ASPECTS OF RADIATION CURING

A thesis submitted for the degree of
Doctor of Philosophy in City University

By

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CONTENTS

Abstract

Free-radical polymerization processes are used in the surface coatings industries.

One of the main problems with the free-radical as opposed to the ionic process is the oxygen inhibition of cure. The latter can be attributed to oxygen scavenging the growing polymeric radicals, scavenging the radicals derived from the photoinitiator or quenching an excited state of the initiator.

Oxygen inhibition can be minimised by incorporating amines into the formulation.

These materials yield radicals which rapidly and efficiently scavenge oxygen, thus depleting the oxygen in the curing layer.

If cure is sufficiently fast, the amine may be able to deplete oxygen at a rate which is greater than the diffusion into the film. A more recent way of overcoming oxygen inhibition, as yet unproved in thin films, is that of the use of sulphur-containing compounds.

Sulphides will transform peroxy radicals into alkoxy radicals (which can initiate polymerization) and reduce hydroperoxides to alcohols. This leads on to the next piece of work which involves regeneratable photosensitisers. Previous work carried out at City University has shown that 2,3 - diphenylquinoxaline, when used in conjunction with a amine is quite a remarkable, if not unique photosensitiser. Through careful work of Moran, as yet unpublished, it was shown that the use of this sensitiser leads to surface cure and hence may find application in 3D - imaging. Current thinking on the mechanism of reaction involves its continuous regeneration by reaction with oxygen.

Various u.v./visible range photoinitiators were prepared:
(i) cyanine borates (ii) cyclopentadienyliron (II) alkylborates and (iii) diazonium salts to show the effect of oxygen on the rate of polymerization.

AUTHORISATION

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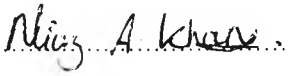

N.A. Khan

CHAPTER ONE

INTRODUCTION TO PHOTOCHEMISTRY

PHOTOCHEMISTRY

INTRODUCTION

Two laws of photochemistry [1,2] are considered that feature in most introductions to the subject.

The Grotthus-Draper Law states that only light absorbed by a molecule can be effective in bringing about chemical change.

The second law is the Stark-Einstein Law, whose re-statement is that the primary photochemical act involves absorption of just one photon by a molecule. This holds true for the vast majority of processes.

Photochemistry then is concerned with reactions of electronically excited states. Here are some general differences between the states and the corresponding ground states.

(i) An electronically excited state is considerably more energetic [3,4]

(ii) The excited state has a very different electron distribution from that in the ground state.

(iii) A further difference is in the electron-donating or electron-accepting abilities of the states

An electronically excited state is both a better donor and a better acceptor of electrons than in the corresponding ground state.

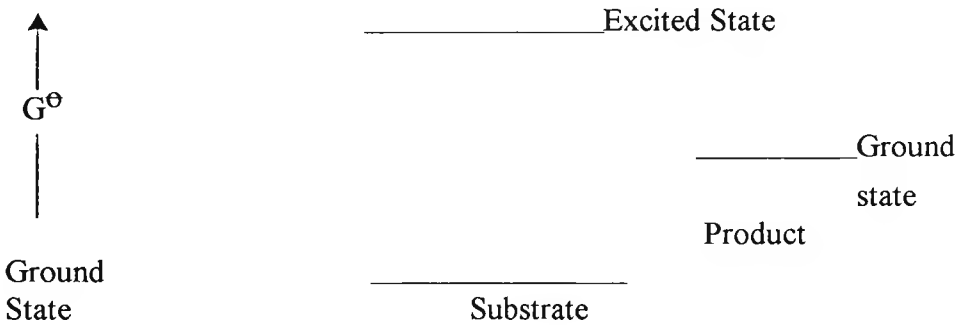

Figure 1.1 :- is a standard free-energy diagram showing the ground state of a molecule, an excited state of the same molecule and a potential product of a chemical reaction.

The reaction leading from ground state to product (in their standard states) involves an increase in free-energy, which will not occur spontaneously.
If the free-energy difference is not large, a small equilibrium concentration of the product might be achieved in homogeneous solution.
However, the photochemical reaction that leads from an excited state to product involves a decrease in free-energy and is much more likely to occur spontaneously.

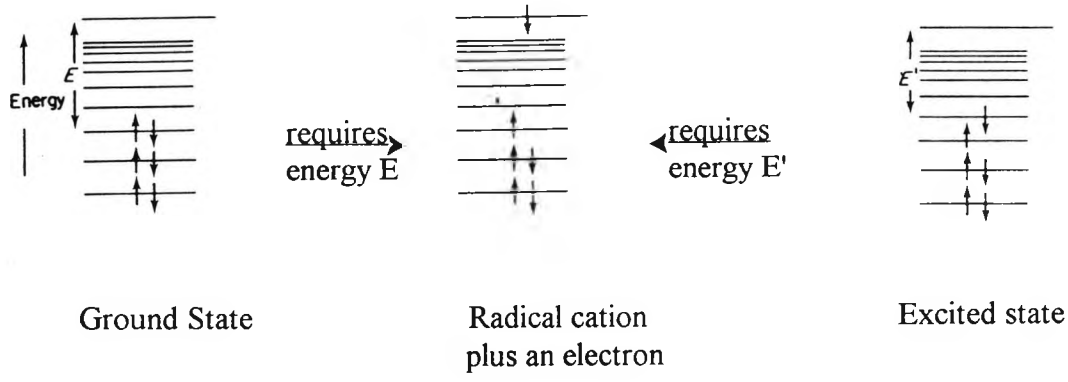

Fig 1.2:- Diagrammatic rationalization of the better electron-donor properties of an excited state.

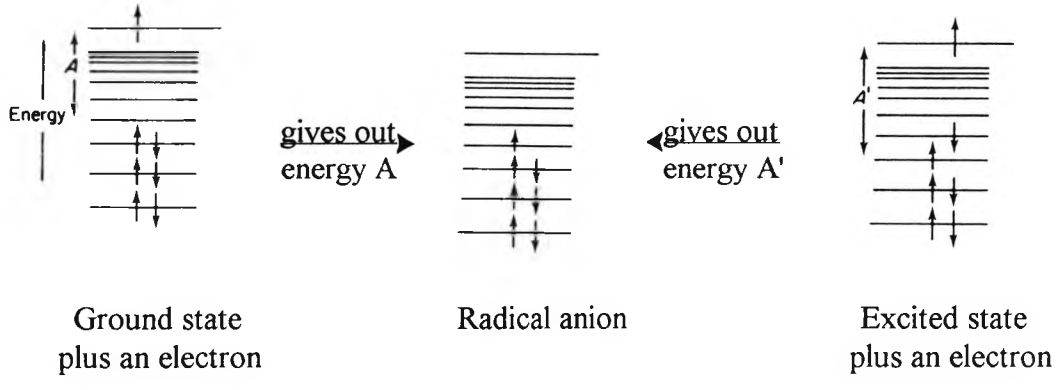

Fig 1.3:- Diagrammatic rationalization of the better electron-acceptor properties of an excited state.

An electronically excited state is both a better donor and a better acceptor of electrons than is the corresponding ground state.

A measure of the electron-donating ability of a species is its ionization potential, the minimum energy required to remove an electron completely from the species . This energy can be equated approximately to the difference in energy between the highest

occupied molecular orbital and the ionization limit, which corresponds to complete removal of the electron and the formation of a radical cation.

The energy is considerably lower for the excited state in which one electron is clearly closer to the ionization limit than for the ground state.

The energy released when an electron comes from outside the influence of the nuclei of a species to occupy the lowest-energy available orbital is called the electron affinity and it offers a measure of electron-accepting ability. The energy is greater for the excited state than for the ground state, because in the former a lower-energy orbital is half-filled.

It is normally assumed that the inner-shell electrons of the consequent atoms of a molecule remain unaltered in the molecule itself, linear combinations of the remaining valence-shell atomic orbitals then provide molecular orbitals that can be used to describe the outer electronic structure in the molecule.

If single atomic orbitals on each of the two adjacent atoms are combined, they produce two molecular orbitals, one of higher energy and one of lower energy than the separate atomic orbitals.

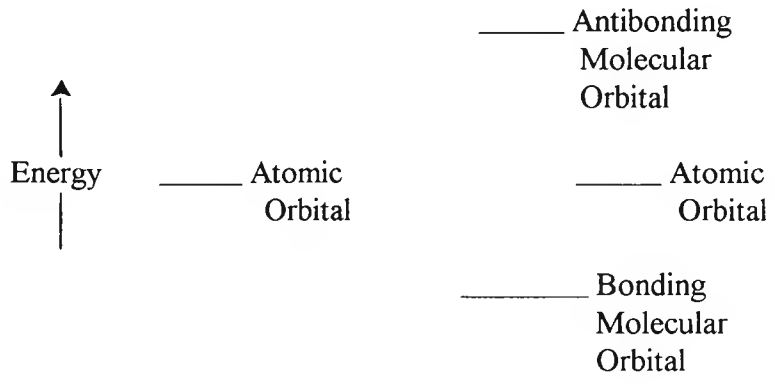

Fig 1.4:- Effect on orbital energy of a linear combination of atomic orbitals.

The lower energy orbital is called a bonding orbital and in a typical situation where there is a two-electron bond between the atoms, a pair of electrons will occupy the bonding orbital in the ground-state electronic configuration. The higher-energy molecular orbital is called an antibonding orbital. It is unoccupied in the ground state, but it may be occupied by one electron in an electronically excited state of the molecule.

Orbitals that are completely symmetrical about the internuclear axis [5,6] are called sigma (σ) or sigma-star (σ^*) orbitals, according to whether they are bonding or antibonding, respectively. Orbitals that are anti-symmetric about a plane that includes the internuclear axis (e.g. those formed by combination of paralled atomic p orbitals) are called pi (π) or pi-star (π^*) orbitals.

In practice two simplifications can be made that affect a more readily visualized model. First it is assumed that there is no interaction between σ and π orbitals because of their different symmetric properties.

Secondly, it is assumed that the σ-framework of an organic molecule can be described in localised orbitals, each covering two nuclei only. Delocalised orbitals that cover more than two nuclei appear in this model only for π-bonding in conjugated organic molecular systems.

A third type of orbital used in such a qualitative description is denoted as an n-orbital. These orbitals are non-bonding, and a pair of electrons occupying an n-orbital is often envisaged as a 'lone pair' of electrons on a particular atom. When a photon interacts with a molecule, the mutual perturbation of electric fields may be of no lasting consequence.

Alternatively, the photon may cease to exist, its energy is transferred to the molecule, and the electronic structure of the molecule changes, the photon having been absorbed

and the molecule excited. Absorption occurs in an extremely short period of time (10^{-18} sec. Franck-Condon principle) and it can be assumed that the positions of the nuclei in the molecule do not change during this period, and the major change is in the electronic structure [12,13,14].

To take a particular example, Fig.(1.5) depicts the orbitals of the carbon-carbon bonds of an alkene and it shows (a) the ground state configuration and (b) an excited state configuration that might be obtained by absorption of a photon of wavelength around 180nm.

The excited state is called a pi, pi-star (π , π^*) excited state and the electronic transition leading to it is a pi to pi-star (π - π^*) transition.

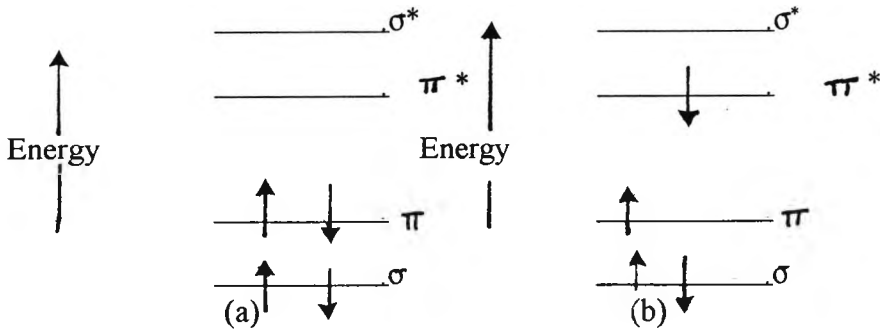

Fig1.5:- Electronic configuration of an alkene, showing the occupancy of the carbon-carbon bond orbitals (a) In the ground state (b) in the (π , π^*) excited single state.

σ^* orbitals are very high-energy orbitals. Molecules containing heteratoms have high energy non-bonding orbitals, and the lowest transitions for such molecules are n-π^* (if multiple bonds are present) or n - σ^* (for saturated molecules).

Although other types of excited state do need to be considered at times, the great majority of organic photochemical reactions carried out with radiation of wavelength greater than 200nm (a limit imposed in part by practical aspects of conducting

preparative reactions in solution) can be accounted for in terms of three general classes of electronically excited state - (n, $\pi\pi^*$), ($\pi\pi$, $\pi\pi^*$) and (n,σ^*).

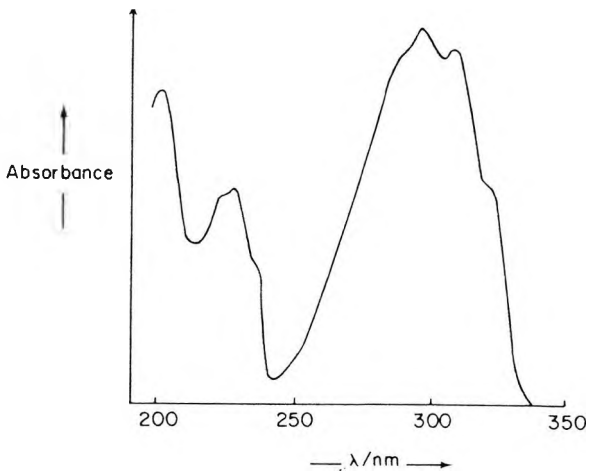

Fig.1.6 Electronic absorption spectrum of trans-stilbene

The probability of absorption [7,8,9,] of a photon by a molecule, and its variation with wavelength are reflected in the electronic absorption spectrum of the compound concerned Fig. 1.6, shows a typical spectrum of an organic compound in solution.

At a particular wavelength the bulk absorption properties can be represented by the Bear-Lambert Law, absorbance (A), which equals the base - 10 logarithm of the ratio of incident light intensity (I_0) to transmitted light intensity (I), is directly proportional to the concentration (c) of the compound and the pathlength (1) of the radiation through the sample.

The proportionality constant (E) is called the absorption coefficient or more specifically the molar absorptivity coefficient (Units:- $1mol^{-1}\ cm^{-1}$), if concentration is in mol^{-1} and path length in cm [10,11].

$$\log (Io/I)=A=Ecl$$

Io/I - ratio of the light intensity (Io)

to the transmitted light intensity (I)

c- Concentration of the compound

E- Molar absorptivity coefficient

l- Path length (cm)

A- Absorbance (i.e. optical density)

The Bear-Lambert Law can also be expressed as: $I_o e^{-Ecl}$

It is shown that the intensity decreases exponentially with the sample thickness and that it decreases exponentially with concentration.

Most solution- phase spectra of organic compounds show broad absorption peaks, unlike atomic spectra which consist of sharp lines. The main reason for this is that there are a large number of vibrational and rotational energy levels associated with polyatomic molecules and absorption of a photon can result in conversion of a portion of its energy into vibrational or rotational energy.

Organic compounds in the vapour phase show vibrational structure. Hence, for the absorption to occur, the energy of the photon does not need to match precisely the energy required simply to change the electronic configuration of the molecule. So there are a large number of slightly separated lines in the spectrum and any fine structure that might remain is lost because solvent molecules cause a broadening of the lines as a result of their influence on the energy levels of the molecules. Despite this the absorption spectrum can provide useful information about the electronic transitions that occur for a particular molecule, and about their relative energies. This is aided by a simple rule of thumb , that bonds corresponding to π - π^* transitions are more usually more intense (E, 5000 - 100,000 $1 mol^{-1} cm^{-1}$) than those corresponding to n-σ^*

transitions (E, 100 - 1000 $1mol^{-1}$ cm^{-1}) or n- π * transitions (E 1-400 l mol^{-1} cm^{-1}) combined with knowledge of the compound's molecular structure and a likely ordering of its orbital energies.

An electronically excited state has two unpaired electrons in different orbitals. In the states depicted so far these have been shown as having opposed spin, so that the state has overall zero spin and is a singlet state [15]. This is the usual situation for excited states that are produced directly by absorption of a photon. If the two spins are parallel the state has a non-zero overall spin and is a triplet state [16,17].

The state corresponding to the arrangement of electrons shown in Fig.1.7 is a (π ,π *) triplet state of an alkene in contrast to the (π , π *) singlet state depicted in Fig. 1.5.

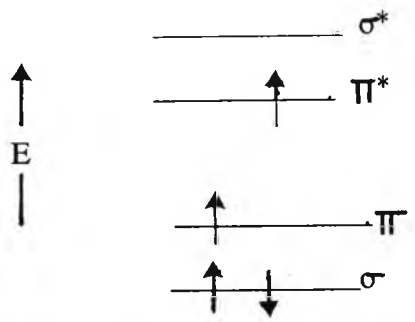

Fig. 1.7 Electronic configuration of the (π,π *) triplet state of an alkene.

The singlet and triplet states are said to be of different spin multiplicity and they are distinct species, with differing properties including chemical reactivity.

The triplet state is of lower energy because of the repulsive nature of interactions between electrons of the same spin (i.e. Hund's rule of maximum multiplicity) but it is not readily produced by direct absorption of a photon because for most molecules the probability of a spin inversion occurring at the same time as absorption is extremely low.

The process of light absorption is extremely fast and at the instant the molecular geometry is unchanged. The nuclei occupies the same relative position as in the ground state. This is an expression of the Franck-Condon principle and is useful in rationalizing the relative intensities within the absorption or emission spectra.

The excited state so produced does not have the most stable geometry for its particular electron distribution and normally relaxation occurs by loss of vibrational and rotational energy to give the excited state in its equilibrium geometry, more so in solution than the vapour phase.

The most stable molecular shape in the excited state may be quite different from that in the ground state, e.g. ethylene is a planar molecule in the ground state but in the relaxed excited state, twisting has occurred around the double bond.

The dipole moment of an excited state can be estimated from an analysis of solvent effects on absorption and emission spectra. The wavelength of maximum emission is particularly sensitive to the nature and polarity of the solvent. The dipole moment, like that of a ground state species gives a measure of the overall electron distribution.

Another property of an excited state is its energy. This is taken to be the energy difference between the relaxed excited state and the lowest vibrational level of the ground state.

The energy of a lowest excited singlet state can be estimated from the absorption spectrum, but not always correctly e.g. if solvation occurs.
If the vibrational fine structure is apparent, the longest wavelength band apparent in the spectrum is often one that corresponds to the energy required.

Spectra for most organic compounds in solution show little or no vibrational structure and in these cases it is very difficult to determine the spectrum.

A more reliable approach to singlet state energies is available from fluorescence emission spectra, which usually show more detailed fine structure than absorption spectra. The shortest wavelength band in the fluorescence spectrum corresponds to the excited state energy.

For the triplet-state energies, estimates from absorption spectra are rarely available because singlet-triplet absorption spectra are very weak and difficult to obtain in useful form.

Triplet energies are generally obtained from phosphorescence emission spectra.

The energy of an excited state is a useful property in devising sensitized photochemical reactions, that is those in which the required excited state is produced indirectly by transfer of energy from another species rather than directly by light absorption.

An excited state has a characteristic lifetime under given conditions of temperature, solvent and concentration of substrate and of other species in the solution. These lifetimes are short, varying from more than 10s at liquid nitrogen temperature for some of the longest-lived triplets to less than 10^{-12}s for some of the shortest- lived singlets.

Intramolecular photophysical processes [18,19] can be divided into two groups (i) radiative (or luminescent) processes in which a photon of ultraviolet or visible radiation is emitted and (ii) non-radiative processes in which no such emission takes place.

The energy of emitted light is less than that of the light used to excite the molecule originally, because some of the energy is converted into vibrational and rotational motion and so visible light emission often occurs as a result of excitation by ultraviolet radiation.

When an excited singlet state emits a photon, the state is normally converted to the ground state which is also a singlet state.

Such a radiative process in which there is no overall change of spin allowed is called fluorescence.

Most commonly it is the lowest excited singlet state whose emission is observed, regardless of which singlet state is formed initially by absorption.

This absorption is one aspect of what is known as Kasha's Rule.[20]

The reason for this is that in solution, higher energy states generally undergo very rapid non-radiative decay to the lowest excited singlet state. Emission from these upper states cannot compete effectively with such very fast decay and in exceptional cases where fluorescence from a higher singlet state is observed, its efficiency and intensity are low.

Because emission is normally from the lowest excited singlet level, a fluorescence spectrum is not normally affected in its profile by the wavelength used to excite the sample.

Another feature of fluorescence is that it is measured absolutely unlike absorption which is measured by difference.

Two useful fluorescence parameters are quantum yield and lifetime.

The efficiency of a photochemical process is defined by the product quantum yield Φ ,where it is a measure of the efficiency with which absorbed radiation causes the molecule to undergo a specified change.

Quantum Yield for fluorescence

$$\Phi_f = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

So for a photochemical reaction, it is the number of product molecules formed or destroyed for each quantum of light absorbed.

Quantum Yield normally falls in the range of 0 - 1.0

The measurement of fluorescence quantum yield is not straightforward. Even with unidirectional monochromatic exciting light, fluorescent emission is in all directions

and is polychromatic (which is relevant because detector response can vary with wavelength).

A common practice is to measure quantum yield relative to that of a standard compound, excited under identical conditions, whose quantum yield is known from previous determinations.

Comparison is made with a standard such as $5x10^{-3}$mol dm^{-3}quinine sulphate in 0.5 mol dm^{-3} H_2SO_4 where $\Phi_f = 0.5 \times 10^{-6}$ mol dm^{-3} of sodium fluorescein in 0.1 mol dm^{-3} NaOH where $\Phi_f = 0.9$.

The lifetime of fluorescence is measured entirely by following the decay of fluorescence intensity with time after the exciting radiation is interrupted. The type of light sources used are various pulsed dye lasers or spark lamps.

Phosphorescence is similar to fluorescence except that in this type of radiative process, the spin multiplicity changes.

Almost all phosphorescence for organic compounds involves luminescence that originates in the lowest excited triplet state, which decays to the ground state in the process. Because it is a 'spin forbidden' process, phosphorescence generally has an associated lifetime that is considerably longer than fluorescence lifetimes for similar molecules. A direct comparison is not always meaningful because fluorescence and phosphorescence are usually studied under different conditions, fluorescence in fluid solution at room temperature and phosphorescence in a rigid glass matrix at a very low temperature, most commonly 77K.

Such conditions are used for phosphorescence because at room temperature in solution, triplet states are generally deactivated very rapidly in bimolecular processes with other molecular species, which greatly reduces the lifetime and quantum yield of phosphorescence and so makes it difficult to detect and study. Their is no doubt that triplet states are formed in fluid solution, because they can be detected by other methods such as flash photolysis, but their luminescence is very weak. Under the low

temperature conditions employed for phosphorescence studies, fluorescence may also be occurring (at shorter wavelength since excited singlet states have energies higher than the corresponding triplet states), and to differentiate between the two, it is normal to incorporate a rapid shutter device into the instrument.

Non-radiative (or radiationless) decay processes involve conversion of one electronic state into another without emission of light.

Like radiative processes they can be divided into two categories according to whether or not there is an overall change in spin multiplicity during the process. If no spin change occurs the non-radiative process is called internal conversion.

This is the means by which higher excited singlet states decay rapidly to the lowest excited singlet state before further photophysical or photochemical reaction occurs.

Similarly, higher triplet states decay rapidly to the lowest triplet state by internal conversion. Internal conversion can also occur from the lowest singlet state to the ground state in competition with fluorescence.

For most molecules this particular internal conversion process is much slower than the process by which higher singlet states decay. This arises because the rate of internal conversion is related inversely to the energy difference between initial and final states and the energy of the lowest excited singlet state is usually much larger than the energy difference between the lowest singlet state and the singlet next higher in energy.

Because internal conversion from the lowest excited singlet state to the ground state is relatively slow, fluorescence can compete effectively with it, and for some molecules the quantum yield for this internal conversion process is negligibly small.

When non-radioactive decay involves a change in spin multiplicity it is called intersystem crossing and for organic molecules there are two important intersystem crossing processes.

The first is the radiationless decay that competes with radiative (phosphorescent) decay of the lowest triplet state to the ground state.

The second is the process that converts the lowest excited singlet state into the lowest triplet state and is therefore in competition with fluorescence and with internal conversion from the lowest singlet state.

The importance of the latter of the intersystem crossing processes is that it provides the means by which many triplet states are produced prior to phosphorescence or photochemical change, namely absorption of a photon to give the excited singlet state followed by intersystem crossing to give the triplet state.

As with other radiationless processes the rate constant for intersystem crossing is related inversely to the energy gap between the initial and final states. This means that intersystem crossing to produce the triplet state is fast and efficient for molecules which have a relatively small singlet - triplet energy difference, such as ketones with low (n, π^*) states but it is slow and inefficient for many molecules which have a much larger singlet - triplet energy gap such as alkenes with low ($\pi\pi$, π^*) states. For this reason direct irradiation of aromatic ketones for example, leads to chemical reaction from the lowest triplet state, whereas direct irradiation of conjugated dienes leads to reaction from the lowest singlet excited state. After this brief description of the various intramolecular photophysical processes that can occur after excitation of a molecule, it is appropriate to bring them together by showing how they can be represented and related on a single diagram, known as a Jablonski Diagram.

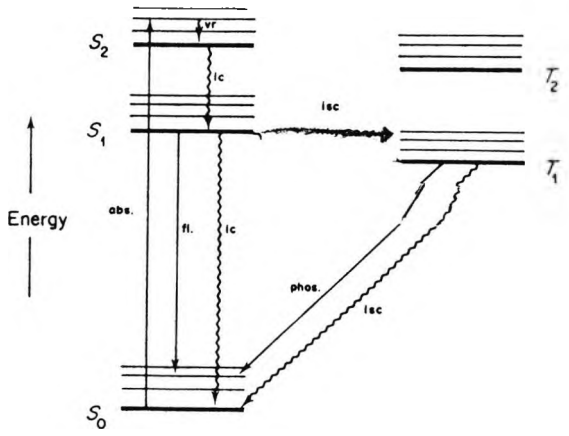

Fig. 1.7 Jablonski Diagram

In the left hand part of the diagram are the singlet states of the molecule, namely the ground state (So) and excited singlet states (S_1, S_2 etc) in a vertical side of increasing energy. In the right-hand part are the triplet states (T_1, T_2 etc) in order of increasing energy. Each horizontal line represents a different electronic state of the molecule. Each electronic state can have varying amounts of vibrational energy as indicated by a series of lighter horizontal lines (vibrational levels) for each state. The radiative processes are represented by the straight line vertically upwards for absorption, vertically downwards for fluorescence, and downwards at an angle for phosphorescence because it involves a change of multiplicity. Wavy lines represent radiationless transition, vertically downwards for internal conversion and at an angle for intersystem crossing.

In addition to the intramolecular deactivation processes there are intermolecular processes that can result from interaction with ground state molecular species. An important type of process that falls into this category is electron transfer.

(1) Electron Transfer

$$A^* + B \longrightarrow A^{\bullet+} + B^{\bullet-} \longrightarrow A+B$$

There are other ways in which excited state decay can be accelerated by other species which cannot be classified as reversible chemical reactions.

The excited state of A is said to be quenched by B. If B is converted into an electronically excited state (B*) during the process an overall transfer of electronic energy takes place between the excited and unexcited partners of the interaction.

$$A^*+B \longrightarrow A+B \text{ (or } B^*)$$

In this representation B might be a second, unexcited molecule of A, which would be the particular case of self-quenching. Self-quenching is a common phenomenon, one outcome of which is that the efficiency of luminescence in fluid solution may depend on the concentration of the substrate. For this reason fluorescence quantum yields are normally measured in a very dilute solutions (10^{-5} to 10^{-6} mol^{-1}) when self-quenching is relatively unimportant.

Of the several mechanisms for quenching, one involves the initial formation of a complex between A* and B. Such an exciplex (or excimer if B is a molecule of ground state A) represents an intermediate of an unusual kind, because it is electronically excited and although the corresponding ground state complex has no separate existence the exciplex can luminesce.

Exciplex fluorescence always occurs at lower energy (longer wavelength) than the normal fluorescence of A* and unambiguous evidence for exciplex formation is the appearance of a new longer wavelength fluorescence that increases in intensity as the concentration of B increases, with a corresponding decrease in the intensity of fluorescence of A*

Even when exciplex luminescence cannot be detected such species may be postulated to account for other aspects of photophysical and photochemical processes.

Apart from exciplex formation there are two major mechanisms by which energy transfer quenching can occur.

The first is known as the dipole-dipole (or coulombic) mechanism, which operates through mutual repulsion of the electrons in the two molecules.

It has the characteristic of being effective over relatively larger distances, and in some systems is efficient at molecular separations up to 5nm or more which means that it does not require the molecules to move into close contact.

A second mechanism is called the exchange mechanism, in which reorganisation occurs within a transient complex formed on close approach of the molecules. This is a shorter range phenomenon than dipole-dipole energy transfer.

The most commonly encountered types of energy transfer are those in which singlet energy is transferred from A to B (eqn 1) or those in which triplet energy is transferred (eqn 2).

In most situations singlet energy transfer takes place mainly by dipole-dipole mechanism, whereas triplet energy transfer occurs largely by the exchange mechanism. An overriding consideration for both types is that efficient transfer occurs only if it is energetically favourable, that is if the excited state energy of A is greater than that of B [21,22].

$$A^*(S_1)+B(S_o) \longrightarrow A(S_o)+B^*(S_1) \text{ (eqn 1)}$$

$$A^*(T_1)+B(S_o) \longrightarrow A(S_o)+B^*(T_1) \text{ (eqn 2)}$$

Electronic energy transfer is an important phenomenon in photochemistry. If a photochemical reaction forms different products from the singlet and triplet excited states, and if the products of the triplet reaction are unwanted, the singlet derived products can be generated alone by carrying out the irradiation with an added triplet quencher in an appropriate quantity.

Conjugated dienes are used as triplet quenchers. The rate of quenching of an excited state, e.g. carbonyl compounds is directly proportional to the concentration of the quencher and hence quantitative studies using a range of quenching concentrations can lead to information from which excited state life times are derived.

Use of a series of quenchers with different energies allows an estimate to be made of the excited state energy, especially for triplet states, since the efficiency of quenching falls markedly when the quencher triplet energy is lower than the energy of the reactive triplet state.

Energy transfer can be employed to produce an excited state of a substrate, rather than to quench it.

This represents a good method for making triplet states (which already can be obtained directly by $So \rightarrow T_1$ absorption of light) especially those whose formation by intersystem crossing from the excited singlet state is inefficient.

Compounds which themselves undergo efficient intersystem crossing can act as triplet sensitisers, the most common being aromatic ketones such as benzophenone.

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CHAPTER TWO

INSTRUMENTATION AND ANALYTICAL TECHNIQUES USED

REAL-TIME INFRARED SPECTROSCOPY

INTRODUCTION

One of the first distinct features of radiation curing lies in the rapidity of the process which transforms almost instantly a liquid resin into a solid material.

One of the problems which is encountered is that it is difficult to evaluate kinetic parameters for in situ u.v. curing reactions. Real-time infrared spectroscopy has been developed to analyse in situ u.v. curing reactions occurring in a fraction of a second.

Cure profiles are directly recorded and the important kinetic parameters are determined quantitatively. The effect of various factors such as chemical composition, film thickness, light intensity, oxygen concentration can be examined for multiacrylic systems exposed to u.v. radiation [1,2,3,4,].

Principle

The basic idea behind the method is to expose the sample at the same time to the polymerizing u.v. beam and to the analyzing i.r. beam which monitors the resulting drop of the absorbance at 812cm $^{-1}$ of an acrylate [5,6,7].

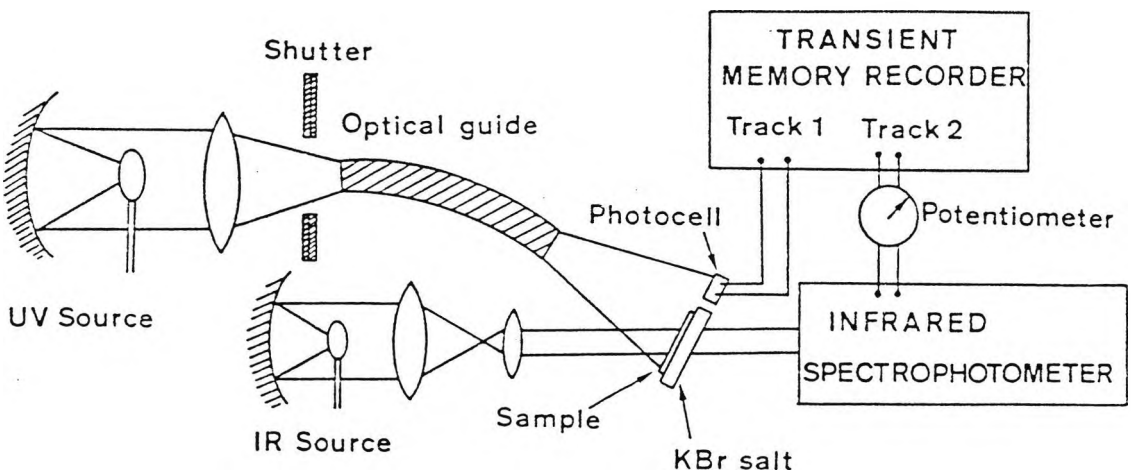

Fig. 2.1 Experimental device for real-time monitoring of uv curing reactions.

Cure Profiles

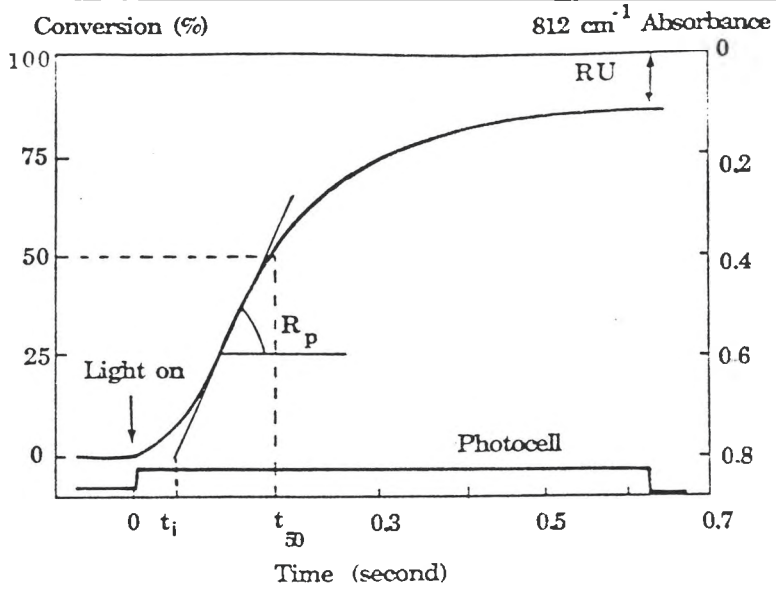

Figure 2.2 Typical cure profile recorded by RTIR spectroscopy for an acrylic coating exposed to u.v. radiation.

Figure 2.2 shows a typical polymerization profile recorded by RTIR spectroscopy. The infrared absorbance at 812cm^{-1} is proportional to the number of acrylate functions which have polymerized, the recorded cure directly translates into the dependence of the percent conversion on irradiation time.

The cure kinetics follow a characteristic 'S' shape profile due first to the inhibition effect of oxygen [8,9,10,11].

Preparation of Thin Films

Thin films were prepared on sodium chloride plates. One of the problems encountered using the sodium chloride plates as the substrate was that the plates were placed vertically in the real-time infrared spectrometer. Some of the monomer would run off the plates. An accurate measurement of film thickness was not obtained.

The formations were tested in the presence and absence of air.

Under anaerobic conditions the formulation was covered with a coverslip.

The formulations were made up of 1% w/w photoinitiator, 10% w/w synergist and a monomer.

The lamp that was used was a 100 watt mercury discharge lamp.

Kinetic Parameters

One of the unique advantages of RTIR spectroscopy is to allow the important kinetic parameters to be evaluated in a single experiment [12,13,14,15].

a. The induction period (ti) which shows how effectively oxygen interfere with the polymerization process.

b. The rate of polymerization (Rp) which can be determined at any moment of the reaction from the slope of the RTIR profile.

c. The quantum yield of polymerization (ϕp) which corresponds to the number of functions polymerized per photon absorbed and is calculated from the ratio of Rp to the absorbed light intensity.

d. The photosensitivity (S) which is usually defined as the amount of energy required to polymerize half of the reactive functions and is determined easily from the 50% conversion time. $S = P \times t_{50}$ in $mJcm^{-2}$.

e. The residual unsaturation content (RU) of the cured polymer which can be evaluated precisely from the i.r. absorbance at 812cm $^{-1}$ of the final product.

1. The rate of polymerisation (Rp) can be determined at any moment of the reaction from the slope of the RTIR curve [16,17].

$$Rp = [M]o \frac{(A_{812})_{t_1} - (A_{812})_{t_2}}{(t_2 - t_1)}$$

Where [M]o is the monomer concentration before exposure to u.v. beam. For photopolymerizations carried out in the presence of air, Rp usually reaches its maximum value at about 25% conversion, since at this point O_2 inhibition has been overcome and gelification has not yet slowed down the polymerization rate.

2. The quantum yield of polymerization (ϕp) reflects the efficiency of this photochemical reaction and corresponds to the number of polymerized functions per photon absorbed. It is calculated from Rp values.

$$\phi p = \frac{Rp(\text{mol } L^{-1} S^{1}) \; l(\text{cm})}{10^{3}(1-e^{-23A}) \; I_{o} \; (\text{einstein } \text{cm}^{-2}S^{-1})}$$

Where A is the absorbance at 363.8nm of the sample and l the film thickness. From ϕp values, the kinetic chain length (ν) of the polymerization can then be evaluated, once the initiation quantum yield (ϕi) is known since $= \phi p/\phi i$

ϕi can be evaluated from the equation as shown below:

$$Ri = \phi i \;\; Io \;\; (1-e^{-2.3A})$$

Where Ri = Rate of initiation

Io = Intensity of light

A = Absorbance

ϕi = Initiation quantum yield

Effect of Film Thickness On The Rate of Polymerization

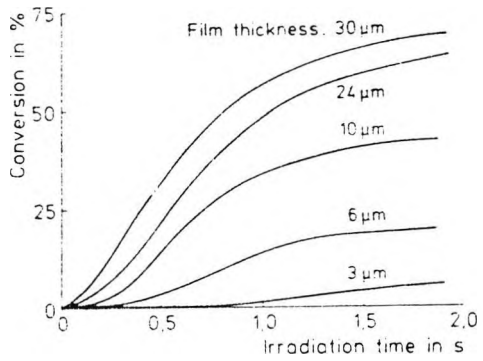

Fig 2.3 Effect of film thickness on the photopolymerization profiles recorded by RTIR spectroscopy for a polyurethane-acrylate.

Fig 2.3 Shows the polymerization curves obtained by varying the thickness of the resin film coated onto the NaCl plate.

As the film thickness decreased to a few µm, the polymerization efficiency dropped drastically. Such a drastic effect was not observed when operating in a nitrogen-saturated atmosphere. It must therefore result from a more pronounced oxygen inhibition in thin films due to a faster replacement of the oxygen consumed by atmospheric oxygen that diffuses through the surface.

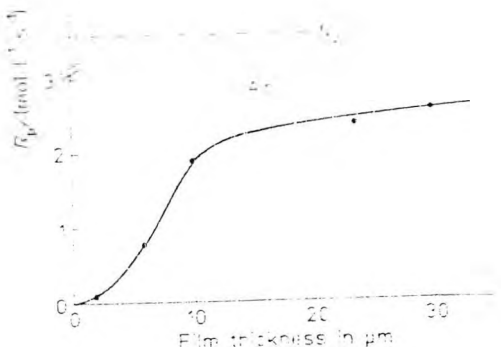

Fig. 2.4 Dependance of the rate of polymerization Rp on the film thickness.

The observed variation of Rp with the film thickness appears to be strongly dependant on the light intensity (I), sharpening the profile as I increases, because of a shorter exposure time during oxygen diffusion occurs.

Advantages of RTIR Spectroscopy

Real-time monitoring

Cure reactions occurring in a fraction of a second can be followed continuously from the very beginning of the process to its ultimate stage. The sensitivity of I.R spectroscopy allows very small changes in the monomer concentration to be detected e.g. less than 1% conversion in a 1μm thick coating (10 μg).

High light intensity operations

RTIR spectroscopy permits the study of the kinetics of cure reactions over a broad range of light intensity, in particular those performed under intense light source and in the presence of air, i.e. experimental conditions very similar to those found in most industrial u.v curing operations.

Quantitative Results

RTIR spectroscopy is the first technique to provide in real-time quantitative information about the important kinetic parameters, induction period, polymerization rate, photosensitivity, residual unsaturation content.

Practical advantages

Since it is based on i.r. spectroscopy, the RTIR technique proved to be reliable and highly sensitive, leading to accurate and reproducible results.

Properties measurements

The cured coating can be examined at any moment of the reaction for evaluation of some of its physical characteristics, like the hardness, abrasion resistance, flexibility, heat resistance.

Versatility

A wide application range is open to this technique of kinetic investigation, since essentially any fast polymerizing system, clear or pigmented, can be analysed in real-time. Besides, it is not restricted to u.v. initiation but can be extended to other types of radiation like lasers, microwaves, electron beams etc. [18,19].

Bulk Polymerization

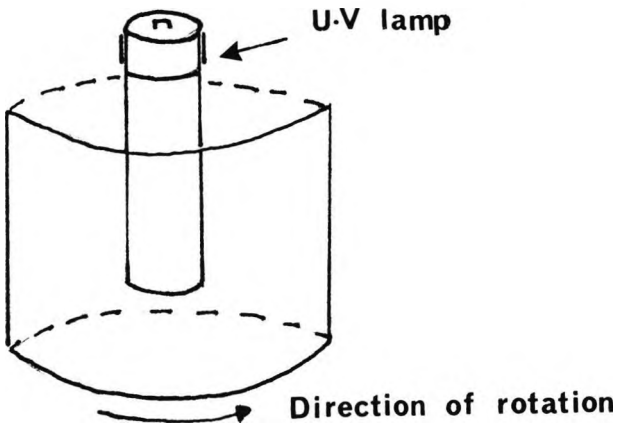

Fig. 2.2 Apparatus used in bulk polymerization

Bulk polymerization consists of a rotary system containing up to six sample tubes, which rotates around a u.v. light source.

The time is taken for the samples to polymerise. The small tubes will contain samples which are normally made up of N-methyldiethanolamine (1g), trimethylolpropane triacrylate (1g) and a photoinitiator.

The amount of photoinitiator used is calculated from the equation shown below.

constant x molecular weight = amount of photoinitiator/10cc dichloromethane

The amount of polymer formed was measured by (i) weighing the amount of polymer formed or (ii) by dissolving the polymer in an appropriate solvent and then removing the solvent under vacuum.

Analytical Techniques

i) Microanalysis - Carlo Erba Model 1106 Elemental Analyser

ii) U.V. Spectrometer - Perkin-Elmer Lambda 5, double beam u.v./visible spectrometer

iii) Nuclear Magnetic Resonance - Jeol PMX 60
Jeol PMX 100, Jeol 270

iv) Perkin - Elmer Infra-red spectrometer:- KBr discs.

Moving Belt System (Colordry)

Colordry

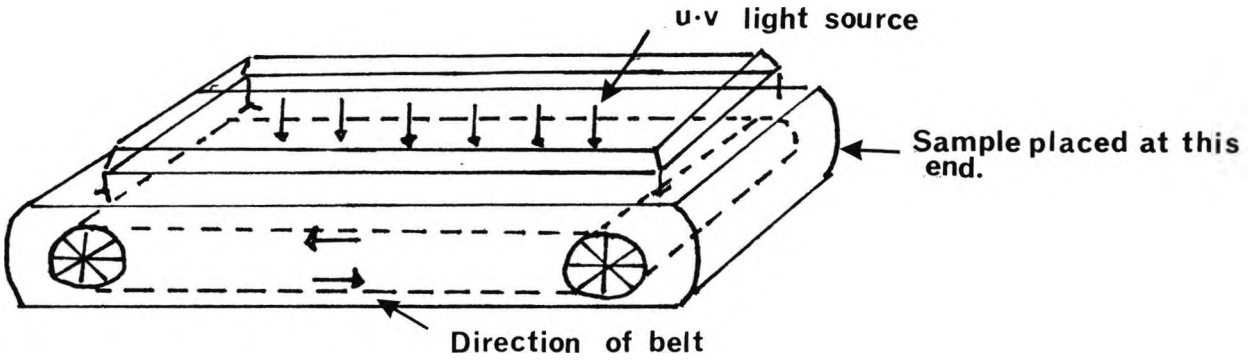

Fig. 2.3 A Moving Belt System

Preparation of the sample was carried out by creating a thin film on paper.

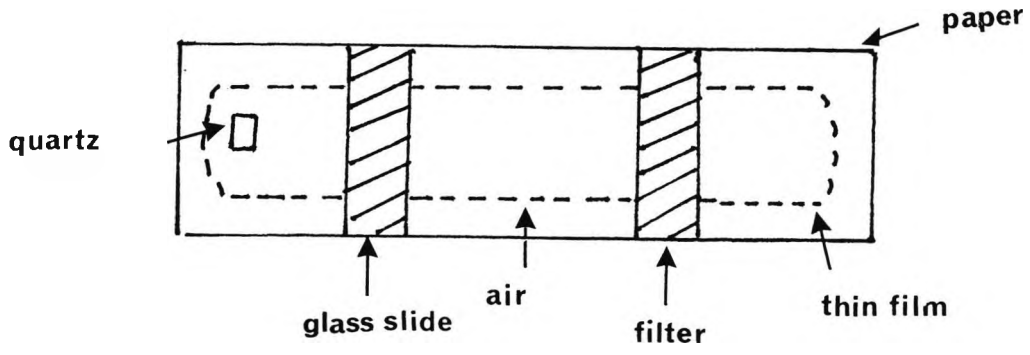

Fig. 2.4 A diagram showing a prepared thin film before exposure to u.v. radiation.

The thin film was then exposed under different environments.

i) Quartz:- Which lets u.v. light through, efficiency of cure determined by transmittance of light.

ii) Glass Slide:- The slide is touching the film, and also absorbs u.v light. These two properties show the effect on the rate of cure, in the absence of 0_2 and u.v. light. The cut-off point for a glass slide is 330nm

iii) Air:- Thin film was exposed to air; which shows effect of 0_2 on the rate of cure.

iv) Filter:- A filter was placed on the film by means of a glass slide raised above the film ; showing the effect of oxygen and the absence of u.v. light on the rate of cure.

The sample is placed at one end of the belt which is then passed under the u.v. source at a relative speed. This is recorded as one pass under the colordry.

The speed of the belt can be increased or decreased depending on the rate of cure, therefore decreasing or increasing the exposure time under u.v. light. The films so produced were usually tested for hardness to assess whether cure had taken place. This was carried out using the test for tackiness (i.e. thumb-print test).

The thickness of the film can be varied according to the K-bars (draw bars) used.

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CHAPTER THREE

DEFEATING OXYGEN INHIBITION OF CURE

DEFEATING OXYGEN INHIBITION OF CURE

3.1 INTRODUCTION

Free-radical polymerization processes are widely used in the printing and surface coatings industries. A problem with free-radical as opposed to the ionic process is the oxygen inhibition of cure.

The latter can be attributed to oxygen scavenging the growing polymeric radicals and the radicals derived from the excited state of the initiator[1].

Scheme 1.

A. PI + Light $\longrightarrow$ PI*

PI* :- Photoinitiator is raised to an electronically excited state.

B. PI $\longleftarrow$ PI* $\xrightarrow{O_2\ (Q)}$ PI

$\downarrow$

I* (I^+)

The lifetime of PI* is short, generally less than 10^{-6}s. During this time, PI* may be partitioned among several processes including:

1. Decay back to PI (with emission of light (or heat)
2. Excited state quenching by O_2, or by a quenching agent (Q).
3. A chemical reaction yielding the initiator species such as I· or I^+ as shown above.

Oxygen occupies a special position in organic photochemistry. It is present in all reaction mixtures exposed to the air, it is a good electron acceptor forming the reactive O_2^- radical anion and it has, unusually a triplet ground state and a very low energy excited singlet state (92.4kJ mol^{-1}) [2].

The last property makes oxygen a very good triplet quencher and excited singlet oxygen is very reactive towards organic compounds.

The majority of the commercial photoinitiators or photoinitiating systems form radicals by direct fragmentation or by bimolecular H-abstraction through their lowest triplet excited state.

As a consequence, the radical formation has to compete with quenching of the excited state by oxygen when the polymerization is carried out in air.

Fortunately, most photoinitiators that survived the extensive screening procedures to reach the stage of commercialisation appear to react to form extremely short-lived triplet excited states ($\tau < 10^{-8}$s) which are not prone to quenching by oxygen from the surrounding air.

Moreover, some photoinitiator systems generate radicals from very efficiently formed exciplexes.

However, oxygen is also known to react readily with carbon-centred radicals, both from the initiator and from growing polymer chains.

The decomposition of benzoin methyl ether has been reported to proceed with an increase in quantum yield in the presence of oxygen, presumably because the radicals generated are prevented from recombining to the starting material, through trapping by oxygen. However, this leads to less reactive peroxy radicals from the standpoint of initiation and as a consequence a slowing down of the rate of polymerization.[3]

This effect is known as oxygen inhibition. It has been concluded that oxygen inhibition results in:

1) an induction period
2) a reduced rate of polymerization
3) an incomplete consumption of unsaturated functionalities

Oxygen inhibition is most pronounced in the u.v. curing of coatings, owing to the unfavourable surface to volume ratio thereby allowing for optimal oxygen diffusion into the film.

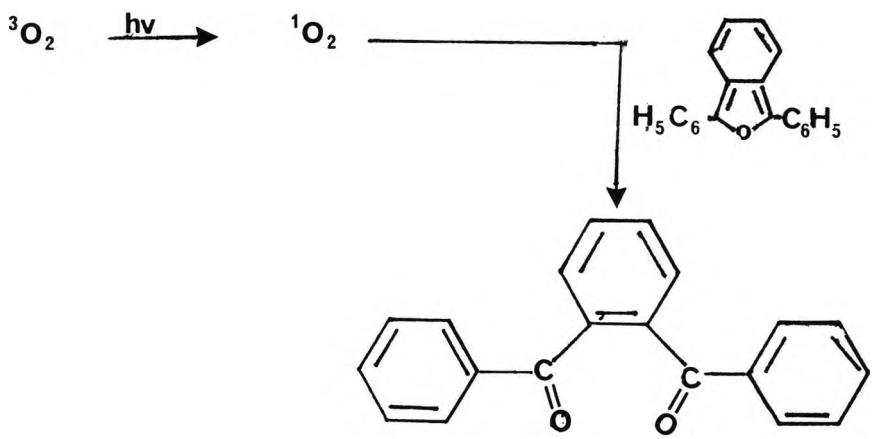
Apart from excluding oxygen by means of an inert atmosphere (e.g. N_2 - blanketing), oxygen inhibition can also be minimised by increasing the intensity of the light source and by the use of various types of additives. Paraffin waxes, for instance have been shown to equal the beneficial effect of an inert atmosphere by acting as a barrier to oxygen. Oxygen inhibition has reportedly been reduced also by the use of additives which eventually lead to depletion of the oxygen present.

Aromatic ketone/tertiary amine combinations are well known examples.

The radicals ultimately derived by H-abstraction from the tertiary amine can act as initiating species on the one hand, and on the other as a trapping agent for the oxygen present. Moreover, the inhibiting oxygen may even be turned into various species capable of initiating of polymerization.

The beneficial effect of added tertiary amines on the curing efficiency of photoinitiators which undergo direct fragmentation (e.g. benzoin ethers, benzil dimethylketal) can be attributed to a similar reaction sequence.

Another interesting approach to overcome oxygen inhibition consists of a dye, a trapping agent for singlet oxygen and a photoinitiator e.g. benzil dimethylketal.



The free-radical chain mechanism of autoxidation [4] has been established by extensive studies of the oxidation of pure hydrocarbons e.g. rubbers and other polymers.
The reaction is autocatalytic because hydroperoxide(ROOH) is formed as the primary product of the reaction and is also a source of free-radicals required to initiate the process.

The formation of a hydroperoxide in the presence of a radical generator involves a removal of a hydrogen atom as the rate-determining step of the autoxidation chain reaction.

$$\text{Initiator} \longrightarrow R\cdot$$
$$R\cdot + O_2 \longrightarrow ROO\cdot$$
$$ROO\cdot + R'H \longrightarrow ROOH + R'$$

The rate of reaction is associated with the stability of the hydrocarbon free-radical R·. In general substituents which stabilise R· give rise to high yields of the hydroperoxide.

Free-Radical Polymerization

Photoinitiators tend to absorb light in the ultraviolet - visible spectral range. The light energy is converted into chemical energy in the form of reactive intermediates such as free-radicals and reactive cations, which subsequently initiate polymerization, [5].

Photoinitiated polymerization and cross-linking of monomers, oligomers and polymers constitute the basis of various commercial processes including photoimaging, u.v. curing of coatings and inks.

Generation of Active Species

In order for light to initiate polymerization in a system of monomers, it is necessary that the molecules to be acted upon are capable of generating active species, either free-radical or Lewis or Brönsted acids.

The first step is a photophysical process in which the molecule containing a chromophoric group is brought to the excited state and therefore to a greater energetic content in order to be activated. This is possible when the absorption spectrum of the photoinitiator overlaps completely or partially with the emission spectrum of the light source and at the same time is significantly different from the absorption spectra of the monomers and pigments.

Photoinitiators for Free Radical Polymerization

These are used to initiate the polymerization of ethylenically unsaturated compounds (vinyl, acrylic, and other monomers).

Upon formation, the radical active species are in a "cage" formed by the substrate molecules, the viscosity of which inhibits the separation and diffusion of the radicals. Therefore the radicals can ultimately recombine in various combinations or can disproportionate within the cage. When the primary radicals are able to escape from the cage they interact with the monomers, beginning the chain reaction which concludes in the formation of the polymer structure. The speed of this reaction depends upon the concentration of the monomer([M]) and the active species ([R.]).

The degree of reactivity of radical initiators towards the monomer is represented by a constant (Ki). Vi is defined as the rate of initiation.

$$Vi = Ki\,[R.][M]$$

It has been experimentally demonstrated that the speed of polymerization depends both on the monomer concentration and on the square root of the photoinitiator concentration and is represented by the equation.

$$Vp = Kp\,[M]\sqrt{\frac{I_o\,\phi Edc}{K_t}}$$

Vp = Rate of propagation

Io = Incident light intensity

ϕ = Quantum Yield of reaction

E = Molar absorptivity coefficient

c = Concentration

d = Path length

Where Kp and Kt are the propagation and the termination constants respectively.

The majority of the photoinitiators which have been studied for triggering free-radical photoinitiated polymerization are aromatic ketones or aromatic aliphatic ketones. This is due to the fact that this chemical class has absorption spectra ranging from 250 to 400 nm and therefore the energetic requirements necessary to initiate photochemical processes.

Within this category there are two types of photoinitiators, the first generate primary radicals by means of homolytic cleavage of a bond inside the molecule itself, while in the second, a hydrogen radical is abstracted from a suitable donor with the formation of a pair of radicals originating from two different molecules.

Intramolecular Bond Cleavage (Type A)

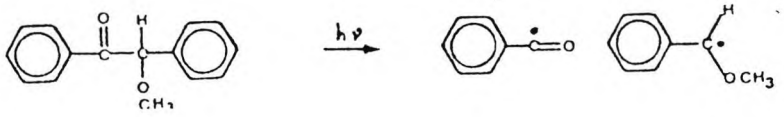
The available excitation energy (71-73 kcal/mole) is sufficient for the intramolecular cleavage of a chemical bond.

There are a great number of compounds in this class, the majority of which are derived from acetophenones.

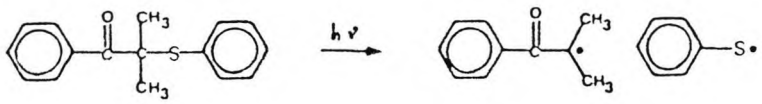
In general electron donor substituents favour alpha cleavage (Norrish type I mechanism), while thio derivatives diminish alpha or favour beta cleavage. Other important classes which have been demonstrated as effective for intramolecular scission include acylphosphine oxides. With particular structures it is also possible to have different fragmentation mechanisms which cause a gamma cleavage, as in certain acyloxime esters.

Fragmentations

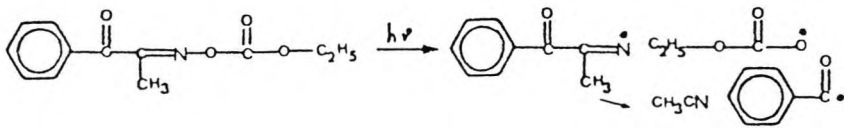
1. Alpha (Norrish 1)



2. Beta



3. Gamma



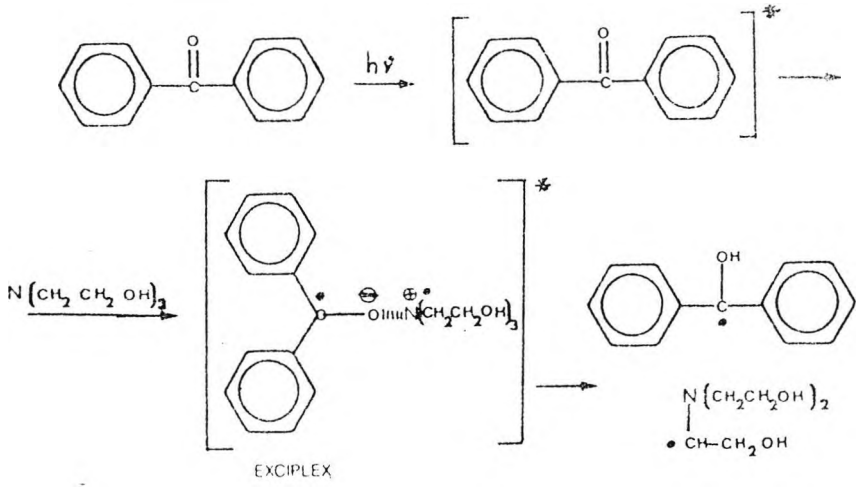
Extraction of Intermolecular Hydrogen (Type B)

Photoinitiators of this type include aromatic ketones such as benzophenones, thioxanthones, quinones and benzils.

For these the excitation energy (max 69 kcal/mole) is not usually sufficient to cause intramolecular cleavage of chemical bonds. Nonetheless, aromatic carbonyls in the excited state have a strong tendency to interact with electron donors (particularly with

molecules bearing hetero-atoms such as nitrogen or oxygen). Thus they form donor-acceptor compounds called exciplexes. When possible the exciplexes decompose into semi-benzpinacol radicals (which generally either pair or end the chains) and alpha amino (or oxa) alkyl radicals through an intramolecular transfer of hydrogen.

Hydrogen Abstraction Mechanism



While the carbonyl undergoes a light-induced reduction, the alpha amino-alkyl radical is the effective initiator species. Tertiary amines are most often used, either aliphatic or aromatic - aliphatic.

The advantages of using hydrogen transfer systems, rather than the fragmentation systems are derived from the absence of quenching by the oxygen if the quantity of amine is sufficiently high.

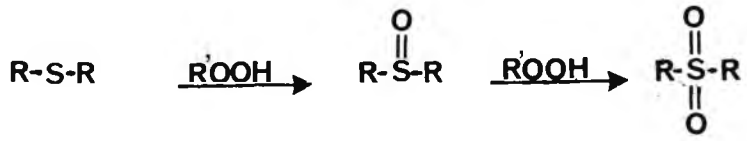
Disadvantages on the other hand are that the speed of polymerization is slower, the films yellow in photo-oxidative conditions, and polymerizable mixtures are sometimes insufficiently stable during storage.

Sulphur-Containing Antioxidants

Denison [6] has made a careful study of the effects of sulphides as antioxidants in purified hydrocarbon oils.

Some of the more effective inhibitors of antioxidation caused an initial rapid uptake of oxygen, followed by autoinhibition.

In separate experiments, it was shown that the antioxidant active sulphides had the power to destroy hydroperoxides and were themselves converted to sulphoxides and sulphones in the process.

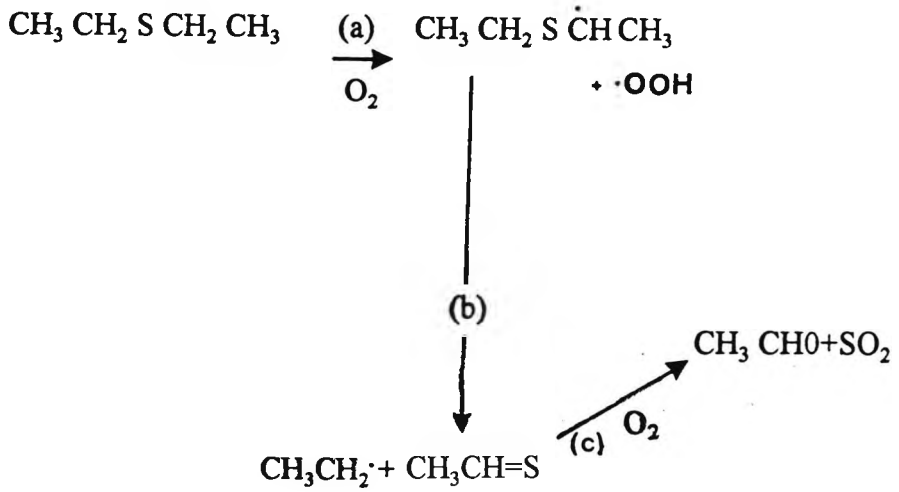


Bateman and his co-workers [7] have more recently found that a variety of simple sulphoxides and thiosulphinates are also effective antioxidants and have a generally higher order of activity than the sulphide from which they are derived.

Denison and Condit [8], had shown that in the case of diacetyl sulphoxide, both the sulphoxide and sulphone were found to autoxidise at a faster rate than the hydrocarbon oil.

However, the sulphone did show some autoinhibition, and the isolation of water-soluble strong acids from the autoxidation products suggests that the inhibitor responsible for sulphide autoinhibition may be formed either through the sulphone or more probably as a by-product during its formation.

Cullis and Rosellar, [9,10] have found that the oxidation of dialkyl sulphides is autoinhibited at temperatures above 170^{o}c due to the formation of SO_2 as one of the reaction products. The mechanism proposed to account for its formation is given by the reaction sequence



SO_2 is also formed from dimethyl disulphide.

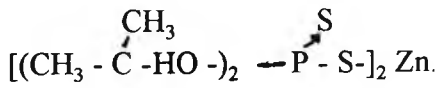
In earlier reviews of basic oxidation processes [11] in elastomers and the fundamentals of stabilisation against thermal autoxidation, it has been noted the two ways in which stabilisers can retard the above oxidation process. They can destroy hydroperoxides and thus reduce the rate of peroxide initiation or they may intercept the chain-propagating free-radicals and thus terminate the chain mechanism.

Scott [12] has classified antioxidants as preventive and chain-breaking respectively. Both types include a variety of compounds that can act in several different ways.

Preventive A. Light absorbers

B. Metal deactivators

e.g. Zinc dialkyl dithiophosphates were found to decompose hydroperoxides



C. Peroxide decomposers (non-radical products)

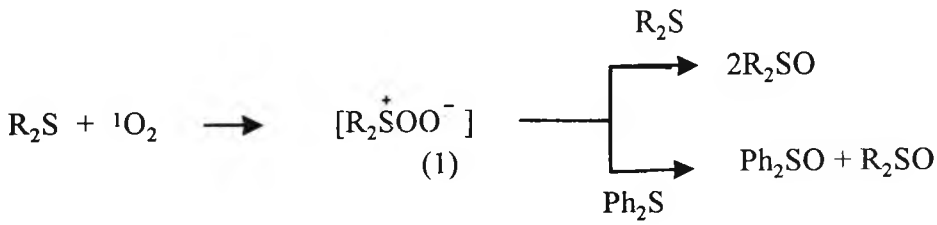
Chain-breaking A. Free-radical traps

B. Electron donors

C. Hydrogen donors

The rate of oxidised organic sulphur compounds as preventive antioxidants relates primarily to their activity as hydroperoxide decomposers to form non-radical products.

In all cases the antioxidant function is preceded by an initial pro-oxidant stage. The pro-oxidant effects are considerable in the case of dialkyl sulphides and result from homolytic cleavage of hydroperoxides induced by oxidised sulphur compounds. Several reports state that the reaction of 'photoxygenation of sulphide' carried out by Foote [13] shows that the primary product of sulphide photoxygenation is a zwitterionic peroxide (a persulphoxide) (1).



The reaction results from the nucleophilic attack of the suphide on $^1O_2$.

The evidence presented was that this intermediate could be trapped by various agents. Among these was diphenyl sulphide, itself unreactive toward $^1O_2$, which gave diphenyl sulphoxide and dialkyl sulphoxide as products of the trapping reaction.

A more recent way of overcoming oxygen inhibition as yet unproved in thin films is that of the use of sulphur-containing acrylates. The compounds were prepared to

increase the rate of cure as compared with normal acrylates. The sulphur acrylates have the function of actually destroying any peroxides formed in the polymerization process. The problem encountered in certain formulations e.g. quinoxalines (will be discussed later) is the formation of hydroperoxides. It is not desirable to have lithographic plate formulations containing peroxides (poor shelf life). Sulphides would transform peroxy radicals into alkoxy radicals (which can initiate polymerization) and reduce hydroperoxides to alcohols.

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot + R'\text{-}S\text{-}R' \longrightarrow RO\cdot + R'\text{-}\overset{\overset{O}{\|}}{S}\text{-}R'$$

$$RO\cdot + R''H \longrightarrow ROH + R''\cdot$$

$\downarrow$

Can initiate polymerization

Of a great number of publications devoted to multiacrylates relatively few consider sulphur-containing acrylates. Of the few reports, work was carried out by Andrzejewska and Wilczynski [14,15] into sulphur-containing acrylates.

3.2 RESULTS AND DISCUSSION

The results obtained from the Colordry and real-time infra-red spectroscopy were from formulations containing

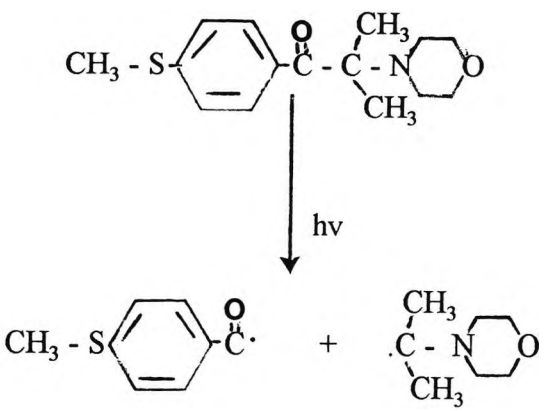
i 1% w/w:- photoinitiator

ii 10% w/w:- N-methyldiethanolamine

iii Monomer:- an acrylate

i) The photoinitiator used was Irgacure 907 A.

A



1% w/w of the photoinitiator was used in the formulations. This photoinitiator was used because it was commercially available, and a very efficient initiator. Only one initiator was used as the rates of polymerization of the acrylates were compared, rather than the efficiency of the initiator itself.

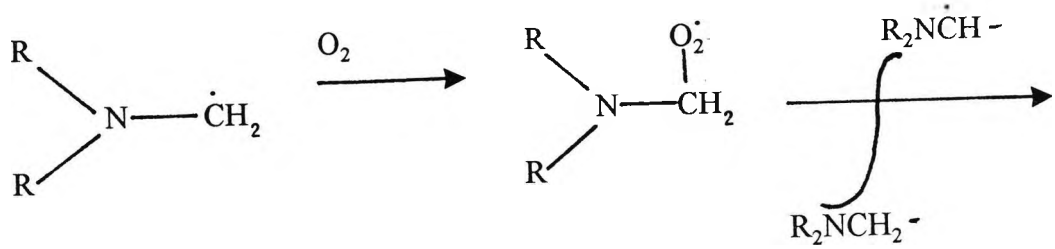
ii) Amines are incorporated into formulations to increase the rate of cure by minimising oxygen inhibition i.e. as a synergist. The basic concept lying behind the design of most of the photoinitiators is that they would in an excited state abstract a hydrogen from a tertiary amine (i.e. a type II initiator). This would probably occur via electron transfer to give an α-aminoalkyl radical which would initiate polymerization.

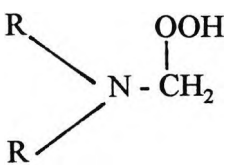
$$PI^* + (R\,CH_2)_3\,N: \rightarrow PIH + \dot{R}CHN\,(CH_2R)_2$$

PI* = Photoinitiator in the excited state

The presence of oxygen, reduces the rate of cure by quenching excited states, scavenging the radicals formed by the initiator and scavenging the radicals of the growing polymer chain.

A second effect of the amine is its role in reducing the effect by oxygen.





R = CH_2CH_2OH

The benefit of amines is that they can quench singlet oxygen and if part of the quenching is chemical, - aminoalkyl radicals are produced. If the cure is sufficiently fast, the amine may be able to deplete oxygen at a rate which is greater than the diffusion into the film. The problem with using amines is that they can cause the photoyellowing of the films.

Previous work conducted by Davidson [16,17,18,19,20], showed that in the case of N-alkylaminoethanols hydrogen abstraction occurs at the alkyl group. Also Davidson and Bartholomew had shown that amines undergo photosensitised oxidation reactions [21,22,23].

U.V. Curing of Acrylates in The Absence of an Amine

The curing of acrylates was carried out using a moving belt system (i.e. Colordry).

2,2 - Thiodiethyl diacrylate (1) was tested in the absence of an amine and the results show that when the film was covered by quartz (i.e. in the absence of oxygen and presence of u.v. visible light), a tack-free film was produced within twelve passes under the colordry. Under aerobic conditions, a tack-free film was not formed after thirty passes under the colordry. This would suggest that the sulphur component of the acrylate does not seem to act as an antioxidant.

1. $CH_2 = CH\ CO_2CH_2CH_2SCH_2CH_2O_2CCH = CH_2$

2,2 - Oxydiethyl diacrylate and 1,4 butanediol diacrylates showed similar results, in the presence and absence of air. The purpose of preparing the oxy derivative and butane-1,4-diol derivative was to compare the rates of cure in the absence of sulphur component in the diacrylate. Due to the poor performance of 2,2 - thiodiethyl diacrylate, it was decided to prepare various acrylates with an increase in the sulphur content of the acrylate e.g. 3,6 - dithia - 1,8 - octane diacrylate and 2,2 - dithiodiethyl diacrylate. The purpose of increasing the sulphur content of the acrylate was to prove whether the rate of polymerization would increase by the antioxidant property of the sulphur component.

$$CH_2 = CH\ CO_2CH_2CH_2SS - CH_2CH_2O_2CCH = CH_2$$

2,2 - Dithiodiethyl diacrylate

$$CH_2 = CH\ CO_2CH_2CH_2SCH_2CH_2\ SCH_2CH_2O_2CCH = CH_2$$

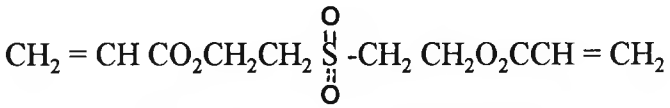
3,6 - Dithia - 1,8 - Octane diacrylate

Under aerobic conditions (i.e. quartz) 3,6 - dithia - 1,8 - octane diacrylate formed a tack-free film in nine passes under the colordry. Whilst 2,2 - dithiodiethyl diacrylate formed a tack-free film in twelve passes.

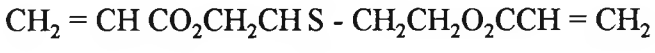
When the film was covered by a touching glass slide (i.e. the result shows the effect of the rate of polymerization in the absence of air and u.v. light (λ >330nm)) the sulphur-containing acrylates did not polymerize efficiently.

3,6 - Dithia - 1,8 - Octane diacrylate, 2,2 - dithiodiethyl diacrylate, butane - 1,4 - diol diacrylate, 2,2 - oxydiethyl diacrylate and 2,2 - thiodiethyl diacrylate did not form a tack-free film in air and in the absence of N-methyldiethanolamine the antioxidant property does not seem to be apparent in the curing of these sulphur-containing acrylates. The reason for the inefficient curing is due to oxygen scavenging the radicals formed, inhibiting the polymerization of the acrylate.

2,2 - Sulphonyldiethyl diacrylate was initially prepared to compare the rates of polymerization of an oxidised sulphur species with 2,2 - thiodiethyl diacrylate.

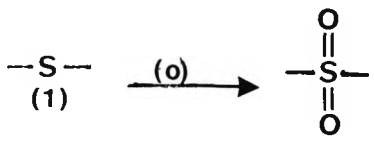


2,2' - Sulphonyldiethyl diacrylate



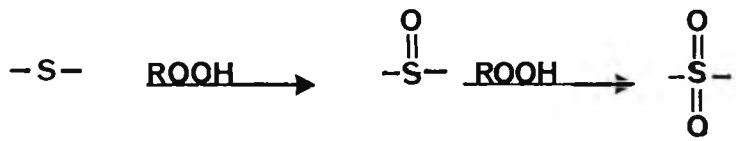
2,2' - Thiodiethyl diacrylate

Theoretically speaking, as the sulphonyl derivative is an oxidised equivalent of 1,



it is not possible for the sulphonyl derivative to destroy hydroperoxides, to form a further oxidised species. Whilst the 2,2 - thiodiethyl diacrylate should polymerize

faster in air, as the sulphur component can be oxidised to form the sulphoxide or sulphone.



The results show that 2,2 - sulphonyldiethyl diacrylate shows some resistance towards oxygen and polymerizes faster in air.

The acrylates were also tested in the presence of a filter (i.e. a raised glass slide). The results show the effect of the rate of cure, in the presence of air and absence of u.v. light (λ >330nm).

The acrylates were compared with a commercial system e.g. Irgacure 907 and 2 - ethyl -2- (hydroxymethyl) - 1,3 - propanediol triacrylate, TMPTA is a triacrylate, and obviously will polymerize a lot faster.

In the presence of a filter, the commercial system formed a tack-free film in ten passes under the colordry. Whilst the sulphur-containing acrylates did not form a film when covered by a filter (i.e. raised glass slide). The result shows the effect of oxygen on the rate of polymerization; it does seem apparent that the sulphur component present in the acrylate does not act as an antioxidant.

It was then proposed to increase the sulphur chain even further and the sulphur content of the acrylate, and see if this affects the rate of polymerization. Various polysulphide acrylates were tested.

ZL1866 and ZL2244 are polysulphide acrylates and were provided by Morton Thiokol.

The polysulphide acrylates are made up of mixtures of mono,di and triacrylates of the polysulphide LP3.

LP3:- HS-($C_2H_4OCH_2OC_2H_4Sx$)n - $C_2H_4OCH_2OC_2H_4$-SH

In the absence of a synergist, ZL1866 and ZL2244 formed a tack-free film within one pass under anaerobic conditions. In the presence of air, the polysulphide acrylates formed a tack-free film in one pass under the colordry. This was compared with the commercial system e.g. Irgacure 907 and TMPTA, which forms a tack-free film within five passes under the colordry. The polysulphide acrylates polymerize remarkably faster in air.

One significant factor is that they polymerize to form a tack-free film, in the absence of a synergist e.g. N-methyldiethanolamine. The speed of the moving belt was increased to 60 and then to 100ft/min, in both cases a tack-free film was produced in one pass under the colordry.

The results show that an increase in the sulphur content of the acrylate does play a vital role in the polymerization process whereby the sulphur compound acts as an antioxidant by decomposing the peroxides formed, therefore increasing the rate of polymerization.

U.V. curing of acrylates in the presence of an amine

The results obtained show that 2,2 - thiodiethyl diacrylate in the presence of N-methyldiethanolamine under aerobic conditions forms a tack-free film within five passes under the colordry.

Butane - 1,4 - diol diacrylate does not polymerize in air. The results show that 2,2 - thiodiethyl diacrylate polymerizes a lot faster than butane - 1,4 - diol diacrylate in air. This could be due to a combination of both the synergistic effect of the amine and the antioxidant property of sulphur.

3,6 - Dithia - 1,8 - octane diacrylate and 2,2 - dithiodiethyl diacrylate form a tack-free film within nine passes in air. The presence of N-methyldiethanolamine increases the rate of polymerization due to oxygen inhibition. Under anaerobic conditions 3,6 - dithia - 1,8 - octane diacrylate and 2,2 - dithiodiethyl diacrylate polymerize efficiently, due to the absence of oxygen.

If the result obtained from 2,2 - thiodiethyl diacrylate is compared with 2,2 - oxydiethyl diacrylate in air, it can be seen that the rate of polymerization is greatly increased in the case of 2,2 - thiodiethyl diacrylate. This could be due to a combination of both the synergistic effect of the amine and the antioxidant property of sulphur. One surprising result is that 2,2 - sulphonyldiethyl diacrylate polymerizes to form a tack-free film in air. A tack-free film was formed after four passes under the colordry. One would have expected the opposite result.

ZL1866 and ZL2244 in the presence of N-methyldiethanolamine form a tack-free film in one pass under the colordry.

The results show that the polysulphide acrylates and Irgacure 907 provide an efficient curing system in the presence of an amine.

U.V. Curing of acrylates in the absence of an amine

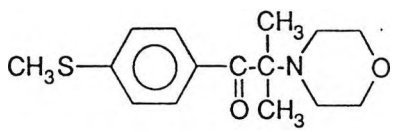
A

Samples	Number of Passes Under Colordry							
	Butane - 1,4 diol diacrylate	2,2 Oxydiethyl diacrylate	2,2 - Thiodiethyl diacrylate	2,2 - Sulphonyl diethyl diacrylate	2,2 - Dithioidiethyl diacrylate	3,6 Dithia -1,8-octane diacrylate	Irgacure 907 + TMPTA	TMPTA
Quartz	9	13	12	9	9	12	1	10
Slide	10	15	13	22	16	14	1	45
Air	30+	30+	30+	9	28	30+	5	50+
Filter	30+	30+	30+	24	30+	30+	10	50+

B

Samples	ZL1866	ZL2244	Speed of Belt (ft/min)
Quartz	1	1	10
	1	1	60
	1	1	100
Slide	1	1	10
	1	1	60
	1	1	100
Air	1	1	10
	1	1	60
	1	1	100
Filter	1	1	10
	1	1	60
	1	1	100

a Normal Speed of belt :- 10 ft/min
b Photoinitiator - Irgacure 907



TMPTA = 2 - Ethyl - 2 (hydroxymethyl) -1,3- propanediol triacrylate

U.V. Curing of acrylates in the presence of an amine

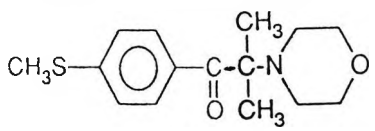
A

Samples	Number of Passes Under Colordry							
	Butane - 1,4 diol diacrylate	2,2 Oxydiethyl diacrylate	2,2 - Thiodiethyl diacrylate	2,2 - Sulphonyl diethyl diacrylate	2,2 - Dithioidiethyl diacrylate	3,6 Dithia -1,8-octane diacrylate	Irgacure 907 + TMPTA	TMPTA
Quartz	3	4	2	6	7	7	1	2
Slide	3	6	4	8	9	8	1	2
Air	30+	15	5	4	9	9	2	40+
Filter	30+	30+	20	6	18	22	2	40+

B

Samples	ZL1866	ZL2244	Speed of Belt (ft/min)
Quartz	1	1	10
	1	1	60
	1	1	100
Slide	1	1	10
	1	1	60
	1	1	100
Air	1	1	10
	1	1	60
	1	1	100
Filter	1	1	10
	1	1	60
	1	1	100

a Normal Speed of belt :- 10 ft/min
b Synergist :- N - methyldiethanolamine (10% w/w)
c Photoinitiator - Irgacure 907 (1% w/w)



TMPTA = Trimethylolpropane triacrylate
(2 - ethyl - 2 (hydroxymethyl) -1,3- propanediol triacrylate)

Real - Time Infra - Red Spectroscopy

Samples	Atmosphere	Rp (%/s)	Total Con-version (%)	R.U. %	I.P. (secs)
2,2'-Thiodiethyl diacrylate + Irgacure 907 + amine	Absence of air	3.64	90	10	2
2,2'-Thiodiethyl diacrylate + Irgacure 907	Presence of air	1.5	24	76	6
2,2'-Thiodiethyl diacrylate + Irgacure 907	Absence of air	2.16	81	19	3
3,6-Dithia-1,8-Octane diacrylate + Irgacure 907 + amine	Absence of air	1.2	80	20	3
3,6-Dithia-1,8-Octane diacrylate + Irgacure 907 + amine	Presence of air	0.4	57	43	5
3,6-Dithia-1,8-Octane diacrylate + Irgacure 907	Absence of air	3.23	69	31	4
2,2'-Sulphonyldiethyl diacrylate + Irgacure 907 + amine	Absence of air	0.9	33	67	5
2,2'-Sulphonyldiethyl diacrylate + Irgacure 907 + amine	Presence of air	1.12	56	44	6
2,2-Oxydiethyl diacrylate + Irgacure 907	Absence of air	2.25	80	20	6
2,2'-Oxydiethyl diacrylate + Irgacure 907	Presence of air	---	26	74	8
Butane-1,4-diol diacrylate + Irgacure 907	Absence of air	1.05	83	17	6
Butane-1,4-diol diacrylate + Irgacure 907 + amine	Absence of air	3.5	85	15	4

1) Rp = Rate of polymerisation (% / s)
2) RU= Residual Unsaturation Content (%)
3) I.P.= Induction period (seconds)
4) Amine used=N-methyldiethanolamine (10% w/w)
5) Photoinitiator used=Irgacure 907 (1% w/w)

Samples	Atmosphere	Rp (%/s)	Total Con-version (%)	R.U. %	I.P. (sec)
ZL1866 + Igacure 907	Absence of air	19	70	30	---
ZL1866 + Igacure 907 + amine	Presence of air	12	90	10	---
ZL2244 + Irgacure 907 + amine	Absence of air	25	100	---	---
ZL2244 + Irgacure 907 + amine	Presence of air	5.3	85	15	---
ZL2244 + Irgacure 907	Absence of air	33	95	5	---
ZL2244 + Irgacure 907	Presence of air	13	100	---	---

Real-Time Infrared Spectroscopy

The results from real-time infrared spectroscopy (R.T.I.R) were obtained using similar formulations as for the colordry. The substrate used was sodium chloride plates.

2,2 - Thiodiethyl diacrylate (TEDA) in the presence of N-methyldiethanolamine and under aerobic conditions has a rate of polymerization (Rp) of 3.64% /s and a total conversion of 90%.

If this result is compared with TEDA in the absence of N-methyldiethanolamine and air, there is a reduction in the rate of polymerization and total conversion. This is due to the absence of the synergist and also oxygen playing more of a role in the reduction of the rate of polymerization.

TEDA was then tested in the absence of an amine and in the presence of air, when it showed a considerable reduction in the rate of polymerization. The result shows that sulphur and its antioxidant property does not play a vital role as one would have expected.

3,6 - Dithia - 1,8 - octane diacrylate in the presence of an amine and air, has an Rp value of 0.4%/s and a total conversion of 57%. In the absence of amine and air, there is an increase in the rate of polymerization and total conversion.

If one compares the results, it shows the effect of oxygen on the free-radical polymerization process.

2,2 - Sulphonyldiethyl diacrylate was tested under anaerobic conditions and in the presence of N-methyldiethanolamine. The result shows very little polymerization and a total conversion of 37%. Whilst in the presence of air and amine, there is an increase in the Rp value and total conversion. This supports the result obtained from the moving belt system (colordry), whereby in the presence of air, there is an increase in the rate of polymerization. One would expect the opposite result-

2,2 - Oxydiethyl diacrylate was tested in the absence of an amine, and absence of air. The rate of polymerization is 1.05% /s and a total conversion of 83%. If this result is compared with TEDA under similar conditions it is shown that there is an increase in the rate of polymerization, which may be due to the presence of the sulphur component, acting as an antioxidant.

1,4 - Butandiol diacrylate in the absence of an amine and air has an Rp value of 1.05%/s and a total conversion of 83%.

If this result is compared with the result obtained under anaerobic conditions and in the presence of N-methyldiethanolamine, the presence of the amine increases the rate of polymerization, but does not affect the total conversion.

ZL1866 in the absence of a synergist and in the presence of air formed a tack-free film and had a total conversion of 70% and a rate of polymerization of 19%/s.

In the absence of air and a synergist, the total conversion was 90%. There was no induction period on the kinetic curve. This shows the effect of the sulphur component present in the acrylate, acting as an antioxidant by destroying the peroxides formed.

ZL2244 in the presence of an amine and air has a total conversion of 100% and an Rp value of 25%/s. Whilst in the absence of an amine and in the presence of air, a total conversion of 95% and a rate of polymerization of 33%/s was obtained.

The polysulphide acrylates polymerize more efficiently in the presence of air as the rate of polymerization is greatly increased.

In the absence of air and in the presence of a synergist, the system should be more efficient, but in this case, the results obtained show that the rate of polymerization is reduced but the total conversion has increased.

Conclusion

The results show that the sulphur component in particular cases does play a vital role in the curing of acrylates.

If the sulphur content is increased in the acrylate, the rate of polymerization is greatly increased.

The sulphur component does act as an antioxidant by destroying the peroxides formed and defeating oxygen inhibition of cure.

In conclusion, the results obtained from real-time infrared spectroscopy and the Colordry show similarities, as expected.

The rate of polymerization is greatly increased with the increase in the sulphur content of the acrylate (i.e. ZL1866 and ZL2244).

3.3 EXPERIMENTAL DETAILS

(A) Preparation of 2,2 - Thiodiethyl diacrylate

$$CH_2=CHCO_2CH_2CH_2SCH_2CH_2O_2CCH=CH_2$$

2,2 - Thiodiethanol (5g, 0.04m) was added to sodium dried ether (30cm^3), which was then added from a dropping funnel to an ice-cool mixture of acryloyl chloride (7.3g, 0.08m), triethylamine (7.5g, 0.08m) and sodium dried ether (150cm^3).

The reaction mixture was refluxed for three hours and then cooled. The precipitate formed was filtered off using filter aid. The solution was dried with sodium sulphate for 48 hours and the solvent was removed using a rotary evaporator to give a yellow viscous liquid.

The product was purified using column chromatography, acetone/alumina and then repurified on the Kugelruhr (i.e. high vacuum distillation). The yield obtained was 45%.

NMR analysis	(100MHz, H NMR)		Solvent - d-acetone/TMS
	6.4-6.2	(m,6H) ,	Acrylate Group
	4.4	(t, 4H) ,	CH_2 protons next to oxygen
	3.0	(t, 4H) ,	CH_2 protons next to sulphur
	2 . 0	(d-acetone) ,	

CHN analysis (%)	Expected	Found
C,	52.2	52.13
H,	6.08	6.32

Formula: $C_{10}H_{14}O_4S$

I.R. analysis

2900cm^{-1}	, (m)	,	aliphatic CH stretch
1725cm^{-1}	, (s)	,	C=O stretch
1632cm^{-1}	, (s)	,	C=C stretch
1195cm^{-1}	, (s)	,	C-O stretch
810cm^{-1}	, (s)	,	CH_2=CH stretch

Boiling point - 72°C/0.1mmHg

(B) Preparation of 2,2 - Oxydiethyl diacrylate

Similar method as for A, using diethylene glycol as the starting material. (Yield = 40%).

$$CH_2=CHCO_2CH_2CH_2OCH_2CH_2O_2CCH=CH_2$$

The product was purified by column chromatography, acetone/alumina and then repurified using the Kugelruhr.

NMR analysis	(100MHz, H' NMR)		Solvent - d-acetone/TMS
	3.6 ,	(t, 4H) ,	CH_2 protons next to oxygen
	4.15 ,	(t, 4H) ,	CH_2 protons next to acrylate group
	6. 3-6.0 ,	(m,6H) ,	Protons on acrylate group

CHN analysis (%)	Expected	Found
C,	56.07	56.16
H,	6.54	6.82
Formula:	$C_{10}H_{14}O_5$	

I.R. analysis

2900cm^{-1} , (m) ,	aliphatic CH stretch
1728cm^{-1} , (s) ,	C=O stretch
1633cm^{-1} , (s) ,	C=C stretch
810cm^{-1} , (s) ,	CH_2=CH stretch

Boiling point - 75°C/0.1mmHg

C Preparation of Butane - 1,4 - diol diacrylate

Similar method as for A, using 1,4 - butanediol as the starting material. (Yield = 40%).

$$CH_2=CHCO_2CH_2CH_2CH_2CH_2O_2CCH=CH_2$$

The product was purified by column chromatography, acetone/alumina and then further repurified by using high vacuum distillation (i.e. Kugelruhr).

NMR analysis (100MHz, H NMR) d-chloroform/TMS

6.4-6.0	, (m, 6H)	,	protons on acrylate group
4.2	, (m, 4H)	,	CH_2 protons next to acrylate group
1.8	, (bs, 4H)	,	CH_2 protons

CHN analysis (%)

	Expected	Found
C,	60.6	60.79
H,	7.07	7.18

Formula: $C_{10}H_{14}O_4$

I.R. analysis

	2961cm^{-1}, (s)	, aliphatic CH stretch
	1722cm^{-1}, (s)	, C=O stretch
	1633cm^{-1}, (s)	, C=C stretch
1061cm^{-1},	1188cm^{-1}, (s)	, C=O stretch
	810cm^{-1}, (s)	, CH_2=CH stretch

Boiling point - 68°C/0.1mmHg

(D) Preparation of 3,6 Dithia - Octane - 1,8 - diacrylate

Similar method as for A, but using 3,6 - dithia - 1,8 - octanediol. (Yield = 40%).

$CH_2=CHCO_2CH_2CH_2SCH_2CH_2SCH_2CH_2O_2CCH=CH_2$

NMR analysis	(100MHz. H' NMR)		CDC1_3/TMS
	6.4-6.0 ,	(m, 6H) ,	protons on acrylate group
	4.2 ,	(t, 4H) ,	CH_2 protons next to acrylate group
	2.9 ,	(m,8H) ,	CH_2 protons next to sulphur

CHN analysis (%)	Expected	Found
C,	49.8	50.07
H,	6.2	6.45

Formula: $C_{12}H_{18}O_4S_2$

I.R. analysis

	$2955cm^{-1}$,	(m) ,	aliphatic CH peak
	$1727cm^{-1}$,	(s) ,	C=O stretch
	$1635cm^{-1}$,	(s) ,	C=C stretch
$1059cm^{-1}$,	$1268cm^{-1}$,	(s) ,	C-O stretch
	$811cm^{-1}$,	(s) ,	CH_2 =CH stretch

Boiling point - 100°C/0.1mmHg

(E) Preparation of 2,2' - Dithiodiethyl diacrylate

Similar method as for A, but using 2,2'- dithiodiethanol as the starting material. (Yield = 40%).

$$CH_2=CHCO_2CH_2CH_2\text{-}S\text{-}S\text{-}CH_2CH_2O_2CCH=CH_2$$

NMR analysis (100 MHz, H' NMR) d-chloroform/TMS

6.5 - 6.3	(m, 6H)	protons on acrylate group
4.6	(t, 4H)	CH_2 protons next to acrylate group
3.0	(t,4H)	CH_2 protons next to sulphur

CHN analysis (%)

	Expected	Found
C,	45.8	45.61
H,	5.3	5.57

Formula: $C_{10}H_{14}O_4S_2$

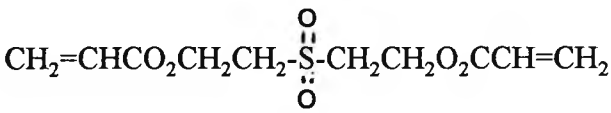
I.R. analysis

	$1725cm^{-1}$	(s)	C=O stretch
	$1633cm^{-1}$	(s)	C=C stretch
$1050\ cm^{-1}$	$1260cm^{-1}$	(s)	C-O stretch
	$810cm^{-1}$	(s)	CH_2=CH stretch

Boiling point - 86°C/0.1mmHg

(F) Preparation of 2,2' - Sulphonyldiethyl diacrylate

Similar method as for A, but using 2,2'- sulphonyldiethanol as the starting material. (Yield = 44%).



The product was purified by column chromatography, methanol/alumina and further purified using the Kugelruhr.

NMR analysis (100MHz, H' NMR) d-acetone/TMS

6.5 - 6.2	, (m, 6H)	,	acrylate group
4.0	, (t, 4H)	,	CH_2 protons next to acrylate group
3.2	, (t,4H)	,	CH_2 protons next to SO_2 group
2.0	, (d-acetone)		

CHN analysis (%)

	Expected	Found
C,	45.8	45.6
H,	5.3	5.50

Formula: $C_{10}H_{14}O_6S$

I.R. analysis

	1725cm^{-1}, (s)	,	C=O stretch
	1632cm^{-1}, (s)	,	C=C stretch
1300cm^{-1},	1190cm^{-1},(s)	,	S=O stretch
1265cm^{-1},	1069cm^{-1},(s)	,	C-O stretch
	810cm^{-1}, (s)	,	CH_2=CH stretch

Boiling point - 120°C/0.1mmHg

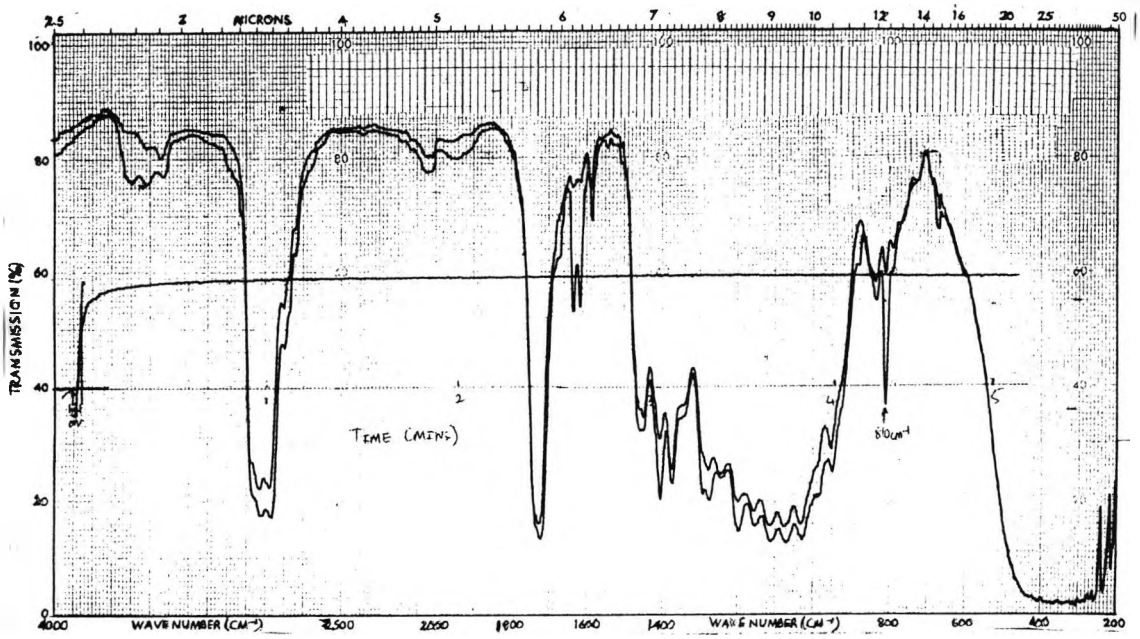
The acrylated liquid polysuphide polymers were provided by Morton International.

1. ZL1866 - reaction product of LP3 and trimethylolpropane triacrylate.
2. ZL2244 - reaction product of LP3 and tripropylene glycol diacrylate.

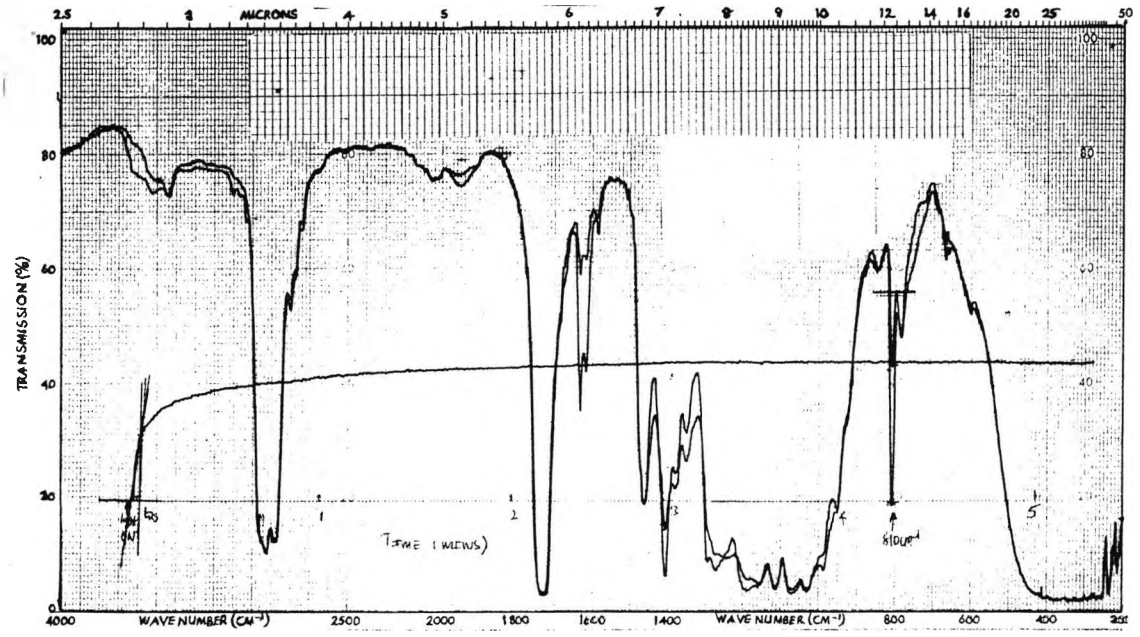
LP3 is a polysulphide polymer.

$$HS\ (C_2H_4OCH_2OC_2H_4\ Sx)_n\text{-}\ C_2H_4OCH_2OC_2H_4SH$$

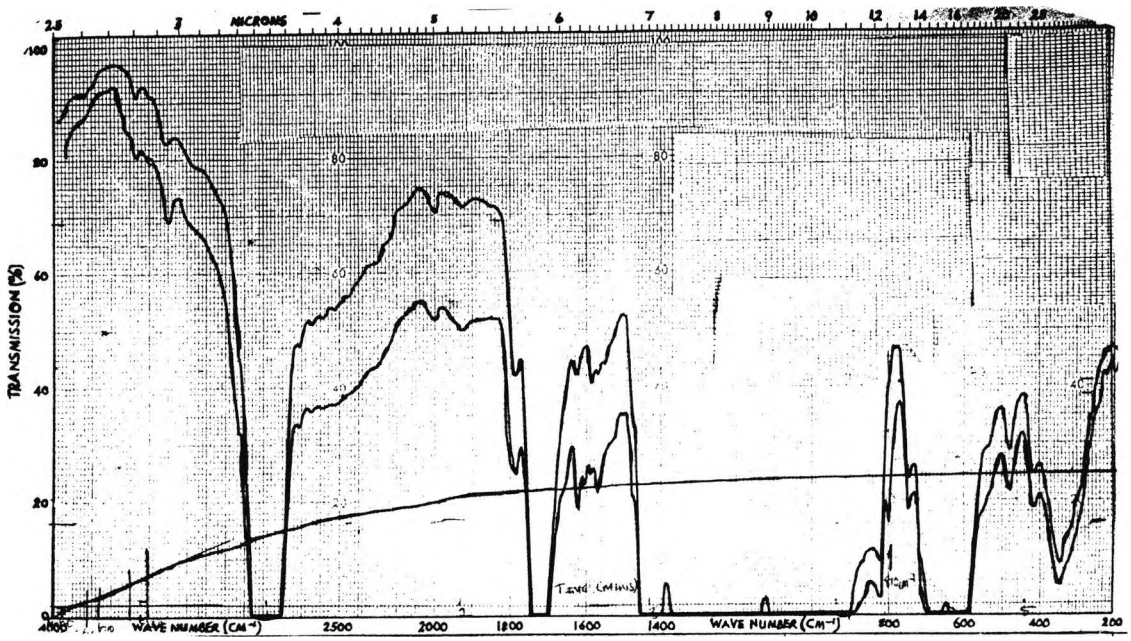
Both products were tested with the colordry and real-time infra-red spectroscopy.



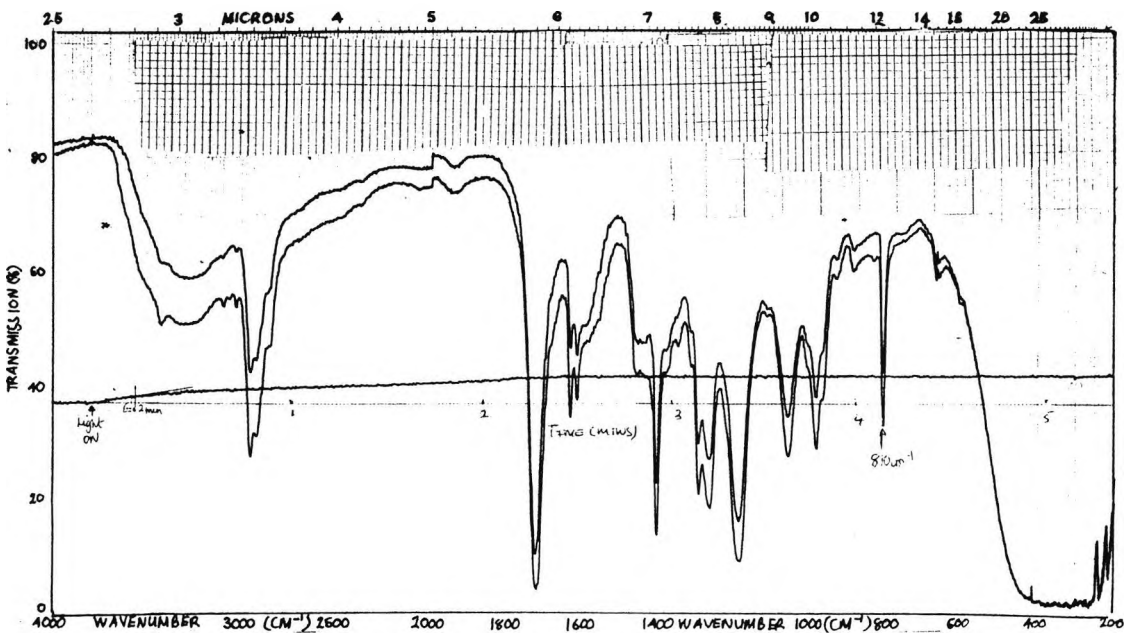
Spectrum 1:- RTIR spectrum, showing the polymerization of ZL2244 in the presence of Irgacure 907 under aerobic conditions.



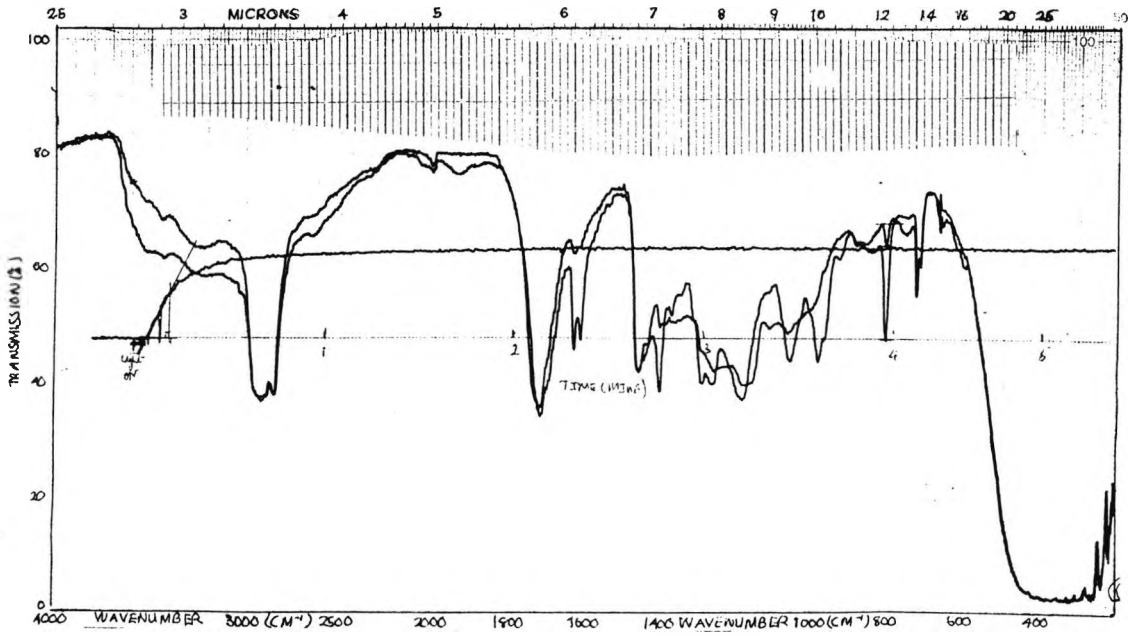
Spectrum 2:- RTIR spectrum, showing the polymerization of ZL1866 in the presence of Irgacure 907 under aerobic conditions.



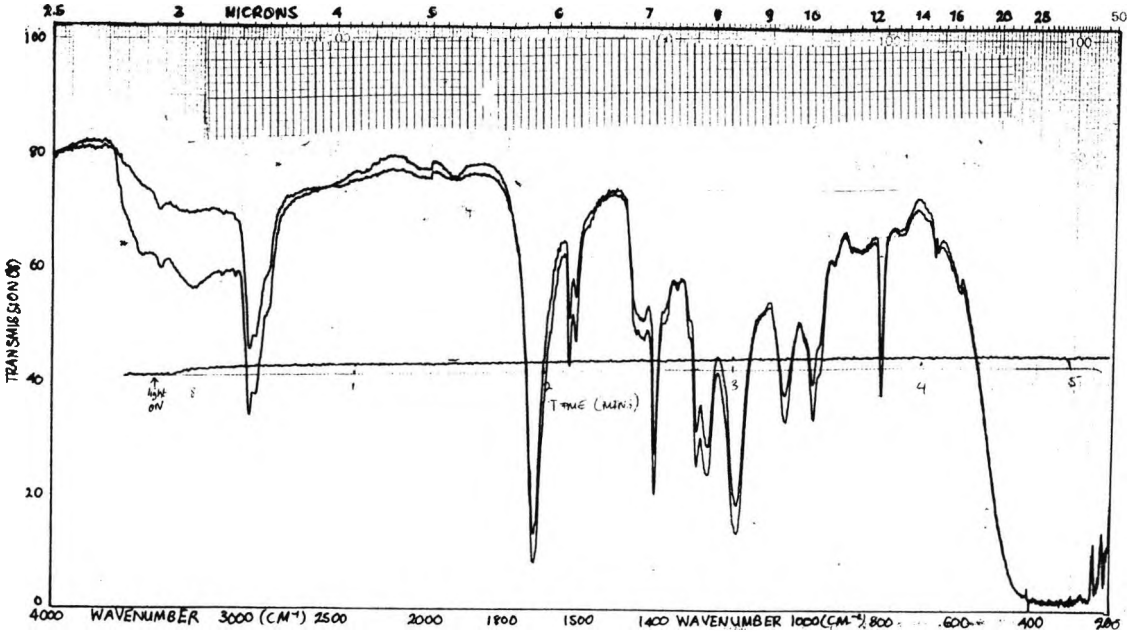
Spectrum 3:- RTIR spectrum, showing the polymerization of 3,6-dithia - 1,8 octane diacrylate in the presence of Irgacure 907 and N-methyldiethanolamine, under anaerobic conditions.



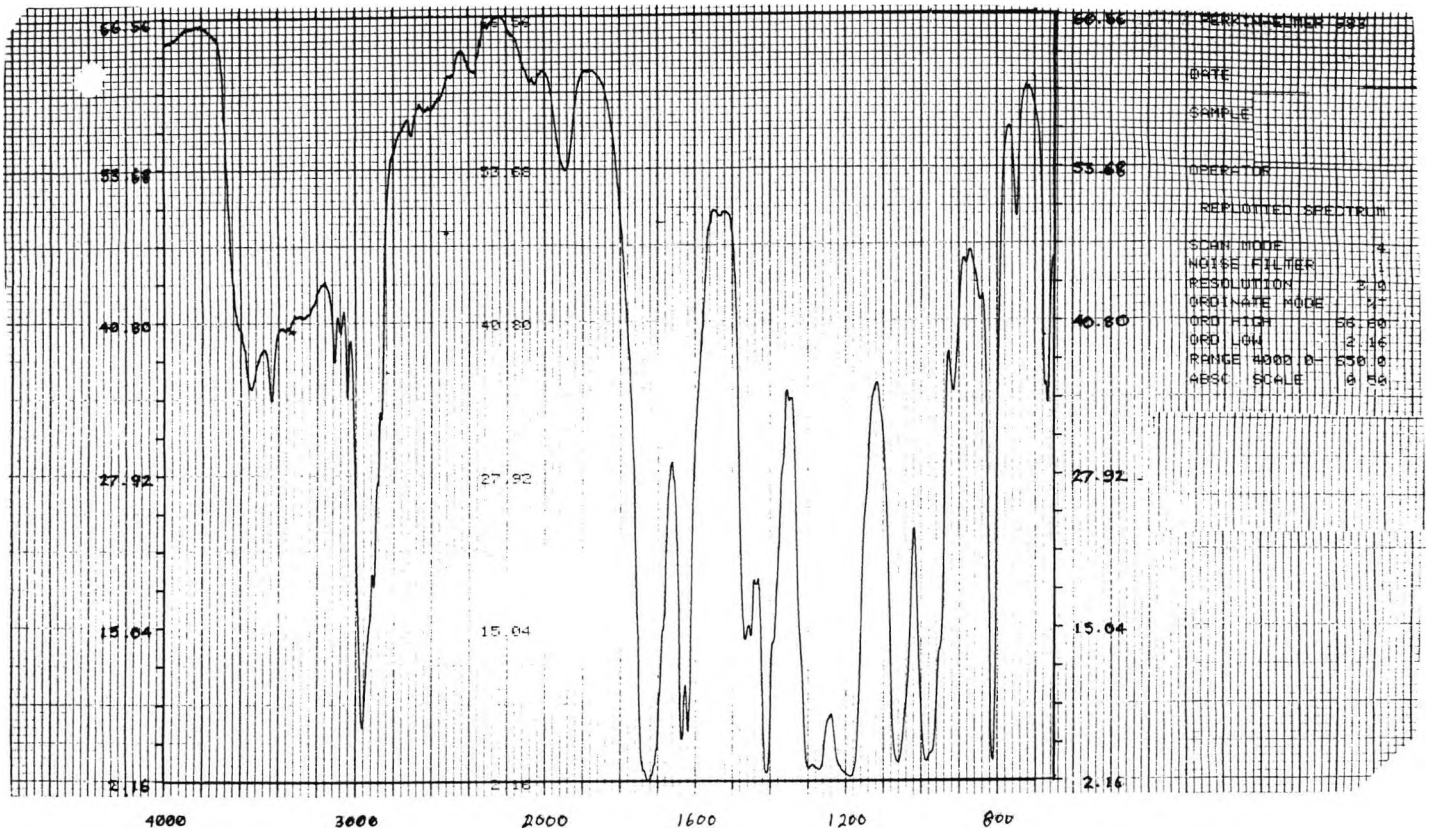
Spectrum 4:- RTIR spectrum, showing the polymerization of 3,6-dithia - 1,8 octane diacrylate in the presence of Irgacure 907 and N-methyldiethanolamine, under aerobic conditions.



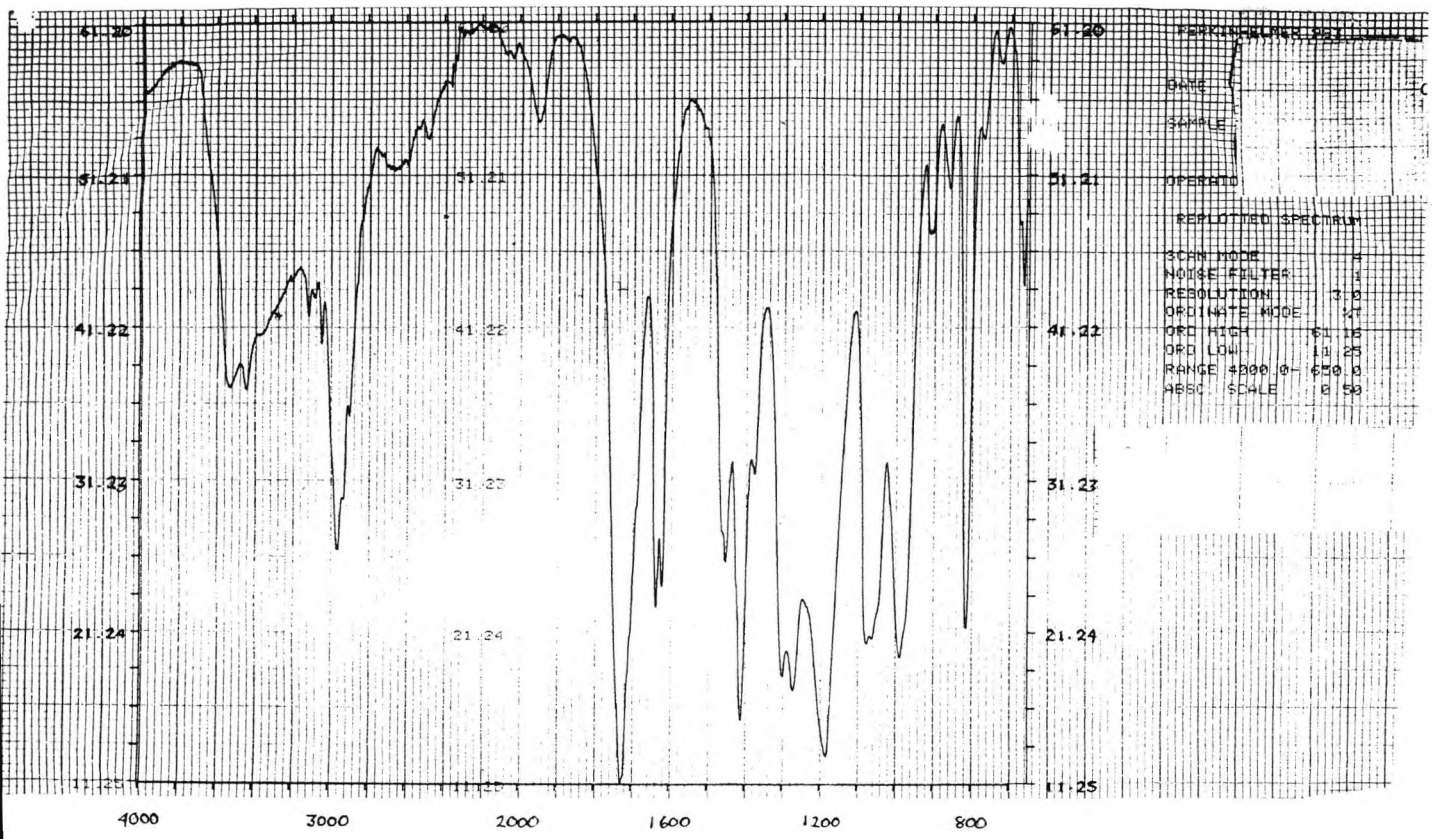
Spectrum 5:- RTIR spectrum showing the polymerization of 2,2-thiodiethyl diacrylate in the presence of Irgacure 907, under anaerobic conditions.



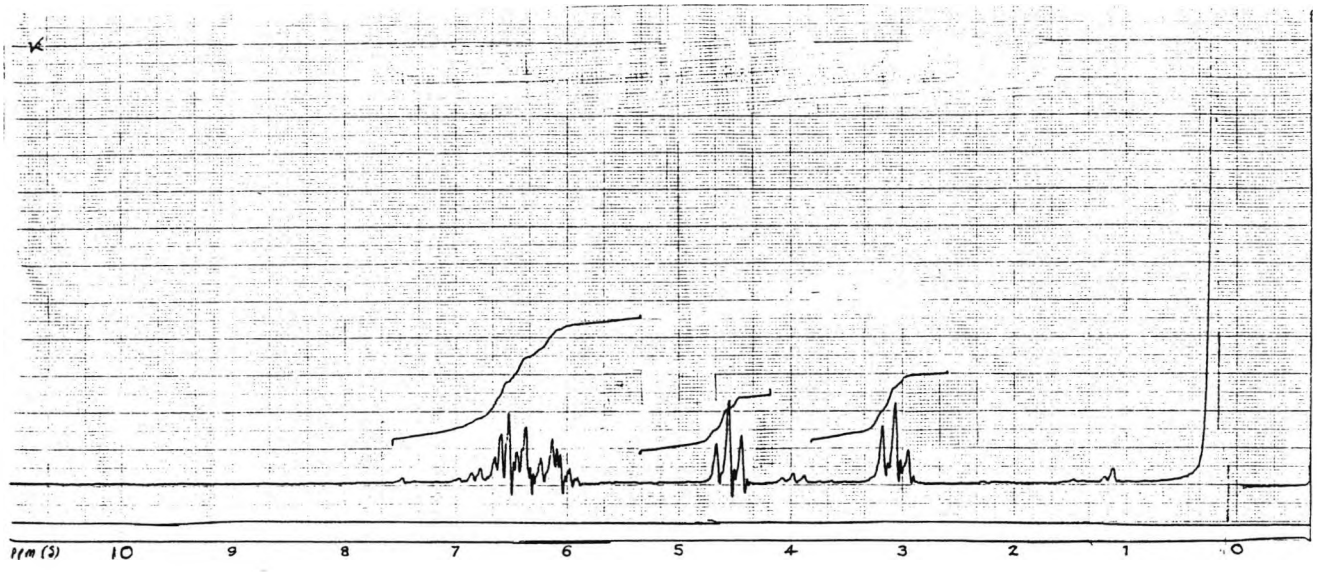
Spectrum 6:- RTIR spectrum showing the polymerization of 2,2-thiodiethyl diacrylate in the presence of Irgacure 907, under aerobic conditions.



Spectrum 7:- Infra-red spectrum of 1,4-butanediol diacrylate.



Spectrum 8:- Infra-red spectrum of 2,2-thiodiethyl diacrylate.



Spectrum 9:- NMR spectrum of 2,2-thiodiethyl diacrylate.

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CHAPTER FOUR

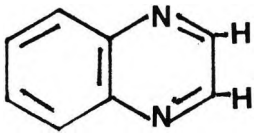
THE USE OF QUINOXALINES AS REGENERATABLE PHOTOINITIATORS

QUINOXALINES

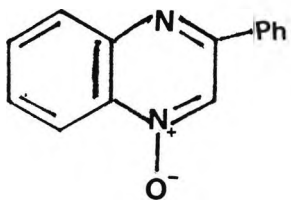
4.1 INTRODUCTION

The quinoxaline nucleus A is to be found in a number of dyes and closely related structures e.g. riboflavin [1,2]

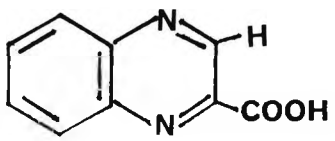
A.



Quinoxalines are in general, comparatively easy to prepare and numerous derivatives have been prepared in work designed to produce biologically active materials e.g. quinoxaline N-oxides, (e.g. 2-phenylquinoxaline - 4 - oxide).

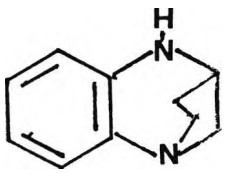


Antibiotics of the triostin and quinomycin series, isolated from cultures of streptomyces aureus, were shown to contain a quinoxaline - 2 - carboxylic acid residue [3]



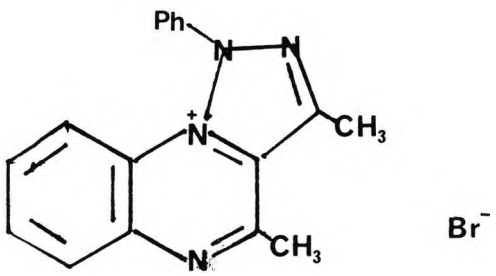
Quinoxaline derivatives such as 1,3 - ethano - 1,2,3,4, - tetrahydro quinoxaline B [4] have been prepared together with many condensed quinoxalines.

(B)



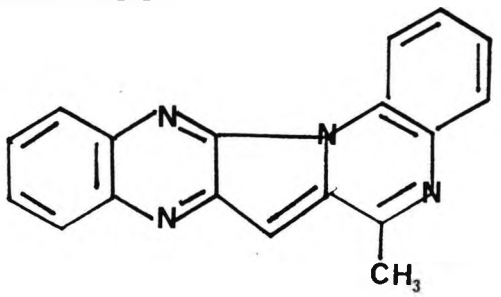
Fusion to the 1,2 - bond is shown by the formation of triazoloquinoxalium salts such as C [5],

(C)

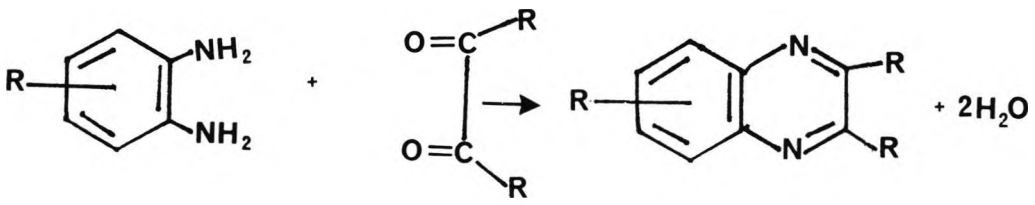


An interesting methylquinoxaline orange D, was obtained by the oxidation of 2 - methylquinoxaline [6],

(D)



The classical synthesis of quinoxalines involves the condensation of an aromatic o-diamine and a dicarbonyl compound (Scheme 1) [7].

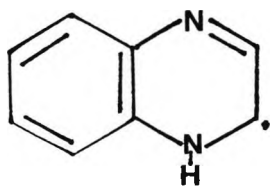


Photochemistry of Quinoxalines

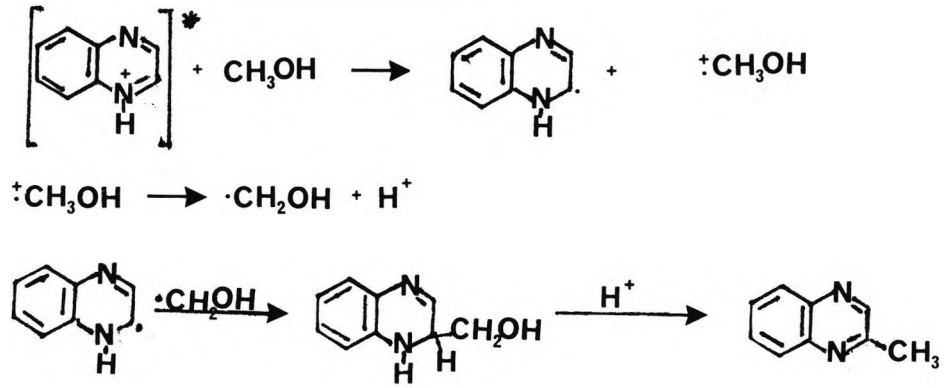
One of the earliest reports of the use of quinoxalines in photochemical reactions was in 1970. [9] It was reported that substitutions of quinoxalines takes place at C_2 when irradiated in either methanol or ethanol.

The intermediate in the reaction is as shown below:

(E)



It was reported that the u.v. irradiation of quinoxaline in methanol yields radicals, by protonation of the first excited singlet state followed by exciplex formation [10]

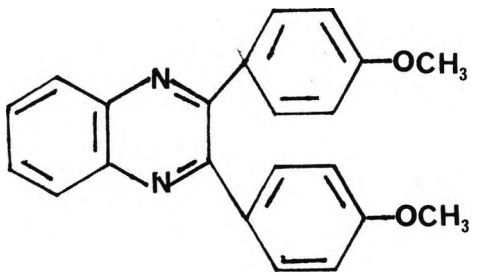


Irradiation of the quinoxaline in acidified methanol produces 2 - methylquinoxaline, and the reaction was suggested to go through a pathway involving electron-transfer from the solvent to an excited state of the protonated quinoxaline. [11]

The use of quinoxalines in the photopolymerization of acrylic and methacrylic monomers has not been widely reported in the literature.

Bauer, Brahm and Dietrich [12], have carried out some work on the photopolymerization of acrylic monomers using 2,3 - bis (p-methoxyphenyl) quinoxaline.

(G)



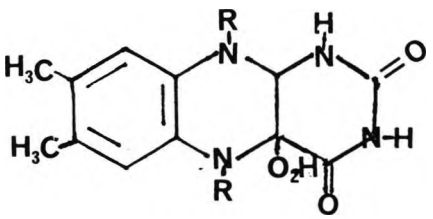
Quinoxalines and azaquinoxalines derivatives were reported to surpass other initiators in accelerating the photopolymerization of certain monomers. [13,14]

Flash photolysis, e.s.r., and CIDEP studies [15] were also carried out on quinoxalines. The results obtained showed that radicals formed from quinoxalines are produced via hydrogen abstraction from a suitable donor.

Also work carried out by Angewandte [16], supported the theory, whereby quinoxalines induce free-radical polymerization via hydrogen abstraction from alkanes.

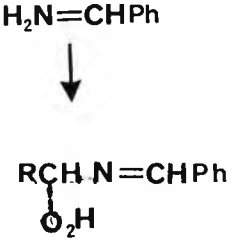
Earlier work by Davidson as yet unpublished showed that quinoxalines can be reduced by tertiary amines to give dihydro compounds, which react with oxygen regenerating the starting material >90% yield. However, some hydroperoxide is generated in this process. This effect is much more noticeable with riboflavin. (H), which upon photoreduction and re-oxidation produces a hydroperoxide.

(H)



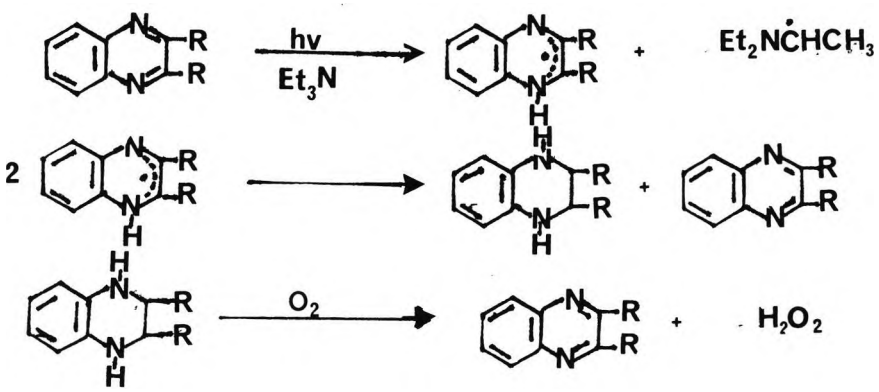
Other materials which generate hydroperoxide upon photo-oxygenation are Schiff bases, (I).

(I) $RCH_2N{=}CHPh$

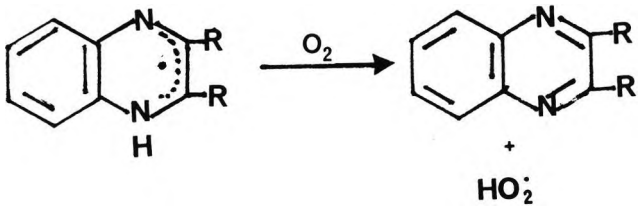


It was noticed that simple quinoxalines on irradiation in degassed solution containing hydrogen donors such as triethylamine undergoes reduction. On admission of air the quinoxaline was regenerated.

A simplified mechanism which explains such a phenomenon is shown in Scheme 2.



If oxygen is present in solution during irradiation it is feasible that it will react with the semi-reduced quinoxaline.



The formation of these hydroperoxides could be used to advantage in lithoplates if catalysts are present which promote the decomposition of peroxides. Whilst normally it is not desirable to have lithographic plate formulations containing peroxides (i.e. poor shelf-life), their formation upon illumination could offer a new method of employing such compounds.

A lot of the earlier work was also carried out by Moran, as yet unpublished. It was shown that the use of this type of sensitizer leads to surface cure and hence may find applications in 3D imaging.

If the quinoxaline and related species promote surface cure in lithoplate formulations, it would prove unnecessary to apply a topcoat.

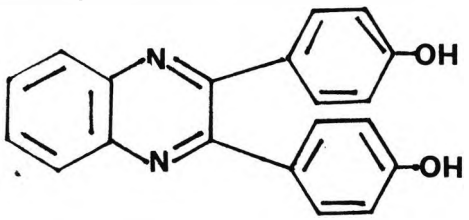
4.2 RESULTS AND DISCUSSION

The results obtained were from formulations of (i) 1% w/w photoinitiator, (ii) 10% w/w N-methyldiethanolamine (i.e. synergist) (iii) monomer :- 2- Ethyl - 2 - (hydroxymethyl) - 1,3 - propanediol triacrylate, (i.e. trimethylolpropane triacrylate (TMPTA)).

The techniques used for studying the photopolymerization processes were the moving belt system (i.e. colordry), real-time infra-red spectroscopy (RTIR) and bulk polymerization.

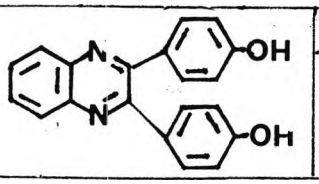
The first compound prepared was 2,3 - bis (4- hydroxyphenyl) quinoxaline (A)

(A)



The purpose in making this compound was to prepare quinoxalines which were soluble in various monomers.

Table (1) U.V. Curing of 2,3-bis (4-hydroxyphenyl) quinoxaline in the presence of an amine

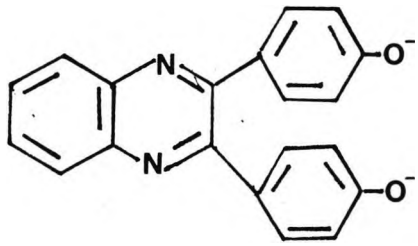
	Quartz	Glass Slide	Air	Filter
	4	9	30+	30+

a) Belt speed:- 10ft/min (b) amine used:- N-methyldiethanolamine

c) Monomer used :- 2-Ethyl - 2(hydroxymethyl) - 1,3 - propanediol triacrylate

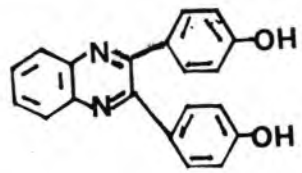
2,3 - Bis (4 - hydroxyphenyl) quinoxaline in the presence of an amine did not polymerize as well as expected under anaerobic conditions (i.e. quartz and touching glass slide), whilst under aerobic conditions no polymerization occurred. One of the

possibilities of the poor performance could be due to the ionisation of the initiator forming the species as shown.



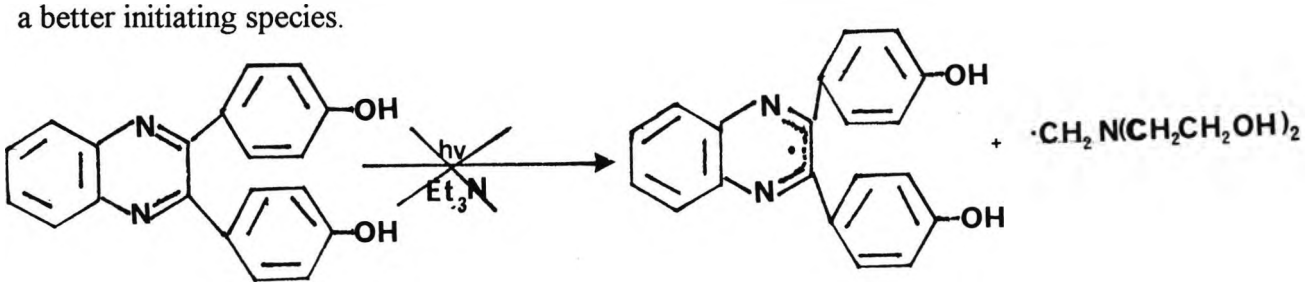
The species formed is a very poor electron acceptor and shows very little polymerization in thin films.

Table 2. U.V. Curing of 2,3 - bis (4 - hydroxyphenyl) quinoxaline in the absence of an amine

	Quartz	Glass Slide	Air	Filter
	30+	30+	30+	30+

The result shows that in the absence of an amine, under aerobic and anaerobic conditions, no polymerization occurred.

In the absence of an amine, it is not possible to form the α-alkylamino radical, which is a better initiating species.



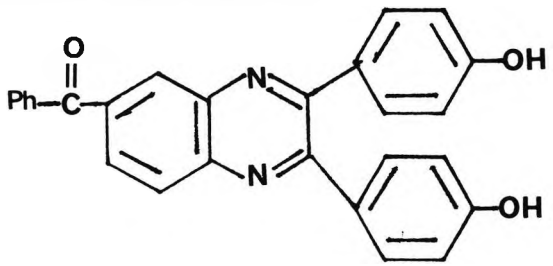
Under aerobic conditions, there was no polymerization due to oxygen inhibition of cure.

Under anaerobic conditions, one would have expected some polymerization of the acrylate by the quinoxaline radical, via hydrogen abstraction of the monomer. Due to

ionisation of the quinoxaline, it is a very poor electron acceptor and shows little polymerization in thin films.

The next compound prepared was the benzoyl derivative of 2,3 - bis (4-hydroxyphenyl) quinoxaline (B)

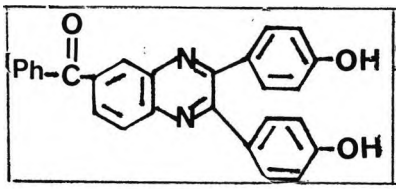
(B)



7 - Benzoyl - 2,3 - bis (4-hydroxyphenyl) quinoxaline

This compound was prepared for three reasons, (i) to prepare more soluble quinoxalines and (ii) the benzoyl group was added to increase the u.v./visible absorption range of quinoxalines (iii) Also, the rates of cure of 2,3 - bis (4-hydroxyphenyl) quinoxaline were compared with the benzoyl derivative to show the effect of the carbonyl group on the rate of polymerization.

Table 3 U.V. Curing of 7-benzoyl - 2,3 - bis (4-hydroxyphenyl) quinoxaline in the presence of an amine

	Quartz	Glass Slide	Air	Filter
	3	7	17	18

(a) Belt speed :- 10ft/min
(b) Amine used :- N-methyldiethanolamine
(c) Monomer :- 2- Ethyl - 2(hydroxymethyl) - 1,3 - propanediol triacrylate

It can be shown that under anaerobic conditions, in the presence of an amine, the benzoyl derivative polymerizes faster than 2,3 - bis (4-hydroxyphenyl) quinoxaline.

Under aerobic conditions, a tack-free film was formed in air and under a filter (i.e. a raised glass slide). This could be due to the presence of the carbonyl group which

undergoes a triplet $\pi \longrightarrow \pi^*$ transition which would produce a better hydrogen abstractor than the quinoxaline itself.

One would have expected the rate of polymerization to be greater. This could be explained by the fact that the benzoyl derivative also undergoes ionisation, and therefore is a poor electron acceptor,forming the species as shown below:

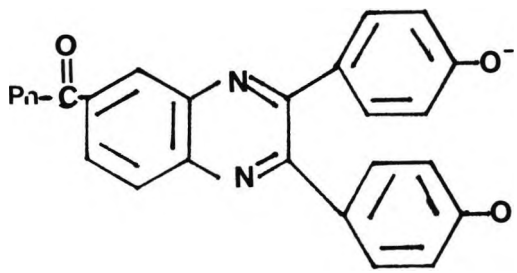
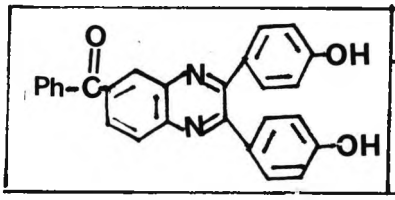
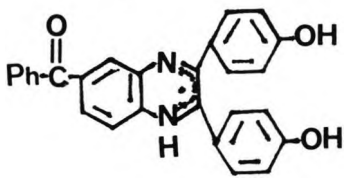


Table 4 U.V. Curing of 7-benzoyl 2,3 - bis (4-hydroxyphenyl) -quinoxaline in the absence of an amine

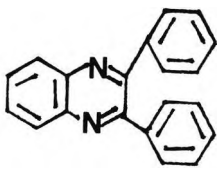
	Quartz	Glass Slide	Air	Filter
	10	10	25	30+

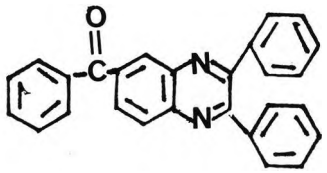
Under anaerobic conditions (i.e. quartz and glass slide) in the absence of an amine, a tack-free film was formed within ten passes under the colordry. If this result is compared with the result obtained in the presence of an amine, it shows that there is an overall increase in the rate of polymerization due to the amine (i.e. synergist). It also proves that the α-aminoalkyl radical formed is a better initiating species than the quinoxaline radical, as shown below:



Under aerobic conditions, (i.e. air and filter), there is very little polymerization due to the presence of oxygen, which inhibits polymerization of the acrylate.

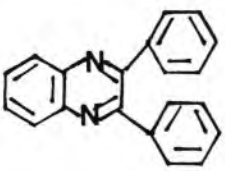
The next two compounds to be tested were 2,3 - diphenylquinoxaline (C) and 7 - benzoyl - 2,3 - diphenylquinoxaline (D).

(C) 

(D) 

The purpose of preparing the above compounds was to show what effect, if any, the carbonyl group in (D) has on the rate of polymerization. Also the reason for preparing the benzoyl derivative was to provide a range in which quinoxalines can absorb in the u.v. and visible regions of the spectrum.

Table 5 U.V Curing of 2.3 - diphenylquinoxaline in the presence of an amine

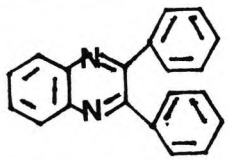
	Quartz	Glass Slide	Air	Filter
	1	1	6	6

(a) Belt speed :- 10ft/min
(b) Amine used :- N-methyldiethanolamine
(c) Monomer :- 2- Ethyl - 2(hydroxymethyl) - 1,3 - propanediol triacrylate

It is shown under anaerobic conditions that a tack-free film is formed in one pass under the colordry. This shows that in the absence of oxygen, and in the presence of an amine, an efficient curing system is obtained.

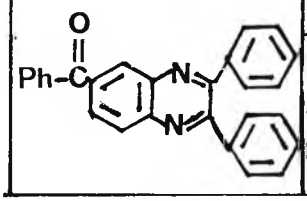
Under aerobic conditions, the rate of polymerization is reduced. This is due to the diffusion of oxygen into the film, inhibiting the polymerization process.

Table 6 U.V. Curing of 2,3 - diphenylquinoxaline in the absence of an amine

	Quartz	Glass Slide	Air	Filter
	2	2	30+	30+

Under anaerobic conditions, the quinoxaline forms an efficient initiating species, which polymerizes 2- ethyl - 2- (hydroxymethyl) - 1,3 - propanediol triacrylate. Under aerobic conditions, the presence of oxygen inhibits the polymerization of the acrylate.

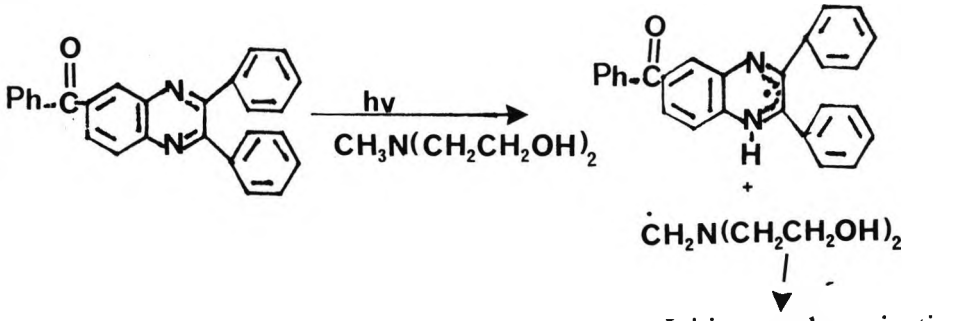
Table 7 U.V. Curing of 7-benzoyl - 2,3 - diphenylquinoxaline in the presence of an amine

	Speed of belt	Quartz	Glass Slide	Air	Filter
	10ft/min	1	1	1	1
	80ft/min	1	1	1	2

(a) Amine used :- N-methyldiethanolamine
(b) Monomer :- 2- Ethyl - 2(hydroxymethyl) - 1,3 - propanediol triacrylate

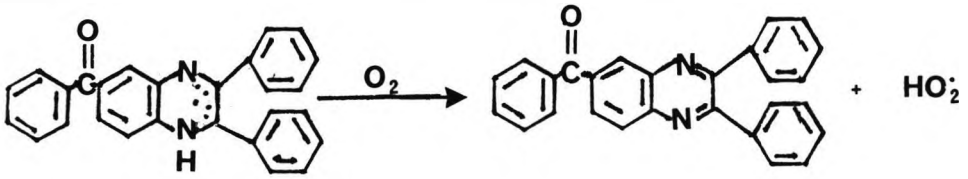
The compound was tested in the colordry at an initial belt speed of 10ft/min. The results showed that a tack-free film was formed in one pass in the colordry. Under anaerobic and aerobic conditions the speed of the belt was then increased to 80ft/min, thereby decreasing the exposure time of the initiator. Under anaerobic conditions (i.e. quartz and glass slide) a tack-free film was formed in one pass under the colordry. Also under aerobic conditions, a tack-free film was formed within two passes in the colordry. The results show that under anaerobic conditions, an efficient curing system is obtained, whereby hydrogen abstraction of the amine occurs, forming an α-aminoalkyl radical

Eqn (1)



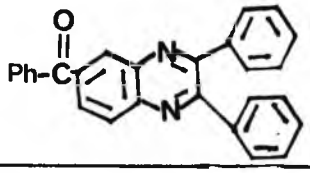
Under aerobic conditions, the quinoxaline is regenerated forming the species, as shown below:

Eqn (2)



If the rate of polymerization of the benzoyl derivative is compared with 2,3 - diphenylquinoxaline, it can be shown the addition of the benzoyl group increases the rate of polymerization. As explained earlier, this could be due to the presence of the carbonyl group which undergoes a triplet π - π^* transition which would produce a better hydrogen abstracter than the quinoxaline itself.

Table 8 U.V. Curing of 7 - benzoyl - 2,3 - diphenylquinoxaline in the absence of an amine

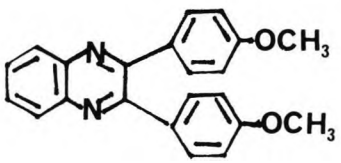
	Quartz	Glass Slide	Air	Filter
	1	1	30+	30+

Under anaerobic conditions, the benzoyl derivative forms an efficient initiating radical, which polymerizes 2-ethyl - 2 (hydroxymethyl) - 1,3 - propanediol triacrylate.

Under aerobic conditions, there is no polymerization due to oxygen inhibition of cure i.e. scavenging the radicals formed.

The problem encountered with 7-benzoyl - 2,3 - diphenylquinoxaline and 2,3 diphenylquinoxaline was their solubility.

2,3 - Bis (4 - methoxyphenyl) quinoxaline (E) and 7 - benzoyl - 2,3 bis (4 - methoxyphenyl) quinoxaline (F), were prepared with the aim of solving the problem of solubility.

(E) 

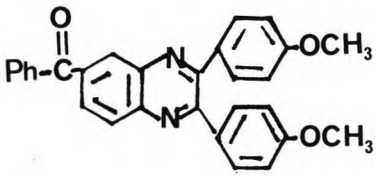
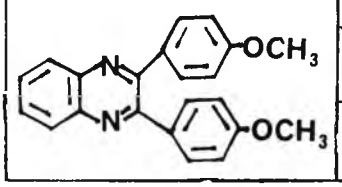
(F) 

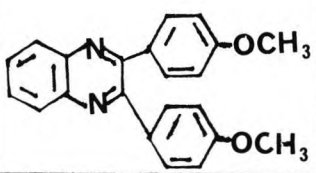
Table 9 U.V. Curing of 2,3 - bis (4 - methoxyphenyl) quinoxaline in the presence of an amine

	Speed of belt	Quartz	Glass Slide	Air	Filter
	10ft/min	1	1	1	1
	80ft/min	1	1	1	2

(a) Amine used :- N-methyldiethanolamine
(b) Monomer :- 2- Ethyl - 2-(hydroxymethyl) - 1,3 - propanediol triacrylate

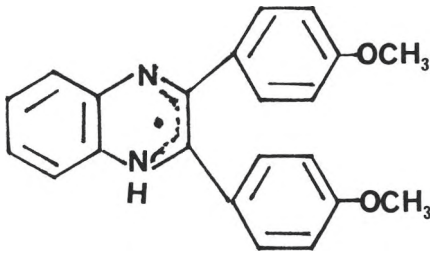
The results show that in the presence and absence of air, 2,3 - bis (4- methoxyphenyl) quinoxaline is an efficient photoinitiator in the polymerization of 2- ethyl- 2-(hydroxymethyl) - 1,3 - propanediol triacrylate.

Table 10 U.V. Curing of 2,3 - bis (4- methoxyphenyl) quinoxaline in the absence of an amine

	Quartz	Glass Slide	Air	Filter
	1	1	30+	30+

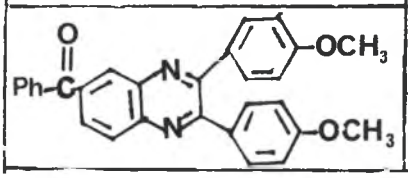
Under aerobic conditions, and in the absence of an amine, the quinoxalines are poor photoinitiators.

Under anaerobic conditions, the radical is formed



by hydrogen abstraction from the monomer itself, resulting in polymerization of the triacrylate.

Table 11 U.V. Curing of 7 - benzoyl - 2,3 - bis (4-methoxyphenyl) quinoxaline in the presence of an amine

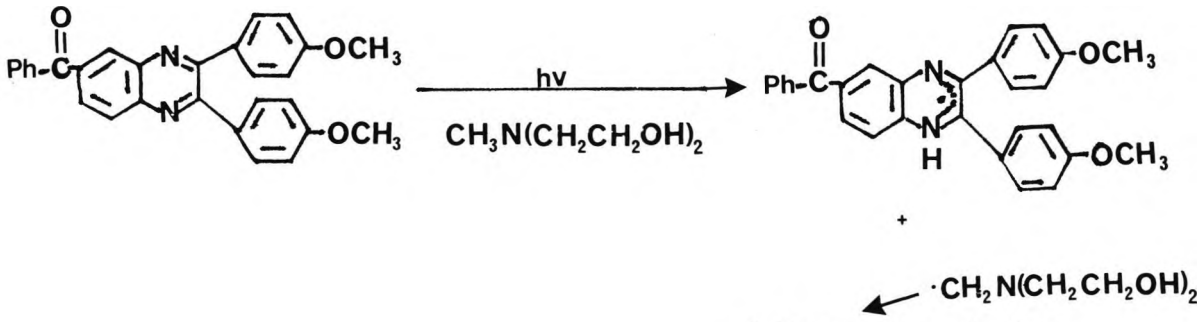
	Speed of belt	Quartz	Glass Slide	Air	Filter
	10ft/min	1	1	1	1
	80ft/min	1	1	1	1

(a) Amine used :- N-methyldiethanolamine(10% w/w)
(b) Monomer :- 2- Ethyl - 2-(hydroxymethyl) - 1,3 - propanediol triacrylate

From the results it can be shown that 7 - benzoyl - 2,3 - bis (4 - methoxyphenyl) quinoxaline and N-methyldiethanolamine and 2 - ethyl - 2- (hydroxymethyl) - 1,3 - propanediol triacrylate produces an efficient curing system.

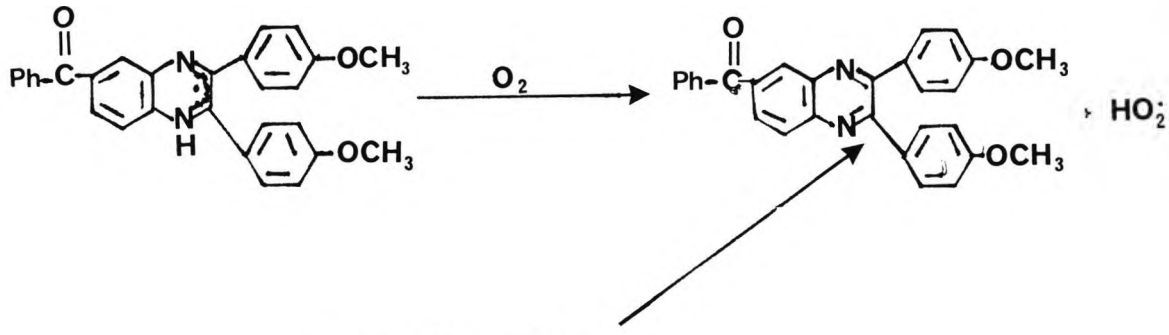
Mechanism

(i)



Initiates polymerization

(ii)

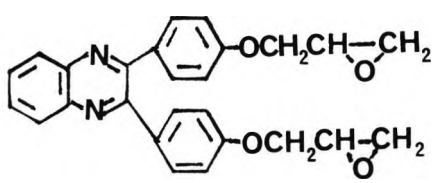


regeneratable sensitizer

For the above compound the amine concentration was reduced to 3% w/w and 4% w/w. This did not affect the rate of polymerization. In the absence of an amine, the results obtained showed that under anaerobic conditions the tack-free film was formed in one pass under the colordry. Under aerobic conditions, no polymerization occurred due to oxygen inhibition of cure.

The preparations of 2,3- bis (4-glycidylphenyl) quinoxaline (G) and 7 - benzoyl - 2,3 - bis (4-gylcidylphenyl) quinoxaline (H) were carried out to offer the possibility of better solubility of quinoxalines in various monomers.

(G)



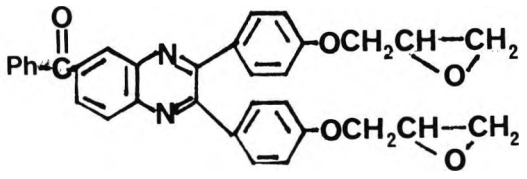
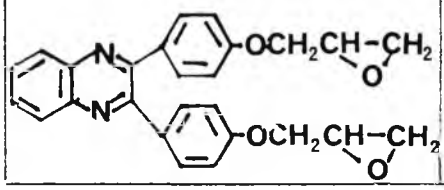
(H) 

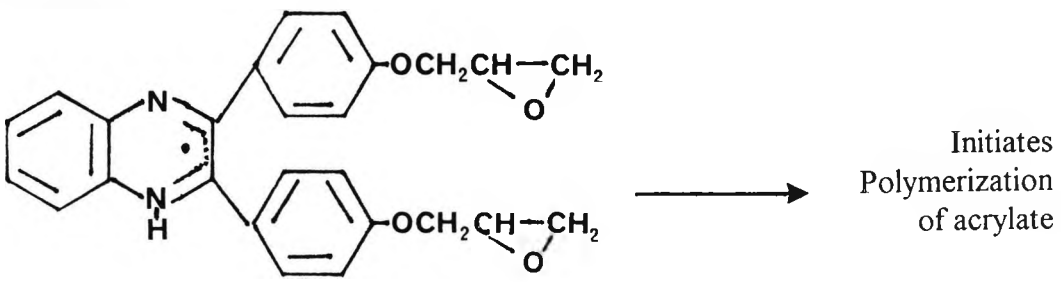
Table 12 U.V. Curing of 2,3 - bis (4-glycidylphenyl) quinoxaline in the presence of an amine

	Speed	Quartz	Glass Slide	Air	Filter
	10ft/min	1	1	1	1
	80ft/min	1	1	1	1

(a) Amine used :- N-methyldiethanolamine
(b) Monomer :- 2- Ethyl - 2- (hydroxymethyl) - 1,3 - propanediol triacrylate

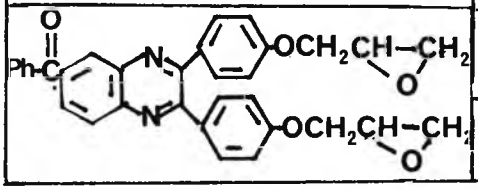
From the results it is shown that the glycidyl derivative is an efficient photoinitiator. The mechanism for the reaction is as explained earlier in the chapter.

In the absence of an amine, and under anaerobic conditions, 2,3 - bis (4 - glycidylphenyl) quinoxaline polymerizes 2 - ethyl - 2- (hydroxymethyl) - 1,3 - propanediol triacrylate. The radical formed is an efficient initiator of the acrylate as shown below:



The radical is formed by hydrogen abstraction from the monomer itself, resulting in polymerization of the acrylate.

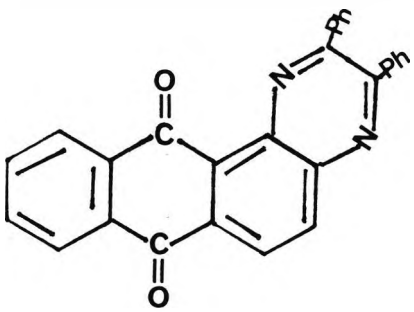
Table 13 U.V. Curing of 7-benzoyl - 2,3 - bis (4 - glycidylphenyl) - quinoxaline in the presence of an amine

	Speed of belt	Quartz	Glass Slide	Air	Filter
	10ft/min	1	1	1	1
	80ft/min	1	1	1	1

(a) Amine used :- N-methyldiethanolamine(10% w.w)
(b) Monomer :- 2- Ethyl - 2- (hydroxymethyl) - 1,3 - propanediol triacrylate

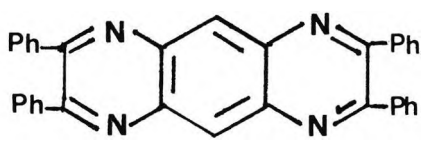
The results obtained for the 7 - benzoyl - 2,3 - bis (4-glycidylphenyl) quinoxaline are similar to 2,3-bis (4-glycidylphenyl) quinoxaline. The quinoxalines were soluble in various monomers. The glycidyl derivatives also provide the opportunity by which the epoxide group can be opened by acrylic acid thereby generating a polymerizable photoinitiator.

1,2 - Anthraquinone - 2,3-diphenylquinoxaline (I) was prepared to provide a range of quinoxalines which absorb in the ultraviolet and also the visible region of the spectrum.

(I) 

The problem encountered with the compound was low solubility.

2,3,7,8, - Tetraphenylpolyquinoxaline (J), was prepared with the intention of using it as an initiator in the visible region.

(J) 

The initial problem of using highly conjugated systems was solubility . When dissolved in the appropriate acrylate, they act as potentially efficient initiators in the visible region.

Table 14:- U.V. Curing of quinoxalines in the presence of a synergist

Samples	No of Passes under Colordry																	
	a + TMPTA	b + TMPTA	c + TMPTA		d + TMPTA		e + TMPTA		f + TMPTA	g + TMPTA		g + TMPTA (3%)		g + TMPTA (4%)		g + TMPTA (5%)		h + TMPTA		i + TMPTA	j + TMPTA
			speed of belt ft / min							speed of belt ft / min											
			10	80	10	80	10	80		10	80	10	80	10	80	10	80	10	80		
Quartz	4	3	1	1	1	1	1	1	Insoluble In	1	1	1	1	1	1	1	1	1	1	1	1
Slide	9	7	1	1	1	1	1	1	TMPTA	1	1	1	1	1	1	1	1	1	1	1	1
Air	30+	17	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	1	1	1
Filter	30+	18	1	1	1	1	1	2		1	1	1	2	1	2	1	2	1	2	3 problem solubility	6

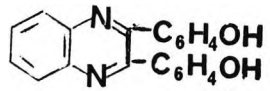
Normal belt speed:- 10ft/min

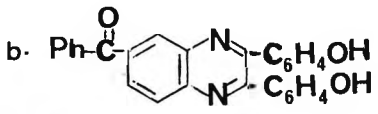
Amine used:- N-methyldiethanolamine

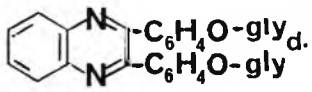
TMPTA-Trimethylolpropane triacrylate - (2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate)

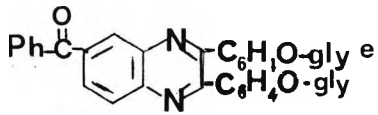
Table 15 U.V. Curing of quinoxalines in the absence of an amine

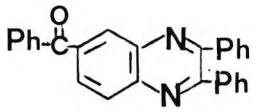
Belt speed :- 10 ft/min Monomer used:- 2-Ethyl-2(hydroxymethyl) 1,3-propanediol triacrylate	No of passes under colordry								
	a	b	c	d	j	e	h	g	i
Quartz	30+	10	1	1	2	1	1	1	3
Slide	30+	10	1	1	2	1	1	1	4
Air	30+	25+	30+	30+	30+	30+	30+	30+	30+
Filter	30+	30+	30+	30+	30+	30+	30+	30+	30+

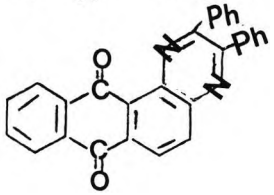
a. 

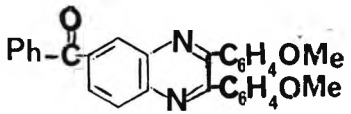
b. 

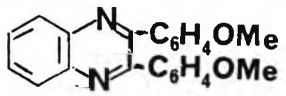
c. 

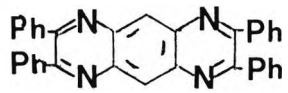
d. 

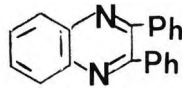
e. 

f. 

g. 

h. 

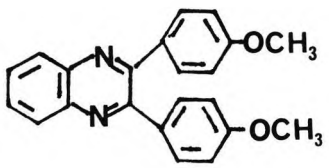
i. 

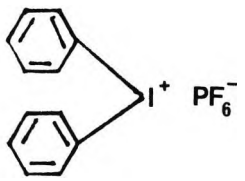
j. 

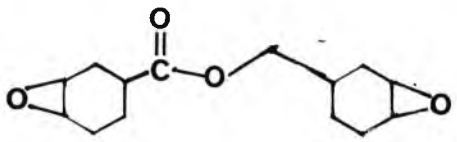
Radiation Curing of 2,3 - bis (4-methoxyphenyl) quinoxaline in the presence of diphenyliodonium hexafluorophosphate:-

The purpose of testing the quinoxaline in the presence of the iodonium salt was to show whether quinoxalines can be used as sensitizers for cationic polymerization.

2,3-Bis (4-methoxyphenyl) quinoxaline (A) was tested in the moving belt system in the presence of diphenyliodonium hexafluorophosphate (B), and an epoxy resin (Degacure K126) (C), [17].

(A) 

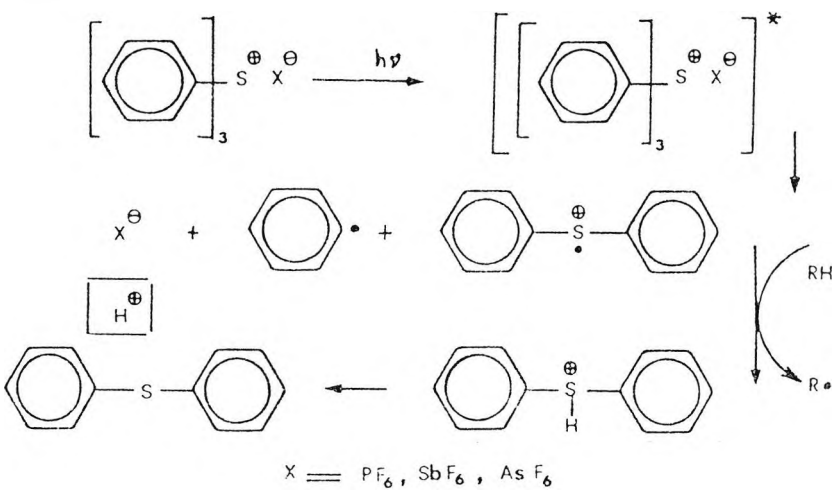
(B) 

(C) 

cycloaliphatic epoxide

The use of onium salts e.g. iodonium and sulphonium salts to initiate the polymerization of epoxides is well reported (i.e. cationic polymerization) [18].

Sulphonium Salts Photolysis



The photoinduced decomposition of the salts leads to the production of Bronsted acids and radicals.

The photodecomposition and sensitized decomposition of diphenyliodonium hexafluorophosphate can induce free-radical polymerization reactions.

$$Ph_2I\,PF_6 \xrightarrow{hv} PhI^{(+)} + Ph\cdot + PF_6^{(-)} \quad (1)$$

$$PhI^{(+)} + RH \rightarrow PhIH^{(+)} + R\cdot \quad (2)$$

$$PhIH^{(+)} + PF_6^{(-)} \rightarrow PhI + HPF_6 \quad (3)$$

The results obtained from the moving belt system showed that diphenyliodonium hexafluorophosphate in the presence of 2 - ethyl - 2- (hydroxymethyl) - 1,3 - propanediol triacrylate under aerobic conditions does not induce efficient polymerization. This is due to the fact that the phenyl radical formed (Eqn (1)) is not a stable radical, and is an inefficient initiator. Under aerobic conditions, the radical is scavenged by oxygen, therefore inhibiting the polymerization of the triacrylate.

In the absence of oxygen and u.v. light (i.e. touching glass slide which absorbs u.v. light $\lambda < 330$nm), there was no polymerization. This is due to the fact that diphenyliodonium hexafluorophosphate absorbs in the u.v. region only, and there is very little absorption of light by the iodonium salt under the glass slide, preventing polymerization.

The iodonium salt was then tested in the presence of an epoxy resin (Degacure K126). Under quartz (i.e. in the absence of oxygen and presence of u.v./visible light), a tack-free film was formed within seven passes under the colordry. The iodonium salt undergoes photodecomposition to form cations, which initiate the polymerization process.

In the absence of oxygen and u.v. light (i.e. touching glass slide), there was no polymerization. This was due to the glass slide absorbing u.v. light, preventing any

absorption of light by the iodonium salt itself. The presence of a filter (i.e raised glass slide) prevents any u.v. absorption ($\lambda < 330nm$) by the photoinitiator, therefore preventing polymerization of the epoxy resin.

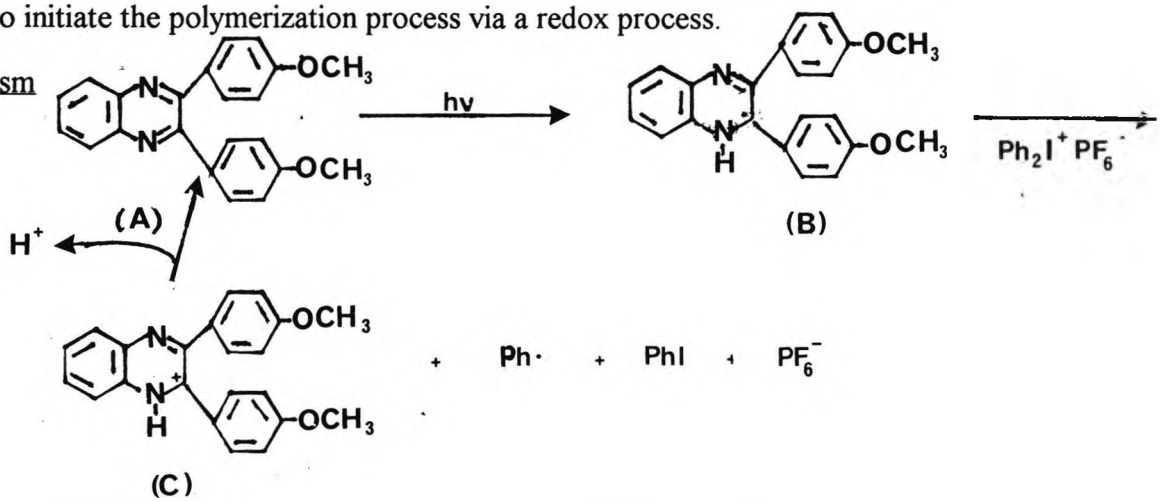
In the presence of air, there was some polymerization due to the fact that oxygen does not affect the rate of polymerization in cationic systems.

The quinoxaline was tested in the presence of diphenyliodonium hexafluorophosphate in an equivalent amount of 2-ethyl -2(hydroxymethyl)-1,3 - propanediol triacrylate and Degacure K126 (an epoxy resin).

Under anaerobic conditions (i.e. under quartz and touching glass slide) a tack - free film was formed in one pass in the moving belt system. When the film was covered by quartz (i.e. in the absence of oxygen and presence of u.v. / visible light) both radical and cationic polymerization . occurred (i.e. a mixed system).

Under a glass slide (i.e. in the absence of oxygen and u.v. light), any light absorbed will be absorbed by the quinoxaline, which may abstract a hydrogen atom from the solvent to initiate the polymerization process via a redox process.

Mechanism



Under aerobic conditions (i.e. air and filter) oxygen scavenges the radical formed (B), preventing polymerization.

The quinoxaline was then tested in the presence of the iodonium salt and Degacure K126 (epoxy resin). Under anaerobic conditions (i.e. quartz and touching glass slide) a tack-free film was formed in two passes under the colordry.

The results show that under anaerobic conditions, the quinoxaline abstracts a hydrogen atom from the solvent and forms radical (B). This reacts with the iodonium salt, forming radicals as shown above. The quinoxaline forms a cation, which initiates the polymerization of the epoxy resin.

Under aerobic conditions (i.e. air and filter), a tack-free film was formed within five passes in the moving belt system. The cation formed, (C) initiated the polymerization of Degacure K126. Cationic polymerization is not affected by the presence of oxygen. It is proposed that the quinoxaline cation formed loses H^+, regenerating the quinoxaline (A).

The results obtained show that quinoxalines can be used as ultraviolet or visible range sensitizers for epoxy resins and are useful in cationic polymerization.

Table 16:- U.V. Curing of 2,3-bis(4-methoxyphenyl) quinoxaline in the presence of an iodonium salt

Samples	No. of Passes Under Colordry				
	Quartz		Glass Slide	Air	Filter
$Ph_2I^+PF_6^-$ + Epoxy Resin	7		30+	25	30+
$Ph_2I^+PF_6^-$ + TMPTA	6		30+	30+	30+
50:50 / TMPTA / Epoxy Resin + $Ph_2I^+ PF_6^-$	1 (Yellow Film)		1 (Yellow Film)	30+	30+
$Ph_2I^+PF_6^-$ + Epoxy Resin	1st pass	Yellow film	Yellow film	Yellow film	Yellow film
	2nd pass	Red Film	Yellow film(cured)	Yellow film	Yellow film
	3rd pass			Red Film	Yellow film
	4th pass			Red Film	Yellow film
	5th pass				Yellow film(cured)

a. Monomer used:- 2-Ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate (i.e. Trimethylolpropane triacrylate (TMPTA))

b. Epoxy resin used:- Degacure K126

c. Belt Speed:- 10ft/min

d. 1% w/w of quinoxaline used

e. 1% w/w of iodonium salt used

The Use of Quinoxalines as Photoinitiators in Bulk Polymerization

(i) Equation to determine weight of initiator to be used in the formulation.

Constant x Molecular weight of initiator
= weight of initiator/10cc CH_2Cl_2

Table 17.

Photoinitiator	Molecular weight of initiator	Weight of initiator (g)10cc CH_2Cl_2	% of Polymer formed	Time taken (mins)
e	386	0.04	100	1
a	314	0.03	10 100	7 14
h	342	0.034	100	0.5
g	446	0.044	100	0.5
f	412	0.04 (problem with solubility)	10 100	15 35
Irgacure 907	279	0.027	100	1

(a) Amine used :- 1g of N-methyldiethanolamine
(b) Monomer :- 1g of 2- ethyl - 2(hydroxymethyl) - 1,3 -propanediol triacrylate

Discussion

The solutions were placed in small pyrex tubes and irradiated vertically with a small diameter beam of light.

The amount of polymer formed was measured by (i) weighing the polymer formed or (ii) dissolving the polymer in an appropriate solvent and then removing the solvent under vacuum.

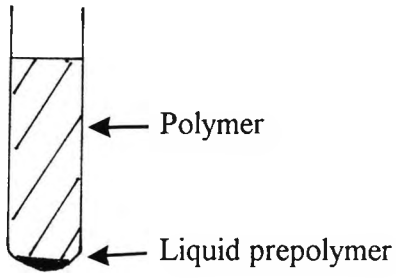
The percentage of polymer formed

$$= \frac{\text{weight of polymer}}{\text{weight of monomer}} \times 100$$

All polymerization reactions were carried out in the presence of oxygen. 2,3 - Bis (4-hydroxyphenyl) quinoxaline polymerized 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate within fourteen minutes.

If the results are compared with 2,3-bis (4-methoxyphenyl) quinoxaline, they show that 2,3-bis (4-hydroxyphenyl) quinoxaline is not an efficient initiator due to ionisation of the quinoxaline.

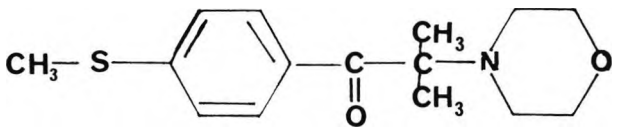
The quinoxalines formed a cylinder of polymer with a very small amount of liquid prepolymer at the bottom of the sample tube.



7-Benzoyl - 2,3 - bis (4-methoxyphenyl) quinoxaline formed a cylinder of polymer after thirty seconds, showing that it is an efficient initiator, thus supporting the result obtained from the moving belt system (i.e. colordry).

7-Benzoyl - 2,3 - diphenyl quinoxaline, also formed a large cylinder of polymer and very small amount of prepolymer. This suggests that the quinoxalines are efficient initiators and may be useful in 3D-imaging

The results obtained were compared with a commercially efficient photoinitiator,. Irgacure 907.



The time taken for the total polymerization of 2- ethyl - 2- (hydroxymethyl) - 1,3 - propanediol triacrylate was one minute.

This shows that the polymerization of the triacrylate containing 2,3-bis (4-methoxyphenyl) quinoxaline and 7-benzoyl-2,3-bis (4-methoxyphenyl) quinoxaline as initiators produces efficient curing systems under aerobic conditions.

1,2 - Anthraquinone - 2,3 - diphenylquinoxaline showed little promise as a visible range photoinitiator, due to the low solubility of the compound.

Table 18 :- Real - Time Infra Red Spectroscopy

Samples	Atmosphere	Rp (% / s)	Total Conversion	Residual Unsaturation Content (Ru)(%)
e +TMPTA	Absence Of Air	1.7	41%	59%
e +TMPTA	Presence Of Air	1.5	41%	59%
g +TMPTA	Absence Of Air	3.75	60%	40%
g +TMPTA	Presence Of Air	0.71	35%	65%
h +TMPTA	Absence Of Air	4.63	66%	34%
h +TMPTA	Presence Of Air	1.1	46%	54%
b +TMPTA	Absence Of Air	0.63	35%	65%
b +TMPTA	Presence Of Air	----	8%	92%
a +TMPTA	Absence Of Air	---	21%	79%
a +TMPTA	Presence Of Air	----	---	---

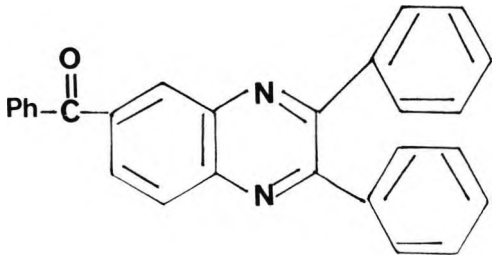
All samples were tested in the presence of a synergist , N-methyldiethanolamine
The formulation was :

(i) 1% w/w of quinoxaline
(ii) 10% w/w of N-methyldiethanolamine
(iii) Monomer 2-Ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

The substrate used was sodium chloride plates. A coverslip was placed above the film to carry out the polymerization process under anaerobic conditions.

Real-Time Infra-red Spectroscopy

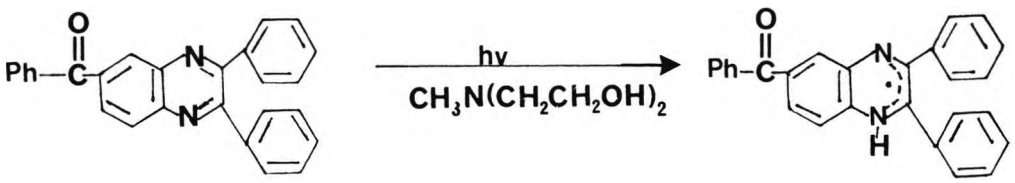
7-Benzoyl - 2,3 - diphenylquinoxaline (A) was tested in the presence of 10% w/w of N-methyldiethanolamine.

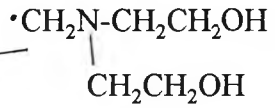


(A)

Under anaerobic conditions the rate of polymerization was 1.7%/s and a total conversion of polymerization of 41% was obtained after 5 minutes.

In the presence of an amine, the quinoxaline in the excited state abstracts a hydrogen atom from the amine, forming an α-aminoalkyl radical (i.e. Type II initiator).

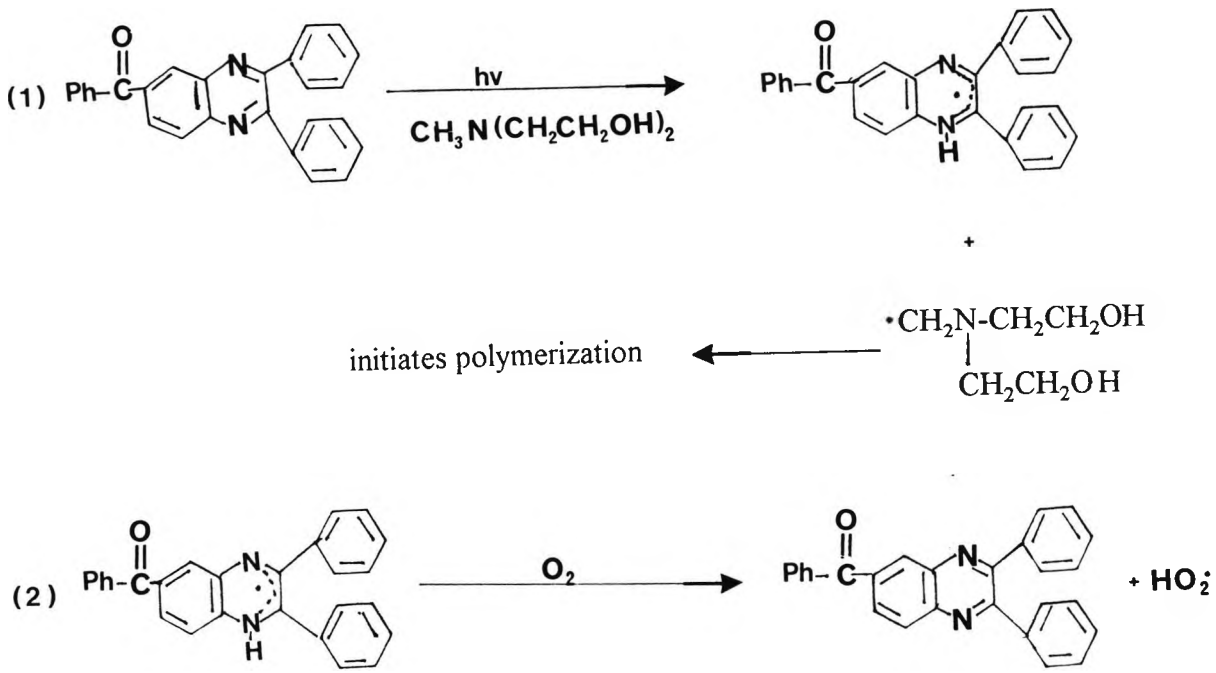




Initiates polymerization of 2 - ethyl - 2 (hydroxymethyl) - 1,3 - propanediol triacrylate

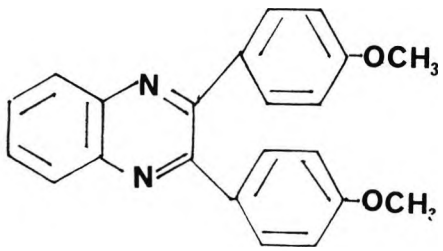
Under aerobic conditions, a rate of polymerization of 1.5%/s and a total conversion of 41% were obtained after five minutes. The results were similar to those obtained under anaerobic conditions.

The results show, that the rate and the total conversion of polymerization are not affected by the presence of oxygen. This is due to the quinoxaline being regenerated on admission of air, as shown :



2,3 - Bis (4-methoxyphenyl) quinoxaline (B), under anaerobic conditions, polymerizes efficiently at a rate of polymerization (Rp) of 4.63%/s and a total conversion of polymerization of 66%.

(B)



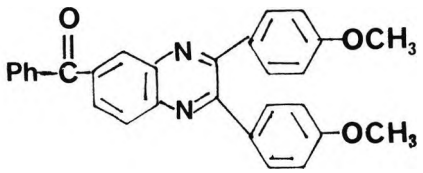
The increase in the rate of polymerization and total conversion as compared to 7-benzoyl -2,3 - diphenylquinoxaline (A) is due to the methoxy derivative being more soluble than (A) in the triacrylate. Obviously, more of the initiator is dissolved in the acrylate, therefore increasing the rate of polymerization and total conversion.

Also, in the case of 7-benzoyl - 2,3 - diphenylquinoxaline it would have been more appropriate to use a xenon-arc lamp, as the benzoyl derivatives absorb more in the far u.v. - visible region of the spectrum.

In the moving belt system, 2,3 -bis (4-methoxyphenyl) quinoxaline polymerizes to form a tack-free film within one pass under aerobic and anaerobic conditions.

Under aerobic conditions, the results obtained from real-time infrared spectroscopy showed an Rp value of 1.1%/s and a total conversion of 46% after 5 minutes . There are circumstances which arise, whereby the results obtained from real-time infrared spectroscopy do not coincide with the results from the moving belt system. In the moving belt system, a more powerful lamp is used, and the heat generated in the system has to be taken into account in the polymerization process.

7-Benzoyl - 2,3-bis (4-methoxyphenyl) quinoxaline (C) polymerizes efficiently under aerobic and anaerobic conditions.

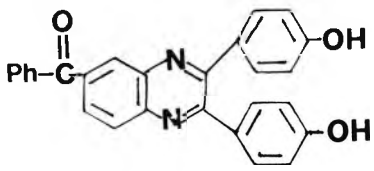
(C) 

Under anaerobic conditions an Rp value of 3.75%/s and a total conversion of 60% were obtained. The results show a reduction in the rate of polymerization and total conversion, when compared with 2,3-bis (4-methoxyphenyl) quinoxaline. The reason may be due to the solubility factor in which the benzoyl derivative is a lot less soluble in the acrylate.

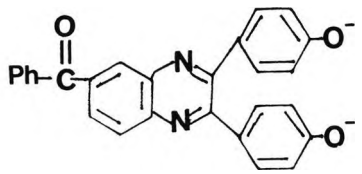
Under aerobic conditions, an Rp value of 0.71%/s and a total conversion of 35% were obtained.

The reduction in the rate of polymerization and total conversion compared to 2,3 - bis (4-methoxyphenyl) quinoxaline, is due to the fact that a mercury lamp was used rather than a xenon-arc lamp, as explained earlier.

7-Benzoyl - 2,3 - bis (4-hydroxyphenyl) quinoxaline (D), was tested under anaerobic conditions, when a rate of polymerization of 0.63%/s and a total conversion of 35% were obtained.

(D) 

One of the reasons for the poor performance of the photoinitiator is due to the ionisation of (D) forming the species, (E) as shown below

(E) 

The above species (E), is a poor electron acceptor, and shows very little promise as an efficient initiator. Under aerobic conditions, there is very little polymerization of the triacrylate. This is due to the ionisation of the species, and also the presence of oxygen, scavenging the radicals formed.

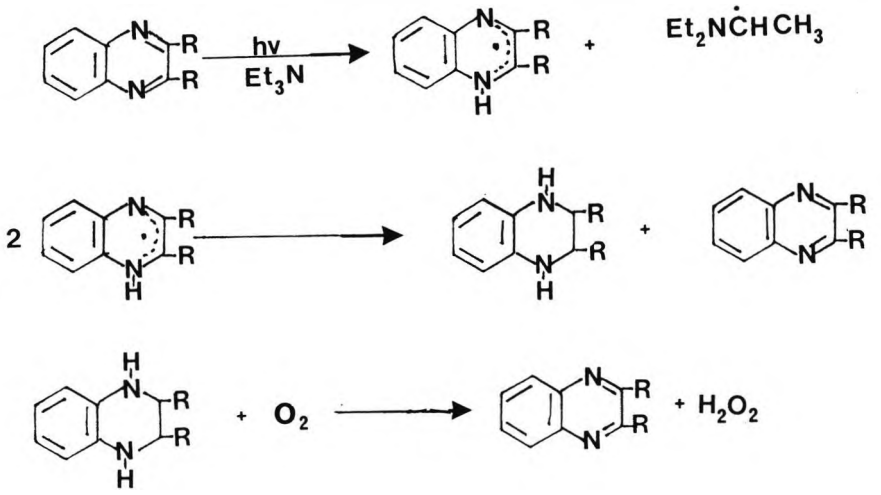
2,3 - Bis(4-hydroxyphenyl) quinoxaline (F) did not induce free-radical polymerization of 2-ethyl - 2(hydroxymethyl) - 1,3 - propanediol triacrylate.

The reason for the poor performance is due to the ionisation of the hydroxy groups.

Conclusion

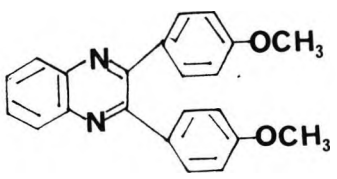
It can be concluded that quinoxalines can initiate the polymerization of acrylates.

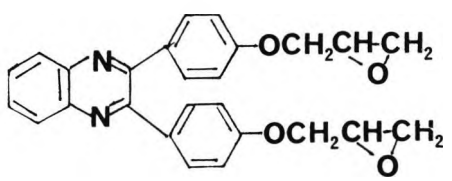
The results obtained from the moving belt system, shows that the quinoxalines can act as photoinitiators in thin films. The results support the earlier mechanism proposed:-



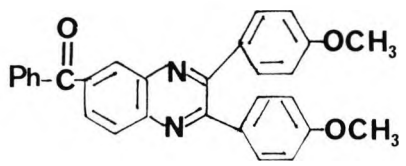
It can be concluded that quinoxalines are regeneratable photoinitiators, whereby on admission of air, the quinoxaline is regenerated.

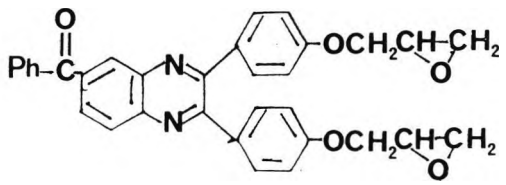
The main problem of using quinoxalines as photoinitiators in thin films is the solubility of the compounds. The problem was solved by preparing the methoxy and glycidyl derivatives ((A)and (B)).

(A) 

(B) 

Also it was proposed to prepare various visible range initiators that are also soluble in various monomers (e.g. compounds (C) and (D)).

(C) 

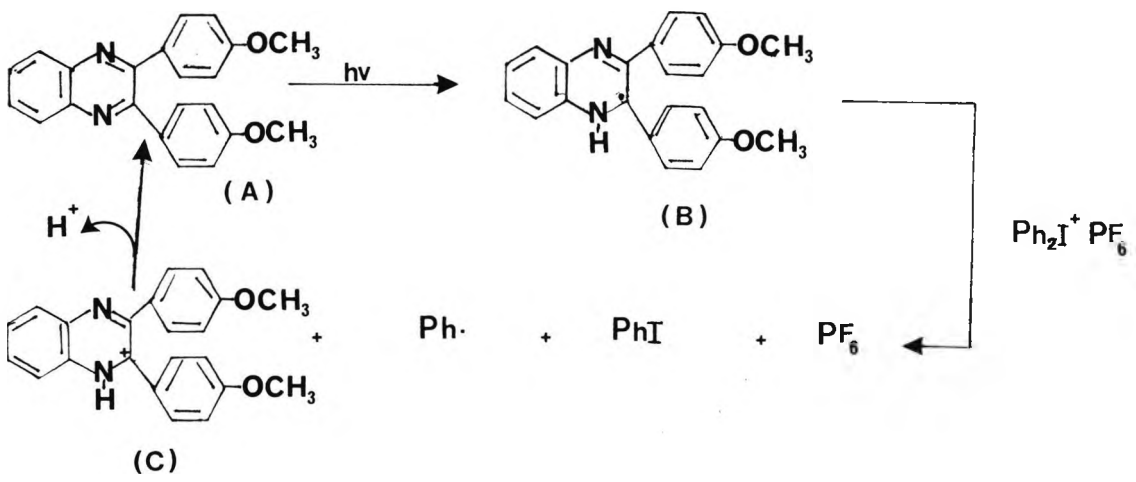
(D) 

The results obtained from bulk polymerization experiments supported the results obtained from the moving belt system. The results also showed that quinoxalines may be useful in 3D imaging.

2,3 - Bis (4-methoxyphenyl) quinoxaline (A), was tested in the presence of diphenyliodonium hexafluorophosphate. The results show that quinoxalines can be used as ultraviolet and visible range initiators in cationic polymerization.

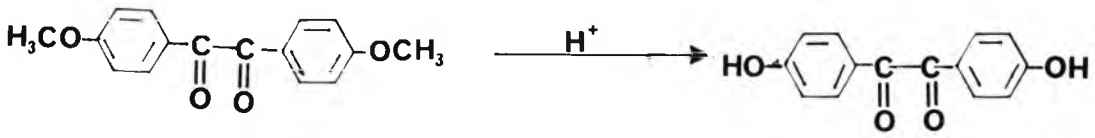
The quinoxalines can be used as initiators in both cationic and free radical polymerization processes.

i.e.



4.3 EXPERIMENTAL DETAILS

A. Preparation of 4,4'-dihydroxybenzil



Dimethoxybenzil (10g) was added to 150ml of hydrobromic acid and acetic acid (120ml). The mixture was refluxed for 24 hours, and the reaction was followed by t.l.c. A brown product was formed, which was recrystallised from methanol forming a yellow crystalline product [19].

NMR analysis (100 MHz, d-methanol/TMS)

7.8 - (m,4H) - Protons next to C=O

6.9 - (m,4H) - Protons next to OH.

Infra-red analysis (KBr disc)

3397cm^{-1} , (s), OH Stretch

1640cm^{-1} , (s), C=O Stretch

1599cm^{-1} , (s), C=C Stretch

1511cm^{-1} , (s), C=C Stretch(aromatic)

CHN analysis (%)

	Expected	Found
C,	69.42	69.56
H,	4.13	4.11

Formula : $C_{14}H_{10}O_4$

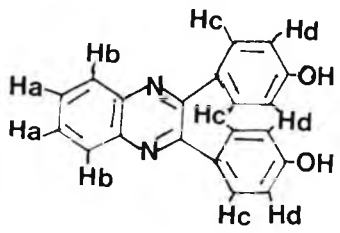
B. Preparation of 2,3 - bis (4-hydroxyphenyl) quinoxaline

4,4' - Dihydroxybenzil (2g, 0.008m) was dissolved in a minimum amount of acetic acid.

An equivalent amount of 1,2 - phenylenediamine was added and the mixture was refluxed for two hours. The reaction was followed by t.l.c. The yield of the reaction was 80% [20,21].

The product was purified by column chromatography on silica gel using dichloromethane as the solvent.

NMR analysis (100 MHz, d-acetone)



8.2 - (m,2H) - Ha

7.8 - (m,2H) - Hb

7.5 - (m, 4H) - Hc

6.9 - (m,4H) - Hd

Infra-red analysis (KBr disc)

3476cm^{-1} , (s), OH Stretch

1606cm^{-1} , (s), C=C Stretch (aromatic)

1516cm^{-1} , (s), C=C Stretch (aromatic)

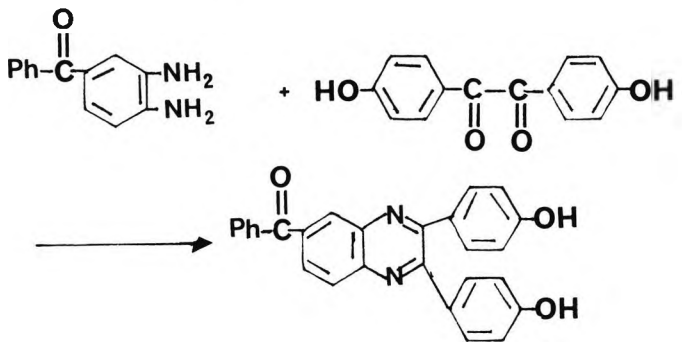
CHN analysis(%)

	Expected	Found
C,	76.4	75.98
H,	4.8	4.59
N	8.91	8.93

Formula : $C_{20}H_{14}N_2O_2$

Melting point:- >200°C

C. Preparation of 7-benzoyl -2,3 -bis (4-hydroxyphenyl) quinoxaline



Method

3,4-Diaminobenzophenone (5g, 0.02m) was dissolved in 150mls of acetic acid.

An equivalent amount of 4,4'-dihydroxybenzil was added and the mixture was refluxed for two hours.

The reaction was followed by t.l.c. (Yield = 85%). The product was purified by column chromatography; dichloromethane/silica gel.

NMR analysis (100 MHz, d-acetone/TMS)

8.3 - (s,1H) - Ha

8.0 - (m,2H) - Aromatic protons next to C=O

7.9-7.0 - (m, 9H) - Aromatic protons

6.9 - (m,4H) - Protons next to OH group

2.9 - Broad peak due to OH

2.0 - d-acetone

After D_2O shake, OH peak disappears

Infra-red analysis (KBr disc)

3404cm^{-1} , (s), OH Stretch

1648cm^{-1} , (s), C=O Stretch

1606cm^{-1} , (s), C=C Stretch (aromatic)

1513cm^{-1} , (s), C=C Stretch (aromatic)

CHN analysis(%)

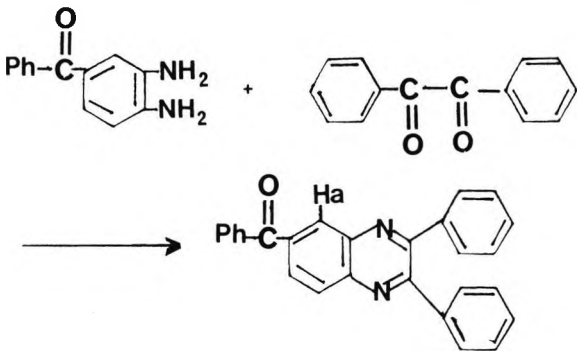
	Expected	Found
C,	77.5	77.97
H,	4.3	4.36
N,	6.7	6.56

Formula : $C_{27}H_{18}N_2O_3$

U.V. Spectrum λ max = 390nm, (E=15,000)

Melting point:- >250°C

D. Preparation of 7 - benzoyl - 2,3 - diphenylquinoxaline



Method

3,4 - Diaminobenzophenone (5g, 0.02m) was dissolved in 200mls of acetic acid. An equivalent amount of benzil was added. The mixture was refluxed for two hours, and the reaction was followed by t.l.c. (Yield=80%). The product was purified by column chromatography on silica gel using acetone as the solvent.

NMR analysis (270 MHz, d-acetonotrile)

8.42 , (s,1H) - Ha

8.25 , (m,2H) - Aromatic protons

8.0-7.6 , (m, 9H) - Aromatic protons

7.4-7.2 , (m,6H) - Aromatic protons

Infra-red analysis (KBr disc)

1660cm^{-1} , (s), C=O Stretch

1612cm^{-1} , (s), C=C Stretch (aromatic)

1491cm^{-1} , (s), C=C Stretch (aromatic)

CHN analysis(%)

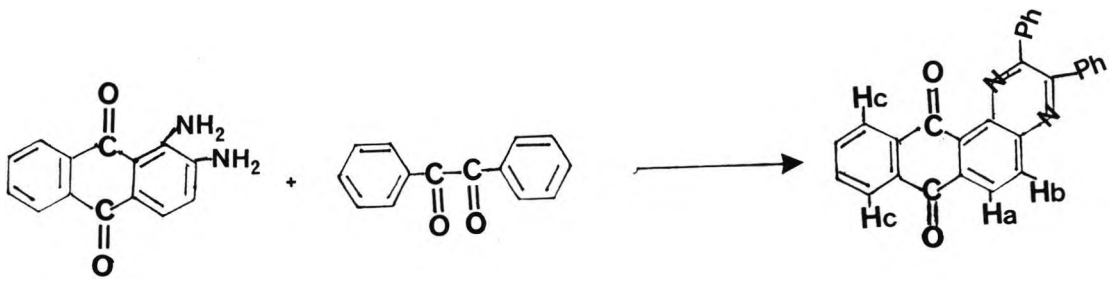
	Expected	Found
C,	83.9	83.59
H,	4.66	4.60
N	7.25	7.16

Formula : $C_{27}H_{18}N_2O$

Melting point:- 138°C - 140°C

U.V. Spectrum:- λ max = 357nm, (E=12000)

E. Preparation of 1,2 - anthraquinone -2,3 - diphenylquinoxaline



1,2-diaminoanthraquinone

Method

1,2-Diaminoanthraquinone (5g, 0.02m) was dissolved in 150ml of acetic acid. An equivalent amount of benzil was added and the mixture was refluxed for two hours. The reaction was followed by t.l.c.

A brown product was formed (Yield=80%). The product was purified by column chromatography on alumina using acetone as the solvent.

NMR analysis (270 MHz, d-chloroform)

8.65 - (d,1H) - Ha

8.40 - (d,1H) - Hb

8.20 - (m,2H) - Hc

7.8-7.0 (m,13H) - Aromatic protons

Infra-red analysis (KBr disc)

1658cm^{-1}, (s), C=O Stretch

1600cm^{-1}, (s), C=C Stretch (aromatic)

1468cm^{-1}, (s), C=C Stretch (aromatic)

CHN analysis(%)

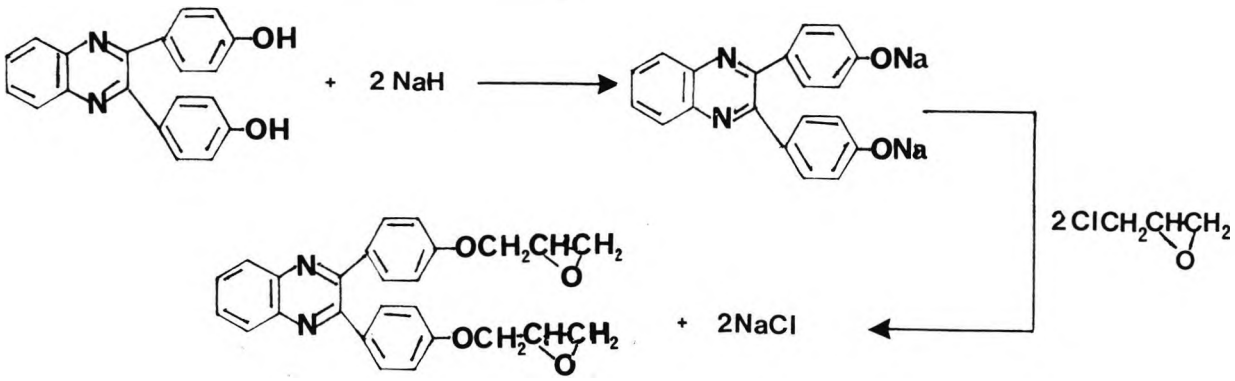
	Expected	Found
C,	81.55	81.23
H,	3.88	3.71
N	6.8	6.5

Formula : $C_{28}H_{16}N_2O_2$

Melting point:- >250°C

U.V. Spectrum:- λ max = 400nm, (E=15000)

F. Preparation of 2,3 - bis (4-glycidylphenyl) quinoxaline



2,3 - Bis (4-hydroxphenyl) quinoxaline (2g, 0.0006m) was dissolved in 150mls of dried tetrahydrofuran the solvent was dried by adding calcium sulphate, which was left to stand for 24 hours. The calcium sulphate was filtered off and sodium strips were added, and left to stand for a further 24 hours.

Sodium hydride (0.28g, 0.01m) was added carefully, and the mixture was refluxed for two hours. Epichlorohydrin was added and the mixture was refluxed for another twenty-four hours.

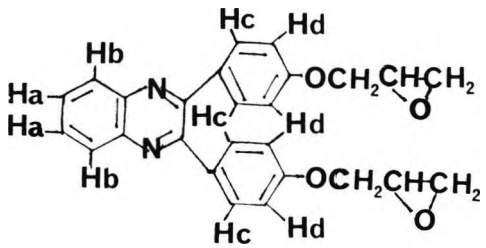
A white precipitate of sodium chloride was formed, which was filtered off. The tetrahydrofuran solvent was removed, using a rotary evaporator.

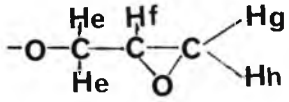
A yellow residue was formed, which was dissolved in acetone and re-precipitated by the addition of water.

The yellow product was filtered off and dried in an oven for twenty-four hours.

NMR analysis (100 MHz, d-dichloromethane/TMS)

8.0 -	(m,2H) - Ha	4.2 -	(m,4H) - He
7.7 -	(m,2H) - Hb	3.8 -	(m,2H) - Hf
7.4 -	(m,4H) - Hc	3.2 -	(m,2H) - Hg
6.8 -	(m,4H) - Hd	2.8 -	(m,2H) - Hh





Infra-red analysis (KBr disc)

$2925cm^{-1}$, (m), CH-aliphatic

$1606cm^{-1}$, (s), C=C Stretch

$1250cm^{-1}$, (s), epoxide linkage

$1029cm^{-1}$, (s), C-O Stretch

$836cm^{-1}$, (s), epoxide linkage

CHN analysis(%)

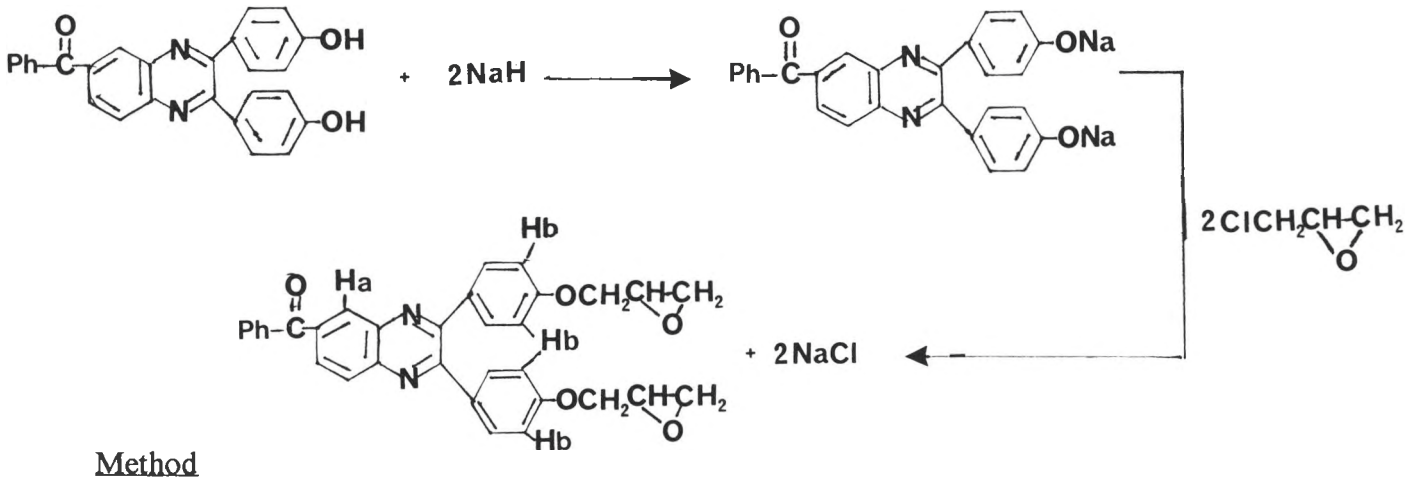
	Expected	Found
C,	73.2	73.18
H,	5.2	5.8
N,	6.5	6.25

Formula : $C_{26}H_{22}N_2O_4$

Melting point:- 120 - 122°C

U.V. Spectrum:- λmax = 372nm, (E=14000)

G. Preparation of 7-benzoyl - 2,3 - bis (4-glycidylphenyl) quinoxaline



Method

As for 2,3 - bis (4-glycidylphenyl) quinoxaline

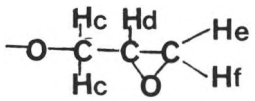
NMR analysis (100 MHz, H'NMR) - d-methanol/T.M.S).

8.2 , (s,1H) - Ha

8.0 , (m,2H) - Aromatic protons

7.8-7.0 , (m, 9H) - Aromatic protons

6.9 , (m,4H) - Hb



4.2 , (m,4H) - H_c

3.8 , (m,2H) - H_d

3.2 , (m,2H) - H_e

2.8 , (m,2H) - H_f

Infra-red analysis (KBr disc)

2926cm^{-1} , (m), CH-aliphatic stretch

1654cm^{-1} , (s), C=O stretch

1606cm^{-1} , (s), C=C stretch

1249cm^{-1} , (s), epoxide linkage stretch

1029cm^{-1} , (s), C-O stretch

836cm^{-1} , (s), epoxide linkage stretch

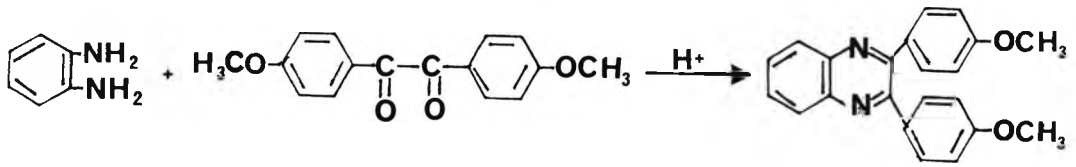
CHN analysis(%)

	Expected	Found
C,	74.7	74.2
H,	4.9	4.7
N,	5.28	5.18

Formula : $C_{33}H_{26}N_2O_5$

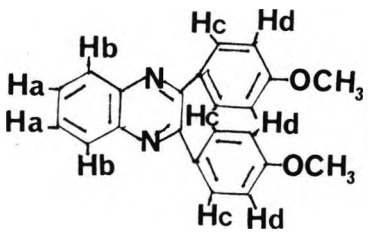
Melting point:- 150 - 152°C

H. Preparation of 2,3 - bis (4-methoxyphenyl) quinoxaline



1,2 - Phenylenediamine (5g) was dissolved in 200mls of acetic acid. 4,4' - Dimethoxybenzil was added and the mixture was refluxed for 6 hours [22,23,24]. The reaction was followed by t.l.c. (Yield=80%). A white product was formed, which was recrystallised from methanol.

NMR analysis (100 MHz, H'NMR), Solvent - d - acetone, TMS



8.0 , (m,2H) - Ha

7.8 , (m,2H) - Hb

7.6 , (m,4H) - Hc

6.9 , (m,4H) - Hd

3.9 , (s,6H) - OCH_3 protons

2.0 - (d-acetone)

Infra-red analysis (KBr disc)

2933cm^{-1} , (m), CH - aliphatic

1606cm^{-1} , (s), C=C stretch (aromatic)

1250cm^{-1} , (s), C–O stretch

1059cm^{-1} , (s), C-O stretch

CHN analysis(%)

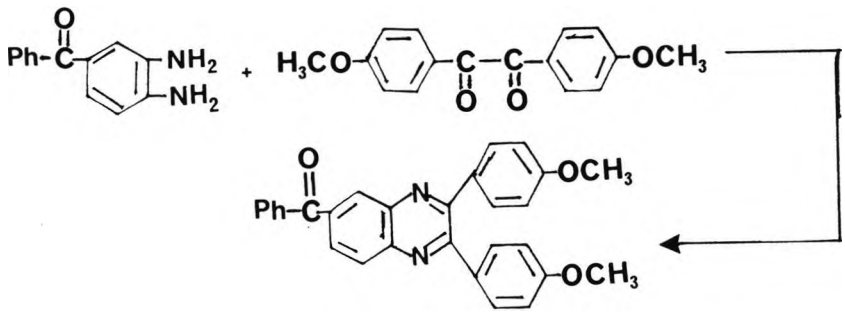
	Expected	Found
C,	77.19	76.89
H,	5.26	5.23
N,	8.1	7.85

Formula : $C_{22}H_{18}N_2O_2$

Melting point:- 138 - 140°C

U.V. Spectrum:- λ max = 367nm, (E=14000)

I. Preparation of 7-benzoyl - 2,3-bis (4-methoxyphenyl) quinoxaline



Method:- As for 2,3 - bis (4-methoxyphenyl) quinoxaline.

NMR analysis (100 MHz, d-acetone /TMS.)

8.3 (s,1H) - Ha

8.1 (m,2H) - Protons next to C=O

8.0-7.5 (m, 9H) - Aromatic protons

6.9-6.7 (m,4H) - Aromatic protons next to OCH_3

3.8 (s,6H) - CH_3 protons

Infra-red analysis (KBr disc)

2956cm^{-1} , (m), CH-aliphatic

1650cm^{-1} , (s), C=O stretch

1605cm^{-1} , (s), C=C stretch (Aromatic)

1249cm^{-1} , (s), C-O stretch

1060cm^{-1} , (s), C-O stretch

CHN analysis(%)

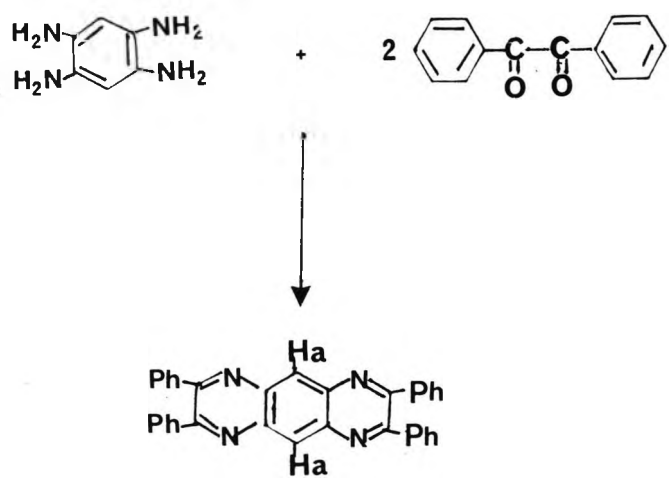
	Expected	Found
C,	78.0	77.5
H,	4.9	4.74
N,	6.2	5.86

Formula : $C_{29}H_{22}N_2O_3$

Melting point:- 158 - 160°C

U.V. Spectrum:- λ max = 390nm, (E=15000)

J. Preparation of 2,3,7,8 - tetraphenylpolyquinoxaline



Method:- As for 2,3-bis (4-methoxyphenyl) quinoxaline

The product was purified by recrystallisation from methanol [25,26].

NMR analysis (100 MHz, d-dichloromethane /TMS.)

8.9 , (s,2H) - Ha

7.7 , (m,8H) - Aromatic protons

7.4 , (m,12H) - Aromatic protons

5.2 , (d-dichloromethane)

A problem encountered with the polyquinoxaline was to find the appropriate nmr solvent, as the quinoxaline was insoluble in a lot of the deuterated solvents.

Infra-red analysis (KBr disc)

1595cm^{-1} , C=C Stretch (Aromatic)

1450cm^{-1} , C=C Stretch (Aromatic)

Melting point:- >280°C (literature = 308-312°C)

U.V. Spectrum:- λ max = 420nm

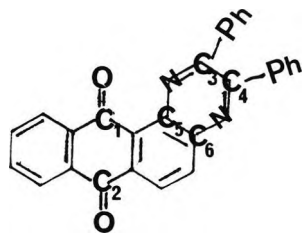
CHN analysis(%)

	Expected	Found
C,	83.9	83.3
H,	4.5	4.24
N,	11.5	11.54

Formula : $C_{34}H_{22}N_4$

^{13}C NMR Spectrum of Quinoxalines:[27]

1. 1,2 - Anthraquinone - 2,3 - diphenylquinoxaline



^{13}C NMR analysis (ppm), d-chloroform/TMS

Carbon

(1.) , C=O - 206.402

(2.) , C=O - 206.110

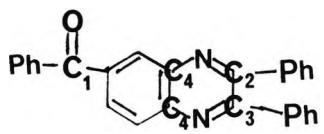
(3) , C=N - 155.949

(4) , C=N - 155.413

(5) , C-N - 143.575 (lit value 145.47)

(6) , C-N - 140.947

(2). 7-Benzoyl - 2,3-diphenylquinoxaline



^{13}C NMR analysis (ppm), d-chloroform/TMS

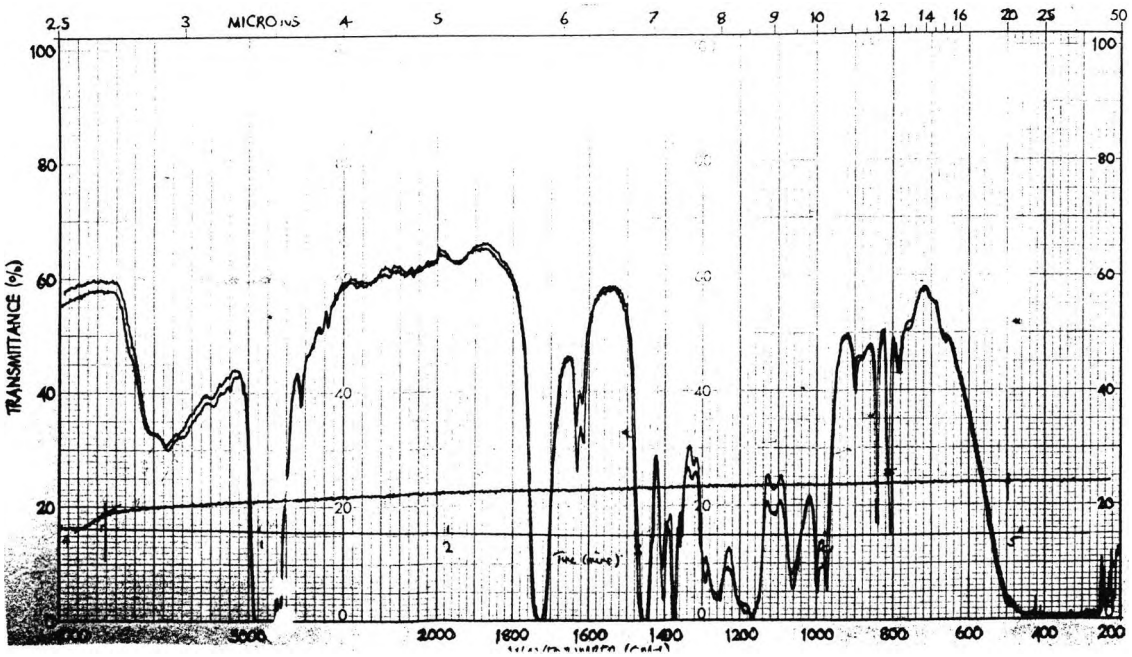
Carbon

(1.) , C=O - 194.563

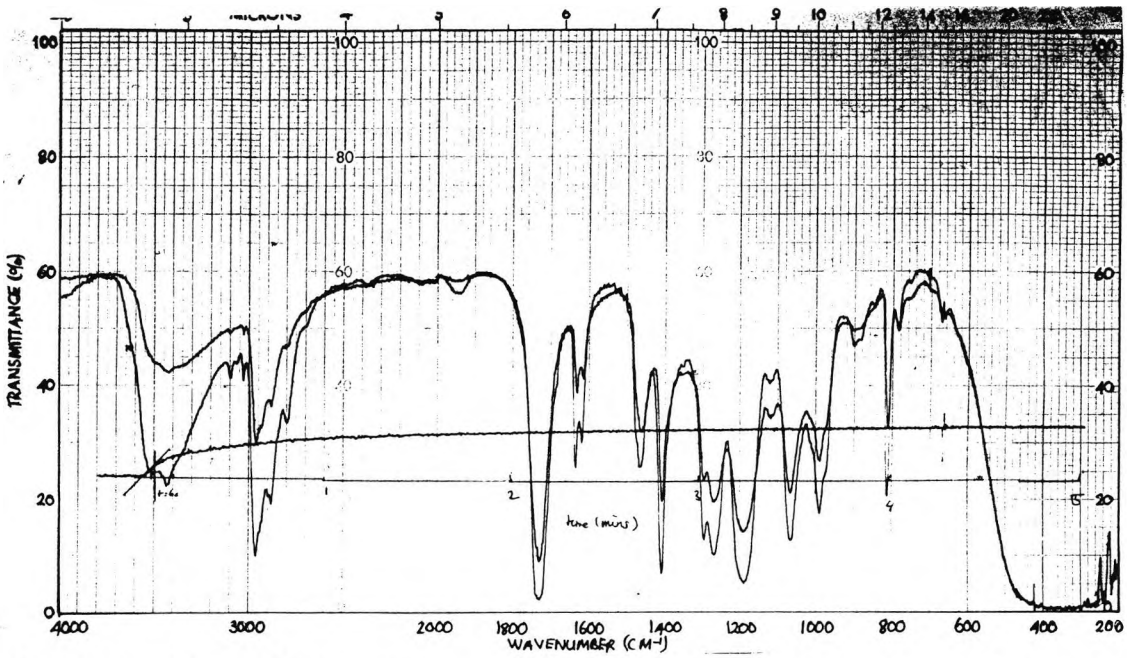
(2.) , C=N - 155.235

(3) , C=N - 154.359

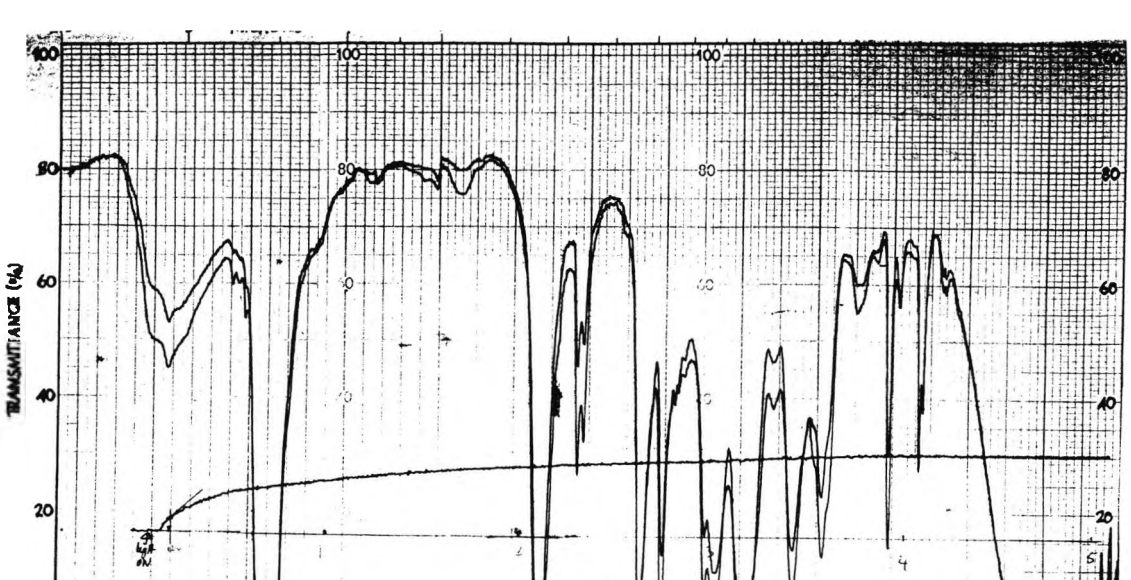
(4) , C=N - 143.039 (Lit value 143.47)



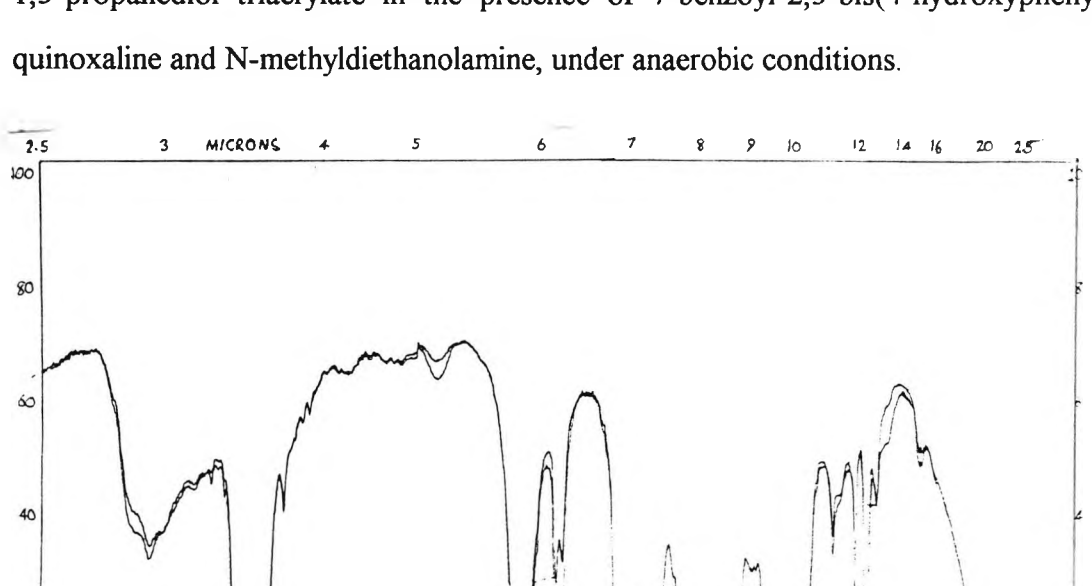
Spectrum 1: RTIR spectrum showing the polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate in the presence of 7-benzoyl-2,3-diphenylquinoxaline and N-methyldiethanolamine, under anaerobic conditions.



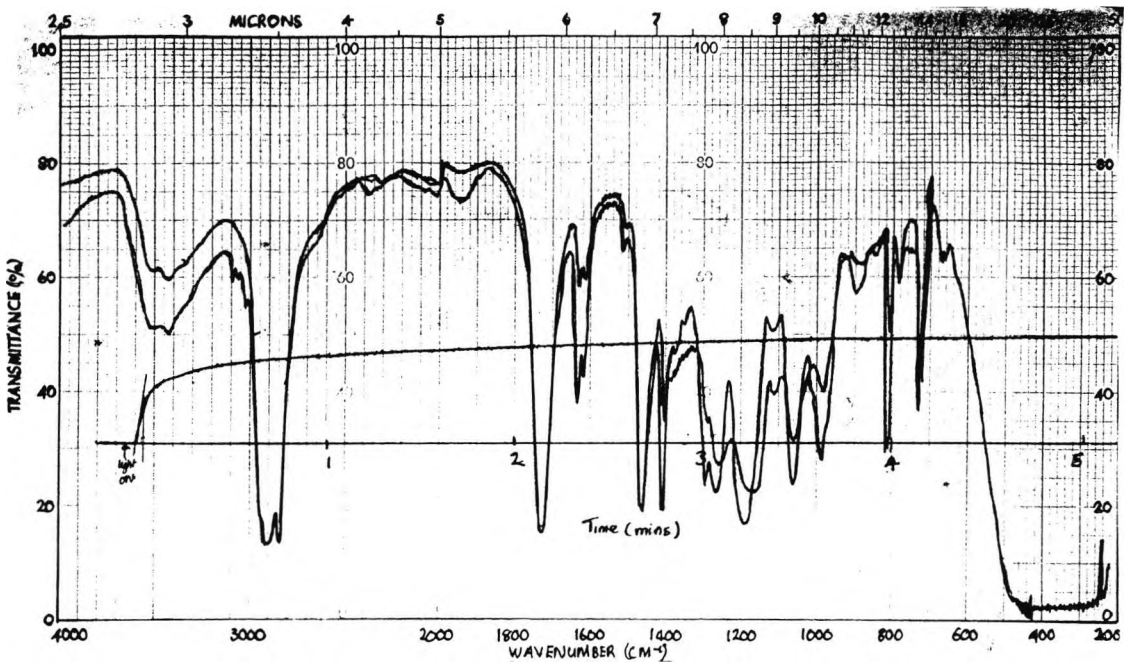
Spectrum 2: RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of 7-benzoyl-2,3-diphenylquinoxaline and N-methyldiethanolamine, under aerobic conditions.



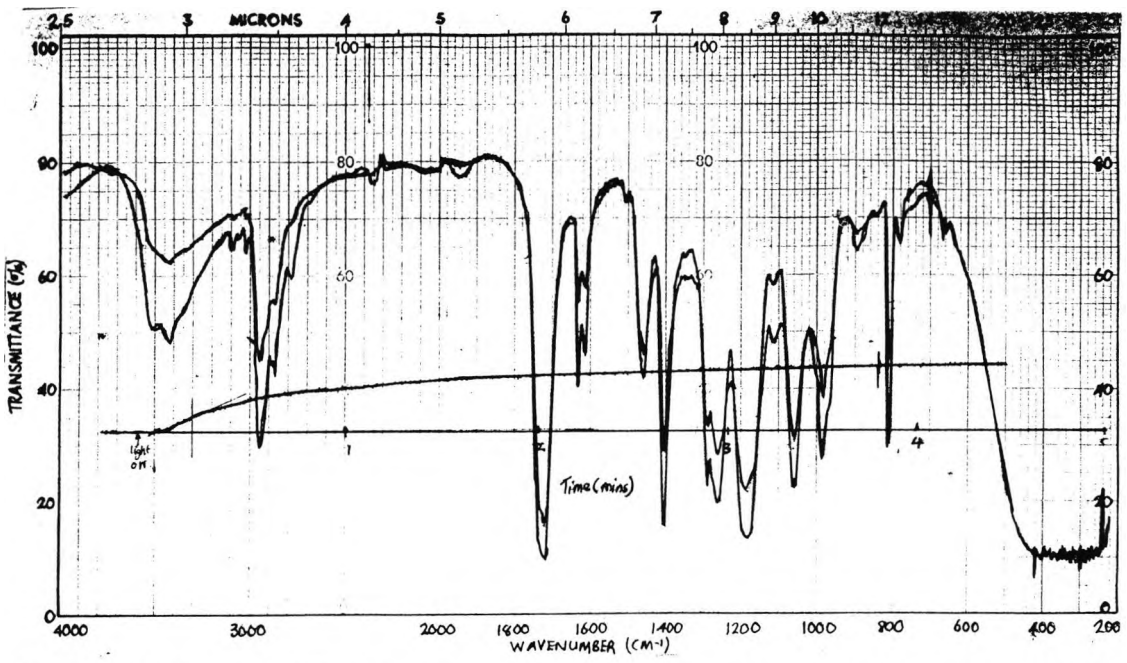
Spectrum 3: RTIR spectrum showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of 7-benzoyl-2,3-bis(4-hydroxyphenyl)-quinoxaline and N-methyldiethanolamine, under anaerobic conditions.



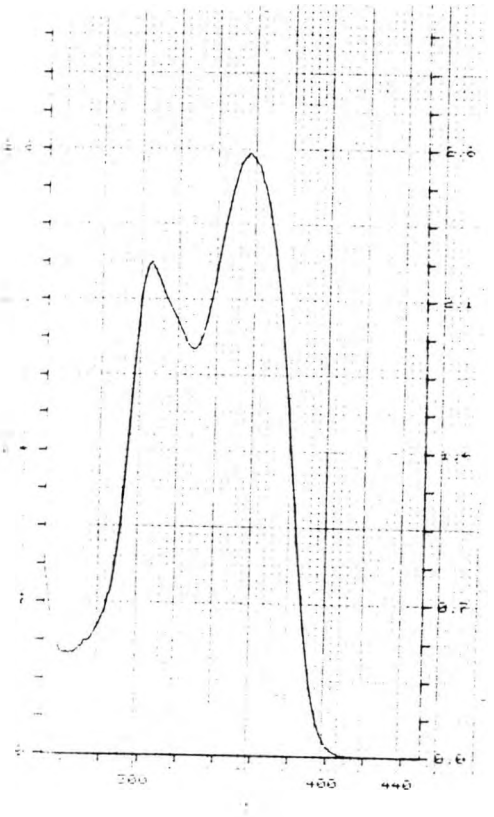
Spectrum 4: RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of 2,3-bis (4-hydroxyphenyl) quinoxaline and N-methyldiethanolamine, under anaerobic conditions



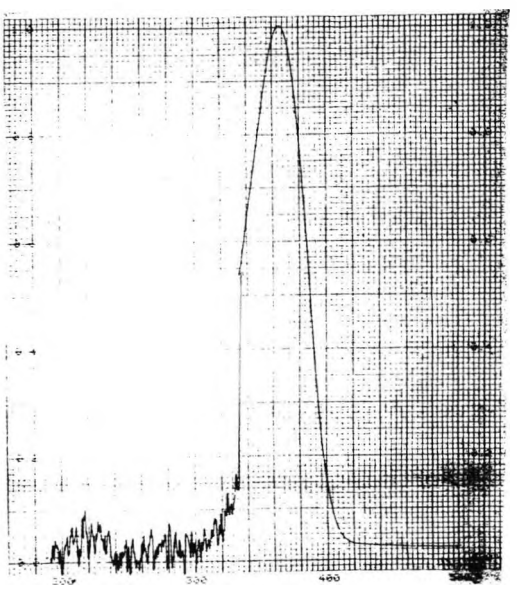
Spectrum 5: RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3 propanediol triacrylate in the presence of 2,3-bis(4-methoxyphenyl) quinoxaline and N-methyldiethanolamine, under anaerobic conditions.



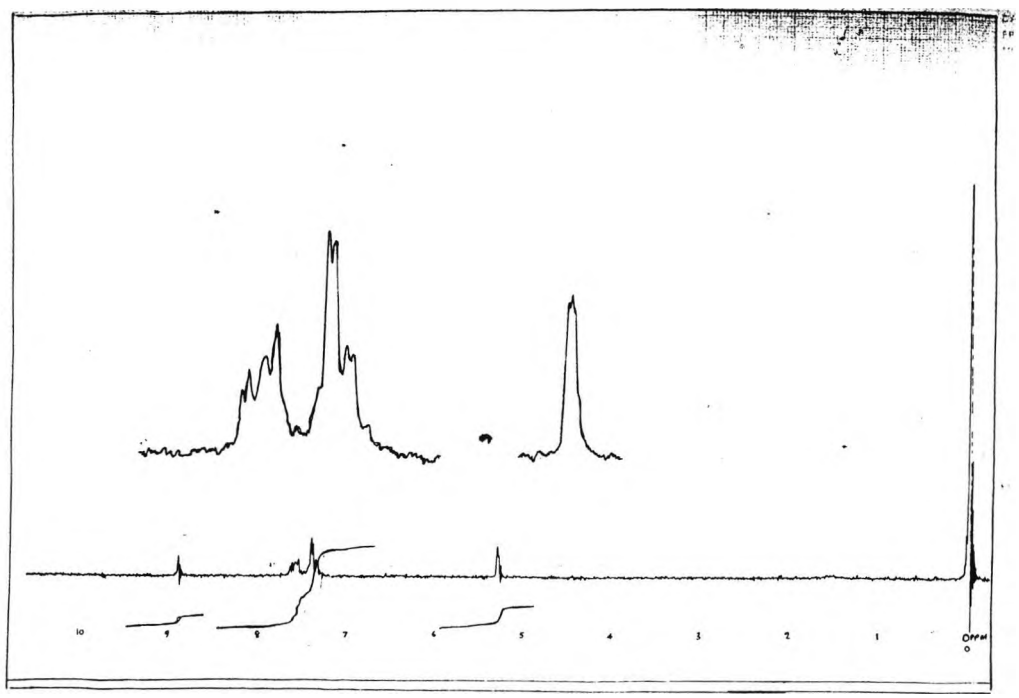
Spectrum 6: RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of 2,3-bis(4-methoxyphenyl) quinoxaline and N-methyldiethanolamine, under aerobic conditions.



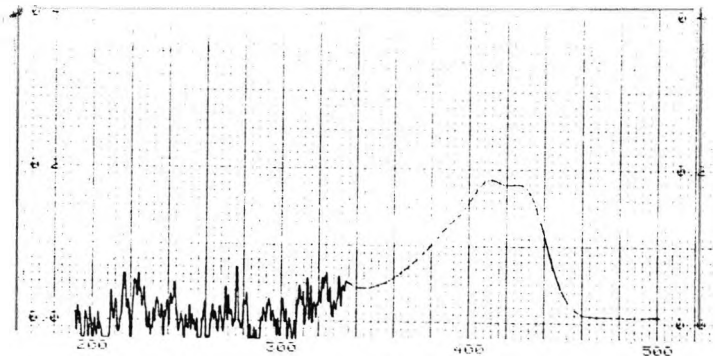
Spectrum 9: U.V. spectrum of 7-benzoyl-2,3-diphenylquinoxaline



Spectrum 10: U.V. spectrum of 2,3-bis (4-methoxyphenyl) quinoxaline



Spectrum 11: NMR spectrum of 2,3,7,8,-tetraphenylpolyquinoxaline



Spectrum 12: U.V. spectrum of 2,3,7,8,-tetraphenylpolyquinoxaline

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CHAPTER FIVE

THE USE OF CYANINE BORATES AS VISIBLE RANGE PHOTOINITIATORS IN THIN FILMS

CYANINE BORATES

5.1 INTRODUCTION

Cyanine dyes [1] are characterised by the presence of a chromophoric system containing an acyclic link or chain.

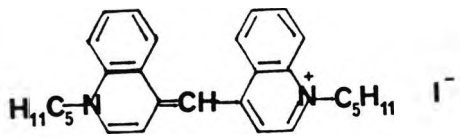
$$-C-(=C-C)_n \text{ (When n=0 or is an integer)}$$

$$\text{or } (-C=C-)_n \text{ (When 'n' is an integer)}$$

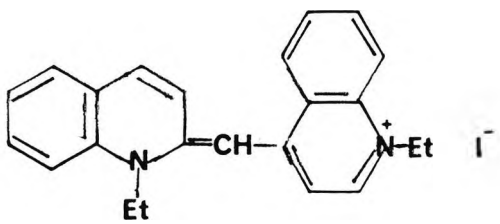
The cyanine dyes form an important class of methine dyes with links or chains of the first type containing an odd number of carbon atoms attached to two basic heterocyclic residues.

The first cyanine dye was discovered by Williams in 1856.[2] He heated crude quinoxaline with isoamyl iodide and caustic soda and obtained a blue dye which he called cyanine.

It was later shown to have the structure (A).

(A) 

The fastness properties of cyanine are poor, but in 1875 Vogel [3] found that it has photosensitivity properties. Vogel's photographic plates in the undyed state were sensitive to blue light only. After treatment with cyanine, the plates became sensitive to green light. Unfortunately, cyanine caused fogging of the plates, but later isocyanines such as structure (B) were found to be of practical value.

(B) 

Photosensitizing Action of Dyes

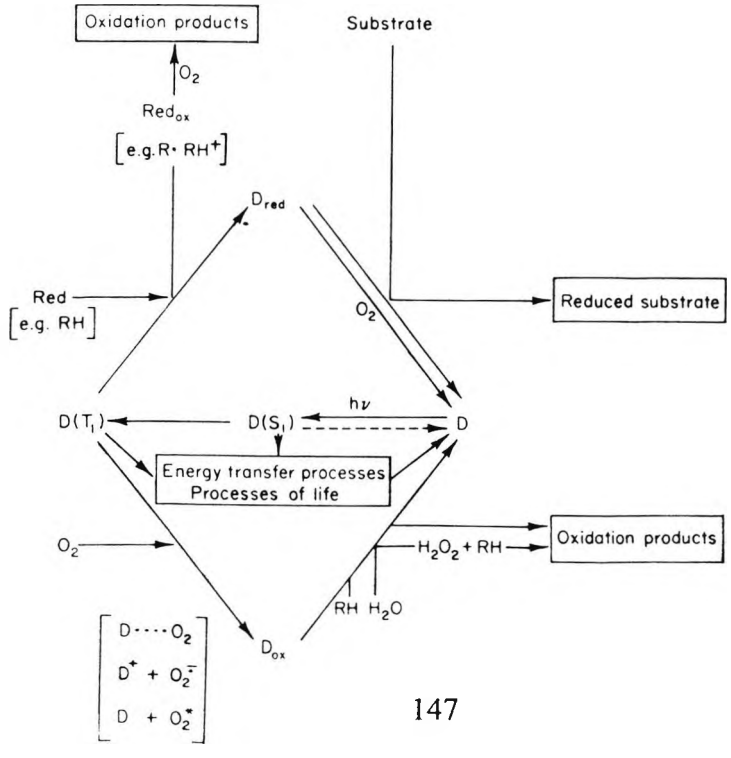
The photo-sensitizing action of dyes results from the ability of the dyes to act as either a strong oxidising or a strong reducing agent in the presence of reducing or oxidising substances, with subsequent regeneration and returning to the normal state. Moreover, in many reactions dyes are predestined sensitizers because the chemically most reactive triplet state is produced in dyes with high efficiency by intersystem crossing from the first excited singlet state.

Dye molecules excited in the triplet state are not only reactive in the course of redox reactions, but they can also transfer energy of the triplet state to other molecules and thereby start specific reactions.

Furthermore, dye molecules as light-sensitive chromophores associated with large molecules of protein can, by absorption of light, initiate key processes of life without any irreversible destruction.

In addition, aggregated dye molecules are able to react in the excited state with contacting systems and thereby induce important physical and chemical processes which could not start without dyes under the influence of visible light.

In fig. 5.1 a survey is given of various processes which are possible in photosensitization with dyes.[4]



The Mead Imaging Process

The Mead Corporation [5] produced a process by which images are formed through exposure controlled release of an image-forming agent from a microcapsule containing a photohardenable composition.

To achieve maximum sensitivities, it is important that an encapsalation technique needs to be used which provides high quality capsules. Urea-resorcinol-formaldehyde and melamine-formaldehyde capsules with low oxygen permeability are preferred. In some cases to reduce oxygen permeability, it is desirable to form a double walled capsule by conducting encapsulation in two stages.

A capsule size should be selected which minimises light attenuation. The mean diameter of the capsules used ranges from approximately 1 to 25 microns (i.e. image resolution improves as capsule size decreases).

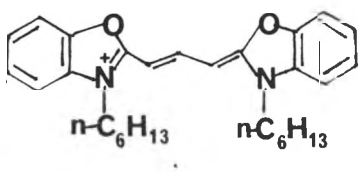
The imaging material is exposed to actinic radiation and subjected to a uniform rupturing force. The image-forming agent is a colour precursor which is released from microcapsules whereupon it reacts with a developer to form a visible image. The problem encountered in designing commercially acceptable panchromatic full colour imaging materials, employing these techniques, was the relatively short wavelengths band to which most photohardenable compositions are sensitive to actinic radiation. In most cases, the compositions are only sensitive to ultraviolet radiation or blue light e.g. 350nm to 480nm.

The imaging materials include a photosensitive layer which contains three sets of microcapsules. Each set of microcapsules is sensitive to a different band of radiation in the ultraviolet or blue spectrum and contains a cyan, magenta or yellow image-forming agent.

There is always some degree of overlap in the absorption curves and sometimes it is substantial.

Exposure conditions therefore must be controlled carefully to avoid cross-exposure. By extending the sensitivity of the photohardenable compositions to longer wavelengths, the amount of overlap in the absorption spectra of these initiators can be reduced, which can lead to a reduction in the cross-exposure. This leads to the preparation of various cyanine borates.

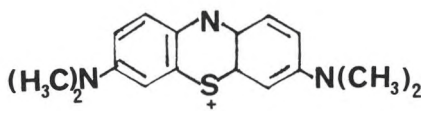
e.g. (i)



$Ph_3\bar{B}$-n - C_4H_9 λmax = 492nm

Dihexyloxacarbocyanine -n -butyltriphenylborate

(ii)



$Ph_3\bar{B}$-n - C_4H_9 λ max = 658nm

Methylene blue - n - butyltriphenylborate

One of the particular advantages of using cyanine borates as initiators is the ability to select from a wide variety of dyes which absorb at substantially different wavelengths. Cyanine borates are useful photoinitiators and have the structure:-

[Cyanine dye]$^{(+)}$ [borate salt]$^{(-)}$

From previous work carried out by Schuster [6,7,8], it has been shown that ionic dye counter-ion compounds, such as cationic dye borate compounds, are useful initiators in the polymerization of acrylates.

Such compounds consist of a visible light absorber (i.e. ionic dye) and a reactive ion (i.e.borate salt). The counter ion is reactive in the sense that upon excitation of the dye, the counter ion donates an electron to the excited state of the light absorbing

dye. Thus the cyanine dye in its excited state accepts an electron from the partner borate and so produces fragments, giving an alkyl radical.

Cycolor [9] was the first commercial product of which it is possible to use visible light systems for the photoinitiation of polymerization of acrylates.

The wavelength of absorption of cyanine borate initiator is tuneable by means of the number of conjugated alkene units, the number 'n' in the cyanine dye.

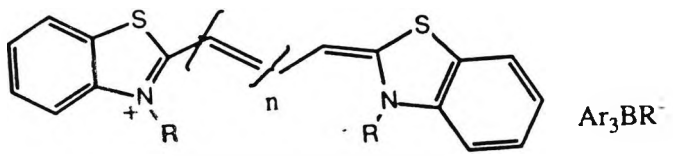


Fig. 5.2, Structure of a thiocyanine borate

The borate anion is designed such that the borate radical generated upon exposure to the light and after electron transfer to the dye, readily dissociates.

For example particularly preferred anions are triphenylbutylborate and trianisylbutylborate anions because they dissociate to triphenylboron ($B(Ph)_3$) or trianisylborane and a butyl radical.

On the other hand tetrabutylborate anion does not work well presumably because the tetrabutylborate radical is not stable and it readily accepts an electron back from the dye in a back-electron transfer and does not dissociate efficiently. Likewise, tetraphenylborate anion is very poor because the phenyl radical is not easily formed.

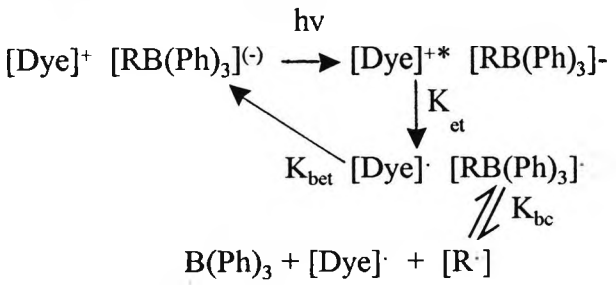
Representative examples of alkyl groups represented by R are methyl, ethyl, propyl, butyl etc. Example of aryl groups R include naphthyl and phenyl.

Boranyl radicals undergo [10,11] carbon-boron bond cleavage to generate an alkyl radical.

The rate of the bond cleavage depends directly on the stability of the alkyl radical formed.

When stabilised alkyl radicals are formed, carbon-boron bond cleavage is faster than the back-electron transfer reaction that regenerates the cyanine borate ion-pair.

Mechanism:- Intra-ion pair electron transfer of cyanine borates.



K_{et} - Rate constant for electron transfer

K_{bet} - Rate constant for back-electron transfer

K_{bc} - Rate constant for carbon-boron bond cleavage

Irradation of the intra-ion pair with visible light generates the excited singlet state of the cyanine dye, which can undergo three possible reactions.

(i) Fluorescence

(ii) Bond rotation to give a photoisomer

(iii) Electron-transfer to form the cyanine and boranyl radicals

The radicals formed might couple to form an alkylated cyanine [Cy-R] or their diffusion from the initial solvent cage will give the free-radicals. In principle the efficiency of formation of free-radicals in this process might be controlled by a decrease in the equilibrium constant for carbon-boron bond cleavage in the series of borates, or it could be due to an increase in the rate constant for back-electron transfer (K_{bet}).

Schuster [12,13], has listed the relative reactivity of the borate salts in forms of free energy of the reaction.

The order of stability of the radicals is as shown below:-

$$NpCH_2\cdot > PhCH_2\cdot > \text{n-Butyl} > \text{Methyl}$$

Various cyanine borates were prepared and tested in thin films using the colordry (i.e. moving belt system). The reason was to show the efficiency of the initiators in the presence and absence of a synergist. Another aim was to see if cyanine borates of the other dyes would act as suitable photoinitiators in thin films.

Boron NMR

Both the naturally occurring isotopes of this element possess nuclei with magnetic moments: boron -10 has a natural abundance of 18.8 per cent and a spin value I=3, and boron -11, of 81.2 per cent natural abundance, has a spin value I=3/2

High resolution nmr investigations of boron resonance [14], invariably feature the more abundant ^{11}B isotope, since this is easier to detect both from the point of view of natural abundance and also in that it has a higher natural sensitivity to nmr detection due to its larger magnetic moment, eg. for ^{10}B, U=1.8006 and for ^{11}B, U=2.6880 nuclear magnetons.

For an external magnetic strength of 14,000 gauss, the respective resonance frequencies of ^{10}B and ^{11}B are 6.405 and 19.124 Mc sec^{-1} .

The most commonly used reference compounds in boron studies are boric acid and boron trifluoride etherate, both which are readily available substances and give rise to sharp ^{11}B absorption bands.

^{11}B Chemical Shifts

Almost all ^{11}B shifts fall between the low field resonance band of $B(CH_3)_3$, where the boron atom is sp^2 hybridised and has a vacant P_z atomic orbital and the higher field absorption band of BH_4^- where the boron atom is sp^3 hybridised.

This state of affairs would be expected if the contribution of the paramagnetic term dominates the overall shielding, since the extent of deshielding depends upon the number of p electrons.

Thus BH_3 adduct formation results in the ^{11}B nucleus becoming more shielded, reflecting the reduced paramagnetic contribution to the shielding, which accompanies electron donation to the empty boron P_z orbital and the change in hybridization from sp^2 to sp^3.

In the series BCl_3, BBr_3 and BI_3, the ^{11}B shielding increases with decreasing halogen electronegativity as can be seen from Table 1.

Compound	Chemical Shift (δppm)
BF_3	+6.6
BCl_3	-29.2
BBr_3	-22.7
BI_3	+23.3

BF_3 has an anomalous ^{11}B chemical shift, which has attributed to the presence of a significant amount of "back donation" (double bond character) from the filled P_z orbital of the fluorine to the empty P_z orbital of the boron atom.

In the relevant boron series, BH_4^-, $B(C_6H_5)_4^-$ and $B(OME)_4^-$, the shielding abilities of the groups directly attached to the boron atom are found to be in the order H> C aromatic >O.

From previous values of ^{11}B chemical shifts it appears that the shielding of the boron nucleus is partially dependent on the degree to which the vacant p-orbital for the trigonal boron atom is occupied, this being at a maximum in the tetrahedrally substituted boron compounds.

Discussion

^{11}B - NMR spectra were run at the University of Kent. The reference sample used was boric acid, $B(OH)_3$.

A spectrum of an empty nmr tube was run to compare the amount of boron in borosilicate glass as with that of the sample.

The spectra obtained were (i) Methylene - blue - n-butyltriphenylborate

(ii) Diethythiacarbocyanine - n- butyltriphenylborate

(i) Methylene - blue - n-butyl triphenylborate

^{11}B Chemical shift (δppm)

-25.966 - $B(Ph)_3$ - C_4H_9

-18.744 - $B(OH)_3$ - Reference sample

(ii) Diethylthiacarbocyanine - n-butyltriphenylborate

^{11}B Chemical shift (δppm)

-25.966 - $B\text{-}(Ph)_3$ - C_4H_9

-18.744 - $B(OH)_3$ - Reference sample

Triphenylboron has a ^{11}B chemical shift of -42.6ppm

5.2 RESULTS AND DISCUSSION

Photopolymerization in thin films was carried out using the moving belt system.

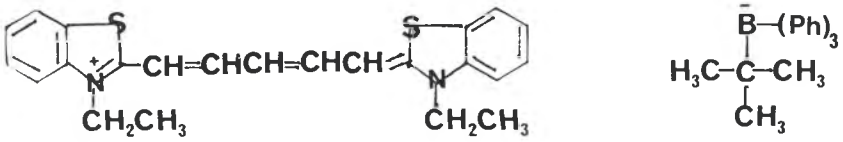
The formulations consisted of:-

a) 0.5% w/w of cyanine borate

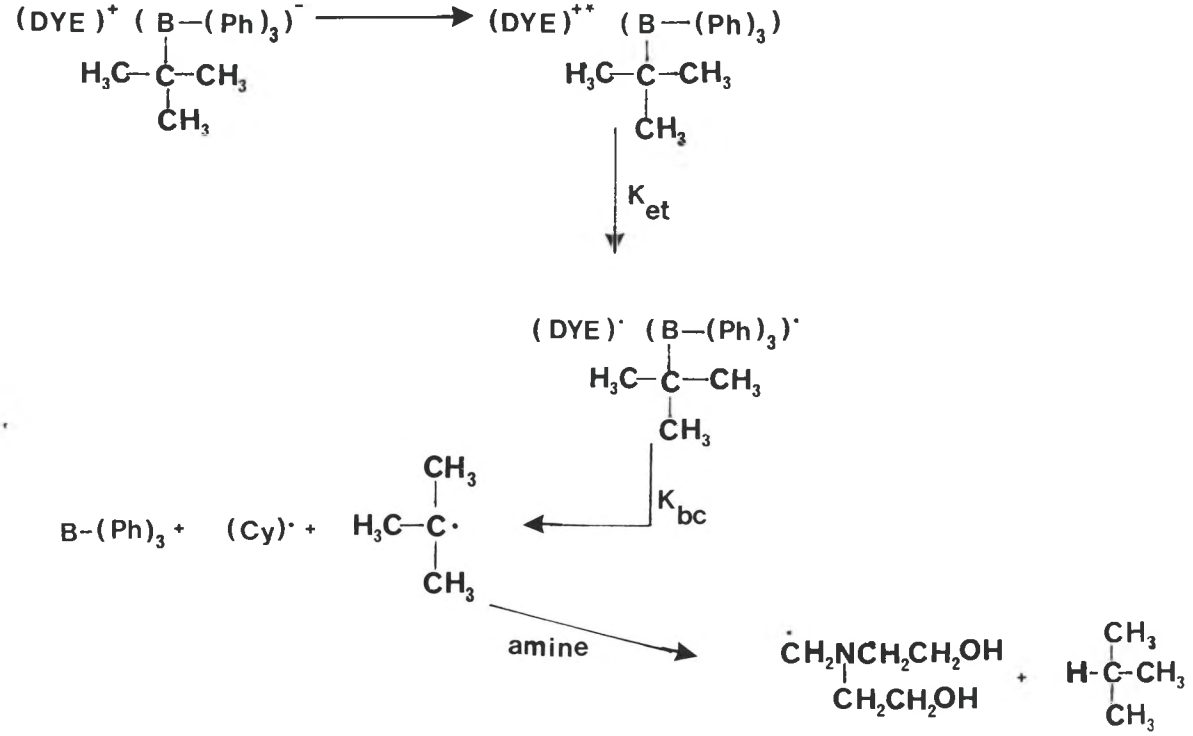
b) 10% w/w of N-methyldiethanolamine (synergist)

c) 2-Ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate

3,3' - Diethylthiacarbocyanine -tert-butyltriphenylborate (A) was tested in the presence of an amine under anaerobic and aerobic conditions.

(A) 

Under anaerobic conditions, in the presence of an amine, a tack-free film was formed within two passes under the moving belt system. This is due to the mechanism proposed as shown below:-

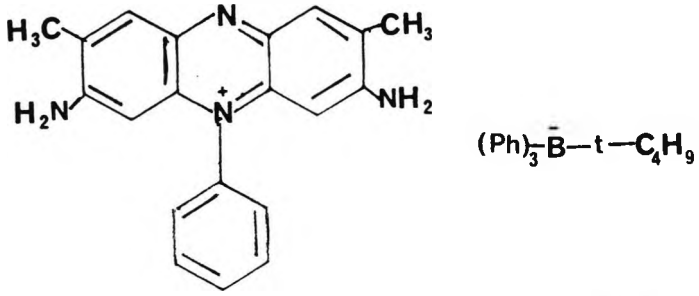


In the presence of an amine, the α-aminoalkyl radical formed is a better initiating species than the alkyl radical.

Under aerobic conditions, the initiation process is inefficient due to the presence of oxygen, which inhibits the polymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanedial triacrylate.

Under anaerobic conditions and in the absence of an amine the rate of polymerisation is reduced, compared with the result obtained under similar conditions in the presence of the amine. This result supports the mechanism, whereby the α-aminoalkyl radical formed in the presence of an amine is a better initiating species than the alkyl radical. Under aerobic conditions, in the absence of an amine there is no polymerization, due to oxygen inhibition of cure.

Safranine 'O' is a dye (B), which was used, but is not classed as a cyanine dye. The dye was used to vary the wavelengths of the light which can be absorbed.

(B) 

Safranine 'O'-t-butyl triphenylborate, λ =516nm

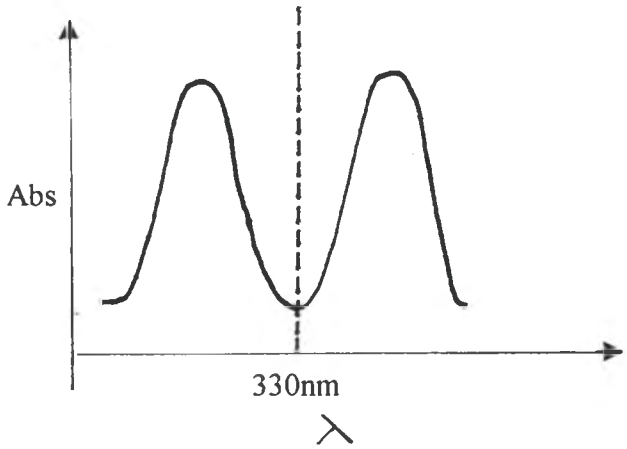
Safranine 'O'-t-butyl triphenylborate was tested in the presence of N-methyldiethanolamine. Under a glass slide, a tack-free film is formed within ten passes under the colordry.

The glass slide absorbs u.v. light (i.e. cut off point for the glass slide is 330nm), therefore the initiation process is created by the absorption of visible light.

The problem encounted whilst using a touching glass slide is that cyanine dyes absorb in the u.v. region as well as the visible region.

The glass slide prevents the absorption of u.v. light, the efficiency of light absorption by the dye is reduced.

The polymerization process is not as efficient as one would expect.



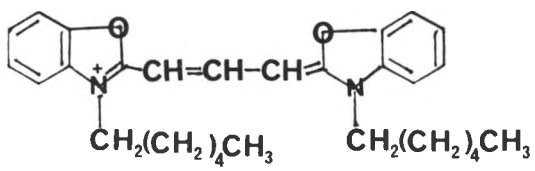
Safranine 'O'-n-butyl triphenylborate, in the presence of an amine, forms a tack-free film under quartz within seven passes under the colordry.

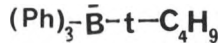
Under the touching glass slide, a tack-free film was formed in twenty-three passes under the colordry.

The reduction in the rate of polymerization as compared with the tertiary-butyl derivative is due to the fragmentation of the borate salt in which there are less n-butyl radicals formed.

In the absence of an amine, safranine 'O'-n-butyl triphenylborate is not an efficient initiator.

Under aerobic conditions, no polymerization occurred, due to oxygen scavenging the radicals formed.

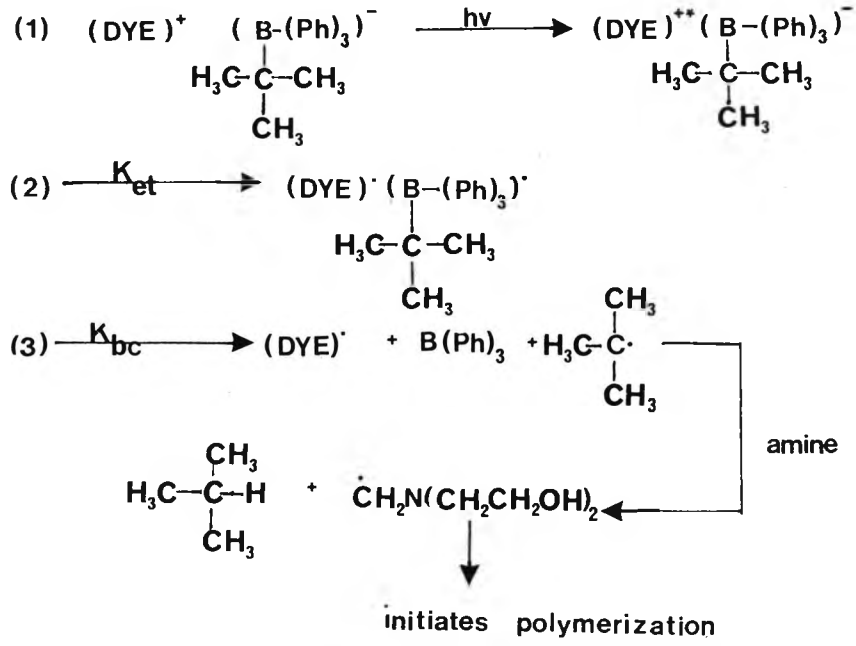
(C) 



Dihexyloxacarbocyanine - t-butyltriphenylborate λ max=484nm

Dihexyloxacarbocyanine-t-butyltriphenylborate was tested in the presence of 10% w/w of N-methyldiethanolamine.

The α-aminoalkyl radical formed initiates the polymerization process.

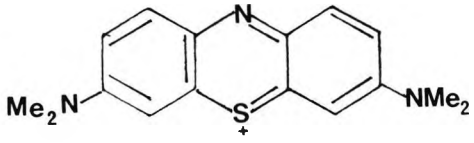


Under anaerobic conditions, in the absence of an amine the polymerization of the triacrylate is initiated by the tertiary-butyl radical.

The results show that there is a reduction in the rate of polymerization in the absence of N-methyldiethanolamine. This is due to the formation of an α-aminoalkyl radical which is a better initiating species than the tertiary-butyl radical.

Under aerobic conditions and in the absence of an amine, there was very little polymerization, due to the presence of oxygen, which inhibits the polymerization process.

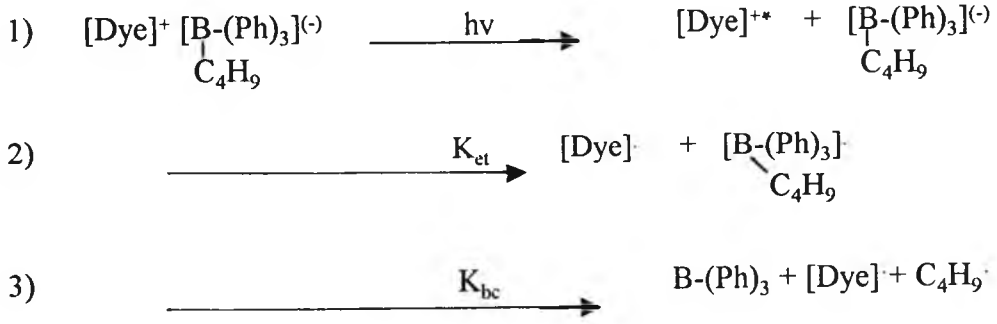
Methylene-blue (D) is a dye which is not classed as a cyanine dye, but was used to vary the wavelength of light which could be absorbed.

(D) 

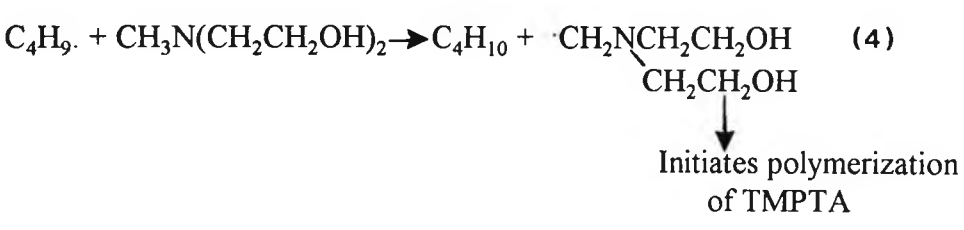
$(Ph)_3\bar{B}-n-C_4H_9$

Methylene-blue-n-butyltriphenylborate λ =654nm

Under anaerobic conditions, in the presence of an amine, a tack-free film is formed within six passes under the colordry. Irradiation of the intra-ion pair with visible light generates the excited state of the dye, which undergoes electron transfer to form the radicals as shown below:-



The boranyl radicals undergo (eqn(3)) carbon-boron bond cleavage to generate an n-butyl radical. In the presence of an amine, hydrogen abstraction by the radical forms an α-aminoalkyl radical, which is a better initiating species (eqn (4)) than the alkyl radical.



Under aerobic conditions and in the absence of an amine, there is no polymerization due to oxygen inhibition, preventing polymerization of the triacrylate.

Under anaerobic conditions and in the absence of an amine, the rate of polymerization is reduced. This is due to the fact that the alkyl radical formed is not as good, as an initiating species, as the α-aminoalkyl radical.

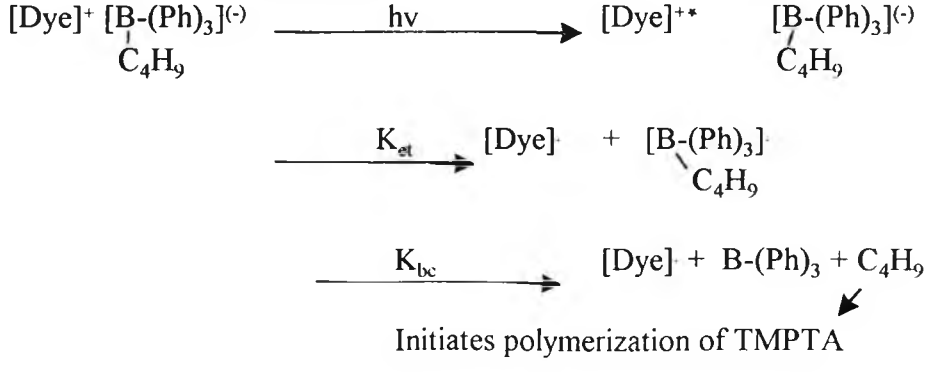


Table 1 U.V. Curing results in the presence of a synergist

	Number of Passes Under Colordry				
Samples	3,3' - Diethylthia carbocyanine - t butyltriphenylborate +amine + TMPTA	Safranine 'O' - t - butyltriphenylborate +amine + TMPTA	Dihexyloxacarbo cyanine - t - butyltriphenylborate +amine + TMPTA	Methylene blue - n - butyltriphenylborate +amine + TMPTA	Safranine 'O' - n - butyltriphenylborate +amine + TMPTA
Quartz	2	8	2	6	7
Slide	9	10	2	20	23
Air	15	30+	7	25	30+
Filter	30+	30+	20	30+	30+

a) 0.5% w/w of initiator
b) Monomer :- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate, TMPTA
c) 10% w/w of N-methyldiethanolamine
Belt Speed - 10ft/min

Table 2 U.V. Curing results in the absence of a synergist

	Number of Passes Under Colordry				
Samples	3,3' - Diethylthia carbocyanine - t butyltriphenylborate + TMPTA	Safranine 'O' - t - butyltriphenylborate + TMPTA	Dihexyloxacarbo cyanine - t - butyltriphenylborate + TMPTA	Methylene blue - n - butyltriphenylborate + TMPTA	Safranine 'O' - n - butyltriphenylborate + TMPTA
Quartz	4	15	7	14	16
Slide	23	30+	15	30+	30+
Air	30+	30+	30+	30+	30+
Filter	30+	30+	20	30+	30+

a) 0.5%w/w of initiator
b) Monomer :- 2-Ethyl-2-(hydroxymethyl) - 1,3-propanediol triacrylate , TMPTA
c) Belt Speed - 10ft/min

Conclusion

From previous work by Schuster,[15, 16] it has been shown that the cyanine borates are efficient photoinitiators in the presence of a synergist, but are poor photoinitiators under aerobic conditions. The results obtained in the present work showed particular similarities. In the absence of a synergist and in the presence of air, they are poor initiators due to oxygen inhibition preventing polymerization of TMPTA.

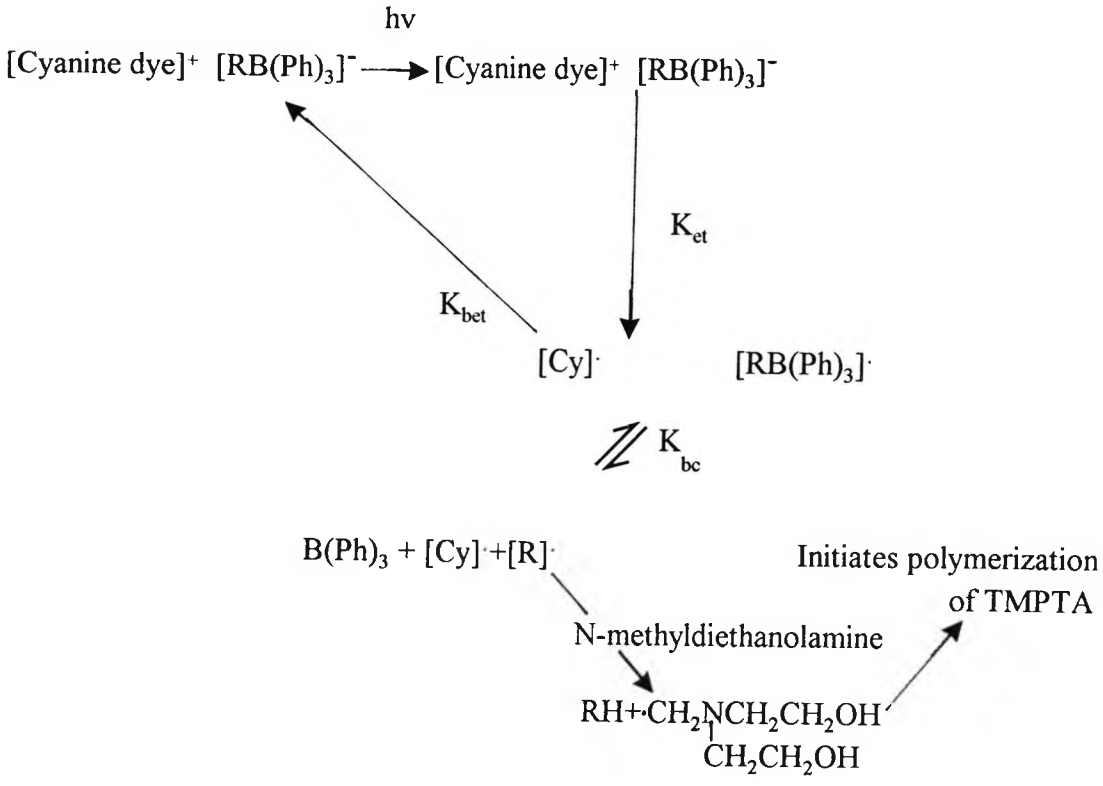
It can be shown from the results that the teriary-butyl radical is formed more efficiently than the n-butyl radical.

The rate of polymerization in the case of the tertiary-butyl derivative under aerobic and anaerobic conditions is greater. Also the results show that the fragmentation of the borate salt determines the efficiency of the initiation stage of the polymerization process.

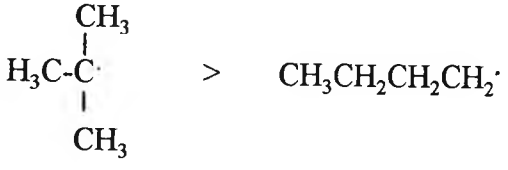
There are discrepancies in the results obtained, since it was difficult to obtain a relatively pure compound for the cyanine borates. It was very difficult to obtain a pure sample of the dye itself.

The cyanine borates seem not to be very efficient initiators in the absence of a synergist and under aerobic conditions. This is due to oxygen preventing polymerization, by scavenging the radicals formed.

Mechanism

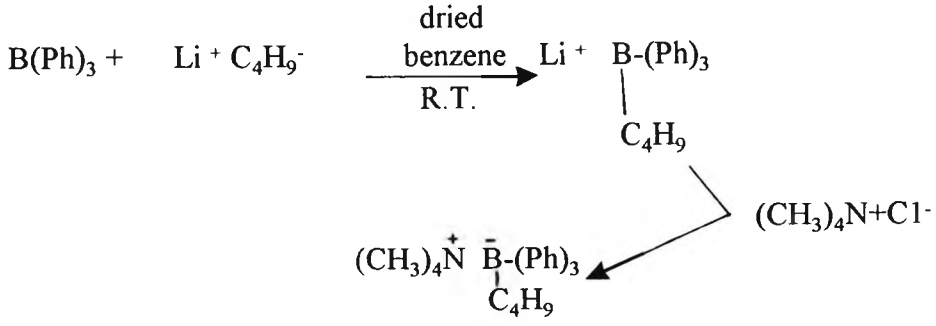


The t-butyl radical is formed in greater concentration than the n-butyl radical.



5.3 EXPERIMENTAL DETAILS

A. Preparation of tetramethylammonium n-butyltriphenylborate



Method

Dried benzene (60ml) was added to a 3-neck round-bottomed flask, flushed with dry nitrogen. Triphenylboron (2.4g, 0.01m) was added to the benzene, and the mixture was stirred for 30 minutes at room temperature. n-Butyllithium (5.8mls of 1.7m solution) was added via a syringe, which was initially flushed with nitrogen. The solution turned pale green, once n-butyllithium was added. The mixture was left to stir under dry nitrogen for 24 hours.

A white precipitate was formed. Hexane (100ml) was added to precipitate out the lithium salt of the borate. The lithium salt was then filtered under nitrogen. The white precipitate was then added to 100mls of distilled water, and stirred under low heat. Tetramethylammonium chloride (1.082g/100mls distilled water) was added to the mixture to form a white precipitate of the tetramethylammonium salt (Yield =30%). The salt was dried in an oven, at low heat for 24 hours.

The product was purified by recrystallisation from methanol

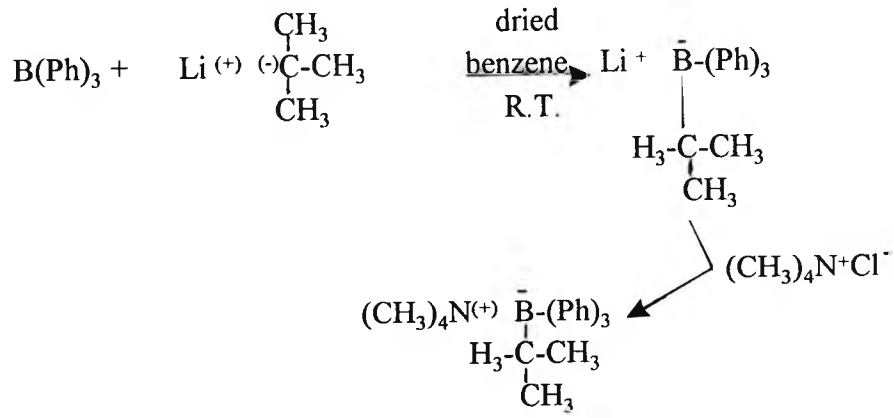
NMR analysis (60MHz, d-acetonitrile/TMS)

7.5-6.9	,	(m,15H)-aromatic protons
3.0	,	(s,12H)-$(CH_3)_4N^+$ protons
2.7	,	(t,2H)-CH_2B protons
2.0	,	-d-acetonitrile
0.7-1.2	,	(m,7H)-n-butyl protons

CHN analysis(%)	Expected	Found
C,	83.64	83.71
H,	9.62	9.66
N,	3.74	3.68

Formula : $C_{26}H_{36}NB$

B. Preparation of tetramethylammonium tertiary-butyltriphenylborate



Method as for compound A.

The product was recrystallised from methanol.

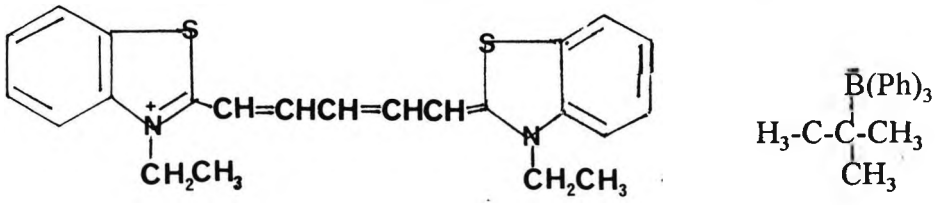
NMR analysis (60MHz H'NMR), solvent-d-acetonitrile/TMS

2.0	,	(d-acetonitrile)
2.2	,	(s,9H)-CH_3 protons on boron
3.0	,	(s,12H)-$(CH_3)_4N^+$ protons
6.9	,	(m,3H) - aromatic protons
7.3	,	(m,6H) - aromatic protons
7.5	,	(m,6H) - aromatic protons

CHN analysis(%)	Expected	Found
C,	83.64	83.85
H,	9.72	9.49
N,	3.75	3.59

Formula : $C_{26}H_{36}NB$

C. Preparation of 3,3' - diethylthiacarbocyanine - tert-butyltriphenylborate



Method

A suspension of the borate salt (1g/10ml) was sonicated in methanol to make a very fine suspension. The flask was protected from light by wrapping with aluminium foil, then one equivalent of the dye was added. The solution was stirred under low heat for 24 hours. The mixture was left to cool to room temperature and then diluted with 5-10 volumes of ice water.

The resultant solid was filtered and washed with water, until washings were colourless.

The compound was left to dry in an oven at low heat for 24 hours (Yield = 50%).

The product was purified by column chromatography:- dichloromethane/alumina.

NMR analysis (100MHz, solvent:- d-acetonitrile/TMS)

1.5	,	(m,6H)-CH_3 protons
2.0	,	d-acetonitrile
2.2	,	(s,9H)-CH_3 protons on boron
4.0	,	(q,2H)-CH_2 protons on N
4.4	,	(q,2H)-CH_2 protons on $N^{(+)}$
5.0	,	(d,1H)-CH proton
5.2	,	(d,1H)-CH proton
5.8	,	(m,3H)-CH proton
7.4-7.0	,	(m,11H) - aromatic protons
7.5	,	(m,6H) - aromatic protons
7.7	,	(m,6H) - aromatic protons

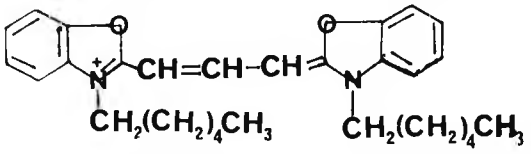
CHN analysis(%)	Expected	Found
C,	78.2	70.91
H,	6.8	6.47
N,	4.2	4.21

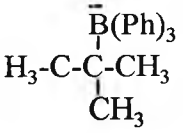
Formula : $C_{45}H_{47}N_2S_2B$

U.V. Spectrum: λ max = 541nm
(solvent-acetonitrile)

Melting Point: >300°C

D. Preparation of dihexyloxacarbocyanine - tert-butyltriphenylborate





Method - As for compound C.

The product was purified by column chromatography:- chloroform/alumina.

NMR analysis (100MHz, H'NMR) - d-acetonitile/TMS

7.8-6.9	,	(m,23H)- aromatic protons
5.8	,	(m,1H)-CH proton
5.2	,	(d,1H)-CH proton
5.3	,	(d,1H)-CH proton
4.2	,	(t,2H)-CH_2 protons on $N^{(+)}$
4.0	,	(t,2H)-CH_2 protons on nitrogen
2.25	,	(s,9H) - CH_3 protons on boron
1.4	,	(m,16H) -CH_2 protons
1.0	,	(m,6H) -CH_3 protons

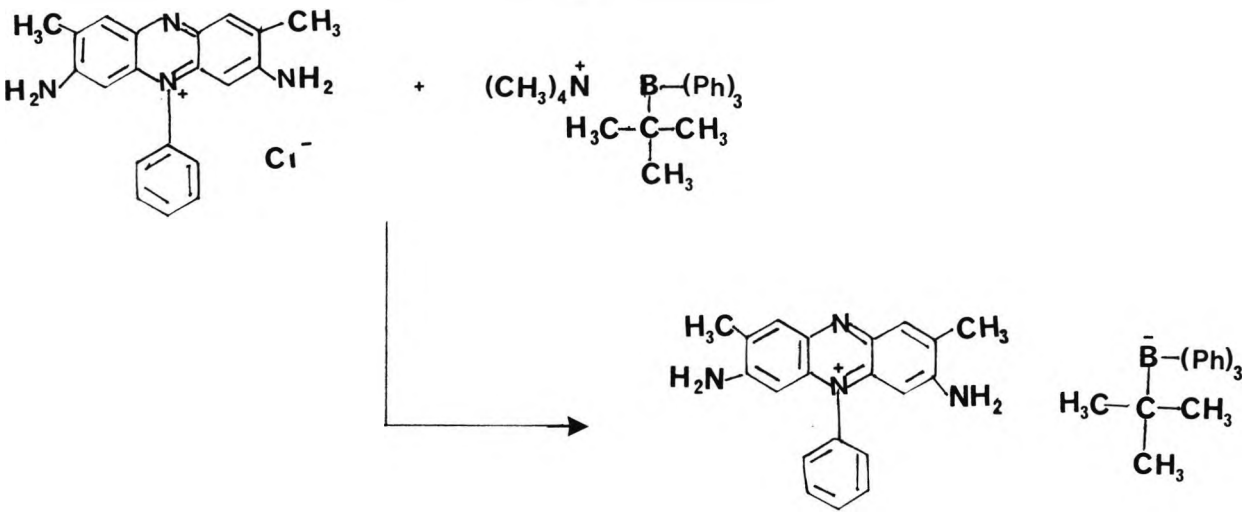
CHN analysis(%)	Expected	Found
C,	82.2	78.4
H,	8.2	7.98
N,	3.76	3.54

Formula : $C_{51}H_{61}N_2O_2B$

U.V. Spectrum: λ max = 484nm (solvent-acetonitrile)

Melting Point: >300°C

E. Preparation of safranine 'O'- tertiary - butyltriphenylborate



Method:- As for compound C.

The product was purified by column chromatography - dichloromethane/alumina.

NMR analysis (60MHz, d-acetonitrile/TMS)

1.9	,	d-acetonitrile
2.1	,	(s,9H)-CH_3 protons on boron
2.3	,	(s,6H)-CH_3 protons on safranine
2.9	,	(s,4H)-NH_2 protons
7.2-6.8	,	(m,24H) - aromatic protons

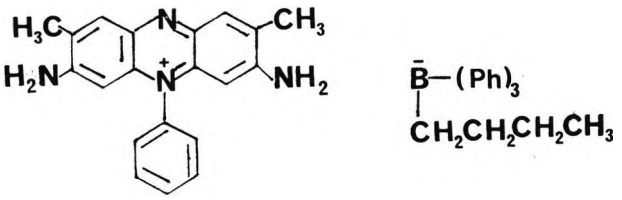
CHN analysis(%)	Expected	Found
C,	82.07	79.62
H,	7.05	7.00
N,	9.12	9.41

Formula : $C_{42}H_{43}N_4B$

U.V. Spectrum: λ = 516nm, 280nm, 250nm (solvent-acetonitrile)

Melting Point: >300°C

F. Preparation of safranine 'O' - n-butyltriphenylborate



Method:- As for compound C

The product was purified by column chromatography - dichloromethane/alumina.

NMR analysis (60MHz, d-acetonitrile)

0.6-1.0	,	(m,7H)- alkyl group of borate salt
1.9	,	d-acetonitrile
2.3	,	(s,6H)-CH_3 protons on Safranine
2.6	,	(m,2H)-CH_2 B group
2.9	,	(s,4H)- NH_2 protons
7.2-6.8	,	(m,24H) - aromatic protons

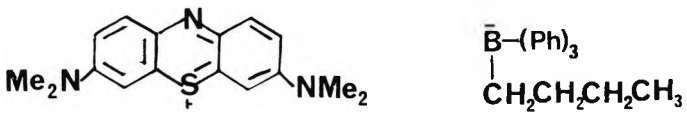
CHN analysis(%)	Expected	Found
C,	82.07	78.73
H,	7.05	6.90
N,	9.12	9.49

Formula : $C_{42}H_{43}N_4B$

U.V. Spectrum: λ = 516.8nm, 280nm, 250nm. (solvent-acetonitrile)

Melting Point: >300°C

G. Preparation of methylene-blue-n-butyltriphenylborate



Method:- As for compound C.

The product was recrystallised from methanol and also purified by column chromatography(i.e. dichloromethane/alumina).

NMR analysis (100MHz, d-acetonitrile /TMS)

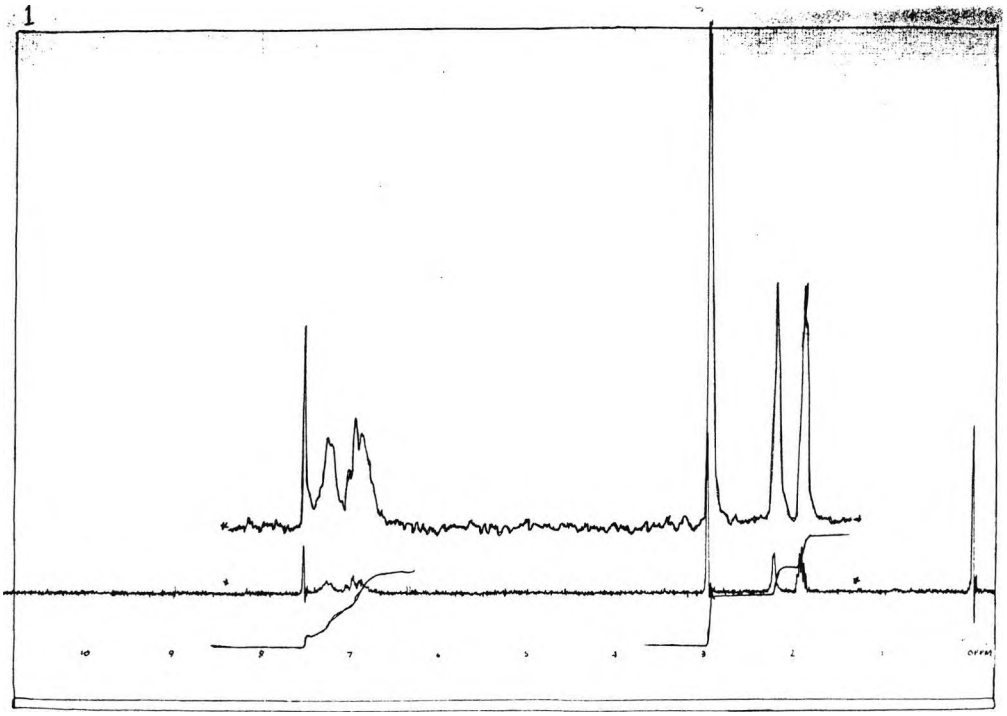
0.8-1.2	,	(m,7H)- $CH_3CH_2CH_2$ group of borate salt
2.0	,	d-acetonitrile
2.5	,	(m,2H)-CH_2 B group
2.8	,	(s,12H)- NMe_2 group
7.7-6.8	,	(m,21H) - aromatic protons

CHN analysis(%)	Expected	Found
C,	78.2	72.68
H,	7.20	6.84
N,	7.20	7.33

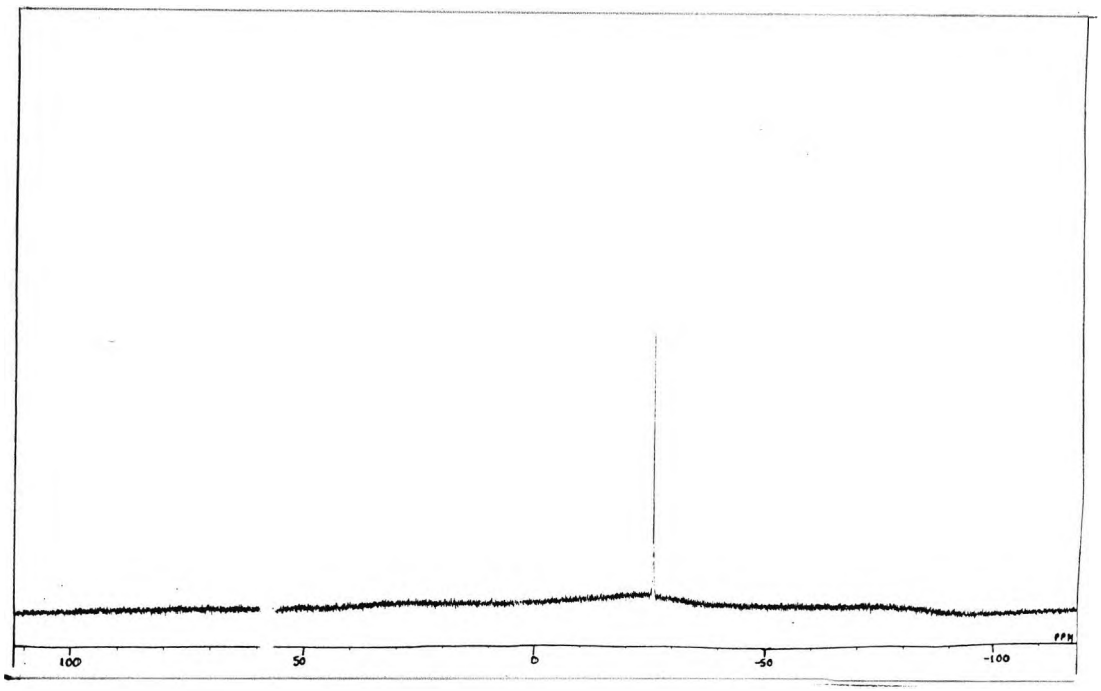
Formula : $C_{38}H_{42}N_3SB$

U.V. Spectrum: λ = 654nm, 292nm (solvent-acetonitrile)

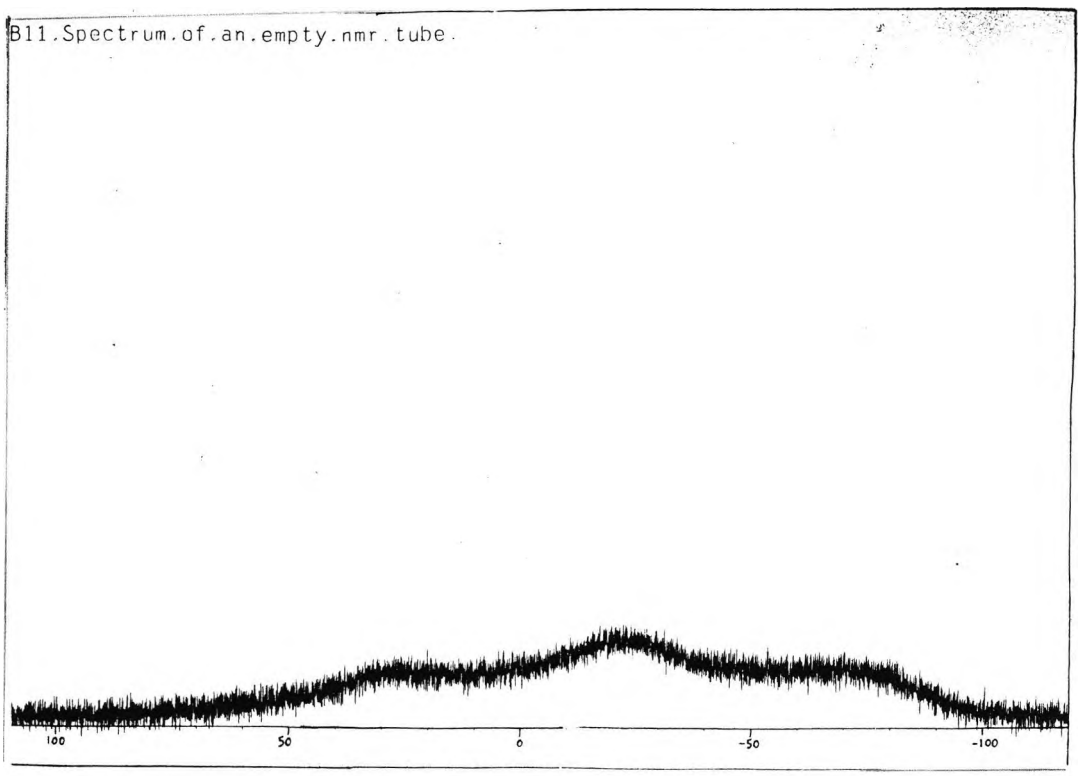
Melting Point: >300°C



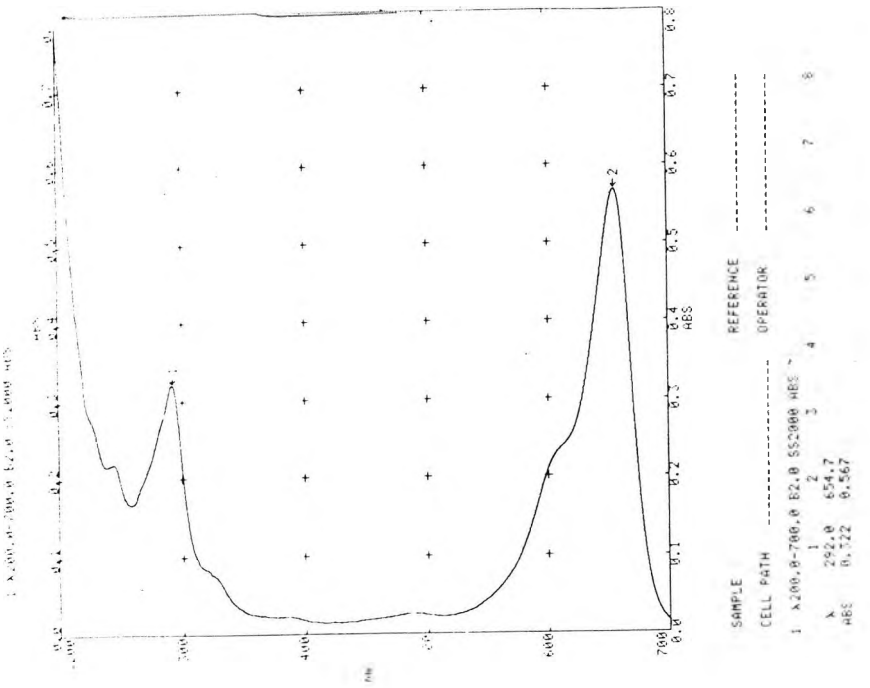
Spectrum 1: NMR spectrum of tetramethylammonium tertiary-butyltriphenylborate



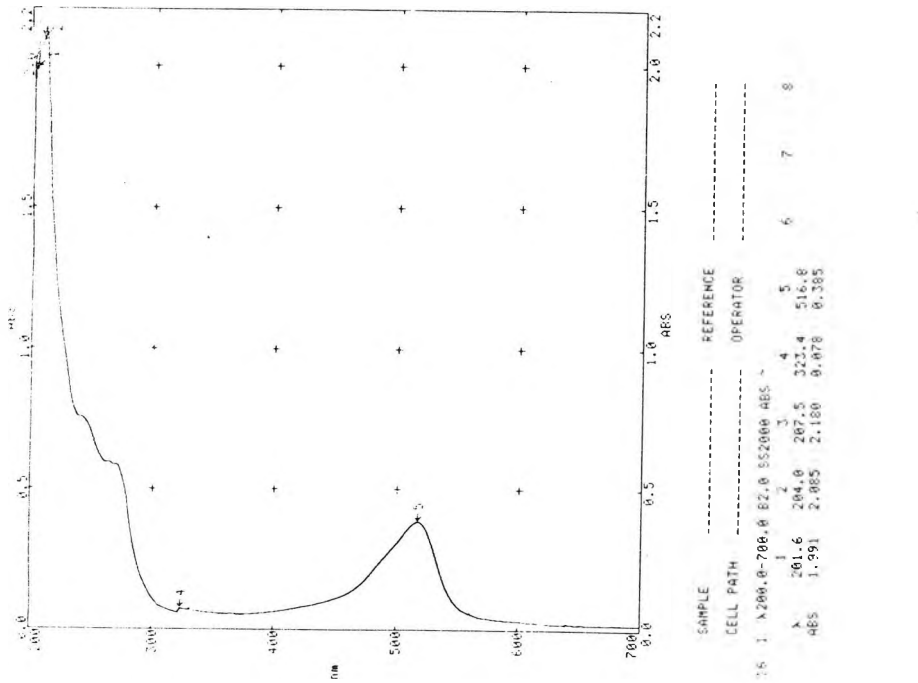
Spectrum 2: ^{11}B spectrum of methylene-blue-n-butyltriphenylborate



Spectrum 3: ^{11}B spectrum of an empty NMR tube



Spectrum 4: U.V. spectrum of methylene-blue-n-butyltriphenylborate



Spectrum 5: U.V. spectrum of safranine 'O'-tert-butyltriphenylborate

5.4

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CHAPTER SIX

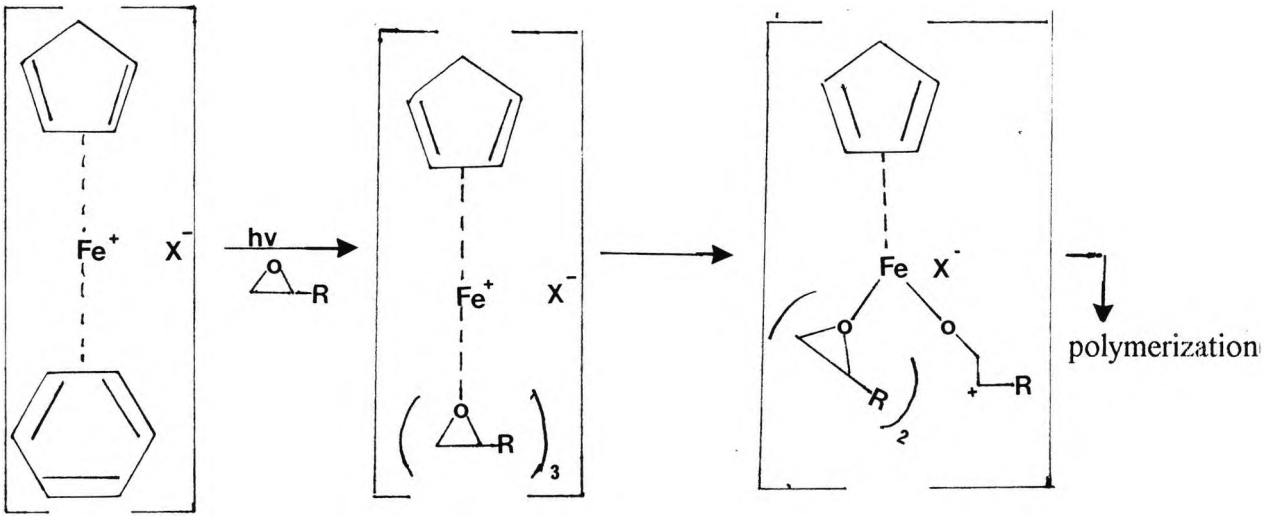
THE USE OF CYCLOPENTADIENYLIRON (II) ALKYLBORATES AS FREE-RADICAL PHOTOINITIATORS IN THIN FILMS

6.1 Photochemistry of cyclopentadienyliron (II) alkylborates

Introduction

In the last few years iron-arene compounds [1,2], have been reported in the literature as cationic photoinitiators.

Mechanism 1



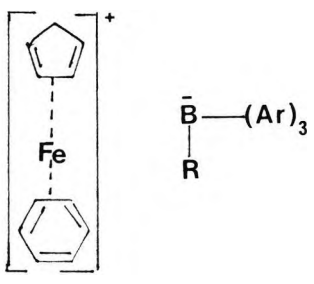
It was found that the photolysis of iron-arene compounds removes the unchanged aromatic ligand and produces a positively charged iron species.

These cationic intermediates are excellent catalysts for the ring opening and polymerization of epoxide resins. The mechanism is as shown above.

More recently, iron arene compounds were reported to act as free-radical photoinitiators [3].

Chrisope and Schuster [4] have carried out work on cyclopentadienyliron (II) alkylborate salts.

e.g.



It was found that irradiation of tetrahydrofuran solutions of appropriate alkylborate $[RB(Ph)_3]^-$ salts of cyclopentadienyliron (II) arene cations $[CpFeArH]^+$ initiates an intra-ion pair electron transfer reaction to form a 19-electron iron (I) species and a boranyl radical $[RB(Ph)_3]\cdot$

Mechanism 2:- Intra-ion-pair electron-transfer of cyclopentadienyliron (II) alkylborates

1. $[CpFeC_6H_5X]^+ [RB(Ph)_3]^- \xrightarrow{hv} [CpFeC_6H_5X]^{+*3}[RB(Ph)_3]^-$
   Ion Pair — isc — Excited Ion Pair

2. $\xrightarrow{K_{et}} [CpFeC_6H_5X]\cdot [RB(Ph)_3]\cdot$
   Radical Pair

3. $\xrightarrow{K_{bet}} [CpFeC_6H_5X]\cdot + [RB(Ph)_3]^-$

4. $\xrightarrow{K_{bc}} [CpFeC_6H_5X]^+ + Ph_3B + R\cdot$
   19 electron Iron(I) Species

5. $R\cdot + R\cdot \longrightarrow R\text{-}R.$

Cleavage of the alkyl carbon-boron bond in the boranyl radical occurs more rapidly than does energy-wasting back-electron-transfer to regenerate the starting salt.

Excitation of the ion-pair leads to the triplet state of the iron - arene complex either directly from u.v. light irradiation or via the singlet excited state by means of a rapid intersystem crossing (isc, eqn (1)). Electron transfer (eqn (2)) can occur despite the short lifetime of the triplet state because ion-pairing ensures the appropriate positioning of the donor (i.e. borate) next to the acceptor (ie. iron arene) at the moment of excitation.

The rate constant for electron transfer, K_{et} will depend on the free energy change for this reaction (ΔG_{et}).

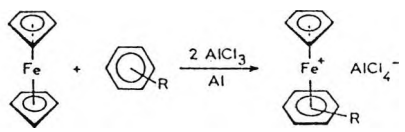
This value may be calculated by means of eqn (6).

(6) $$\Delta G_{ET} = E_{OX} - E_{red} - E^{*3} + E_{work}$$

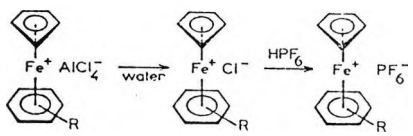
The oxidation potential of the borate and reduction potential of the iron complex can be estimated by cyclic voltammetry.

Electron - transfer from the borate to the excited iron complex generates a radical pair, as explained earlier. In many such reactions back-electron transfer to regenerate ground state starting materials (eqn (4)) overwhelms other reaction paths. In the present case, cleavage of carbon-boron bond in the boranyl radical (eqn (5)) must be sufficiently rapid to give a measurable yield of the alkyl radical, whose dimerization (eqn 6) completes the reaction sequence.

The synthesis of iron-arene compounds using ferrocene involves a ligand exchange reaction between one ring of ferrocene and arenes. It has attracted interest as it is a straightforward way to complex arenes with the $CpFe^+$ unit [5,6].



The reaction is carried out at 70°C during 1-16 hours in the arene as a solvent. $AlCl_3$ is the most common Lewis acid including the reaction and aluminium powder is added to inhibit oxidation of ferrocene to ferricinium.



After hydrolysis with ice water, the aqueous phase contains $CpFe^{+}$ (arene) cation. Aqueous HPF_6 or PF_6^- salt is added to the filtrate to precipitate the water insoluble PF_6^- salt.

Organoiron Electron-Reservoir Complexes

The geometry of transition-metal organometallic compounds and the accessibility of multiple oxidation states provide a unique opportunity to design molecular electron reservoirs. This concept is implicit for biological electron-carriers. Molecular electron reservoirs are compounds [7] which store and transfer electrons stoichiometrically or catalytically without decomposition.

The unusual Fe(I) oxidation state can be obtained either by one electron oxidation of electron rich Fe^{o} complexes [8] or by one electron reduction of Fe (II) complexes [9]. The latter approach is specially noteworthy because it can lead to the 19-electron structure if no decoordination occurs. Whereas organomettalic complexes are commonly known with 8 to 18 electrons in the metal valence shell, violation of the 18-electron rule by an excess of electrons is rare because loss of a ligand usually occurs. The discovery that 19 electron Fe (I) species could be stabilised and isolated provides the possibility to gain an insight into the chemistry of this oxidation state.

The 19 electron structures have very negative redox potentials suggesting the use of these complexes as molecular electron reservoirs

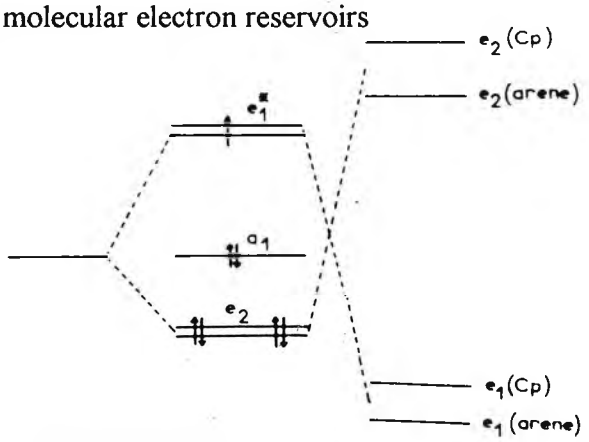


Fig. 1. - Molecular - orbital diagram for transition metal sandwiches d^7, 19 electron CpFe (I) (arene) complex

6.2 RESULTS AND DISCUSSION

Photopolymerization in thin films was carried out by using a moving belt system (i.e colordry)

The moving belt system gives an indication of the efficiency of the cyclopentadienyliron (II) alkylborates salts in thin films.

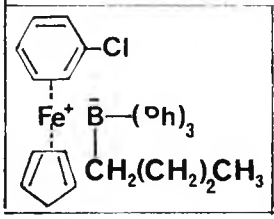
The formulations were made up of :-

a) 1% w/w of initiator

b) 10% w/w of N-methyldiethanolamine

c) Monomer:- 2-Ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate

Table 1. U.V. Curing of n^6-chlorobenzene -n^5-cyclopentadienyliron(II) n-butyl triphenylborate in the presence of an amine

No. of Passes Under Colordry				
	Quartz	Glass Slide	Air	Filter
	1	2	4	12

(a) Belt Speed:- 10ft/min (b) Amine used:- N-methyldiethanolamine

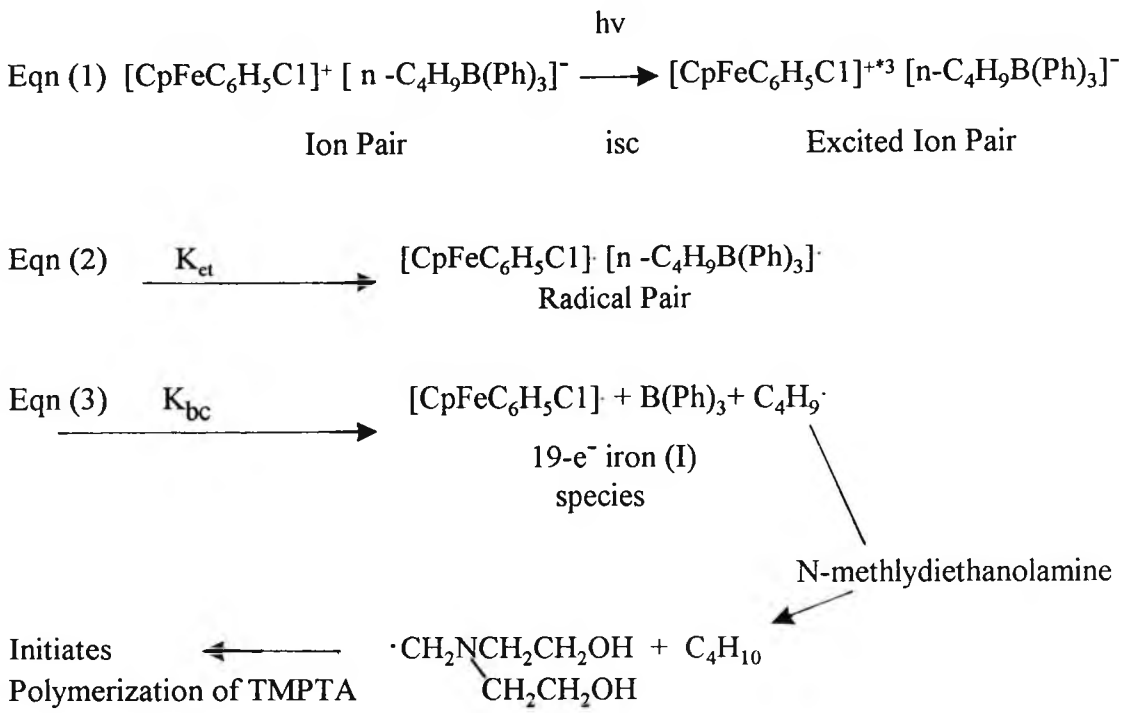
(c)Monomer:- 2-Ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate

In the presence of an amine, and under quartz, a tack-free film was formed in one pass under the colordry. The result shows that cyclopentadienyliron (II) alkylborates initiate the polymerization of 2-ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate, under anaerobic conditions and in the presence of u.v./visible light.

Under a touching glass slide, a tack-free film is formed within two passes under the colordry.

Under anaerobic conditions, and in the presence of an amine, n^6 - chlorobenzene - n^5 - cyclopentadienyliron (II)-n-butyltriphenylborate forms an excited ion pair (eqn (1)), which then undergoes electron transfer to form a radical pair (eqn (2)). The cleavage of alkyl carbon-boron bond produces an alkyl radical which abstracts a hydrogen

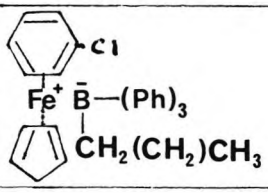
forming an α-aminoalkyl radical, which is a better initiating species than the alkyl radical formed.



In the presence of air, a tack-free film was formed within four passes under the colordry. Under aerobic conditions, the rate of polymerization is reduced due to inhibition by oxygen. When the film is covered by a filter (i.e. raised glass slide, which absorbs u.v. light, λ <330nm), a tack-free film is formed within twelve passes under the colordry.

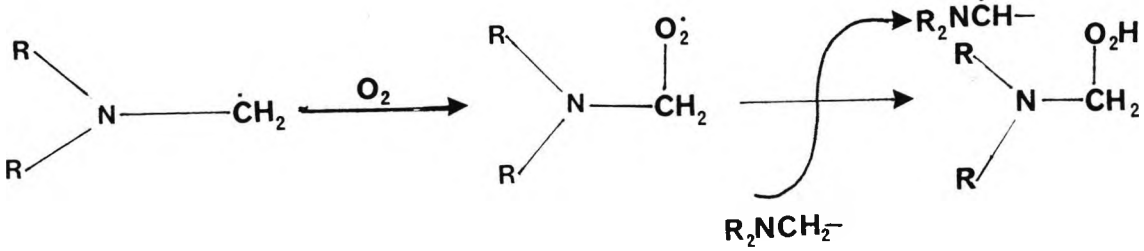
In this case, the rate of polymerization is reduced, due to the fact that the glass slide absorbs u.v. light. The initiator absorbs in the u.v. region of the spectrum, and therefore does not absorb as much (i.e. cut off point of glass slide is 330nm) u.v. light. Also, the radicals formed are scavenged by oxygen, inhibiting the polymerization process.

Table 2. U.V. Curing of η^6-chlorobenzene-η^5-cyclopentadienyliron (II)-n-butyl triphenylborate in the absence of an amine

No. of Passes Under Colordry				
	Quartz	Glass Slide	Air	Filter
	4	9	20	30+

In the absence of an amine and under anaerobic conditions the rate of polymerization is reduced.

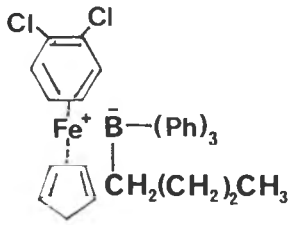
This is due to the absence of α-aminoalkyl radical which is a better initiating species than the alkyl radical formed.



Under aerobic conditions (i.e. air and filter), the rate of polymerization is reduced, due to oxygen inhibition of cure which prevent the polymerization of the triacrylate.

Under a filter, the rate of polymerization is reduced even further, due to the glass slide absorbing u.v. light. The cyclopentadienyliron(II) alkylborates absorb in the u.v. region and are not able to absorb u.v. light, therefore reducing the rate of polymerization.

Table 3 U.V. Curing of η^6-dichlorobenzene-η^5-cyclopentadienyliron (II)-n-butyl triphenylborate in the presence of an amine

No. of Passes Under Colordry				
	Quartz	Glass Slide	Air	Filter
	1	2	4	11

(a) Belt Speed:- 10ft/min (b) Amine used:- N-methyldiethanolamine

(c)Monomer:- 2-Ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate

Under anaerobic conditions (i.e. quartz and touching glass slide) a tack-free film was formed within two passes under the colordry.

This is due to the mechanism mentioned previously, whereby a radical pair is formed, as shown below:-

(1) $K_{et} \longrightarrow [CpFeC_6H_4Cl_2]\cdot\ [n\text{-}C_4H_9B(Ph)_3]\cdot$

The cleavage of the carbon-boron bond, produces alkyl radicals.

(2) $K_{bc} \longrightarrow [CpFeC_6H_4Cl_2]\cdot + B(Ph)_3 + C_4H_9^-$

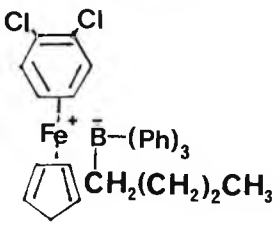
N-methyldiethanolamine

$C_4H_{10} + \dot{C}H_2NCH_2CH_2OH$

CH_2CH_2OH

Under aerobic conditions (i.e. air and filter), oxygen inhibits the polymerization process by scavenging the radicals formed and therefore reducing the rate of polymerization.

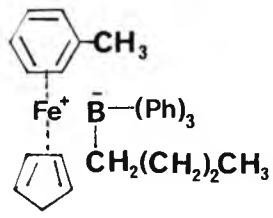
Table 4 U.V. Curing of η^6-dichlorobenzene-η^5-cyclopentadienyliron (II)-n-butyl triphenylborate in the absence of an amine

No. of Passes Under Colordry				
	Quartz	Glass Slide	Air	Filter
	3	8	30+	30+

Under anaerobic conditions (i.e quartz and touching glass slide), the reduction in the rate of polymerization is due to the absence of the synergist i.e N-methyldiethanolamine.

Under aerobic conditions (i.e. air and filter), a tack-free film is not formed. This is due to the presence of oxygen, which inhibits the polymerization of 2-ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate, by scavenging the radicals formed.

Table 5 U.V. Curing of n^6-toluene-n^5-cyclopentadienyliron (II)-n-butyl triphenylborate in the presence of an amine

No. of Passes Under Colordry				
	Quartz	Glass Slide	Air	Filter
	1	2	4	12

(a) Belt Speed:- 10ft/min (b) Amine used:- N-methyldiethanolamine

(c)Monomer:- 2-Ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate

Under anaerobic conditions (i.e quartz and touching glass slide) a tack-free film was formed within two passes under the colordry.

This is due to a radical pair being formed as shown below:-

(1) $h\nu \longrightarrow [CpFeC_6H_5CH_3]^{+*3}\ [n\text{-}C_4H_9B(Ph)_3]^-$

Excited Ion Pair

(2) $K_{et} \longrightarrow [CpFeC_6H_5CH_3]\cdot\ [n\text{-}C_4H_9B(Ph)_3]\cdot$

Electron transfer Radical Pair

(3) $K_{bc} \longrightarrow [CpFeC_6H_5CH_3] + B(Ph)_3 + C_4H_9\cdot$

Cleavage of carbon-boron bond

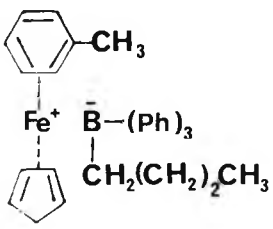
19-e^- iron (I) Species

N-methyldiethanolamine

Initiates polymerization of TMPTA $\longleftarrow$ $C_4H_{10} + CH_2NCH_2CH_2OH$ / CH_2CH_2OH

In the presence of N-methyldiethanolamine the rate of polymerization is increased, due to the amine acting as a synergist, forming an α-aminoalkyl radical, which is a better initiating species.
Under aerobic conditions, the rate of polymerization is reduced, due to oxygen inhibition of cure.

Table 6 U.V. Curing of η^6-toluene-η^5-cyclopentadienyliron (II)-n-butyl triphenylborate in the absence of an amine

No. of Passes Under Colordry				
	Quartz	Glass Slide	Air	Filter
	4	8	30+	30+

a) Belt Speed:- 10ft/min
b) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

Under aerobic conditions (i.e. air and filter), it is shown that a tack-free film is not formed due to the presence of oxygen, preventing polymerization of the acrylate, by scavenging the radicals formed.

Under quartz, a tack-free film was formed within four passes under the colordry. Whilst in the presence of a touching glass slide, a tack-free film is formed within eight passes under the colordry.

The difference in the rate of polymerization is due to the glass slide absorbing ultraviolet light. The cyclopentadienyliron (II) alkylborate salts absorb in the u.v. region of the spectrum it is not possible for the initiator to absorb u.v. light λ <330nm to initiate the polymerization process.

Mechanism:- Intra-ion-pair electron transfer of cyclopentadienyliron (II) alkylborates

A.

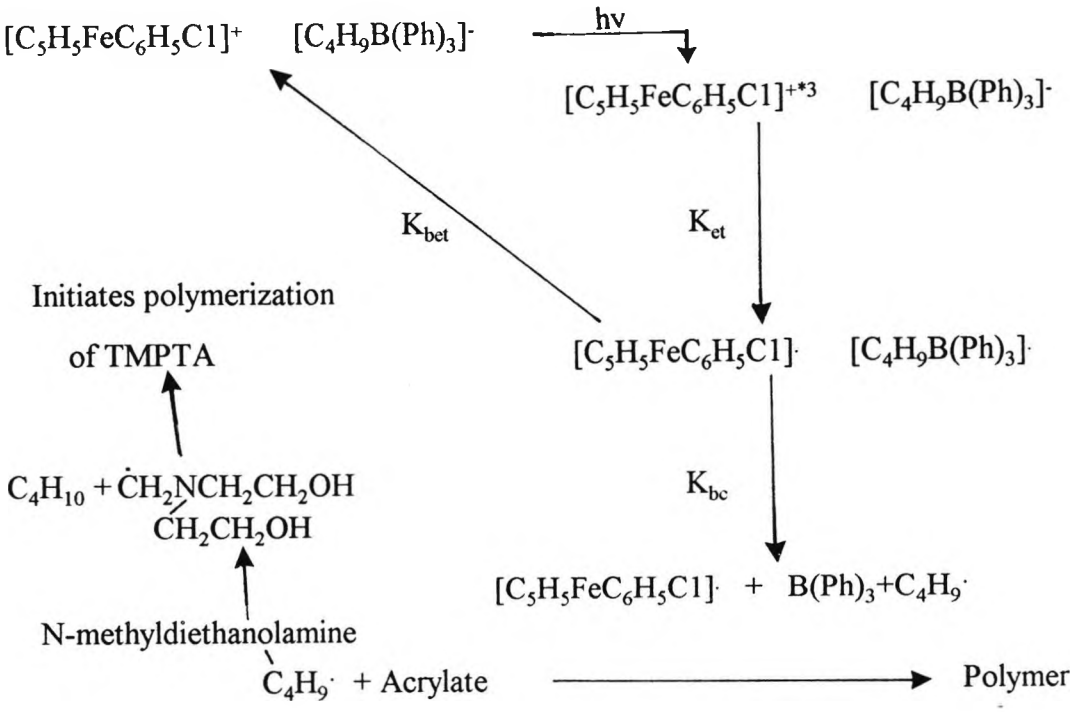
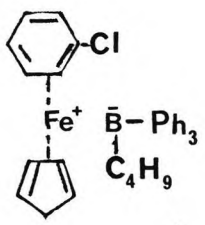
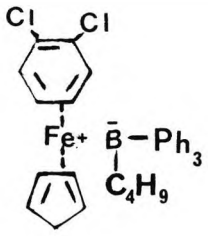


Table 1 U.V. Curing of cyclopentadienyliron (II) alkylborates in the presence of an amine

	Number of passes under colordry		
Samples	a	b	c
Quartz	1	1	1
Slide	2	2	2
Air	4	4	4
Filter	12	11	12

(a) 

(b) 

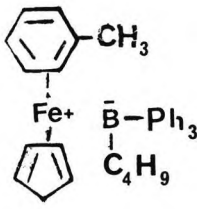
(c) 

Table 2 U.V. Curing of cyclopentadienyliron (II) alkylborates in the absence of an amine

	Number of passes under colordry		
Samples	a	b	c
Quartz	4	3	4
Slide	9	8	8
Air	20	30+	30+
Filter	30+	30+	30+

A. Belt Speed:- 10ft/min
B. Synergist Used:- N-methyldiethanolamine (10% w/w)
C. 2-Ethyl-2(hydroxymethyl)1,3-propanediol triacrylate

Real-Time Infra-Red Spectroscopy

Samples	Atmosphere	Rp (%/s)	Total conversion (%)	Residual unsaturated content (%)
b +N-methyldiethanolamine	In the absence of air	0.89	53	47
b	In the absence of air	0.5	32	68
b	In the presence of air	-	4	96

(a) Amine used:- 10% w/w of N-methyldiethanolamine
(b) 1% w/w of initiator
(c)Monomer:- 2-Ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate

n^6-Dichlorobenzene - n^5-cyclopentadienyliron (II) - n-butyltriphenylborate, in the presence of an amine under anaerobic conditions, gave a rate of polymerization of 0.89% /s and a total conversion of polymerization of 53% after five minutes.

The result supports the conclusions obtained from the colordry, whereby a radical pair is formed (eqn(1)), which undergoes carbon-boron bond cleavage to form a 19e iron (I) species and alkyl radicals (eqn (2)). In the presence of an amine, an α-aminoalkyl radical is formed, which is a better initiating species than the alkyl radical.

(1) $h\nu \longrightarrow [CpFeC_6H_4Cl_2]^{\cdot} \quad [n\text{-}C_4H_9B(Ph)_3]^{\cdot}$

Radical Pair

(2) $K_{bc} \longrightarrow [CpFeC_6H_4Cl_2]^{\cdot} \quad + \quad (Ph)_3B + C_4H_9^{\cdot}$

19-e⁻ iron (I) Species

N-methyldiethanolamine

$C_4H_{10} + \dot{C}H_2N(CH_2CH_2OH)CH_2CH_2OH$

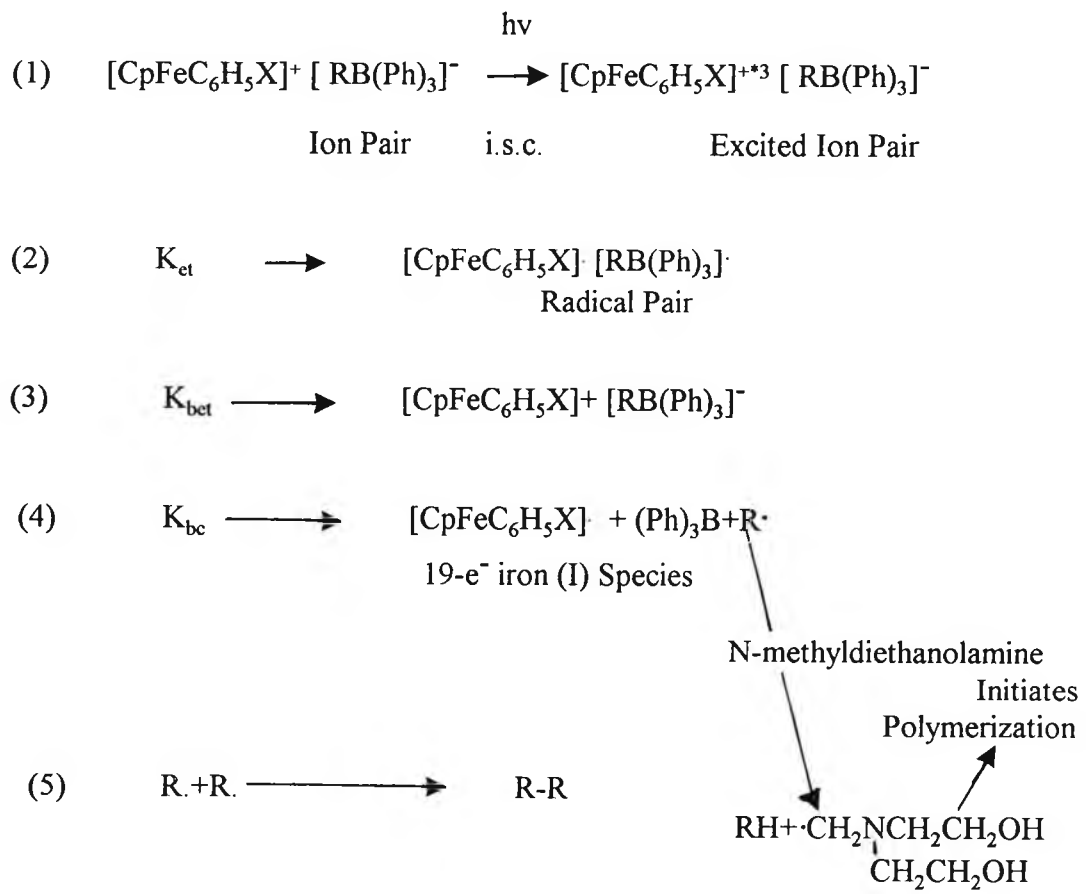
In the absence of an amine; and under anaerobic conditions, the rate of polymerization is reduced to 0.5%/s and a total conversion of 32% is obtained. The result shows that the inclusion of a synergist increases the rate of polymerization and total conversion. The result also shows that the α-aminoalkyl radical is a better initiating species than the alkyl radical.

η^6-Dichlorobenzene - η^5-cyclopentadienyliron (II) - n-butyltriphenylborate was also tested in the presence of air and in the absence of an amine. There was very little polymerization. This is due to the presence of oxygen, which scavenges the radicals formed, preventing polymerization.

Conclusion

The results obtained show that cyclopentadienyliron (II) alkylborate salts are efficient radical initiators in the presence of a synergist (i.e. N-methyldiethanolamine), under anaerobic and aerobic conditions. The mechanism shows the effect of the amine in the system, whereby an α-aminoalkyl radical is formed.

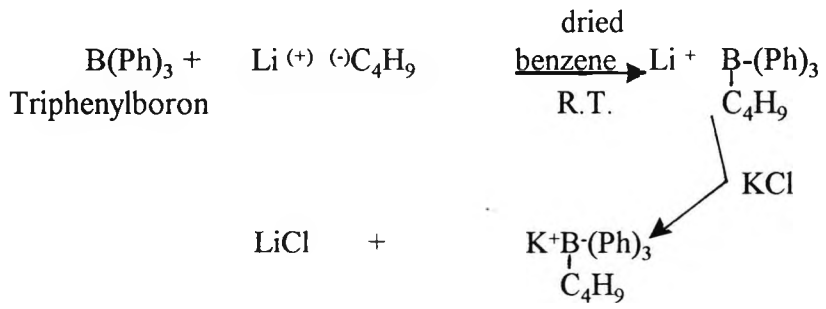
Mechanism:- Intra-ion pair electron-transfer of cyclopentadienyliron (II) alkylborates.



In the presence of an amine, the α-aminoalkyl radical is a better initiating species than the alkyl radical formed. In the absence of an amine, cyclopentadienyliron (II) alkylborates are not efficient initiators under aerobic and anaerobic conditions. Under aerobic conditions, the oxygen present scavenges the radicals formed, preventing polymerization of the acrylate.

6.3 EXPERIMENTAL DETAILS

Preparation of potassium n-butyltriphenylborate



Dried benzene (100mls) was added to a 3-neck round-bottom flask, which was flushed with nitrogen.

Triphenylboron (2.4g, 0.01m) was added and the mixture was stirred for fifteen minutes.

n-Butyllithium (5.8ml of 1.7m solution, 0.01m) was then added via a syringe.

The solution turned pale green, once the n-butyllithium was added. The mixture was left to stir at room temperature for 24 hours. A white precipitate was formed and hexane (100ml) was added to precipitate out the lithium salt of the borate.

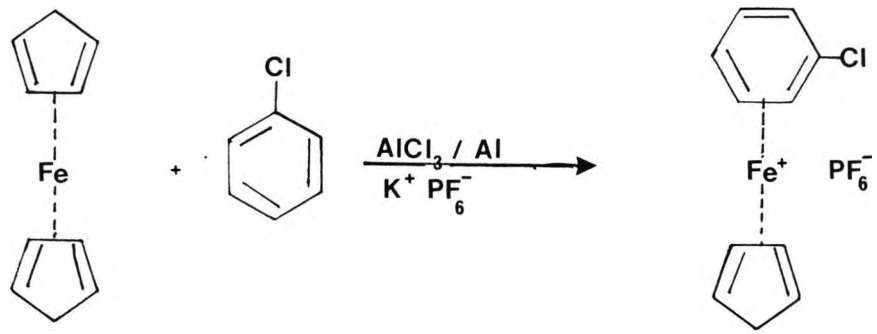
To form the potassium salt, the white precipitate was filtered and then added to 100mls of distilled water and stirred under low heat.

An equivalent amount of potassium chloride in 100mls of distilled water was added to the mixture to form the white precipitate of the potassium salt (Yield = 35%).

NMR analysis (60MHz, d-methanol/TMS)

7.4-6.8	,	(m,15H)	-	aromatic protons
2.7	,	(t,2H)	-	CH_2B protons
0.7-1.1	,	(m,7H)	-	n-butyl protons

A. Preparation of n^6-chlorobenzene, n^5-cyclopentadienyliron (II) hexafluorophosphate



Method

Powdered anhydrous aluminium chloride (4.0g, 30mmol) and aluminium powder (0.35g) were added to a solution of ferrocene (3.0g, 16mmol) in chlorobenzene (70ml), and the mixture was refluxed for six hours. The colour of the solution changed from orange to red/brown.

The mixture was cooled, water (150ml) was added carefully and the solution was stirred vigorously. The aqueous layer was then separated and washed with petroleum ether to remove the unreacted ferrocene. An aqueous solution of potassium hexafluorophosphate was added (Yield 30%).

Purification:- The product was purified by column chromatography, methanol/alumina.

NMR analysis (100MHz, H'NMR) , solvent - d-acetone

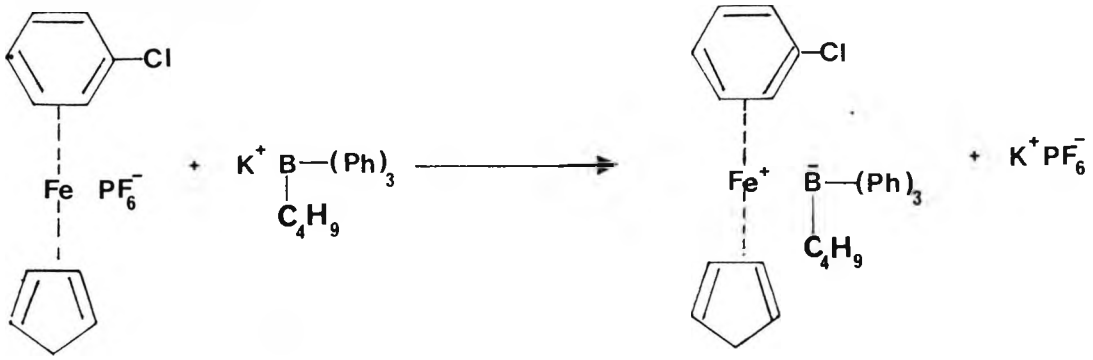
7.0	,	(m,2H)	-	arene - protons
6.8	,	(m,3H)	-	arene - protons
5.4	,	(s,5H)	-	cyclopentadienyl protons
2.0	,	(d-acetone)		

CHN analysis (%)

	Expected	Found
C,	34.8	34.58
H,	2.65	2.51

Formula : $C_{11}H_{10}FeCl\,PF_6$

B. Preparation of n^6 - chlorobenzene, n^5-cyclopentadienyliron - n-butyltriphenylborate



Method (II)

n^6-Chlorobenzene, n^5-cyclopentadienyliron (II) hexafluorophosphate (0.01g) was added to methanol (30ml) and stirred for 30 minutes.

Potassium n-butyltriphenylborate was added and refluxed for two hours. A white precipitate was formed of the hexafluorophosphate salt. This was filtered off and the remaining solution was removed using a rotary evaporator. A small amount of distilled water was added to the solution. The iron salt had precipitated out and was then filtered under vacuum. The salt was dried in an oven at low heat for 24 hours (Yield = 50%).

Purification was carried out by using methanol as the solvent and alumina plates.

NMR analysis (270MHz, d-acetonitrile/TMS)

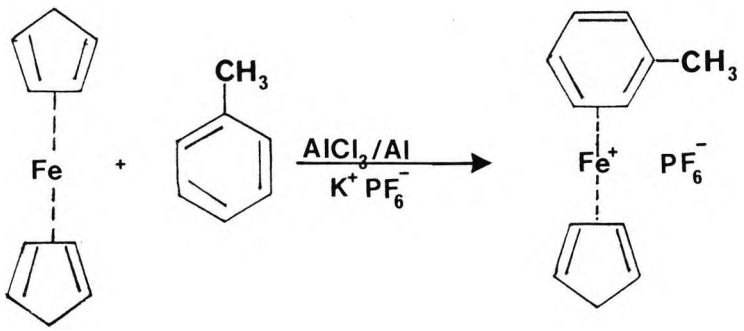
7.4-7.2	,	(m,6H)	-	aromatic protons
7.0	,	(m,6H)	-	aromatic protons
6.8	,	(m,3H)	-	aromatic protons
6.6	,	(m,2H)	-	arene - protons
6.2-6.4	,	(m,3H)	-	arene - protons
5.0	,	(s,5H)	-	cyclopentadienyl protons
2.8	,	(t,2H)	-	CH_2B protons
0.7-1.2	,	(m,7H)	-	n-butyl protons

CHN analysis(%)

	Expected	Found
C,	74.3	73.4
H,	6.38	6.45

Formula : $C_{33}H_{34}Fe\ B\ Cl$

C. Preparation of n^6-toluene - n^5-cyclopentadienyliron (II) hexafluorophosphate



Method

As for n^6-chlorobenzene - n^5 cyclopentadienyliron (II) hexafluorophosphate.

Purification was carried out by using methanol and alumina plates.

NMR analysis (100MHz, d-acetone)

6.5	,	(s,5H)	- aromatic protons
5.2	,	(s,5H)	- cyclopentadienyl protons
2.6	,	(s,3H)	- CH_3 protons

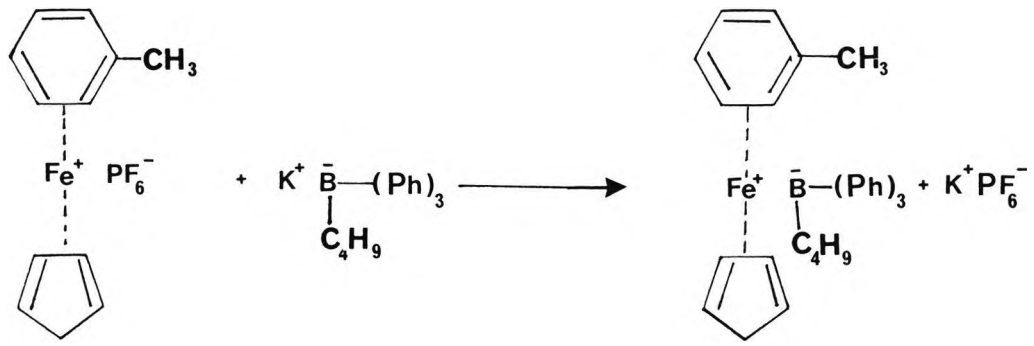
CHN analysis(%)

	Expected	Found
C,	40.22	39.89
H,	3.63	3.47

Formula : $C_{12}H_{13}Fe\,PF_6$

U.V. Spectrum:- λ max = 240nm

D. Preparation of η^6-toluene - η^5-cyclopentadienyliron (II) n-butylriphenylborate



Method:- As for compound B.

Purification was carried out by using alumina plates and methanol.

NMR analysis (270MHz, d-acetonitrile/TMS)

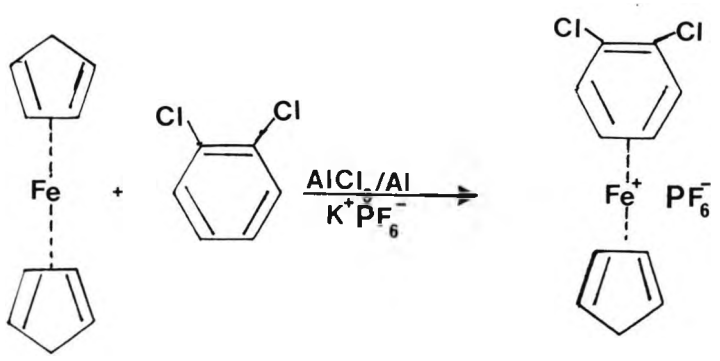
7.4-7.2	,	(m,6H)	-	B-$(Ph)_3$ protons
7.0	,	(m,6H)	-	B-$(Ph)_3$ protons
6.8	,	(m,3H)	-	B-$(Ph)_3$ protons
6.2	,	(s,5H)	-	arene - protons
4.9	,	(s,5H)	-	cyclopentadienyl protons
2.8	,	(t,2H)	-	CH_2B protons
2.5	,	(s,3H)	-	CH_3 protons
0.7-1.1	,	(m,7H)	-	n-butyl protons

CHN analysis(%)

	Expected	Found
C,	79.68	79.48
H,	7.22	6.85

Formula : $C_{34}H_{37}Fe\,B$

E. Preparation of η^6-dichlorobenzene - η^5-cyclopentadienyliron (II) hexafluorophosphate



Method:- As for compound A.

Purification was carried out by using methanol and alumina plates.

NMR analysis (100MHz, d-acetone)

7.0	,	(m,2H)-	aromatic protons
6.6	,	(m,2H)-	aromatic protons
5.4	,	(s,5H) -	cyclopentadienyl protons
2.0	,	(d-acetone)	

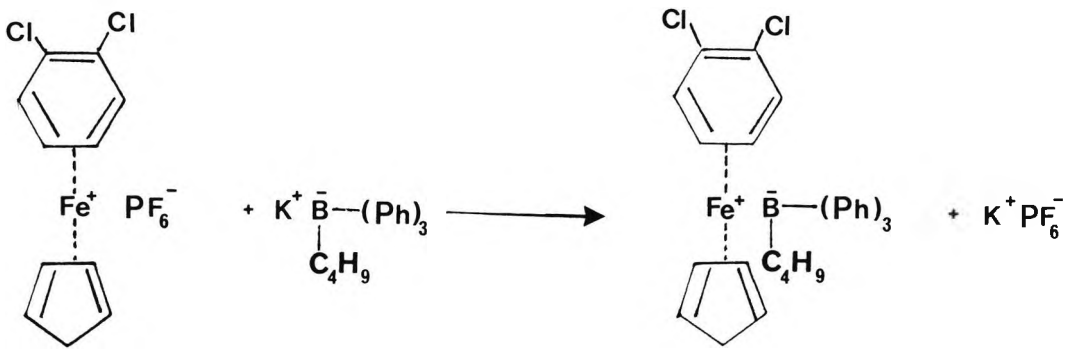
CHN analysis(%)

	Expected	Found
C,	31.96	31.35
H,	2.17	2.20

Formula : $C_{11}H_9Fe\,Cl_2\,PF_6$

U.V. Spectrum:- λ max = 232nm

F. Preparation of η^6-dichlorobenzene-η^5- cyclopentadienyliron(II) n-butyltriphenylborate



Method:- As for compound B.

Purification was carried out by using methanol and alumina plates

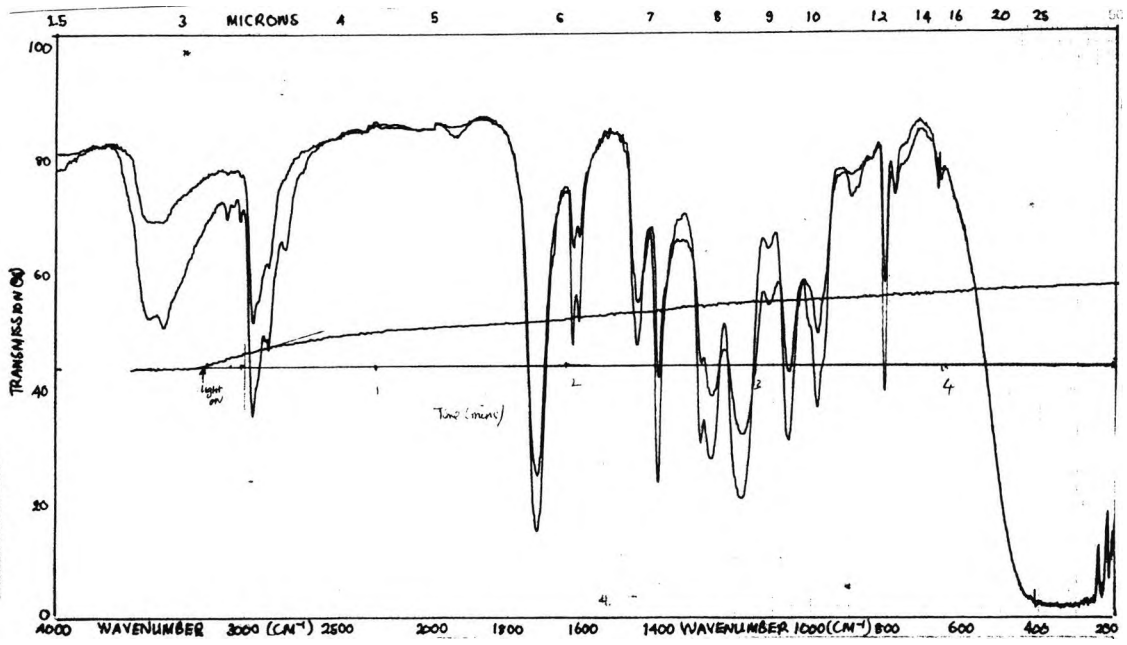
NMR analysis (270MHz, H'NMR, solvent - d-acetonitrile)

7.4-6.8	, (m,17H)	-	Aromatic and arene protons
6.3	, (m,2H)	-	arene - protons
5.2	, (s,5H)	-	cyclopentadienyl protons
2.8	, (bs,2H)	-	CH_2B protons
2.0	,	-	d-acetonitrile
0.7-1.2	, (m,7H)	-	n-butyl protons

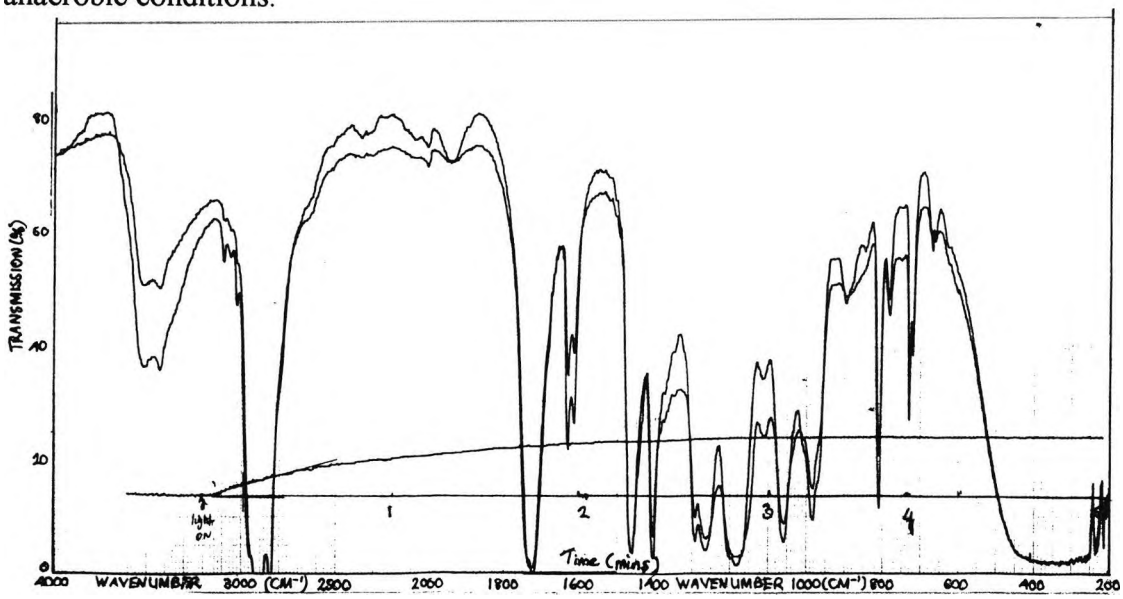
CHN analysis(%)

	Expected	Found
C,	69.8	69.49
H,	5.82	5.74

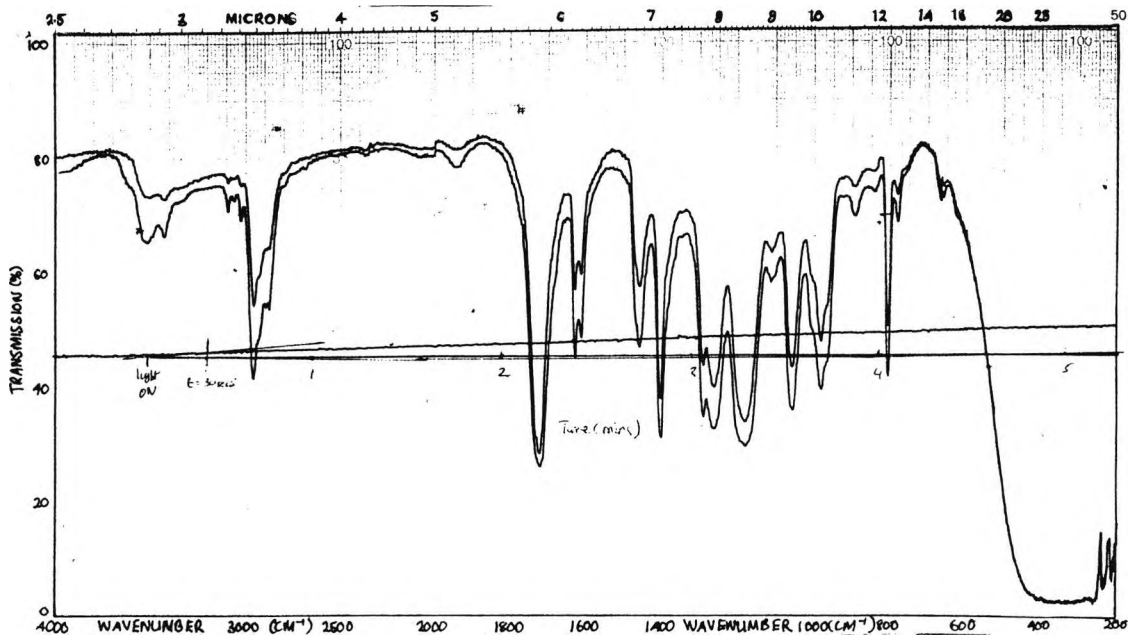
Formula : $C_{33}H_{33}Fe\,Cl_2\,B$



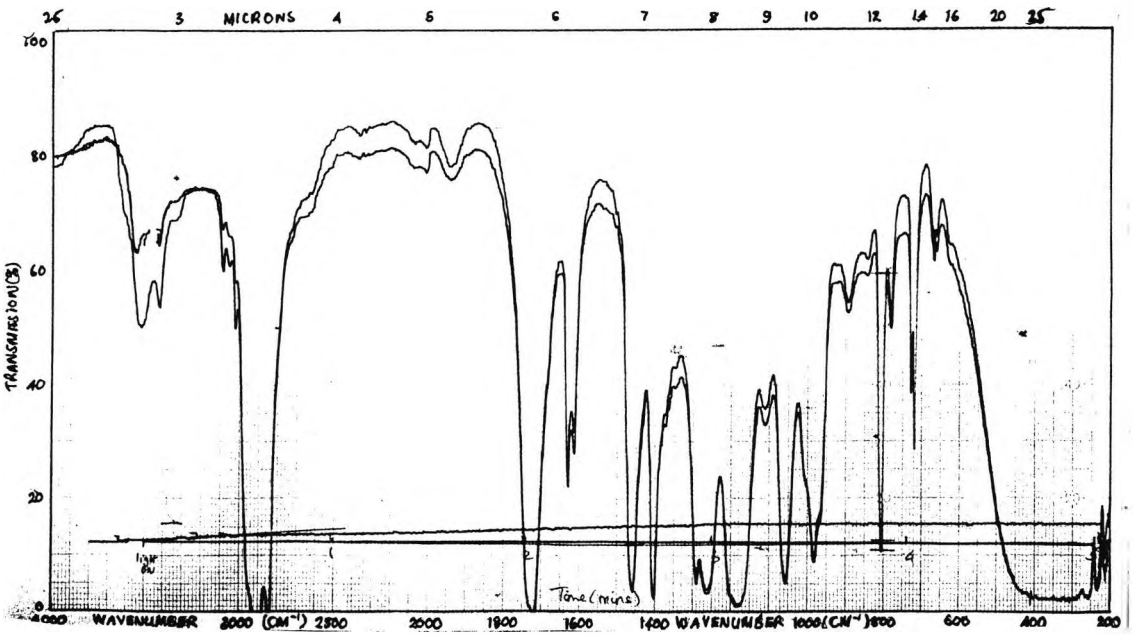
Spectrum 1:- RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of n^6-dichlorobenzene-n^5-cyclopentadienyliron(II)-n-butyltriphenylborate and N-methyldiethanolamine, under anaerobic conditions.



Spectrum 2:- RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of n^6-dichlorobenzene-n^5-cyclopentadienyliron(II)-n-butyltriphenylborate and N-methyldiethanolamine, under aerobic conditions.



Spectrum 3:- RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of η^6-dichlorobenzene-η^5-cyclopentadienyliron(II)-n-butyltriphenylborate, under anaerobic conditions.



Spectrum 4:- RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of η^6-dichlorobenzene-η^5-cyclopentadienyliron(II)-n-butyltriphenylborate, under aerobic conditions.

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CHAPTER SEVEN

PHOTOCHEMISTRY OF DIAZONIUM SALTS IN THIN FILMS

Diazonium Salts

7.1 INTRODUCTION

Eqn A. Diazotisation:-

$$ArNH_2 + NaNO_2 + 2HX \xrightarrow[0\text{-}5^oC]{\text{cold}} ArN_2^+X^{(-)} + NaX + 2H_2O$$

Diazonium salt

When primary aromatic amines are treated with sodium nitrite and a mineral acid, diazonium salts are formed (eqn (a)). The reaction also occurs with primary aliphatic amines, but aliphatic diazonium ions are extremely unstable in solution (eqn (b)). [1]

Eqn B.

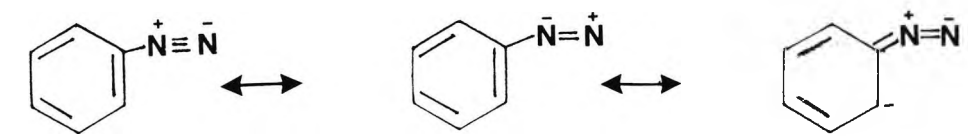
$$R\text{-}NH_2 + NaNO_2 + HX \rightarrow [R\text{-}N_2^{(+)}X^{(-)}] \xrightarrow{H_2O} N_2 + \text{mixture of alcohols and alkenes}$$

unstable

The amine present in the reaction reacts with "nitrous acid", (HONO), which is generated from the mineral acid and sodium nitrite.

Aromatic diazonium ions are more stable, because of the resonance interaction between the nitrogen atoms and the ring.

Eqn C.



(A) (B) (C)

etc.

Species (A) contributes more to the hybrid than (B). This is due to the bond distance measurements, e.g. in benzenediazonium chloride, the C-N distance is approximately 1.08 Å, which is similar to the bond distance in a triple bond rather than to two double bonds (i.e. species 'C').

Even aromatic diazonium salts are stable only at low temperatures (usually only below 5°C), though more stable ones, such as the diazonium salt obtained from suphanilic acid, are stable up to 10-15°C. Diazonium salts are usually prepared in aqueous solution and used without isolation, although it is possible to prepare solid diazonium salts if desired. For aromatic amines, the reaction is very general. Despite the fact that diazotisation takes place in acid solution, the actual species attacked is not the salt of the amine, but the small amounts of free amine present. This is because aromatic amines are weaker bases than aliphatic ones, that at low pH values there is enough free amine present for the aromatic amine to be diazotised.

In dilute acid solution, the actual attacking species is N_2O_3 which acts as a carrier of $NO^{(+)}$. Evidence for this is that the reaction is second order in "nitrous acid" and at sufficiently low acidities,the amine does not appear in the rate expression.

Under these conditions the mechanism is :-

Mechanism 1

Step 1. $2\,HONO \xrightarrow{slow} N_2O_3 + H_2O$

Step 2. $Ar\text{-}NH_2 + N_2O_3 \longrightarrow Ar\text{-}\overset{H}{\underset{H}{N^{(+)}}}\text{-}N{=}O + NO_2^-$

Step 3. $Ar\text{-}\overset{H}{\underset{H}{N^{(+)}}}\text{-}N{=}O \xrightarrow{-H^{(+)}} Ar\text{-}\overset{(-)}{N}\text{-}N{=}O$ (H)

Step 4. $Ar\text{-}\overset{(-)}{N}\text{-}N{=}O \longrightarrow Ar\text{-}N = N\text{-}OH$ (H)

Step 5. $Ar\text{-}N = N\text{-}O\text{-}H \xrightarrow{H^{(+)}} Ar\text{-}N^{(+)} \equiv N + H_2O$

There exists other evidence for this mechanism. Other attacking species may be NOCl, $H_2NO_2^+$, and at higher acidities NO^+ (as shown below).

1. $HONO + H_3O^+ \rightleftharpoons H_2O^+\text{-}NO + H_2O \rightleftharpoons 2H_2O + \overset{(+)}{N}{=}O$

$Ar\text{-}\overset{H}{N}: + {}^+N{=}O \longrightarrow Ar\text{-}\overset{H}{\underset{H}{N^+}}\text{-}N{=}O \xrightarrow{-H^+} Ar\text{-}N\text{-}N{=}O$ (H)

1· aryl or alkylamine — N-nitrosoammonium ion, — N-nitrosoamine

Proton Shift: $Ar\,\ddot{N}{=}N\text{-}OH \overset{H^{(+)}}{\rightleftharpoons} Ar\,\ddot{N}{=}N\text{-}\overset{+}{O}H_2$

Diazohydroxide: $\rightleftharpoons Ar\,N{\equiv}N: \rightleftharpoons Ar\,\ddot{N}{=}\overset{+}{N} + H_2O$

Diazo and related compounds

Diazoalkanes, $[R_2C=\overset{+}{N}=\overset{-}{N} \leftrightarrow R_2\bar{C}-\overset{+}{N}=N \leftrightarrow R_2\overset{+}{C}-N=\overset{-}{N}]$ exhibit a weak absorption band in the visible region (400-500nm),which is attributed to a $n \rightarrow \pi^*$ transition [2].

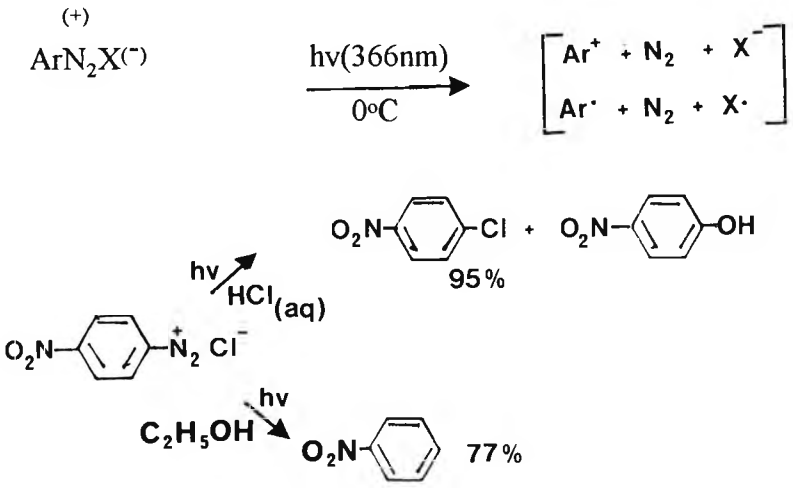
The corresponding excited states fragment readily to give molecular nitrogen and a carbene, and this is a widely used method for the generation of these divalent carbon species. Direct irradiation leads initially to a singlet excited state of the diazo compound, and hence to a singlet carbene. Although collisional deactivation to give triplet carbene before further reaction occurs, is important for the carbenes whose triplet state is lower in energy than the singlet state, especially at higher pressures in the vapour phase or in solution.

Triplet sensitized decomposition of diazoalkanes gives rise directly to triplet carbene by way of the triplet excited state. These processes provide a valuable route to carbenes and are employed for intramolecular reaction as in the ring-contraction of cyclic diazoketones.

Diazonium Salts

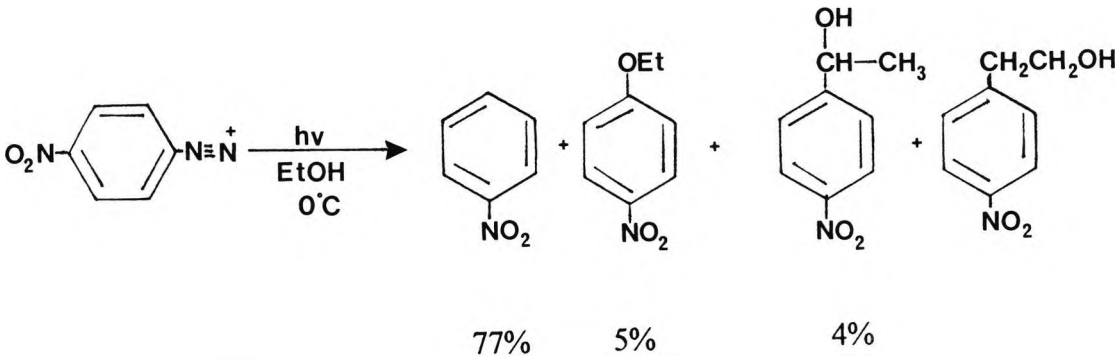
Aromatic diazonium salts on photolysis in solution undergo efficient loss of nitrogen in two primary processes with a combined quantum efficiency approaching unity. One of the processes leads to a carbonium ion and the other to a carbon radical. The relative importance of the two pathways varies with the solvent used and is controlled by the degree of association of the diazonium cation with the anion.

The difference is seen in the photochemistry of p-nitrobenzene diazonium chloride. In aqueous hydrochloric acid the products are largely p-nitrophenol and p-nitrochlorobenzene formed in an ionic process, but in ethanol as solvent, the major product is nitrobenzene formed by a radical mechanism.



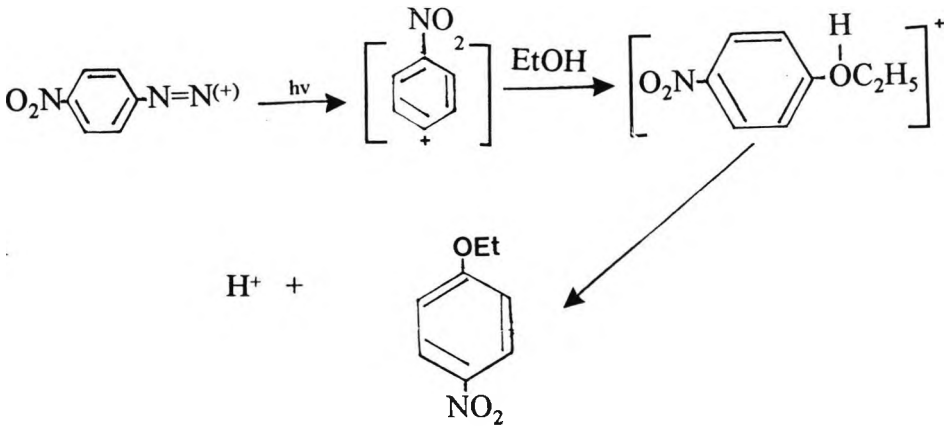
Photochemistry of Aromatic Diazonium Salts

Previous work carried out on the photolysis of diazonium salts [3], especially using various alcohols as solvents, showed that aromatic ethers and aromatic hydrocarbons are the main products formed.



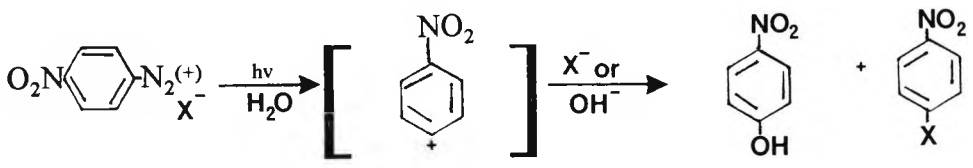
These products are thought to result from attack of an intermediate p-nitrophenyl radical on the solvent. Evidence for this intermediate was obtained by scavenging the radical with diphenylpicrylhydrazyl radical halogens, and nitric acid.

The formation of 4-nitrophenetole in the presence of iodine, which effectively eliminates most other radical products, suggests that another mechanism involving a phenyl carbonium ion may also be operative.



Indeed the acidity of the reaction mixture was found to increase upon continued photolysis in accord with the carbonium ion mechanism.

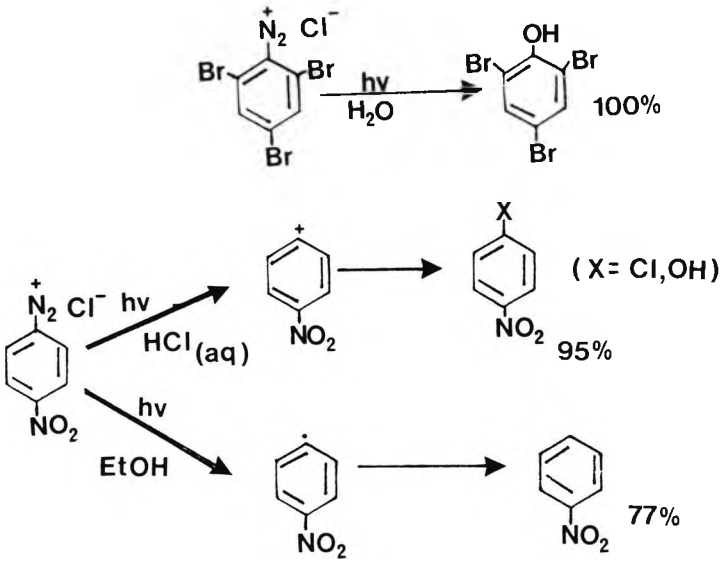
In aqueous solution, diazonium salts produced products corresponding to an anion addition to an intermediate carbonium ion.



74% 4% X=Cl

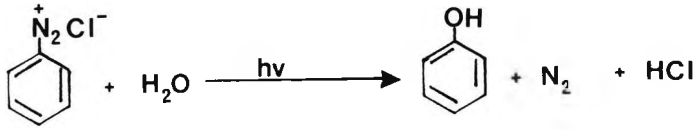
The photochemistry of diazonium salts ($ArN_2^+X^-$) [4], is important because these compounds have for a long time been widely used for photoimaging. Materials impregnated with a diazonium salt are exposed to light through a 'mask' of the object recorded. In the exposed areas the diazonium salt is destroyed and development of the image using a coupler (such as a phenolate salt) that reacts with the unchanged diazonium salt to produce an azo-dye provides a direct, positive record of the original. The resolution is very high, the materials are not expensive and development is simple, so this long standing process is still used for reproduction of such items as detailed technical plans. There are many variations in the method of development, but all of these diazo imaging systems rely on the photochemical breakdown of diazonium salts by loss of nitrogen. As explained earlier, in some hydroxylic solvents irradiation of a diazonium salt can lead to a phenol in high yield and this suggests that cleavage to give an aryl cation is a likely mechanism.

However, replacement of $-N_2^+$ by hydrogen may also occur and this implies an aryl radical is an intermediate. In many systems it is possible that both cationic and radical mechanisms operate.



At the end of the last century, Andressen[6] established that aqueous solutions of diazo compounds decompose under the influence of light.[5] The mechanism of the photochemical decomposition is not completely understood, it appears to be largely determined by the environment and by the chemical species present.

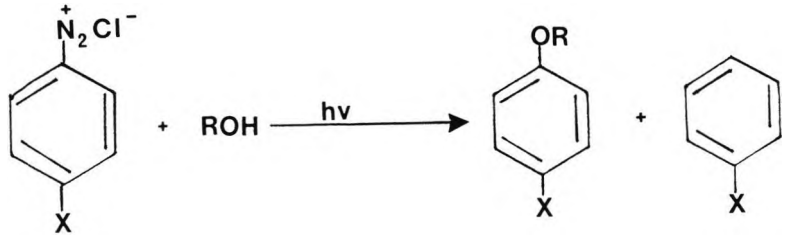
The effect of substituents on the light sensitivity of diazo compounds has been studied by many investigators.



According to Andressen [6], diazonium salts irradiated in aqueous solution are decomposed into a phenol and nitrogen.

Orton and co-workers [7] investigated the photolysis of diazonium salts in aqueous solutions and found a noticeable increase in the rate of decomposition as compared to that of a dark reaction.

When para-substituted benzene diazonium derivatives are irradiated by u.v. light in methanol as the solvent, the formation of the phenol ether is rather a minor process, while the main reaction is the substitution of hydrogen for the diazo group.



Substitution of the diazonium group by fluorine

In the photolysis of crystalline diazonium fluoroborate and hexafluorophosphates, the corresponding fluoroarenes are usually the only volatile product as in pyrolysis[8].

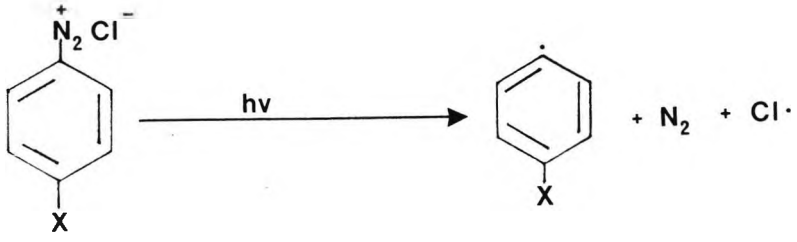
In some cases, the yield of fluoroarenes was higher than that obtained by pyrolysis of these salts (the Balz-Schiemann reaction), which remains the most generally used means of introducing a fluorine substitute into an aromatic ring [9].

$$ArN_2^+ BF_4^- \text{ (or } PF_6^-) \xrightarrow{hv} ArF + N_2 + BF_3 \text{(or } PF_5)$$

Lewis and co-workers [10] compared photochemical and thermal reactions of diazonium salts in aqueous solutions and concluded definitely that there was no single intermediate common to both.

Substitution of the diazonium group by chlorine or by hydroxy groups

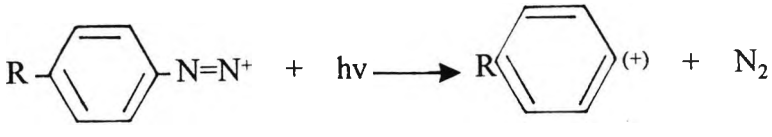
Solid anhydrous chlorides completely free of polar influences were observed to be photolysed with a quantum efficiency of well over unity. These results can be explained by considering the covalent diazo tautomer of the diazonium chloride, which decomposes symmetrically in the first step [11],



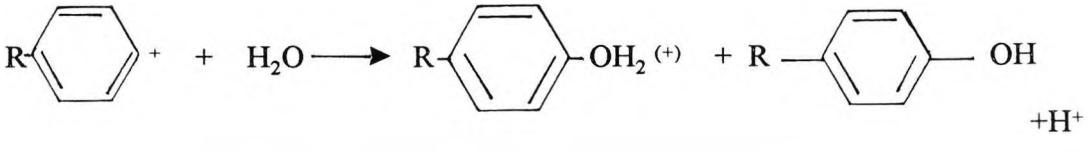
Free chlorine atoms and phenyl radicals so produced are capable of continuing the original function of the utilized photon.

The products of the photodecomposition of diazonium salts in aqueous solution seem well explained through a simple cleavage to form molecular nitrogen and a carbonium ion [12].

Eqn 1.

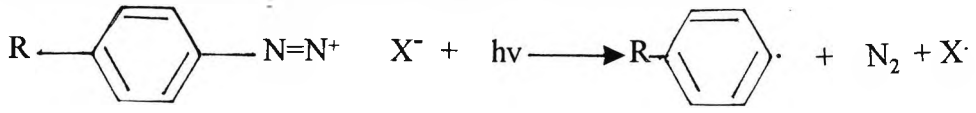
e.g. 

The ion formed in equation (1), either hydrates to form the phenol as a final product

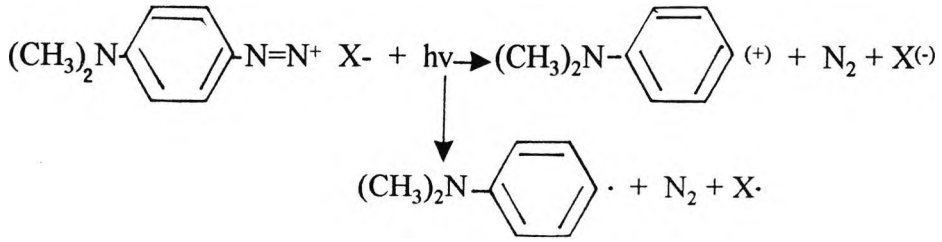


or combines with a negative ion (i.e. $Cl^{(-)}$) at high concentrations of added ions. Ring collapse of the primary carbonium ion products occurs in part in the o - hydroxy substituted compounds in water.

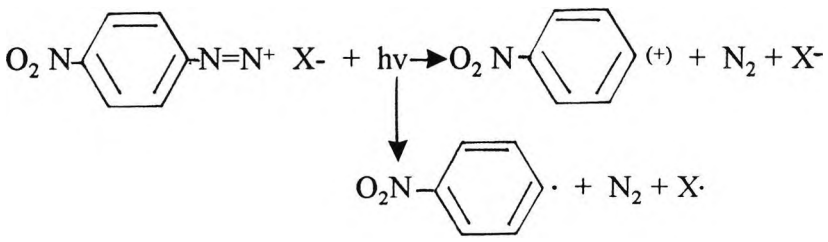
In less polar solvents, such as ethanol, the formation of free radicals by electron transfer may compete favourably with the ion forming process.



Eg.1 p-Diazo - N, N-dimethylaniline - zinc chloride complex (dihydrate). [13]



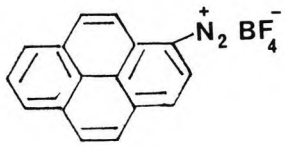
Eg. 2 p-Nitrobenzene diazonium chloride - stannic chloride complex. [14]



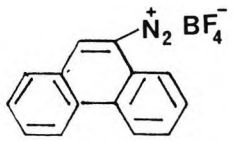
7.2 RESULTS AND DISCUSSION

Pyrenediazonium tetrafluoroborate (A), phenanthrenediazonium tetrafluoroborate (B), 3-diazonium-2-methoxy-dibenzofuran p-toluenesulphonate (C), 4-diazonium - diphenylamine p-toluenesulphonate (D), and 4-diazonium-3-methoxydiphenylamine mesitylene sulphonate/bis (methylether)- diphenyl ether condensate (E) were all tested on the moving belt system to give an indication of the efficiency of the salts as free radical photinitiators in the polymerization of acrylates.

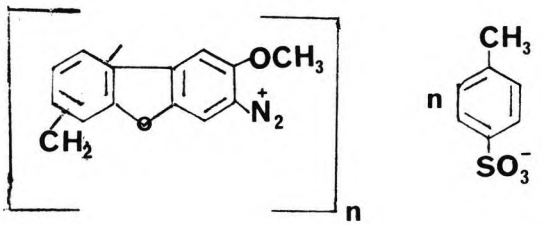
A)



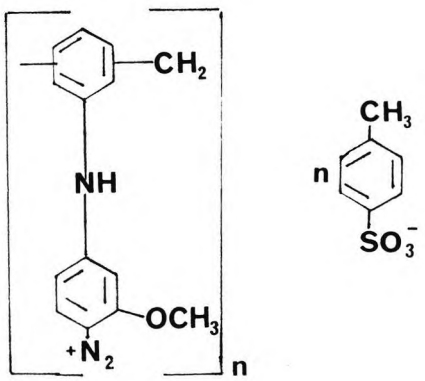
(B)



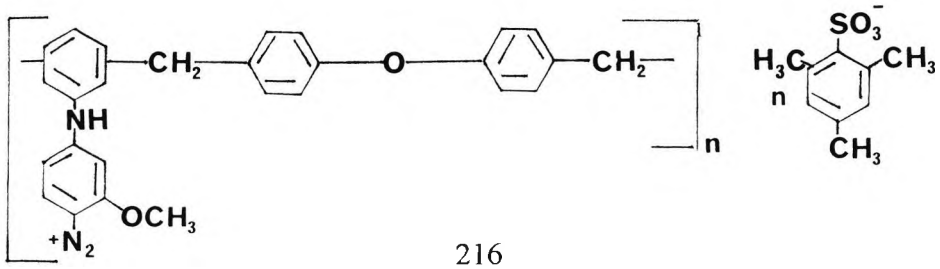
C)



D)



E)



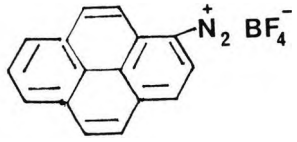
The formulation consisted of (i) 1% w/w of diazonium salt

(ii) 10% w/w of N-methyldiethanolamine

(iii) Monomer:- 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate

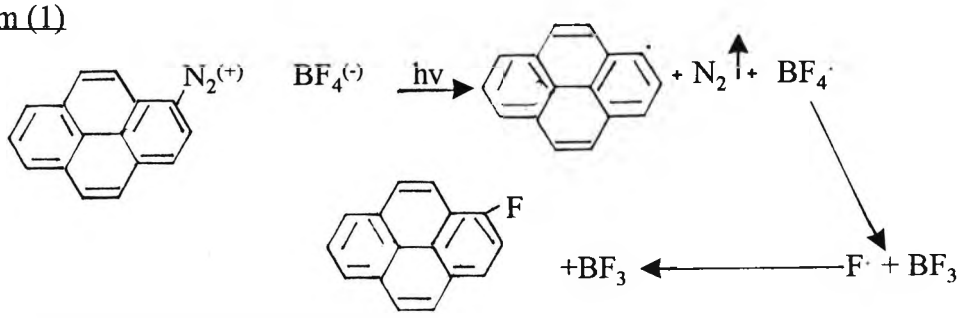
U.V. Curing of diazonium salts in the presence of an amine

Pyrenediazonium tetrafluoroborate (A), was tested in the presence of 10% w/w of N-methyldiethanolamine.

A. 

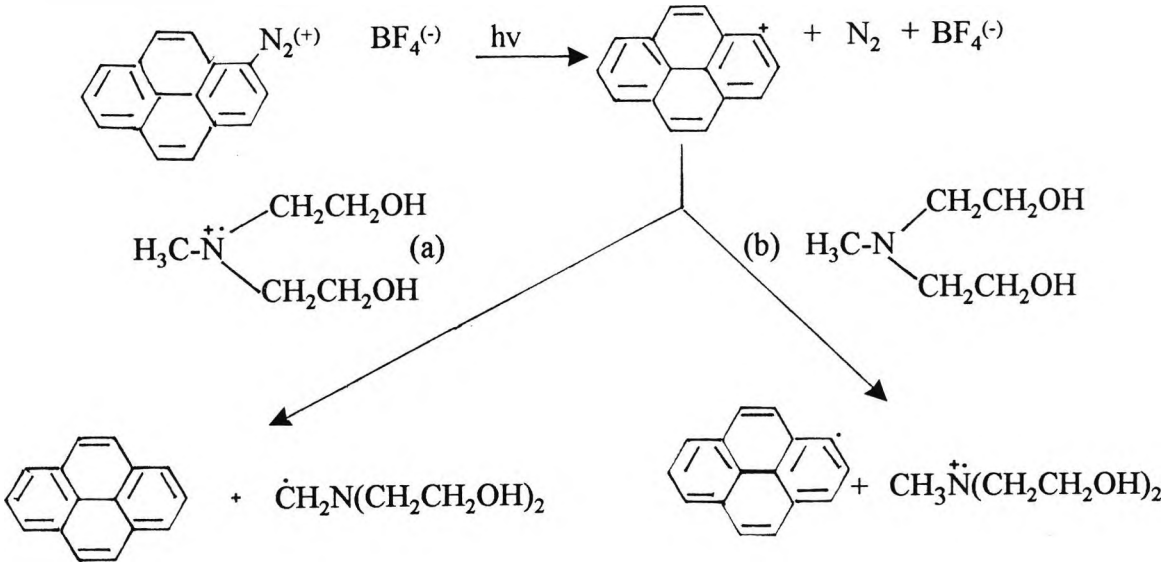
Under anaerobic conditions (i.e. quartz and a touching glass slide), the results suggest that upon absorption of u.v./visible light, the diazonium salts dissociates and liberates nitrogen. The mechanism for the photodecomposition of diazonium salts in thin films is uncertain. The diazonium salts can decompose to form aryl radicals, which are inefficient initiators.

Mechanism (1)



Also the salts could decompose via a non-radical pathway, forming a cation (mechanism (2)).

Mechanism (2)



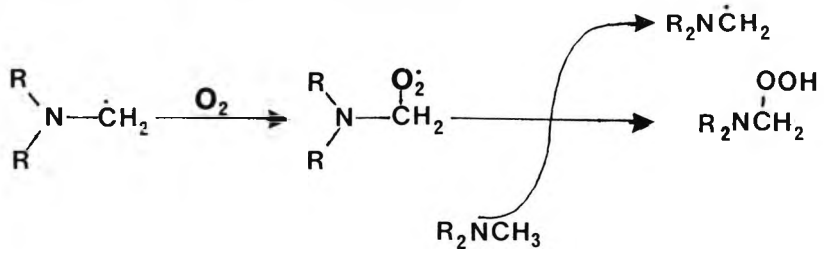
In the presence of an amine, there are two possible pathways in which free-radical polymerization could occur.

Pathway (a), shows the formation of an α-aminoalkyl radical via the intermediate radical cation.

The α-aminoalkyl radical is formed via proton transfer from the radical cation. The α-aminoalkyl radical is a better initiating species than the aryl radicals formed, and would initiate the polymerization of the triacrylate.

Pathway (b), shows the formation of an aryl radical, which is an inefficient initiator in the polymerization of acrylates.

The presence of the amine in the formulation reduces the effect by oxygen of inhibition of the polymerization process as shown below:

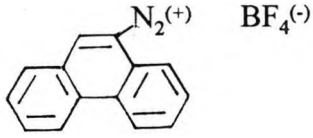


Also the amine provides a source of initiating radicals i.e. α-aminoalkyl radicals.

$\dot{C}H_2N(CH_2CH_2OH)_2$

The α-aminoalkyl radical is a better initiating species than the aryl radicals formed.

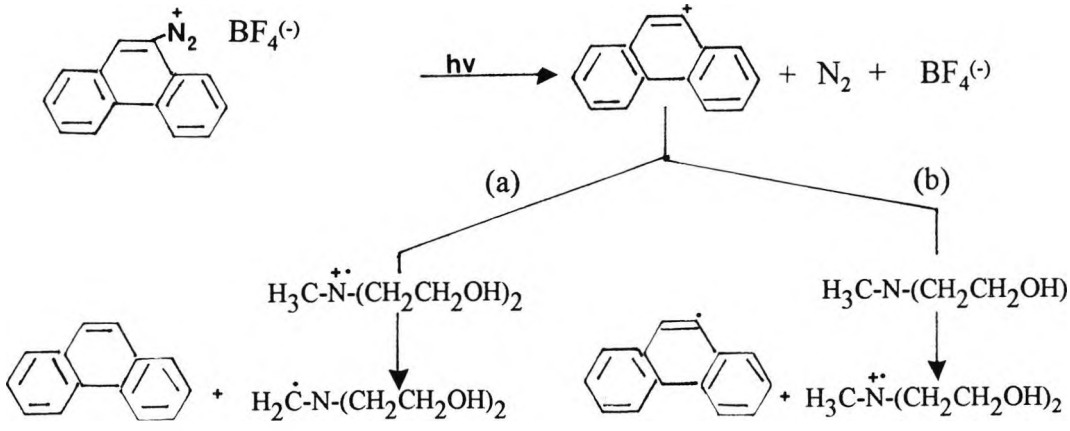
Under aerobic conditions, the reduction in the rate of polymerization is due to the presence of oxygen inhibiting the polymerization process. The film formed contained bubbles, which were most likely due to the production of nitrogen. Phenanthrenediazonium tetrafluoroborate (B) was tested in the presence of 10% w/w of N-methyldiethanolamine.

(B) 

Under anaerobic conditions (i.e. quartz and touching glass slide), a tack-free film was formed within two passes under the colordry.

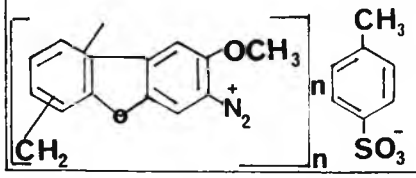
The mechanism for the photodecomposition of the phenanthrene derivative is as described for the pyrenediazonium tetrafluoroborate.

Mechanism (3)



Under aerobic conditions (i.e. air and filter), there is a reduction in the rate of polymerization, due to oxygen scavenging the radicals formed. The film also contained bubbles, due to the production of nitrogen.

Table 1. U.V. Curing of 3-diazonium-2-methoxydibenzofuran p-toluenesulphonate in the presence of an amine

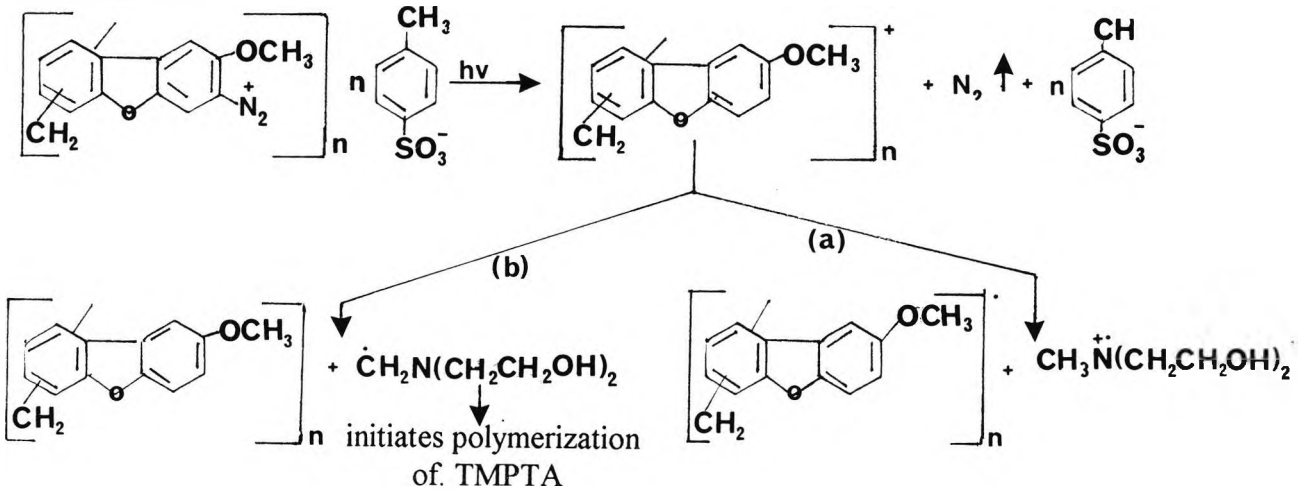
	No of passes under Colordry			
	Quartz	Glass Slide	Air	Filter
	1	1	15	15

a) Belt Speed:- 10ft/min
b) Amine:- N-methyldiethanolamine
c) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

Under anaerobic conditions (i.e. quartz and touching glass slide), a tack-free film is formed in one pass under the colordry.

Upon absorption of u.v. light, 3-diazonium-2-methoxydibenzofuran p-toluenesulphonate decomposes to form a cation and liberates nitrogen.

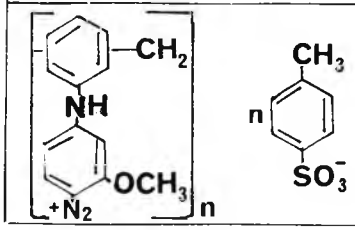
Mechanism (4).



The most probable pathway will be (b), as the α-amino-alkyl radical is formed, which is a better initiating species than the aryl radical formed.

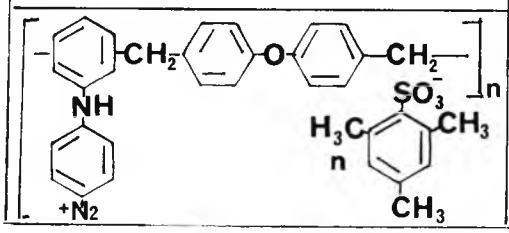
Under aerobic conditions, the reduction in the rate of polymerization is due to oxygen scavenging the radicals formed.

Table 2 U.V. Curing of 4-diazonium-3-methoxydiphenylamine p-toluenesulphonate in the presence of an amine

No of passes under Colordry			
Quartz	Glass Slide	Air	Filter
	1	3	27	27

a) Belt Speed:- 10ft/min
b) Amine:- N-methyldiethanolamine
c) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

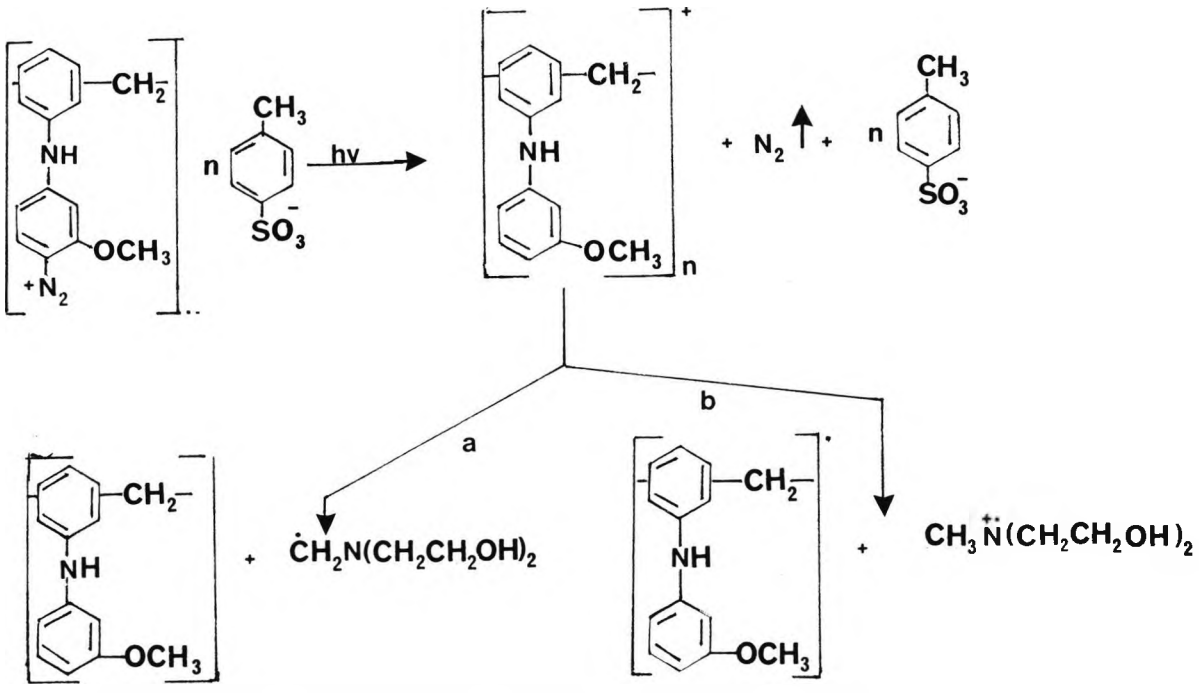
Table 3. U.V. Curing of 4-diazonium-3-methoxydiphenylamine mesitylene sulphonate, bis (methylether)-diphenyl ether condensate, in the presence of an amine

No of passes under Colordry			
Quartz	Glass Slide	Air	Filter
	1	1	20	23

a) Belt Speed:- 10ft/min
b) Amine:- N-methyldiethanolamine
c) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

Under anaerobic conditions (i.e. quartz and touching glass slide), a tack-free film is formed with 4-diazonium-3-methoxydiphenylamine p-toluenesulphonate and 4-diazonium-3-methoxydiphenylamine mesitylene sulphonate,bis(methylether) - diphenyl ether condensate in the presence of N-methyldiethanolamine.

Both diazonium salts contain amino groups which provide a good source of electrons. The diazonium salts photodecompose to form cations as shown:



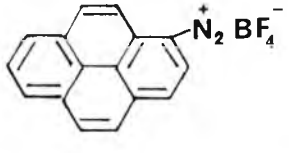
Pathway (a) involves proton transfer, which results in the formation of an α-aminoalkyl radical, which is a good initiating species.

Whereas pathway (b) involves electron transfer, producing aryl radicals, which are not as efficient as α-aminoalkyl radicals in the polymerization of acrylates.

Under aerobic conditions (i.e. air and filter), the reduction in the rate of polymerization is due to oxygen scavenging the radicals formed.

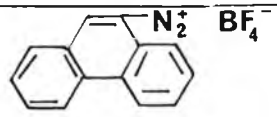
U.V. Curing of diazonium salts in the absence of an amine

Table 4. U.V. Curing of pyrenediazonium tetrafluoroborate in the absence of an amine

	No of passes under Colordry			
	Quartz	Glass Slide	Air	Filter
	4	5	30+	30+

a) Belt Speed:- 10ft/min
b) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

Table 5. U.V. Curing of phenanthrenediazonium tetrafluoroborate in the absence of an amine

No of passes under Colordry				
	Quartz	Glass Slide	Air	Filter
	5	6	23	30+

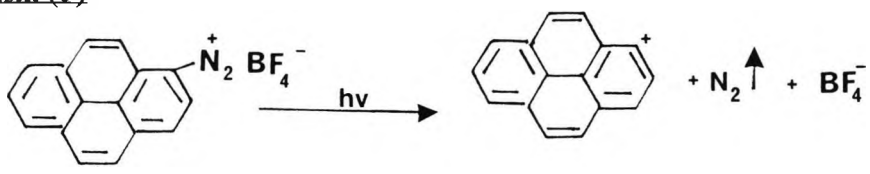
a) Belt Speed:- 10ft/min
b) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

Under anaerobic conditions (i.e. quartz and touching glass slide), pyrenediazonium tetrafluoroborate forms a tack-free film within five passes under the colordry. There is a reduction in the rate of polymerization as compared with the result in the presence of an amine. This shows the effect of the amine on the rate of polymerization whereby the amine provides a source of initiating radicals, i.e. α-aminoalkyl radicals and also prevents inhibition by oxygen.

$$\dot{C}H_2N(CH_2CH_2OH)_2$$

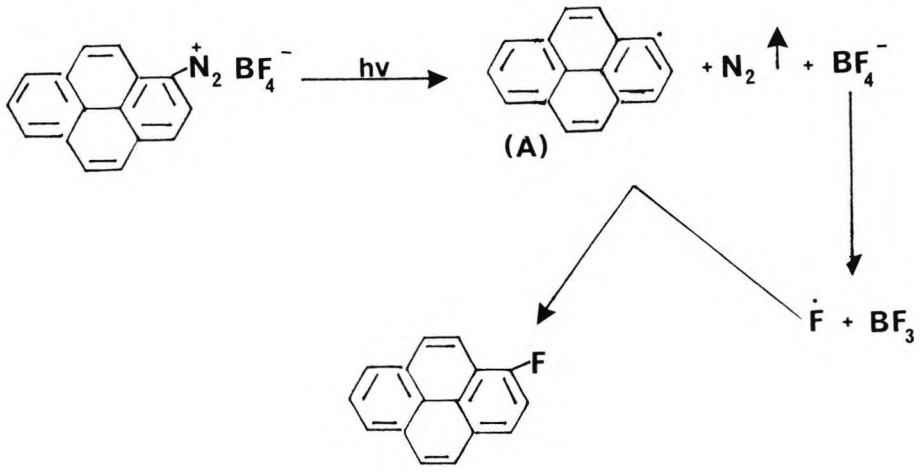
In the absence of an amine, the pyrene derivative undergoes photodecomposition to liberate nitrogen. It is uncertain whether an aryl radical or a cation is formed. A mechanism which is proposed is shown below.

Mechanism (5)



In the absence of an amine, the cation formed has to react with the triacrylate via electron transfer followed by hydrogen transfer, to initiate the polymerization process.

Mechanism(6)



The radical intermediate (A) could be formed via the photodecomposition of pyrenediazonium tetrafluoroborate. The aryl radical formed is a poor initiator for the polymerization of acrylates.

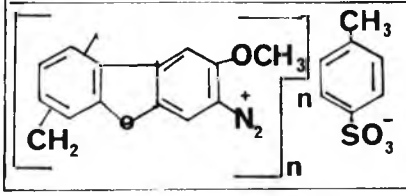
Mechanism 5 seems to show the most appropriate pathway for the photodecomposition of pyrenediazonium tetrafluoroborate.

Under anaerobic conditions both the phenanthrene and pyrene derivatives photodecompose to form a cation.

Under aerobic conditions, both the phenanthrene and pyrene derivatives did not initiate the polymerization of the triacrylate. This was due to oxygen scavenging the radicals formed, inhibiting the polymerization process.

All the films tested contained bubbles, due to the formation of nitrogen.

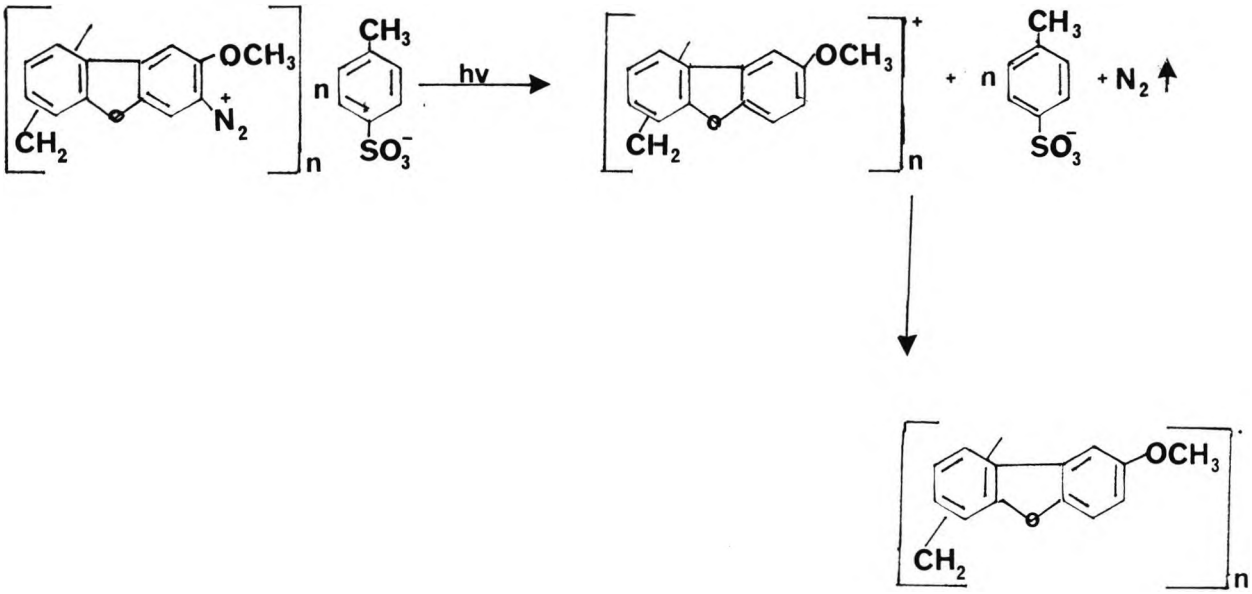
Table 6. U.V. Curing of 3-diazonium-2-methoxydibenzofuran, p-toluenesulphonate in the absence of an amine

No of passes under Colordry				
	Quartz	Glass Slide	Air	Filter
	3	7	30+	30+

a) Belt Speed:- 10ft/min
b) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

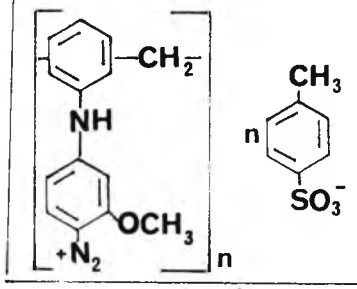
Under anaerobic conditions (i.e. quartz and touching glass slide), a tack-free film was formed.

The diazonium salt photodecomposes to form a cation and liberates nitrogen.
The benzylic species may undergo electron transfer with a reducing species to form a radical cation and an aryl radical.



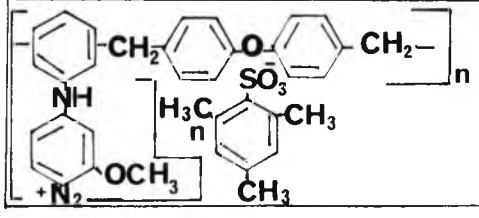
Under aerobic conditions, there was no polymerization, due to oxygen scavenging the radicals formed. The films contained bubbles, due to the formation of nitrogen.

Table 7. U.V. Curing of 4-diazonium-3-methoxydiphenylamine, p-toluenesulphonate in the absence of an amine

No of passes under Colordry				
	Quartz	Glass Slide	Air	Filter
	10	25	30+	30+

a) Belt Speed:- 10ft/min
b) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

Table 8. U.V. Curing of 4-diazonium-3-methoxydiphenylamine-p-toluenesulphonate, bis (methyl ether) diphenyl ether condensate in the absence of an amine

No of passes under Colordry				
	Quartz	Glass Slide	Air	Filter
	10	27	30+	30+

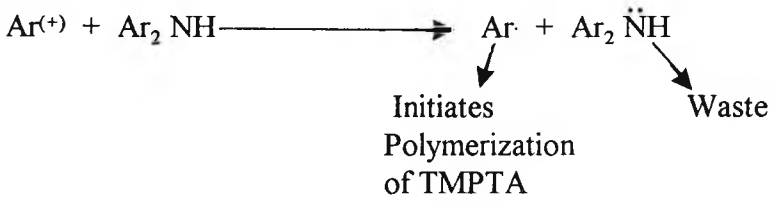
a) Belt Speed:- 10ft/min
b) Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

Under anaerobic conditions, a tack-free film was formed under quartz and a touching glass slide.

The results show that in both 4-diazonium-3-methoxydiphenylamine p-toluenesulphonate and 4-diazonium-3-methoxydiphenylamine mesitylene sulphonate, bis (methyl ether) diphenyl ether condensate, there is a reduction in the rate of polymerization as compared with the pyrene and phenanthrene derivatives. This can be explained as follows:

When the diazonium salts contain amino groups, they provide a good source of electrons.

When the diazonium salts decompose, they can form cations and liberate nitrogen. The cation undergoes electron transfer to form an aryl radical. This may occur via the amino group which is a good source of electrons.



The reduction in the rate of polymerization, under anaerobic conditions, may be due to the formation of poor initiating radicals.

Under aerobic conditions, there is no polymerization, due to oxygen scavenging the radicals formed.

The films contained bubbles, due to the formation of nitrogen.

Table 9

No of Passes Under Colordry					
	a	b	c	d	e
Quartz	4	5	3	10	10
Glass Slide	5	6	7	25	27
Air	30+	23	30+	30+	30+
Filter	30+	30+	30+	30+	30+

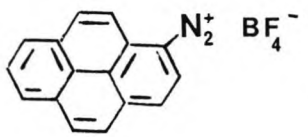
U.V. Curing of diazonium salts in the absence of an amine

(i) 1% w/w of initiator

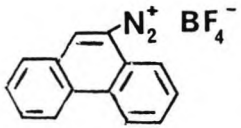
(ii) Monomer:- 2-ethyl-2(hydroxymethyl) -1,3-propanediol triacrylate

(iii) Belt Speed:- 10ft/min

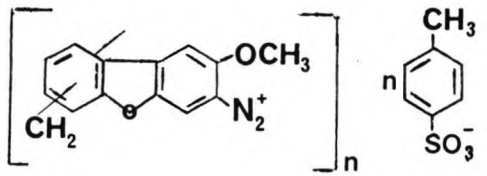
a.



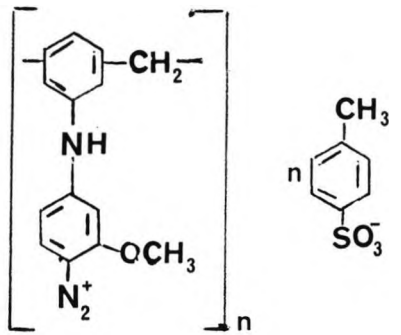
b.



c.



d.



e.

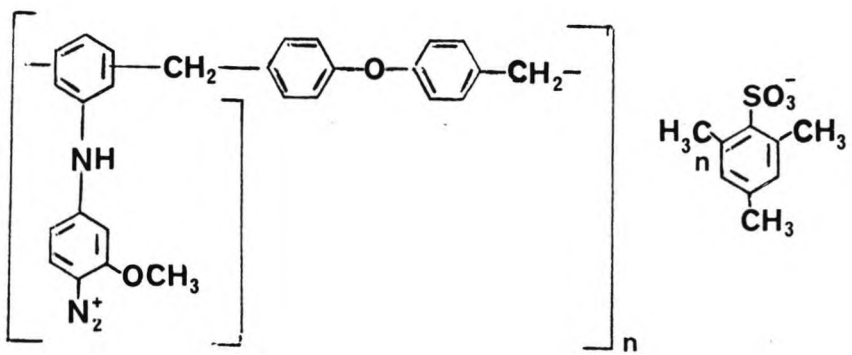


Table 10

No of Passes Under Colordry					
	a	b	c	d	e
Quartz	1	1	1	1	1
Glass Slide	1	2	1	3	1
Air	4	8	15	27	20
Filter	7	16	15	27	23

U.V. Curing of diazonium salts in the presence of an amine

(i) 1% w/w of initiator

(ii) 10% w/w of N-methyldiethanolamine

(iii) Monomer:- 2-ethyl-2(hydroxymethyl) -1,3-propanediol triacrylate

(iv) Belt Speed:- 10ft/min

Real Time Infra-red Spectroscopy

	Atmosphere	Rate of polym (Rp - % / s)	Total Conversion (%)	Residual Unsaturation Content - (%)
Pyrenediazonium tetrafluoroborate + N-methyldiethanolamine	Absence of air	4.7	45	55
Pyrenediazonium tetrafluoroborate + N-methyldiethanolamine	Presence of air	1.18	39	61
Pyrenediazonium tetrafluoroborate	Absence of air	0.5	14	86
Pyrenediazonium tetrafluoroborate	Presence of air	---	10	90
Phenanthrenediazonium tetrafluoroborate + N-methyldiethanolamine	Absence of air	2.15	43	57

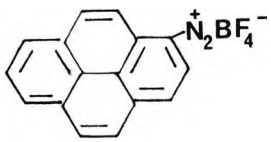
a 1% w/w of initiator used
b 10% w/w of N - methyldiethanolamine
c Monomer:- 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate

The results from real-time infra-red spectroscopy were obtained by using similar formulations as for the moving belt system.

The thin films were prepared on sodium chloride plates.

A coverslip was placed over the film to exclude oxygen from the polymerization reaction.

Pyrenediazonium tetrafluoroborate (A), was tested in the presence of an amine under anaerobic conditions.

A. 

The results obtained showed a rate of polymerization of 4.7%/s and a total conversion of 45% after 5 minutes.

Under aerobic conditions a rate of polymerization of 1.18%/s and a total conversion of 39% were obtained.

The results show that the rate of polymerization was reduced due to the presence of oxygen, which scavenges the radicals formed, inhibiting the polymerization process.

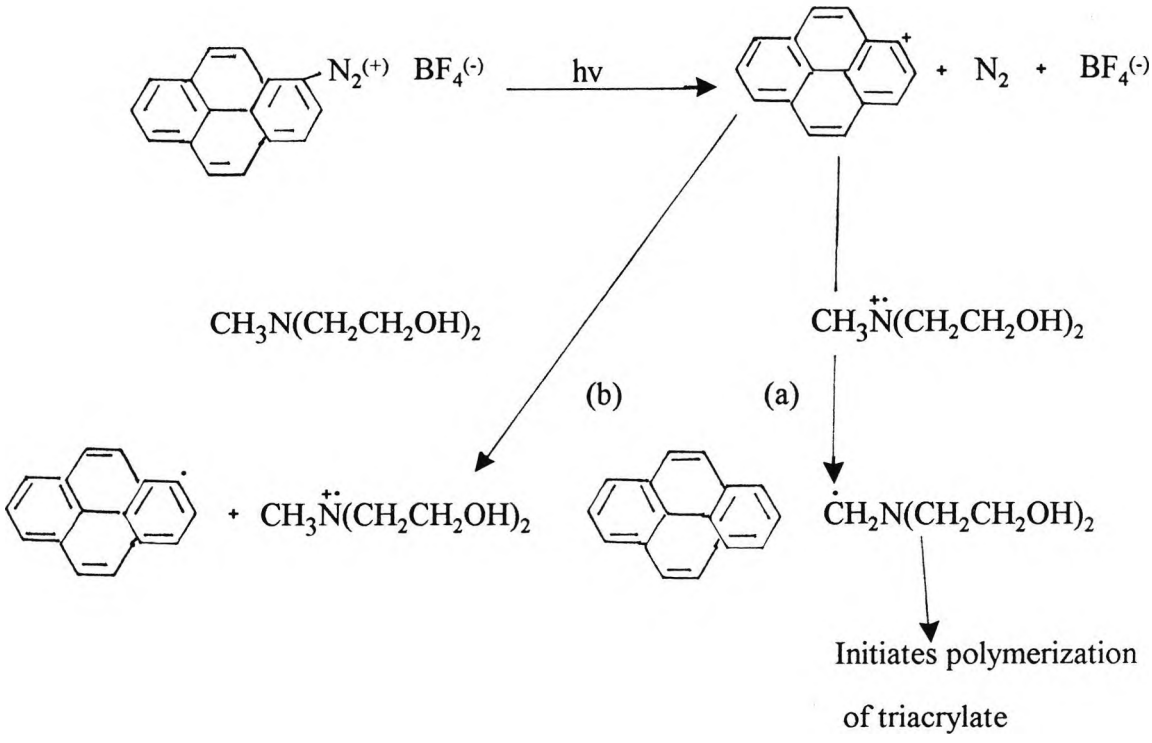
Pyrenediazonium tetrafluoroborate was tested in the absence of an amine under anaerobic conditions.

A rate of polymerization of 0.5%/s and a total conversion of 14% were obtained.

There is a considerable reduction in the rate of polymerization and total conversion.

The results show the effect of the amine on the rate of polymerization whereby a good source of initiating radicals is produced, i.e. α-aminoalkyl radicals.

Mechanism



From the results obtained from real-time infra-red spectroscopy, and the moving belt system, pathway (a) seems the more appropriate pathway, as the production of α-aminoalkyl radicals provides a good source initiating species.

The aryl radicals formed via pathway (b) are inefficient photoinitiators of acrylates.

Pyrenediazonium tetrafluoroborate was tested in the absence of N-methyldiethanolamine under aerobic conditions. A total conversion of 10% was obtained after 5 minutes. The polymerization process is inhibited by oxygen, scavenging the radicals formed, preventing polymerization of the acrylate.

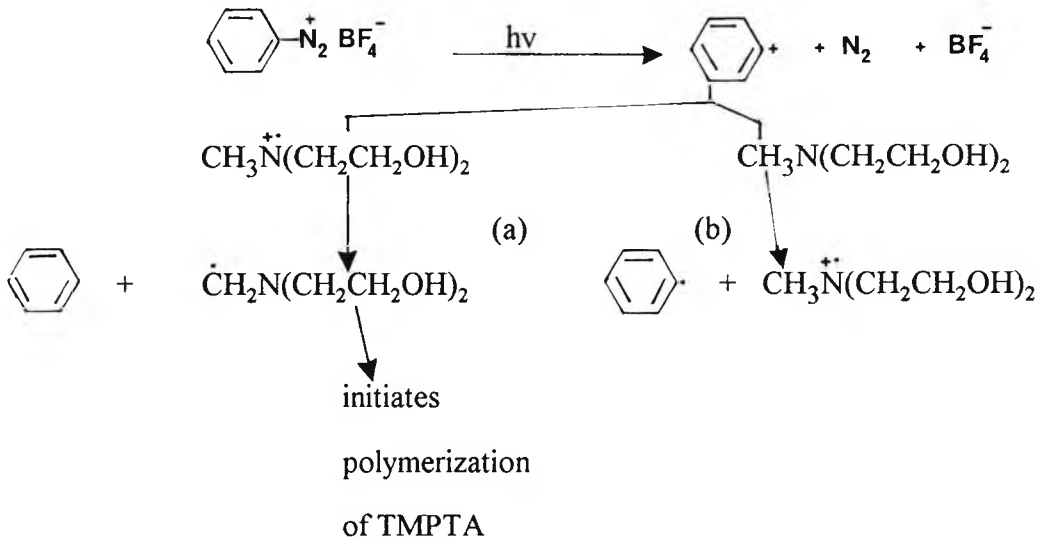
Phenanthrenediazonium tetrafluoroborate (B), was tested in the presence of an amine, under anaerobic conditions. A rate of polymerization of 2.15%/s and a total conversion of 43% were obtained.

If the result is compared with pyrenediazonium tetrafluoroborate under similar conditions, there is a reduction in the rate of polymerization in the case of phenanthrenediazonium tetrafluoroborate. One possible reason for this is that the

phenanthrene derivative absorbs less u.v./visible light than the pyrene derivative, therefore the initiation process is inefficient.

Conclusion

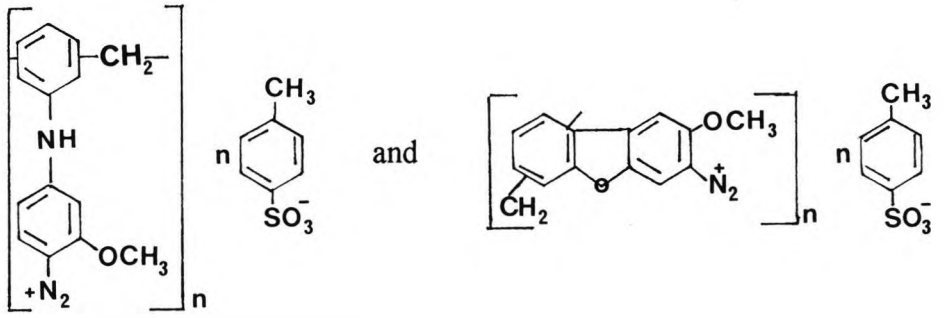
It can be concluded that diazonium salts upon absorption of u.v./visible light undergoes photodecomposition to produce nitrogen. The mechanism for the decomposition of diazonium salts is quite a problem. A mechanism for the photo-decomposition of diazonium salts in the presence of an amine is proposed, as shown below:



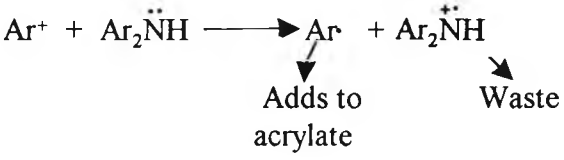
The diazonium salt decomposes to form a cation. Pathway (a) involves an aryl cation which undergoes proton transfer to form a neutral species and an α-aminoalkyl radical. The radical formed is a good initiating species.

Pathway (b) involves electron transfer, forming an aryl radical, which is an inefficient initiator of the polymerization of acrylates.

For systems containing heteroatoms, e.g. nitrogen and oxygen they provide a good source of electrons.

e.g. 

It is possible for the cation formed to be converted to an aryl radical, via electron transfer.



In the absence of an amine the aryl cation formed will react with the acrylate, via electron transfer followed by proton transfer.

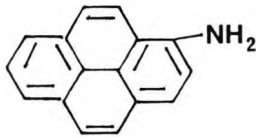
As previously reported, the problem encountered with diazonium salts is that they have poor thermal stability.

Also decomposition of these compounds produces nitrogen, which forms bubbles in thin films and adversely affects the image.

Diazonium salts are efficient free-radical photoinitiators under anaerobic conditions. Under aerobic conditions, they are poor initiators, due to oxygen scavenging the radicals formed, inhibiting the polymerization process.

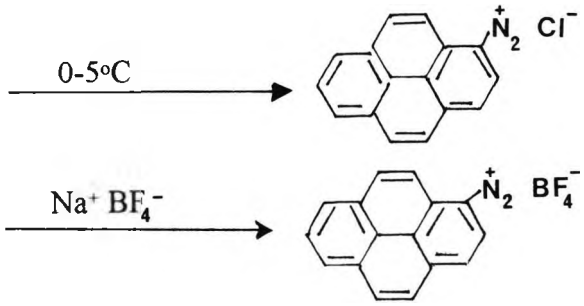
7.3 EXPERIMENTAL DETAILS

A. Preparation of pyrenediazonium tetrafluoroborate



+ $NaNO_2$ +HCl

1- aminopyrene



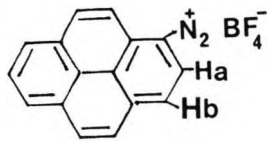
Method

1-Aminopyrene (1g, $3.2x10^{-3}$m) was added to distilled water (100ml) containing 2.5 to 3 equivalents of HCl and stirred for thirty minutes under low heat. The mixture was cooled to 0°C. An aqueous solution of sodium nitrate was added portion-wise, until after allowing 3-4 minutes for a reaction, the solution gave an immediate test for excess nitrous acid with an external indicator, moist KI-starch paper. An equivalent amount of sodium tetrafluoroborate was added and stirred, for 30 minutes. the precipitate formed was filtered and dried in a vacuum desiccator (Yield = 35%).

The product was purified by column chromatography, acetone/alumina

NMR analysis (270 MHz, H'NMR) solvent = d-acetonitrile/TMS

9.2	-	(d,1H)	-	H_a
9.0	-	(d,1H)	-	H_b
8.9-8.2-		(m,7H)	-	Aromatic protons
2.0	-	(d-acetonitrile)		



I.R. analysis 2207cm^{-1} , (s) - N_2^+ group

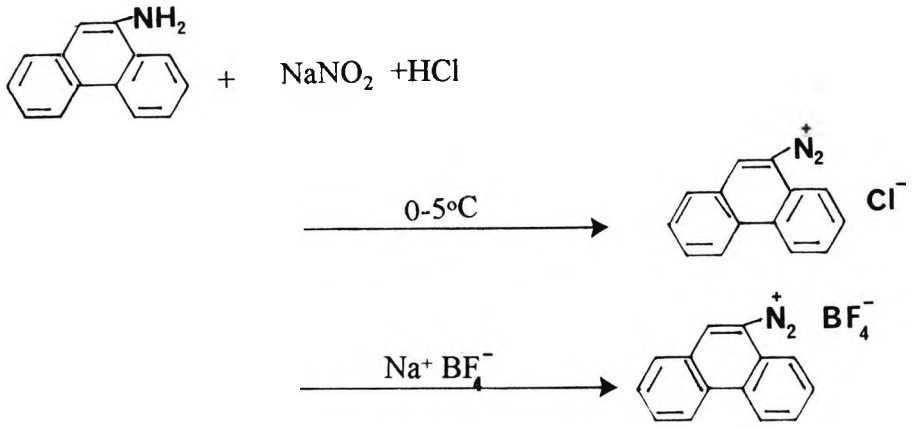
CHN analysis (%)

	Expected	Found
C,	60.75	59.93
H,	2.86	2.66
N,	8.9	8.51

Formula : $C_{16}H_9N_2BF_4$

U.V. Spectrum:- λmax = 460nm, (E=6000)

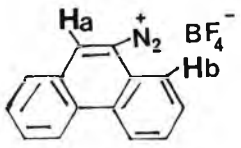
B. Preparation of 9-phenanthrenediazonium tetrafluoroborate



Method:- As for compound (A)

The product was purified using column chromatography dichloromethane/alumina. (Yield = 35%)

NMR analysis (270 MHz, d-acetonitrile/TMS)



10.0	-	(s,1H)	-	Proton H_a
9.2	-	(m,1H)	-	Proton H_b
8.5-7.5	-	(m,7H)	-	Aromatic protons
2.0	-	(d-acetonitrile)		

I.R. analysis 2237cm^{-1} , (s) - N_2^+ group

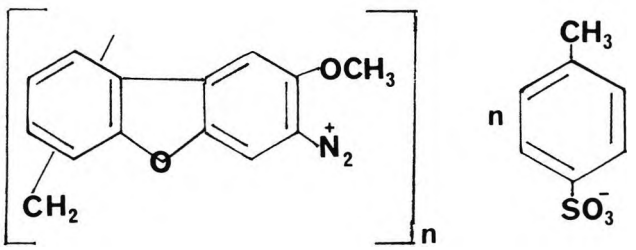
CHN analysis (%)

	Expected	Found
C,	57.7	57.5
H,	3.0	2.8
N,	9.6	9.3

Formula : $C_{14}H_9N_2BF_4$

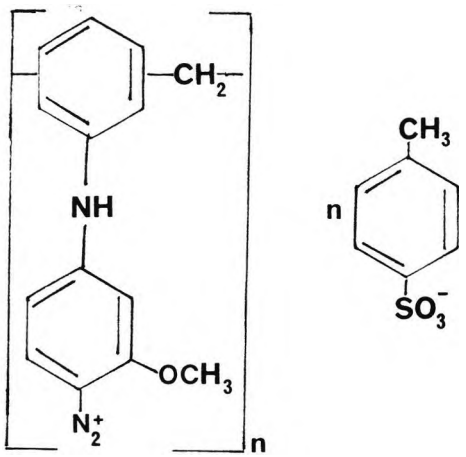
The following diazonium compounds were provided by Cookson's Graphics.

1)



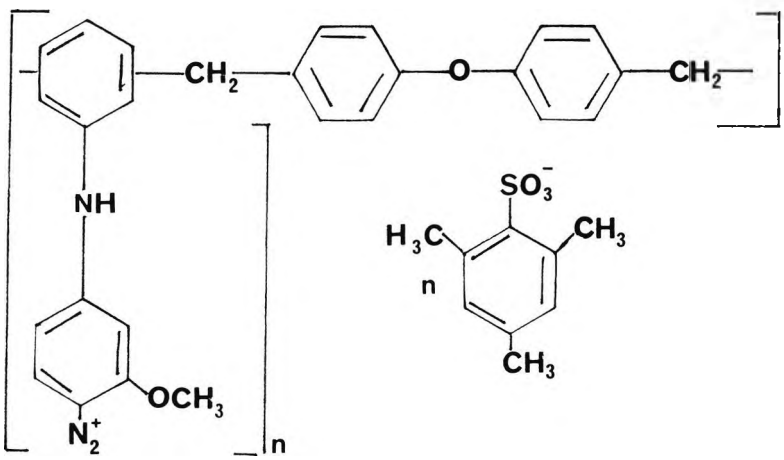
3-diazonium-2-methoxy-dibenzofuran p-toluenesulphonate

2)

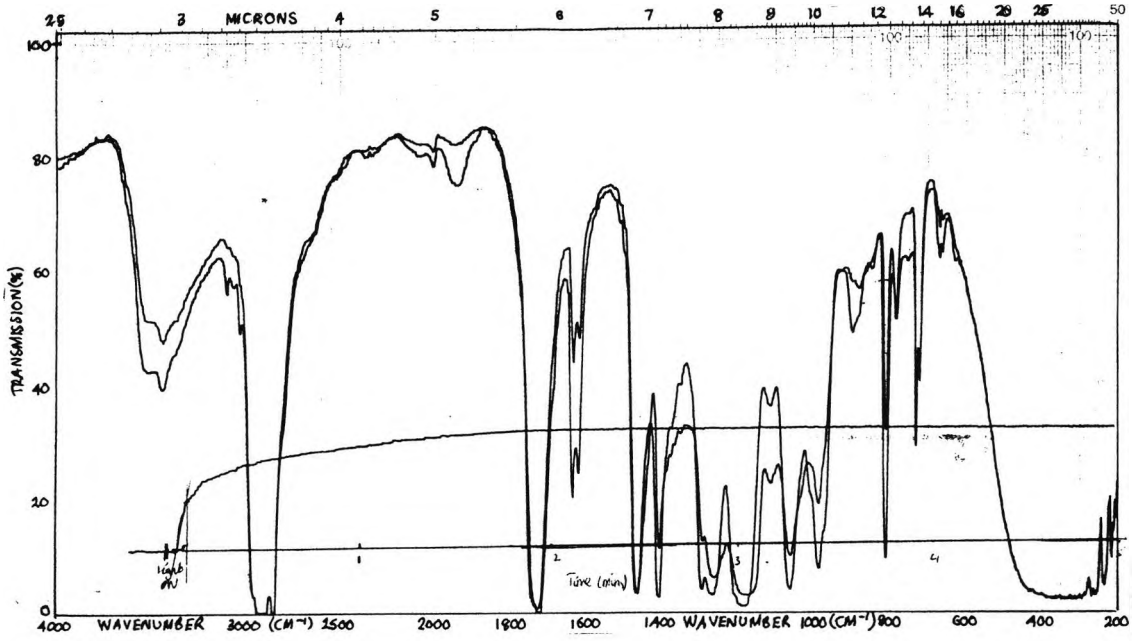


4-diazonium-3-methoxydiphenylamine p-toluenesulphonate

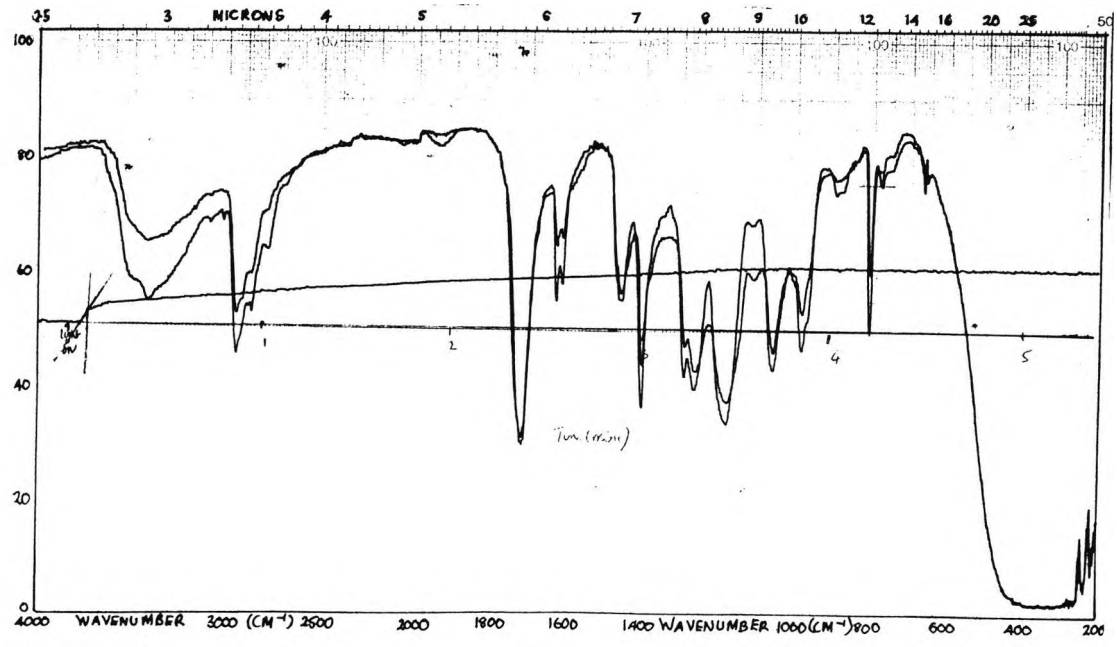
3)



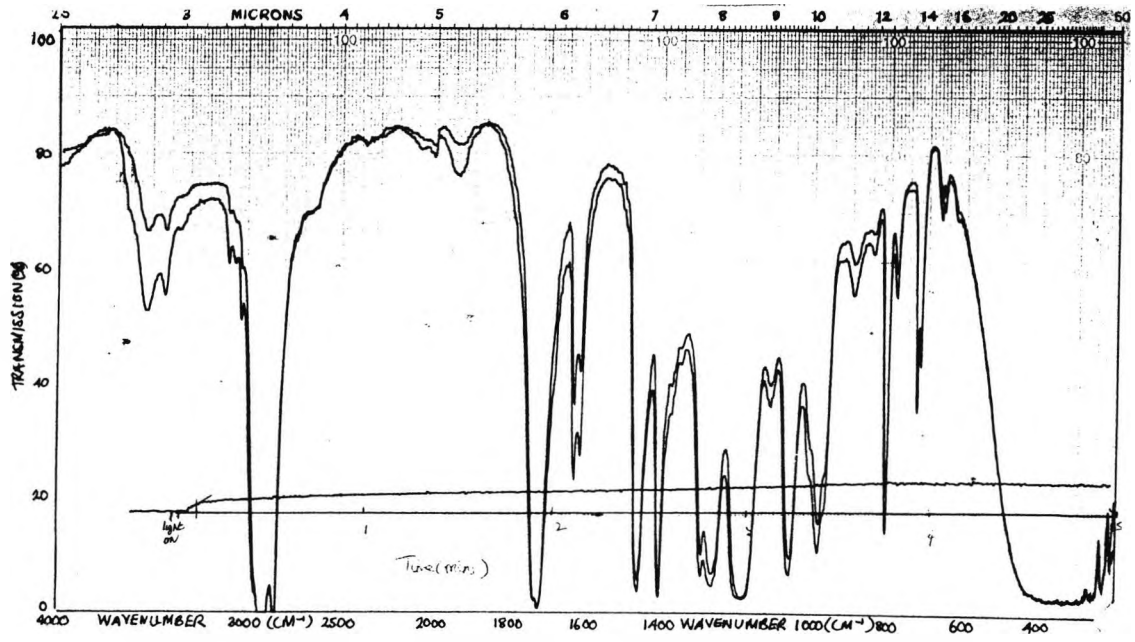
4-diazonium -3-methoxydiphenylamine mesitylene sulphonate/bis (methyl ether) diphenyl ether condensate.



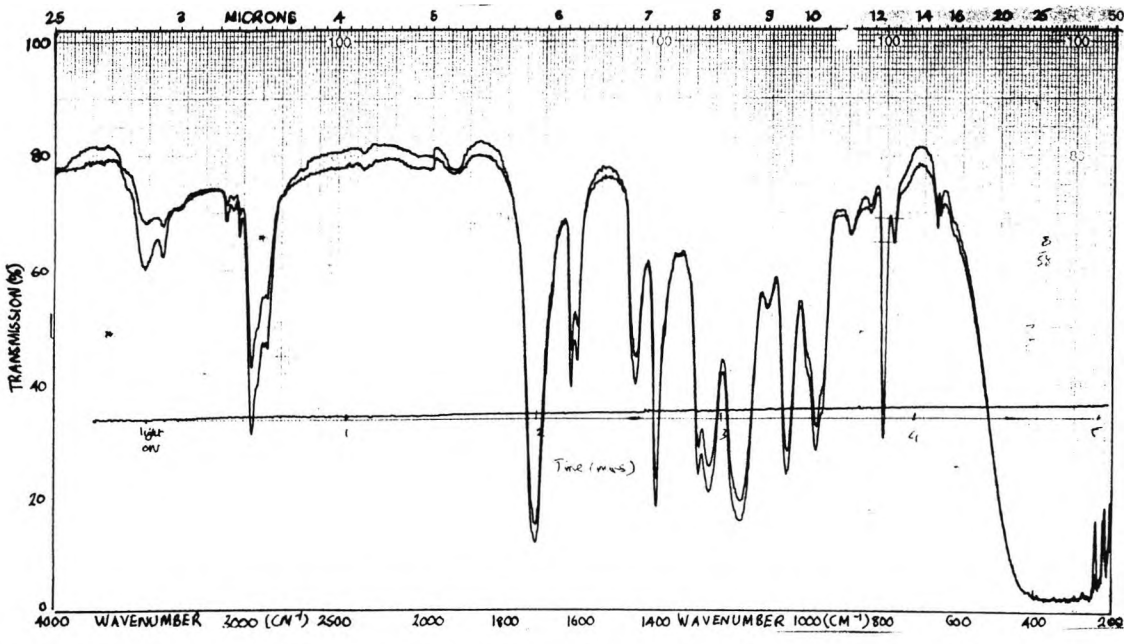
Spectrum 1: RTIR spectrum, showing the polymerization of 2-ethyl-2 (hydroxymethyl)-1,3-propanediol triacrylate in the presence of an amine and pyrenediazonium tetrafluoroborate, under anaerobic conditions.



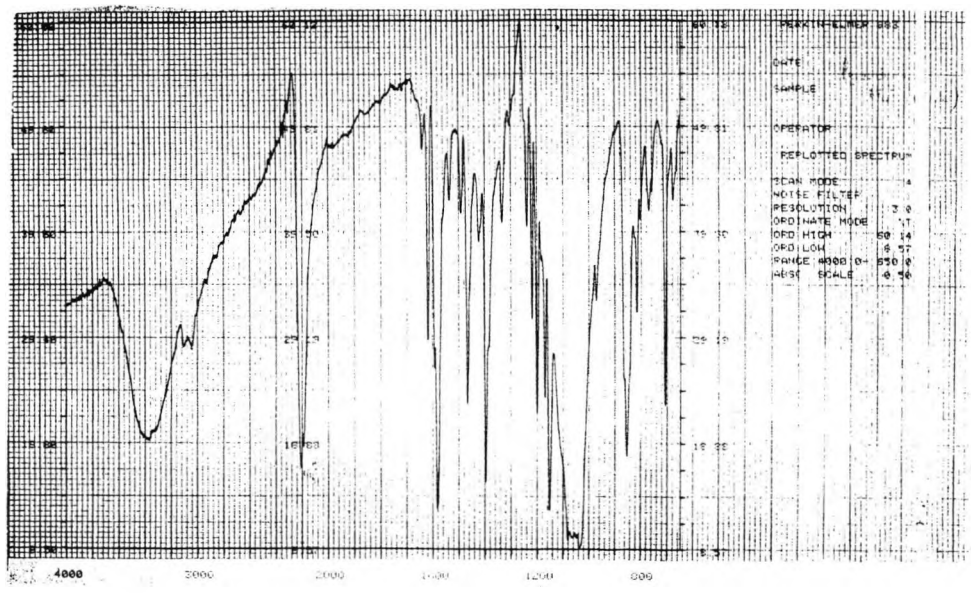
Spectrum 2:- RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of an amine and pyrenediazonium tetrafluoroborate, under aerobic conditions.



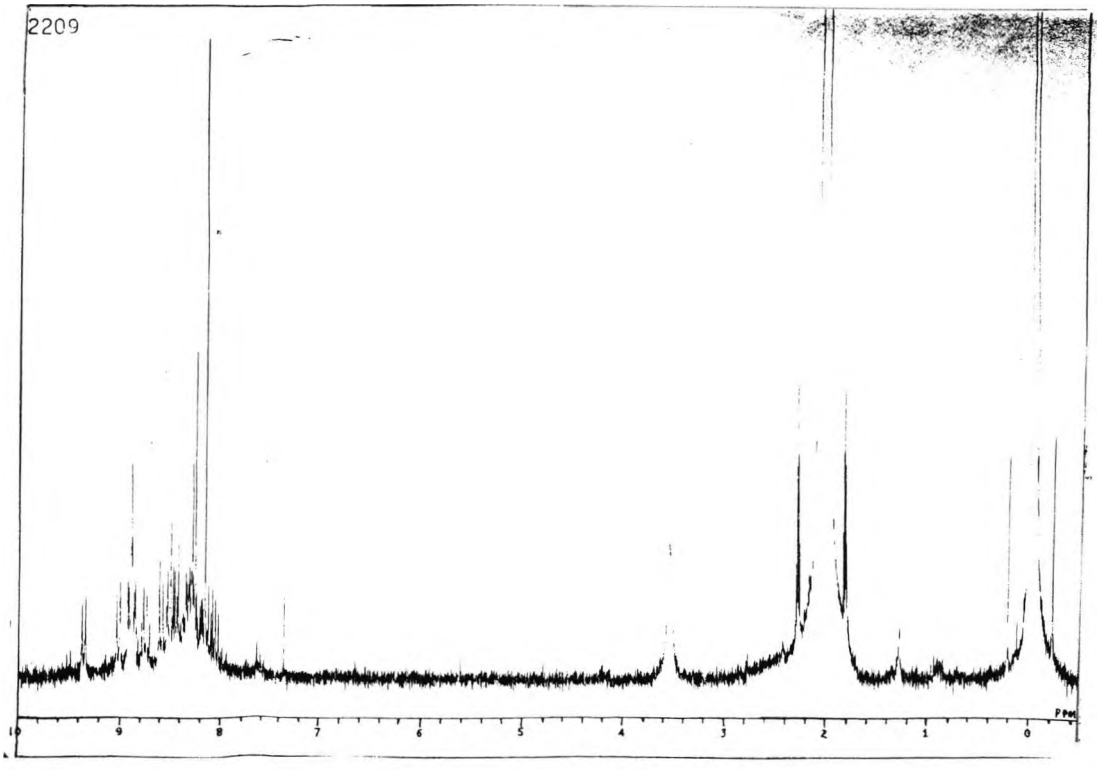
Spectrum 3:- RTIR spectrum, showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of pyrenediazonium tetrafluoroborate, under anaerobic conditions.



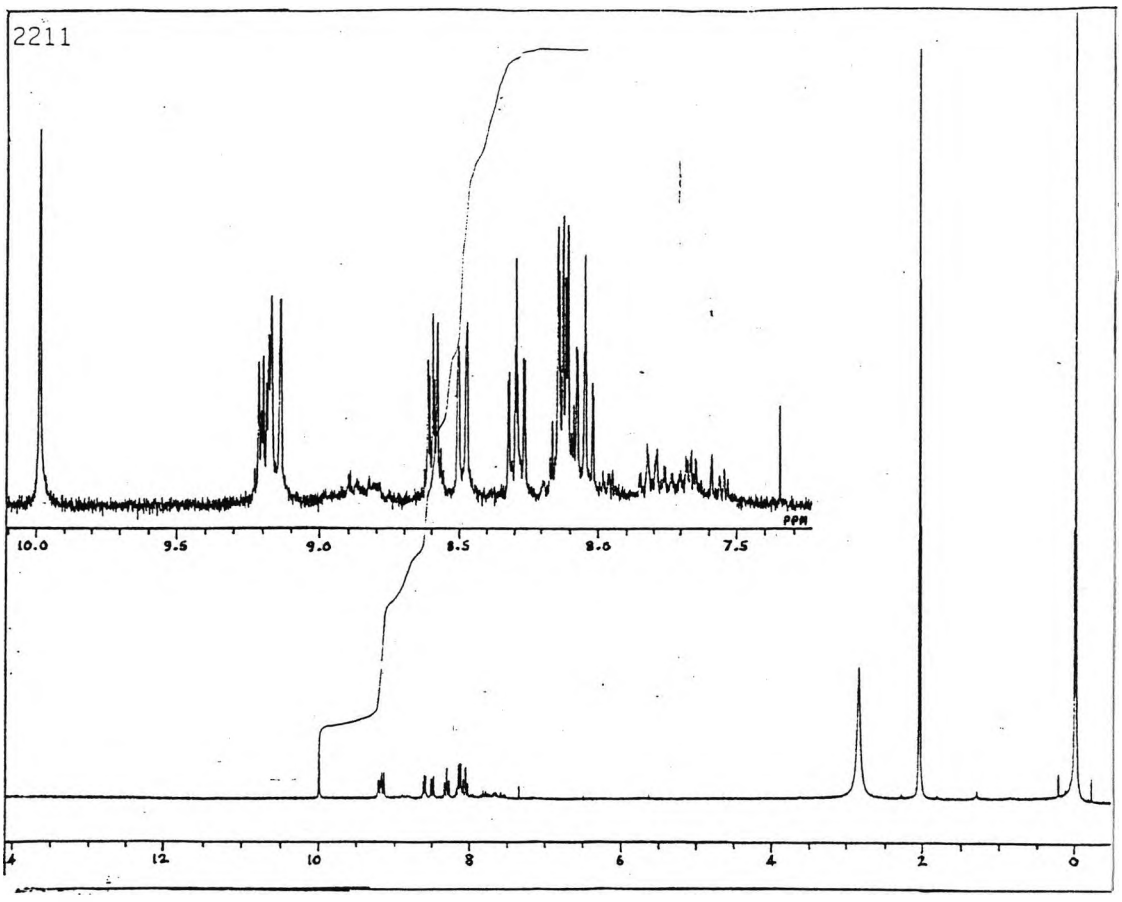
Spectrum 4:- RTIR spectrum showing the polymerization of 2-ethyl-2(hydroxymethyl)-1,3-propanediol triacrylate in the presence of pyrenediazonium tetrafluoroborate, under aerobic conditions.



Spectrum 5:- Infra-red spectrum of pyrenediazonium tetrafluoroborate



Spectrum 6:- NMR spectrum of pyrenediazonium tetrafluoroborate



Spectrum 7:- NMR spectrum of phenanthrenediazonium tetrafluoroborate.

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Further Work

A. Defeating Oxygen Inhibition of Cure

The results show that the polysulphide acrylates (i.e. ZL2244 and ZL1866) show potential of defeating oxygen inhibition of cure.

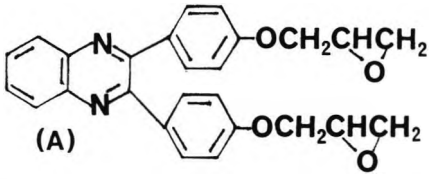
Further work could be carried out, preparing various polysulphide acrylates and testing them with other photoinitiators.

B Photochemistry of Quinoxalines

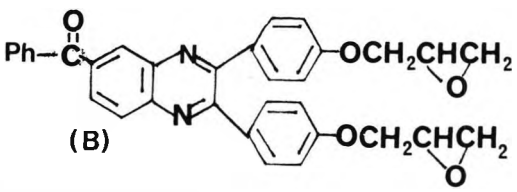
The quinoxalines show potential as being very good regeneratable photoinitiators.

Further work could be carried out, whereby the quinoxalines could be used as photoinitiators in the visible region, i.e. preparation of various polyquinoxalines.

The glycidyl derivatives can be used to prepare a polymerizable photoinitiator,



(A)



(B)

whereby the epoxide group can be opened by acrylic acid.

The results also show that the quinoxalines can be used as photosensitisers in cationic polymerization. Further work could be carried out using different quinoxalines in cationic polymerization.

C The use of cyanine borates as visible range photoinitiators in thin films

Cyanine borates have been shown to be potentially efficient initiators under anaerobic conditions. Under aerobic conditions, they are poor photoinitiators, due to the presence of oxygen scavenging the radicals formed.

It would be suitable to test the cyanine borates in the polysuphide acrylates. This may produce an efficient curing system in the absence of an amine.

D. The use of cyclopentadienyliron (II) alkylborates as free-radical initiators in thin films

Cyclopentadienyliron (II) alkylborates have been shown to be potentially efficient free-radical initiators under anaerobic conditions, in the presence of an amine.

Under aerobic conditions, in the absence of an amine, they are poor initiators, due to the presence of oxygen scavenging the radicals formed.

It would be more appropriate to test the cyclopentadienyliron (II) alkylborates in the polysulphides acrylates. This would solve the problem of oxygen inhibiting the polymerization process. Also, this would produce a curing system containing no synergist (i.e. N-methyldiethanolamine). Further work could be carried out, in preparing various other cyclopentadienyliron (II) alkylborate salts, which can provide more stable radicals e.g. $NpCH_2$. radical.