M}_n$ in the region of 2-3,000 was desired to give oligomeric, rather than polymeric,photoinitiators. This $\overline{M}_n$ value corresponds to a value of approximately 0.12 for the ratio $^{M}/\overline{M}_n$. By extrapolating the Mayo plot to this region it could be seen that a thiol concentration of approximately 14% is required to give the desired molecular weight average under the conditions employed.

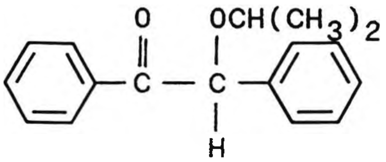
3.3.4 SCREENING OF PHOTOINITIATORS

3.3.4.1 Laser Nephelometry



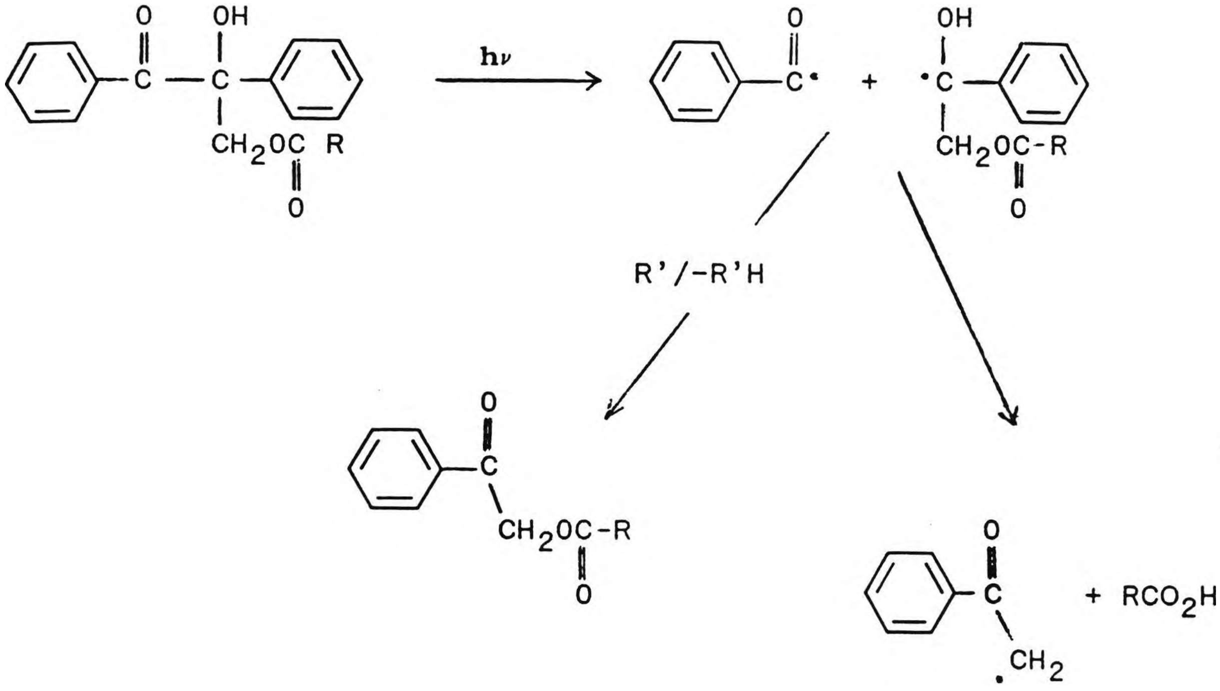
Laser nephelometric analyses were performed with a number of benzoin derivatives. Benzoin isopropyl ether (BIPE) was used as a reference compound.

Photo-initiator	Induction Period/s	Polymerization Rate x 10^{-3}/mol $l^{-1}s^{-1}$
BIPE	35.5	3.48
$R=C_6H_5$	35.3	4.48
$R=CH_3$	37.5	4.48
$R=CH_3(CH_2)_9CH_2$	36.1	4.48
$(CH_3)_2CH$	33.9	4.66
$(CH_3)_3C$	40.5	4.79



BIPE

The tabulated results show the expected trend in dependence of polymerization rate on the substituents R. Carboxylic esters of α-methylolbenzoin undergo UV-initiated α-cleavage to yield a benzoyl/ β-acyloxyketyl radical pair[70]. Elimination of carboxylic acid with formation of the benzoylmethyl radical has been observed as a minor secondary reaction[71].



Whilst the nature of R will have no effect upon the major secondary reaction, in which the phenacyl ester is formed, it will clearly be a factor in the elimination of acid. R groups which exert a positive inductive effect will favour acid elimination by stabilizing RCO_2^+. This is reflected in the observed order of polymerization rates.

BIPE, for which acid elimination is not a possibility, was found to give the lowest polymerization rate. In the case of BIPE only one initiating radical would be formed per photoinitiator molecule. The elimination of acid afforded two initiating radicals (the benzoyl and benzoylmethyl radicals) for one molecule of each of the carboxylic ester photoinitiators. This result was, therefore, to be expected.

Attempts to perform laser nephelometric measurements on solutions of the polymeric photoinitiators proved unsuccessful, since these photoinitiators were insoluble in the standard solvent system.

3.3.4.2 Photoinitiated Solution Polymerization of Methyl Methacrylate

The efficiencies of the copolymeric photoinitiators were compared to those of their corresponding model compounds, as well as to those of other low molecular weight compounds. A blank solution was also used which contained no photoinitiator, in addition to a solution of the commercial photoinitiator benzoinmethyl ether (supplied by Aldrich Chemical Company; no further purification carried out).

Photoinitiator	Polymer yield per mmol of Photoreactive Groups/g
Blank	-
Benzoin Methyl Ether	7.3
I	6.9
II	7.0
III	9.8
IV	7.3
VII	8.0
VIII	7.7
IX	6.1
MA 120	9.6
MMA 70	9.0
MB 2:1	17.2
KM/MA 70	7.5
MB/MMA 120	15.0

NMR analysis of the polymeric product samples showed no signs of the photoinitiators being present.

In general, the results tabulated above demonstrate that the photoinitiators in which the photoreactive functionalities are pendant to a polymeric chain show greater efficiency in the polymerization of methyl methacrylate in benzene solution than the corresponding monomeric parent and model compounds. This observation is in agreement with the findings of Ahn et al.[30], who similarly produced photosensitive polymers with benzoin methyl ether sidechains. In the photopolymerization of vinyl monomers in benzene solution they, too, demonstrated greater efficiency than several monomeric benzoin ether derivatives. Ahn attributed the higher conversion to polymer as achieved by the macromolecular photoinitiators to gel formation during the polymerization process. Such gel formation would hinder the termination of radicals contained within the polymer coil and thus lead to longer chains than would be afforded by the monomeric compounds. This explanation was also suggested to rationalize the observations of Neckers et al.^{2}.

3.3.4.3 UV Curing of Thin Films

Results for Thin Films of UVE 74/TEGDA Cured in the Absence of a Tertiary Amine

Liquid films of UVE 74/TEGDA on satinized paper were cured under a high pressure Philips HOK-6 mercury lamp. 0.1M photoinitiator concentrations were used. An Erichsen rod was used to produce liquid films of the desired thickness.

Photo-initiator	Film Thickness/ μm	No. of Passes to Cure at Belt Speed 8m min^{-1}	Irradiation time to Cure/s
I	50	15	18.0
II	"	12	14.4
III	"	18	21.6
IV	"	23	27.6
V	"	9	10.8
VII	"	19	22.8
VIII	"	21	25.2
IV	"	11	13.2
BME*	"	15	18.0
MA 120	"	8	9.6
MMA 70	"	11	12.0
MB 2:1	"	4	4.8

*BME = Benzoin methyl ether, used as supplied by Aldrich without further purification

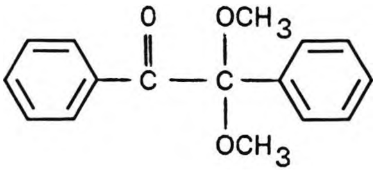
A tertiary amine has been shown to enhance the efficiency of photoinitiators which undergo Type I cleavage, presumably by acting as a scavenger for atmospheric oxygen[49]. The UV curing results tabulated on the previous page were obtained in the absence of a tertiary amine and thus reflect the efficiencies of the various photoinitiators under conditions of high exposure to atmospheric oxygen.

A marked difference is immediately seen between the photoinitiating efficiencies of the copolymeric materials and their monomeric model compounds. For each type of copolymer the irradiation time required to effect complete cure of a 50 μm TEGDA/UVE 74 film was less than half that for the corresponding monomeric model. This confirms the results of the solution polymerization experiments, which indicated an enhancement of the photoinitiating efficiencies of the benzoin derivatives by their attachment to a polymeric chain.

The (meth)acrylate monomers show higher photoinitiating efficiency than the corresponding non-polymerizing model monomers, as would be expected. Clearly, the unsaturated (meth)acrylate functionality affords the possibility for copolymerization of unreacted radical fragments into the polymer network and would thus be expected to yield higher rates of cure than the saturated model monomers. This is in accordance with the findings of Baeumer et al.[73].

Comparing the cure times obtained with that of benzoin methyl ether - which is known to be an efficient photoinitiator for polymerizations[49] - it can be seen that those systems in which the photoreactive benzoin structure is pendant to a polymeric chain are highly efficient photoinitiators for the UV curing of thin films of UVE 74/TEGDA.

Due to the small quantities of polymeric samples available, and the difficulties associated with characterizing any further samples, it was not possible to repeat the previously mentioned measurements in the presence of a tertiary amine. However, the later copolymeric systems, MA 060 MA P45, were cured in the presence of N-methyl diethanolamine. Comparisons were again made with the monomeric model compound, but the commercial Type I photoinitiator Irgacure 651 was also tested.



Irgacure 651

As before, 0.1M photoreactive group concentrations were used with a 0.6M amine concentration. TEGDA alone was used as the prepolymer (supplied by Aldrich and used without further purification). Irgacure 651 and N-methyl diethanolamine were supplied by Ciba-Giegy and Aldrich Chemical Company, respectively, and were both used without further purification. 6μm films of the TEGDA solutions were coated onto strips of G.N.T. paper and were passed beneath a medium pressure 80W cm^{-1} mercury lamp by means of a moving belt arrangement. Approximate belt speeds were determined by measuring the time for the metal plate, to which the substrate would be attached, to pass beneath the UV source. This was repeated several times for each belt setting, and average velocities calculated. The wet film thickness was determined by means of a No. 1 K bar as supplied by R.K. Print-Coat Instruments Ltd.

TEGDA Films Cured in the Presence of N-Methyl diethanolamine

Photo-iniator	Wet Film Thickness/μm	No. of passes to Cure at Given Belt Speed/m min^{-1}									
		14	16	20	21	30	36	43	51	58	72
VII	6	10	10	12	13	16	19	22	27	30	-*
Irgacure 651	6	4	4	5	5	7	8	9	11	15	17
MA P45	6	5	5	5	6	8	10	13	17	19	22
MA 060	6	4	4	4	6	8	9	13	17	20	23

*- Indicates more than thirty passes required to cure film.

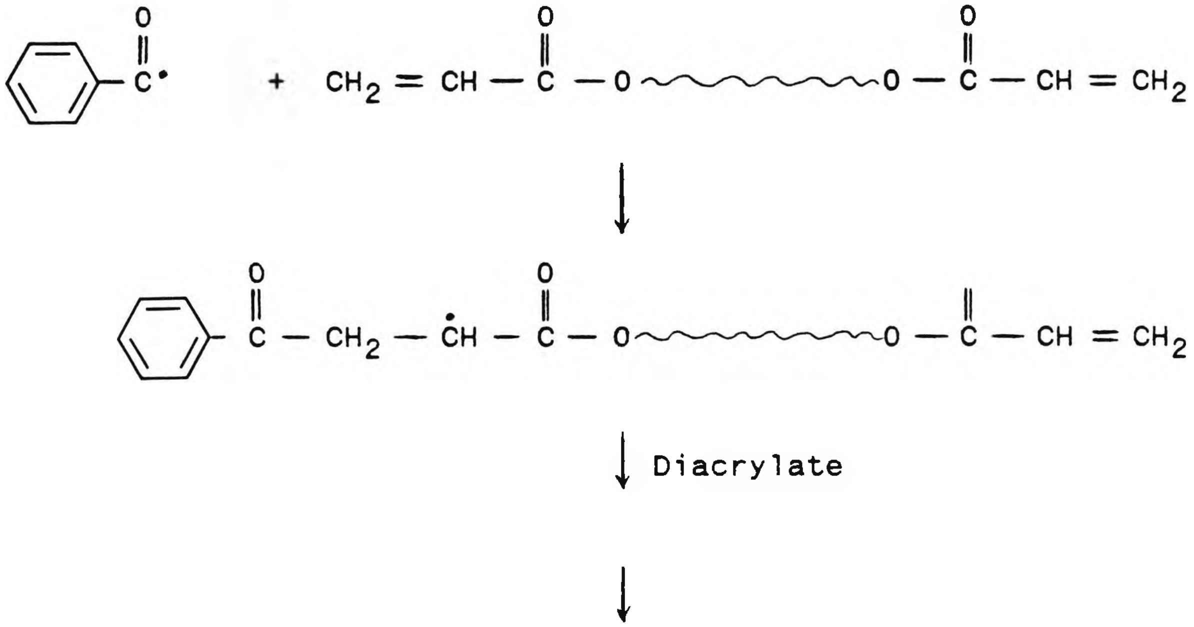
As expected the addition of a tertiary amine enhanced the efficiencies of the copolymeric photoinitiators and their monomeric model. This enhancement is attributed to the amine scavenging oxygen and thus reducing the inhibitory effects of the latter on the curing process[49]. A considerable improvement is still seen when going from the monomer to the polymeric systems, and confirms the results obtained when curing in the absence of an amine and when performing photopolymerizations in solution. No significant difference can be seen between the photoinitiating efficiencies of the two copolymeric photoinitiators, however, which suggests that molecular weight has little, if any, effect for the types of copolymers prepared. In order to investigate further whether rates of cure with the MA copolymers would be affected by molecular weight differences, films of UVE 74/TEGDA were cured on satinized paper, using the Philips HOK-6 mercury lamp/moving belt arrangement. No N-methyl diethanolamine was used on this occasion.

Photo-iniator	Wet Film Thickness/μm	No. of Passes to Cure Film at Given Belt Speed/m min^{-1}						
		10	15	20	25	30	35	40
VII	20	8	16	29	-	-	-	-
Iracure 651	20	12	14	17	20	26	30	-
MA P45	20	-	-	-	-	-	-	-
MA 060	20	25	22	-	-	-	-	-
VII	50	7	13	25	-	-	-	-
Iracure 651	50	2	8	13	19	22	23	24
MA P45	50	19	-	-	-	-	-	-
MA 060	50	12	18	-	-	-	-	-

The results tabulated on the previous page are clearly in disagreement with all the other results recorded so far. Contrary to all the previous observations, the measurements shown indicate that considerably better curing efficiency is obtained with the monomeric model than with the copolymeric photoinitiators. Since these results are so inconsistent with all of the others - for which there seems to be no apparent reason - they will not be included in any further discussions.

It can be seen, then, that the UV curing results,both in the absence and presence of a tertiary amine, confirm that the photoinitiators in which the photoreactive benzoin groups are pendant to a polymeric backbone give greater efficiency than their monomeric counterparts. The radical trapping experiments with TMPO and DTE demonstrate that the copolymers undergo type I cleavage upon irradiation with UV light, and that the benzoyl radical is thus liberated from the polymeric chain. The fate of the β-acyloxyketyl radical is not so clear, however, and whilst the species trapped indicate that this undergoes secondary cleavage, it is possible that some of the radicals are still attached to the polymeric chain. Whereas the benzoyl radical is generally accepted to initiate polymerization, there is considerable evidence to suggest that the benzyl ether radicals produced by benzoin and derivatives is largely consumed in the terminating step[74].

UV irradiation of multifunctional monomers, with a suitable photoinitiator, leads to the initial formation of a linear polymer chain with pendant double bonds.



Scheme for initial polymerization of a diacrylate monomer, initiated by benzoyl radicals.

Once one of the acrylate double bonds starts to polymerize, the radical becomes attached to the polymer network and loses its mobility. Provided that monomer molecules are able to approach closely to the radical sites and be scavenged, the polymer chain will continue to grow. In the case of a monomeric photoinitiator being used the β-acyloxyketyl radical, which is active in termination, will be sufficiently small to easily gain access to the growing polymer radical and terminate growth. If the ketyl radical is polymer bound, however, its mobility will be considerably less than that of the monomeric molecules as the network develops. Termination will thus be hindered, allowing more rapid development of the highly crosslinked, cured coating. As polymerization continues, mobility will eventually reach the point at which all free radical approach to the polymeric centre is prevented. At this point chain growth will cease and the radical will remain alive, but occluded in the polymer network[75]. Both post-polymerization and electron spin resonance (ESR) investigations have confirmed this by demonstrating the presence of stable radicals trapped in UV-cured acrylic coatings[76,77].

Thus the enhanced curing efficiency of the polymeric photoinitiators relative to the low molecular weight model compound can be attributed to the reduced rate of termination, resulting from reduced mobility of the polymer-bound terminating radicals.

3.3.4.4 Dependence of Curing Efficiency on Photoinitiator Concentration

Photo-initator	Photoinitiator Concentration/M	No. of Passes to Cure Film	Equivalent Irradiation Time for Cure/s (Approximate)
Irgacure 651	0.10	7	7.8
	0.15	5	5.6
	0.20	5	5.6
	0.25	4	4.5
	0.30	4	4.5
	0.40	4	4.5
VII	0.05	24	26.9
	0.10	16	17.9
	0.15	11	12.3
	0.20	6	6.7
	0.25	6	6.7
	0.30	6	6.7
	0.40	6	6.7
MA 060	0.05	-*	-
	0.10	8	9.0
	0.15	5	5.6
	0.20	5	5.6
	0.25	5	5.6
	0.30	5	5.6
	0.40	5	5.6

*More than thirty passes required to cure film; no equivalent irradiation time determined.

The graphs clearly show that, for each photoinitiator, rate of cure increases with increasing photoinitiator concentration up to an optimum concentration. Increasing the amount of photoinitiator present beyond this value leads to no further increase in the rate of surface cure. With the equipment available it was not possible to monitor the effect of increasing photoinitiator concentration upon the degree or rate of through-cure. Since only surface cure was considered, the observed results are in complete agreement with expectations.

The rate of initiation, and thus the rate of cure, increases with increasing photoinitiator concentrations. For low photoinitiator concentrations, the generation of radical fragments occurs fairly evenly throughout the film. As the concentration increases an increasing number of radicals are produced in areas closest to the UV source. These high concentrations of radicals at the surface screen the lower layers from the incident radiation, resulting in a slower rate of through-cure. Thus it can be seen that, whilst high photoinitiator concentrations allow efficient curing of the film to a tack-free condition, they may be counterproductive from considerations of through-cure.

Optimum photoinitiator concentrations of approximately 0.15M, 0.25M and 0.25M again were found for MA 060, its monomeric model analogue and Irgacure 651, respectively, corresponding to irradiation times of 5.6, 6.7 and 4.5s. Thus the oligomeric photoinitiator gives a greater maximum rate of cure, and at a lower photoreactive group concentration, than the monomeric model compound. As expected, the fastest cure rates are obtained with the commercial Type I photoinitiator Irgacure 651. These results again point to an enhancement of photoinitiating efficiency when the derivatized benzoin unit is pendant to a macromolecular chain.

3.3.4.5 Real-Time Infrared Spectroscopy

Photoinitiator	Relative Rate of Polymerization Following Exposure to UV Irradiation for t secs. t = 0	3	6	30	Induction Period (secs.)
Irgacure 651	12.00	0.29	0.02	0.00	0.00
VII	4.62	0.30	0.14	0.07	0.00
MA P45	3.75	0.34	0.11	0.01	0.00
MA 060	4.62	0.46	0.20	0.01	0.00

With all four photoinitiators, curing, in the presence of N-methyldiethanolamine,began immediately upon exposure of the samples to UV radiation. The highest rates of polymerization in all cases were obtained at the start of the reaction, and decreased as irradiation continued. This was as expected, since the amount of photoinitiator would be progressively depleted as reaction continued. The curing process was completed very rapidly with Irgacure 651, whilst a more gradual tailing off was observed with the other three photoinitiators.

3.4 SUMMARY

Polymeric photoinitiators are expected to offer a number of advantages over similar monomeric compounds[1,20]. In many cases, this has been found to be true[2-4,17,30].

A number of photoinitiators were prepared in which photoreactive benzoin-derived units were attached as pendant groups to a polymeric backbone. This was achieved by the copolymerization of a benzoin derivative with either methyl acrylate or methyl methacrylate. Radical trapping experiments showed these polymeric photoinitiators to undergo Norrish Type I photocleavage, similarly to analogous monomeric benzoin derivatives.

The molecular weights of the polymeric photoinitiators were found to decrease with increasing polymerization times. This observation is consistent with a polymerization mechanism in which primary radical termination is important.

By performing the polymerizations in the presence of a chain transfer agent, it was possible to control the molecular weights of the products formed. In this manner an oligomeric photoinitiator was prepared in addition to the earlier polymeric samples. No significant difference was observed between the photoinitiating efficiencies of the oligomeric and polymeric photoinitiators.

The efficiencies of the polymeric photoinitiators were compared to those of similar monomeric compounds in the initiation of photopolymerizations both in solution and in UV-curable formulations. In both situations the macromolecular compounds were found to afford higher efficiencies than the low molecular weight initiators. This efficiency enhancement is attributable to protection of the propagating radicals by the polymer coils, allowing more extensive chain growth[2,30].

Some hyperchromism was observed with the copolymers, suggesting that the polymeric chains adopted conformations in which the interaction of pendant chromophoric groups was a possibility.

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CHAPTER IV :

WATER-COMPATIBLE, POLYMERIC TYPE I PHOTOINITIATORS

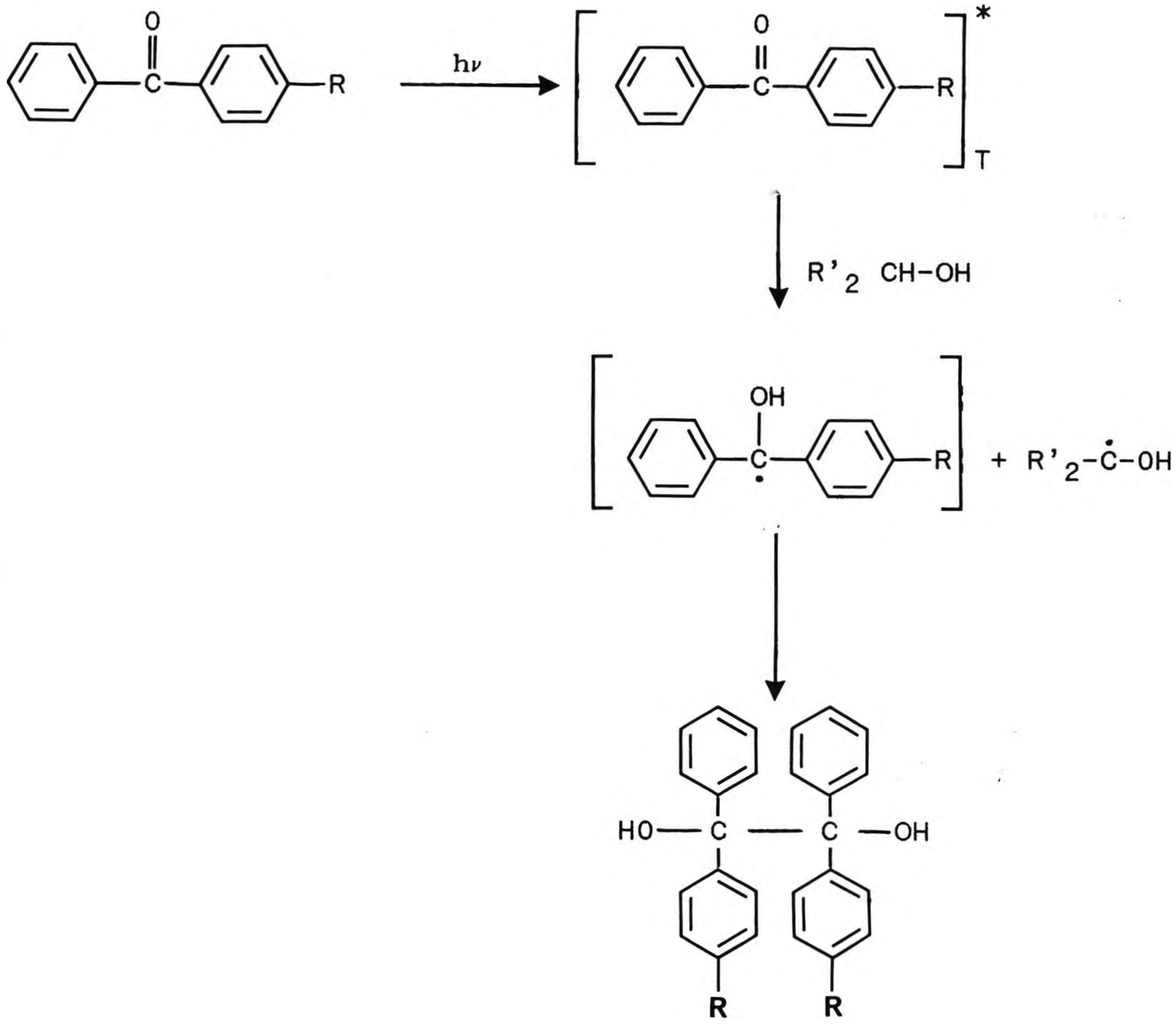
4.1 INTRODUCTION

UV-curable compositions generally consist of a prepolymer, monomer and photoinitiator, all of which are usually lipid-soluble. Such formulations afford high quality finished products, but the monomers which they contain are frequently skin irritants. Furthermore, the addition of organic solvents is sometimes necessary to achieve the desired formulation viscosity. These problems could be overcome if aqueous curing formulations were used, but very few photoinitiators suitable for use in aqueous media are available. It has been observed that the activity of conventional photoinitiators is greatly reduced upon transfer from organic to aqueous solutions. Solubility is often an additional problem, and attempting to overcome this by the attachment of solubilizing substituents frequently reduces the activity of the photoinitiators even further.

Suitably modified benzil and benzophenone derivatives have been reported to efficiently initiate photograft copolymerizations in aqueous media[1,2]. Water-soluble benzophenones have been observed to exhibit a similar reactivity to that of analogous photoinitiators in organic solution[3,4]. However, this is not the case with benzil derivatives. Benzil initiates free radical photopolymerizations via an intermolecular hydrogen abstraction mechanism[5]. Good hydrogen donors have been found to increase the photoactivity of benzil in organic solvents[5]. Investigations carried out with a water-soluble benzil sodium salt, however, revealed that the photodecomposition was totally unaffected by the presence of a hydrogen donor[3]. Thus it was concluded that the mechanism by which benzil derivatives in aqueous media generate initiating radicals is different to that which operates in organic media. No photodecomposition mechanism was postulated for the water-soluble photoinitiators.

Water-soluble thioxanthones have also been observed to operate via a different mechanism to similar oil-soluble types[6,7]. It was suggested that photoreaction of the water-soluble derivatives takes place from the singlet state, whilst it is the triplet state of the oil-soluble thioxanthones which is photoactive[6,8,9].

As mentioned previously, the reactivity of benzophenones in aqueous media is similar to that in organic solvents. The presence of a water-soluble group was found to have little effect upon the photoreactivity of 4-(trimethylammoniummethyl) benzophenone chloride, BP2[3]. Photoreduction of BP2 was only effected when a hydrogen donor was present.



Photoreduction of Benzophenone Derivatives by Alcohols

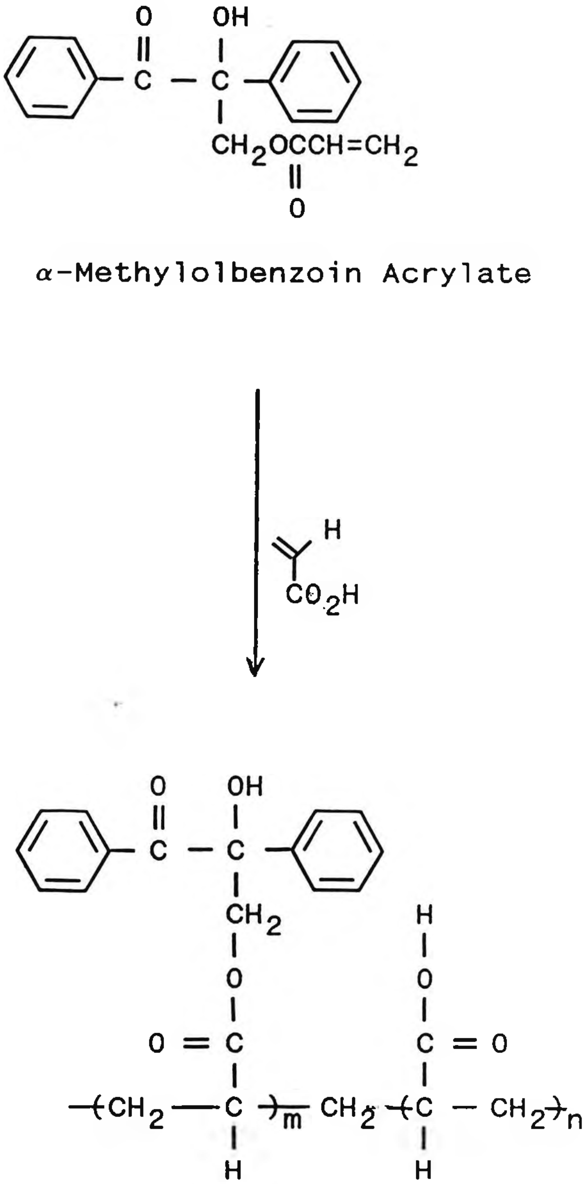
Phosphorescence quantum yields, triplet lifetimes and transient formation on conventional flash photolysis all indicate that photoreaction of benzophenone derivatives in aqueous media occurs via the lowest triplet state[4].

In 1989 a series of highly efficient, copolymerizable, water-soluble benzophenone derivatives was reported[10]. Only very small quantities of material were extracted into water from the cured coatings obtained with the copolymerizable photoinitiators. This was in contrast to the situation with the coatings produced with similar, non-polymerizable photoinitiators. Further advantages afforded by the copolymerizable photoinitiators were high water solubility, low coloration and odourless cured coatings[10].

The use of polymeric photoinitiators has been suggested as an alternative means of avoiding the problems of migration and extractability of low molecular weight photodegradation products[11]. It was decided, therefore, to attempt to produce novel copolymeric photoinitiators which would be water-compatible. All of the commercially available water-soluble photoinitiators are of the Type II photoinitiator/tertiary amine type . Consequently, it was decided to aim to produce a polymeric photoinitiator with pendant benzoin moieties, which are known to undergo Type I cleavage[12,13]. The preparation of such polymers and their evaluation as water-compatible photoinitiators is described.

4.2 EXPERIMENTAL

4.2.1. PREPARATION OF PHOTOINITIATORS



α-Methylolbenzoin Acrylate

AA Copolymers

Copolymerization of α-Methylolbenzoin Acrylate with Acrylic Acid, I

Procedure

2.40g (8.10×10^{-3} mol) α-methylolbenzoin acrylate, 1.72g (2.40×10^{-2} mol) acrylic acid and 0.32g (1.95×10^{-5} mol) azobisisobutyronitrile were dissolved in methyl isobutylketone. Solvent was added to bring the solution to a volume of 32ml. The solution was then deaerated with argon gas for approximately 10 mins, and the sealed reaction vessel placed in oil bath at 80^{o}C. 8ml aliquots were removed from the reaction mixture after heating for 10, 30, 120 and 180 mins. Precipitation of the powdery copolymers was effected by pipetting the aliquots into an excess of petroleum ether (60-80^{o}C fraction). The solid products were isolated by filtration and dried for several hours in a vacuum oven at 45^{o}C. The copolymers thus prepared are denoted copolymer 10, 30, 120 & 180.

NMR Spectra (Acetone - d_6):δ 8.10-7.77 (m,2H, benzoyl); 7.73-7.07 (m,6H, aryl) 5.10-4.07 (2m,2H, $-CH_2O-$); 2.90-0.73 (m, alkyl protons in polymer chain);

IR Spectra (KBr Disc): 3441 (H-bonded -O-H), 3240-2800 (carboxylic acid O-H str.), 1730 (ester C=O str.); 1681 (ketone C=O str.), 1597 & 1492 (aryl C-C str.), 1449 (C-H def. of $-CH_2-$), 1243 (carboxylic acid C-O str./O-H def.); 761 and 701 (monosubstituted aromatic out-of-plane C-H def.)cm^{-1}.

Copolymerizion of α-Methylolbenzoin Acrylate with Acrylic Acid. II

Attempts to repeat the copolymerization as previously described led to gellation at the bottom of the reaction vessel. In the hope of overcoming this problem an overhead mechanical stirrer was used in the procedure described below.

Procedure

9.60g (3.24×10^{-2} mol) α-methylolbenzoin acrylate, 6.88g (9.56×10^{-2} mol) acrylic acid and 1.28g (1.78×10^{-3} mol) azobisisobutyronitrile were dissolved in methylisobutylketone. The solution was made up to a volume of 128ml and deaerated with argon gas for approximately 20 mins. The reaction vessel was fitted with a mechanical stirrer, sealed and placed in an oil bath. After heating at 80°C for 30 mins, stirring vigorously, the reaction mixture was poured into petroleum ether (60-80°C fraction). Despite vigorous stirring of the reaction mixture whilst heating, a considerable amount of gel still formed on the base and walls of the reaction vessel. This was isolated by triturating with petroleum ether and filtering . The precipitated copolymer was also isolated by filtration, and both sets of product were dried for several hours in a vacuum oven at 45°C.

The gel which was isolated by trituration is referred to as AA2, whilst the precipitated solid is referred to as AA1. Both samples gave very similar NMR and IR spectra to those obtained with the first copolymers prepared.

Copolymerization of α-Methylolbenzoin Acrylate with Acrylic Acid. III

In the third procedure attempted, nitrogen gas was bubbled through the reaction mixture throughout, rather than deaerating with argon before heating.

Procedure

9.60g (3.24×10^{-2} mol) α-methylolbenzoin acrylate, 1.16g (1.62×10^{-2} mol) acrylic acid and 1.28g (7.80×10^{-3} mol) azobisisobutyronitrile were dissolved in methylisobutyl ketone and made up to a volume of 128ml. The reaction vessel was fitted with a mechanical stirrer and was placed in an oil bath at 80^{o}C. The mixture was heated for 30 mins. whilst bubbling nitrogen gas through the solution continuously and stirring vigorously. After 30 mins. the product was precipitated by pouring the hot solution into petroleum ether (60-80^{o}C). Filtration followed by drying for several hours in a vacuum oven afforded the white, crystalline copolymer AA3 in 79% yield.

The NMR and IR spectra obtained for this product were again very similar to those of the other acrylic acid copolymers prepared. In all cases the absence of signals/ absorption peaks in the NMR and IR spectra from acrylate functionalities confirmed that polymerization had taken place.

All NMR spectra were recorded on a Jeol JNM-PMX 60 SI spectrometer; IR spectra were recorded on a Perkin-Elmer 983G infra-red spectrophotometer.

4.2.2 CHARACTERIZATION OF COPOLYMERIC PHOTOINITIATORS

4.2.2.1 Determination of Photoreactive Group Contents

When attempting to determine the photoreactive group contents of the copolymeric photoinitiators by UV spectroscopic analysis in the preceding chapter, hyperchromic effects were observed. These led to inaccuracies in the photoinitiator compositions as determined by UV spectral analysis. Consequently, it was decided to rely upon NMR spectroscopy as the sole method of determination of photoreactive group contents.

Whilst the α-methylolbenzoin (meth)acrylate/methyl(meth) acrylate copolymers afforded two signals in the NMR spectra which were clearly and unambiguously associated with each of the two components, such a situation did not arise with the copolymers with acrylic acid. It was, therefore, necessary to use an alternative method to determine the photoreactive group contents. NMR spectra of solutions of the copolymers and their monomeric model analogue were run consecutively on the same spectrometer. The instrumental settings remained unchanged throughout and the same solvent was used in each case. In this way the photoreactive group contents of each copolymer could be determined by comparison of its aromatic signal integral to that of the model compound. The samples were all dissolved in acetone-d_6 (supplied by Aldrich Chemical Company), with tetramethylsilane (Aldrich) as internal standard. NMR spectra were recorded on a Jeol JNM-PMX 60 SI spectrometer.

4.2.2.2 Molecular Weight Determination by G.P.C. Analysis

The copolymer samples were dissolved in acetone for analysis by G.P.C. Polystyrene-divinylbenzene columns of pore size 1000 Å were supplied by Poly Labs. U.K. The columns were eluted with tetrahydrofuran at a flow rate of 1ml min^{-1}. A 254nm UV detector was used and molecular weights were determined using a narrow standards calibration curve.

4.2.3 MOLECULAR WEIGHT CONTROL OF COPOLYMERIC PHOTOINITIATORS

4.2.3.1 Determination of a Chain Transfer Constant for the α-Methylolbenzoin Acrylate/Acrylic Acid Copolymers with 1-Dodecanethiol as Chain Transfer Agent

Since 1-dodecanethiol was found to be a suitable chain transfer agent for the α-methylolbenzoin acrylate/methyl acrylate copolymers, it was decided to use the same chain transfer agent for the α-methylolbenzoin acrylate/acrylic acid copolymers. As before, a series of small-scale copolymerizations were performed in the presence of the chain transfer agent in order to construct a Mayo plot[14].

Procedure

A similar procedure to that described on p.146 was used, replacing methyl acrylate by acrylic acid and using 0-6% 1-dodecanethiol concentrations. Acrylic acid and 1-dodecanethiol were supplied by Aldrich Chemical Company; methylisobutyl ketone and azobisisobutyronitrile were supplied by Baker and Merck, respectively. All materials were used without further purification.

4.2.3.2 Preparation of AA Copolymer in the Presence of 1-Dodecanethiol

Procedure

14.80g (0.05 mol) α-methylolbenzoin acrylate, 10.80g (0.15 mol) acrylic acid, 0.082g (5.00×10^{-4} mol) azobisisobutyronitrile and 2.02g (0.01 mol) 1-dodecanethiol were dissolved in methylisobutylketone and made up to a volume of 148ml. The solution was deaerated with nitrogen gas for approximately 40 mins. and the reaction vessel was sealed. After heating to 80°C in an oil bath for 30 mins., the hot solution was poured into an excess of petroleum ether (60-80°C fraction). Some gellation had occurred whilst heating, and the gel thus formed in the reaction vessel was removed by trituring with petroleum ether. The gel and the copolymer precipitated by pouring the hot reaction mixture into petroleum ether were isolated by filtration and washed several times with petroleum ether. Both sets of copolymer were dried overnight in a vacuum oven at 45^{o}C. The powdery precipitate is hereafter referred to as AA4, the gel as AA5.

A combined product yield of 88% was isolated. Very similar NMR and IR spectral data were obtained for the two samples.

NMR Spectra (Acetone-d_6): δ 8.05-7.87 (m,2H,H_a); 7.69-7.52 (m,2H,H_b), 2.79-0.70 (m,4H,phenyl); 4.97-4.72 & 4.48-4.18 (2m,2H,-CH_2-); 2.79-0.70 (m,polymer chain alkyl protons);

IR Spectra (KBr Disc): 3432 (benzoin H-bonded O-H str.); 3300-2840 (carboxylic acid H-bonded O-H str.); 1711 (ester C=O str.), 1680 (ketone C=O str.); 1597, 1576 & 1492 (aryl C-C str.); 1448 (alkyl C-H def.), 1244 (carboxylic acid C-O str./O-H def.); 761 and 701 (monosubstituted aromatic out-of-plane C-H def.) cm^{-1}.

The photoreactive group contents of AA4 and AA5 were determined similarly to those of AA1, AA2 and AA3. Values of 51% and 46% were obtained for AA4 and AA5, respectively.

NMR spectra were recorded on a Bruker WH 270 spectrometer, using tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin-Elmer 983G infra-red spectrophotometer.

4.2.4 SCREENING OF PHOTOINITIATORS

The potential of the AA copolymers to function as photoinitiators for thin film UV curing was tested with solutions of water in tetraethyleneglycol diacrylate (T.E.G.D.A.). A 7% water content was used initially, but it was found that better results were obtained when this was increased to give a 15:85 v:v water/T.E.G.D.A. mixture. Solutions of 0.1M and 0.2M with respect to photoreactive units were cured on strips of G.N.T. paper supplied by Wiggins-Teape, U.K. Wet film thicknesses of 6 μm (produced by a No. 1 K-bar supplied by R.K. Print-Coat Instruments Ltd.) were used. The earlier curing measurements were obtained using a Colordry system consisting of two 80W cm^{-1} medium pressure mercury lamps over a moving belt arrangement. For later measurements a single, new, medium pressure mercury lamp was used.

In order to determine the effect of photoinitiator concentration on curing efficiency, solutions of varying concentration were cured with AA4 and its monomeric model ester as the photoinitiators. It was hoped that the effect of adding a tertiary amine synergist could be observed also. Several amines were tried, including N-methyldiethanolamine and triethylenetetramine, but all led to salt formation and, therefore, could not be used in conjunction with the copolymers to enhance their performance. To construct the concentration/performance curves, films of the 85:15 (v/v) T.E.G.D.A./water mixture were cured on strips of G.N.T. paper. A film thickness of 6 μm was used. Curing was carried out with the Colordry system, using only one of the two available medium pressure mercury lamps.

4.3 RESULTS & DISCUSSION

4.3.1 CHARACTERIZATION OF COPOLYMERIC PHOTOINITIATORS

4.3.1.1 Determination of Photoreactive Group Contents by NMR Spectral Analysis

Copolymer	[a]AA/Photo-initiator Molar Ratio	Deaeration Method	Stirring Whilst Heating	Photo-reactive Group Content (Weight %)
Copolymer 10	3.0	[b]Ar Prior	No	55
Copolymer 30	3.0	Ar Prior	No	53
Copolymer 120	3.0	Ar Prior	No	59
Copolymer 180	3.0	Ar Prior	No	56
AA1	3.0	Ar Prior	Yes	41
AA2	3.0	Ar Prior	Yes	41
AA3	0.5	[c]N_2 During	Yes	68
AA4	3.0	[d]N_2 Prior	No	51
AA5	3.0	N_2 Prior	No	46

[a]AA = acrylic acid

[b]Ar Prior = solution deaerated with argon gas prior to sealing the reaction vessel and heating

[c]N_2 During = solution deaerated by passing nitrogen gas through whilst heating

[d]N_2 Prior = solution deaerated by passing nitrogen gas through prior to sealing the vessel and heating

As expected, the photoreactive group content of AA3 was found to be considerably higher than those of the other copolymers. The photoreactive group contents of the six copolymers prepared without stirring were all found to be quite similar, whilst the values for AA1 and AA2 were notably lower. No clear explanation for this observation is apparent.

4.3.1.2 Molecular Weight Determination by G.P.C. Analysis

Molecular weights were determined for AA2, AA4 and AA5. Whereas no means of molecular weight control was employed in the preparation of AA2, a chain transfer agent was present when preparing AA4 and AA5.

Copolymer	$\bar{M}_n$	$\bar{M}_w$
AA2	10901	27962
AA4	1655	2938
AA5	2011	4774

As expected, the presence of a chain transfer agent led to dramatically lower product molecular weights.

The molecular weight values for AA4 (isolated by precipitation from petroleum ether) were found to be lower than those for AA5 (formed by gellification whilst heating), although both samples were prepared in the presence of a chain transfer agent. It is possible that, once gellation began, movement and interaction of the molecules in that region were progressively restricted, thus limiting the efficiency of the chain transfer agent. This would explain the higher molecular weights of AA5, relative to AA4.

4.3.2 CONTROL OF COPOLYMERIC PHOTOINITIATOR MOLECULAR WEIGHTS

4.3.2.1 Determination of a Chain Transfer Constant for AA Copolymerization System, with 1-Dodecanethiol as Transfer Agent

The chain transfer constant for the α-methylolbenzoin acrylate/acrylic acid system was determined from a Mayo plot[14].

Sample No.	M	$\overline{M}_n$	[RSH]/ mol l^{-1}	[M]/ mol l^{-1}M	$M/\overline{M}_n$	[RSH]/ [M]
1	296	5961	3.33×10^{-9}	3.33×10^{-7}	0.050	0.01
2	296	5551	6.66×10^{-9}	3.33×10^{-7}	0.053	0.02
3	296	5697	9.99×10^{-9}	3.33×10^{-7}	0.052	0.03
4	296	4899	1.33×10^{-8}	3.33×10^{-7}	0.060	0.04
5	296	4102	1.67×10^{-8}	3.33×10^{-7}	0.072	0.05
6	296	4823	2.00×10^{-8}	3.33×10^{-7}	0.061	0.06
7	296	4156	2.33×10^{-8}	3.33×10^{-7}	0.071	0.07

The Mayo plot produced from the afore-mentioned data gives a chain transfer constant of 0.36 for the AA copolymer/1-dodecanethiol system. Being less than unity, this chain transfer constant value indicates that telomerization is taking place instead of 1:1 copolymerization[15]. In the case of transfer solely to a chain transfer agent, the chain transfer constant is defined as $^{k}tr/_{kp}$[16] k_{tr} denotes the rate constant for the chain transfer of a propagating radical with the transfer agent; k_p is the rate constant for propagation of the radical.

The chain transfer constant is smaller for 1-dodecanethiol with the AA copolymerization system than with the MA copolymerization system. The only difference between the two is the acrylated monomer. Hence it follows that the acrylic acid-derived propagating radical must be less reactive towards the abstraction of hydrogen from the transfer agent than is that derived from methyl acrylate. Thus a smaller quantity of chain transfer agent will be required to limit the molecular weight of the MA copolymers to a given value than to produce the same results with the AA copolymers. This is reflected in the chain transfer agent concentrations needed to give number average molecular weights in the 2-3,000 range. Extrapolation of the Mayo plot shows that a thiol concentration of approximately 20% is required for the AA copolymers, compared with 14% for the MA copolymers.

4.3.3 SCREENING OF PHOTOINITIATORS

4.3.3.1 UV Curing of Thin Films

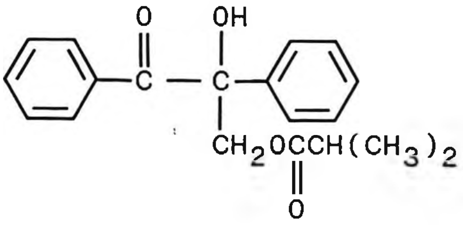
In all of the following measurements, a wet film thickness 6 μm was used. G.N.T. paper was used as the substrate (supplied by Wiggins Teape, U.K.).

T.E.G.D.A. Films with a 7% Water Content

Both of the 80W cm^{-1} medium pressure mercury lamps were utilized in these first experiments. Copolymer 10 and Copolymer 30 were chosen to be representative of the first batch of copolymers produced.

Photoinitiator	Photoreactive Group Concentration/M	No. of Passes to Cure Film at Specified Belt Speed/m min^{-1}		
		30	43	58
Copolymer 10	0.2	5	7	12
Copolymer 30	0.2	4	7	11

The amount of water present was then increased to give a 15:85 (v/v) water/T.E.G.D.A. solution. Since the two copolymeric photoinitiators performed with such similar efficiencies in the tests recorded on the previous page, it was decided to use only one of them in the next set of measurements. AA1 and AA3 were also used to cure the water/T.E.G.D.A. mixture of increased water content. Comparisons were made with the monomeric model compound, α-methylolbenzoin isobutyrate (ISO)



Curing Films of an 85:15 T.E.G.D.A./Water Mixture

As in the previously mentioned experiments, both of the available mercury lamps were used. For AA1, AA3 and ISO, photoreactive group concentrations of 0.1M were tried in addition to 0.2M. An insufficient quantity of Copolymer 10 (or Copolymer 30) was available to allow this also to be used at two different concentrations.

Photo-initiator	Photoreactive Group Concentration/M	No. of Passes to Cure Film at Specified Belt Speed/m min^{-1}				
		16	20	30	43	58
Copolymer 10	0.2	1	1	1	1	2
AA1	0.2	1	2	3	5	11
AA3	0.2	2	2	3	6	12
ISO	0.2	2	2	4	6	10
AA1	0.1	4	6	10	23	-
AA3	0.1	5	6	11	24	-
ISO	0.1	5	6	10	21	-

As expected, reducing the amount of photoinitiator in the solutions led to a corresponding decrease in the rate of cure. More interesting is the dramatic increase in the rate of cure with Copolymer 10 when the water content of the T.E.G.D.A./water mixture is increased, all other conditions remaining the same. It can only be assumed that this is the result of some physical effect. Possibly, the increased water content leads to more efficient mixing of the constituents of the formulation, which, in turn, affords a higher rate of cure.

Whilst all of the copolymers gave fairly good rates of cure at a photoreactive group concentration of 0.2M, Copolymer 10 was considerably better than the other two. The reason for this observation is not clear but, since the measurements for AA1, AA2 and ISO were made some time after those for Copolymer 10, it is possible that the lamp intensities were not the same. (Curing with AA1, AA2 and ISO was performed on the same day.) The probability of this being the case is even greater on consideration of the fact that the lamps had to be replaced shortly after the experiments with AA1, AA2 and ISO were carried out.

With this in mind, comparisons can only be considered valid between AA1, AA3 and ISO. Little difference can be seen between the rates of cure obtained with these three photoinitiators, and there appears to be no benefit gained by attaching the photoreactive moiety to a polymeric backbone.

In order to observe whether lowering the molecular weights of the copolymeric photoinitiators would improve their performance, films were also cured with AA4 as photoinitiator. These measurements were carried out with a new set of UV lamps and, furthermore, only one of the two lamps was switched on at any given time. Comparisons were again made with the monomeric model compound.

Photo-initiator	Photo-reactive Group Con-centration/M	No. of Passes to Cure Film at Specified Belt Speed/m min^{-1}					
		14	16	20	30	36	43
AA4	0.1	-	-	-	-	-	-
ISO	0.1	-	-	-	-	-	-
AA4	0.2	15	17	27	-	-	-
ISO	0.2	21	22	27	-	-	-

Whilst AA4 affords faster cure rates at the lowest belt speeds, both photoinitiators give the same rate of cure at a belt speed of 20m min^{-1}. It was not possible to obtain a cured film with either photoinitiator at a photoreactive group concentration of 0.1M. Thus, whilst curing of the T.E.G.D.A./water 85:15 mixture can be effected with photoreactive group concentrationsof 0.2M and above, the rate of cure was found to be very low with the reduced lamp intensity.

From the UV curing results, it can be seen that, whilst the acrylic acid/α-methylolbenzoin acrylate copolymers are able to initiate the photocuring of a T.E.G.D.A./water mixture, they offer no higher efficiency than their monomeric counterpart.

Further information regarding the efficiency of the copolymers and their monomeric counterpart in initiating the photopolymerization of the T.E.G.D.A./water mixture was obtained by measuring the relative rates of cure with varying photoinitiator concentrations.

4.3.3.2 Construction of Concentration/Performance Graphs for the Curing of 6 μm Films of T.E.G.D.A./Water 85:15 (v/v)

Photo-initiator	Photo-initiator Concen-tration/M	No. of Passes to Cure Film at Belt Speed 14m min^{-1}	Equivalent Irradiation Time Required to Cure Film/s
AA4	0.05	-	-
	0.10	-	-
	0.15	-	-
	0.20	15	35.4
	0.25	11	25.9
	0.30	9	21.2
ISO	0.05	-	-
	0.10	-	-
	0.15	27	63.6
	0.20	21	49.5
	0.25	17	40.1
	0.30	15	35.4

Due to problems with solubility it was not possible to use photoreactive group concentrations in excess of 0.30M. The results tabulated above show that curing of the films can be achieved with a lower concentration of the monomeric model than of the copolymeric photoinitiator. Nevertheless, once a workable concentration is reached AA4 affords a faster rate of cure for each of the concentrations used than does the monomeric model.

From these results it appears that some benefit is to be gained from copolymerizing the benzoin-derived unit with a water-soluble monomer. The enhanced photoinitiating efficiency possibly originates from two sources. First of all, copolymerization with a water-solubilizing monomer should improve the compatibility of the photoreactive group with the T.E.G.D.A./water mixture. Secondly, the polymer coils would be expected to protect the propagating radicals from termination and thus allow more rapid development of the polymerization process[17,18].

As expected, the rate of cure increases when increasing the concentration of each of the photoinitiators. The difference in curing efficiencies between them remains constant, however, throughout the range of concentrations.

4.4 SUMMARY

By copolymerizing α-methylolbenzoin acrylate with acrylic acid it was hoped to produce a polymeric photoinitiator to initiate the photopolymerization of acrylate monomers in the presence of water. Tetraethyleneglycol diacrylate, T.E.G.D.A., was found to be compatible with water up to ratios of around 85 T.E.G.D.A./15 water. The results presented in the preceding section show that the copolymers formed are able to initiate the photocuring of such a mixture, and that they do so with greater efficiency than the monomeric ester α-methylolbenzoin isobutyrate. The curing results show that the rate of reaction increases with increasing photoinitiator concentration. However, due to problems with solubility at higher concentrations, the optimum photoreactive group concentration was found to be in the region of 0.3M.

Whilst curing can be achieved with the formulations used the rates of cure are not exceptionally high. Reasonable rates were achieved with the higher photoinitiator concentrations, but better results would, doubtless, be achieved if a suitable copolymeric photoinitiator/tertiary amine combination could be found. As stated earlier, attempts to combine various amines with the photoinitiators resulted in insolubility in the T.E.G.D.A./water mixture.

It can be concluded that the polymeric acrylic acid/α-methylolbenzoin photoinitiators are capable of functioning as photoinitiators for UV curing in the presence of water. However, the rate of cure afforded by these photoinitiators is insufficiently high for them to be of commercial interest.

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