Some new developments in radiation curing

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ABSTRACT Decomposition of cationic photoinitiators in the
solid state is used in a remote cure process ie. one in which
photoinitiator is not present in the polymerisable monomer. An
application of this process to a dual cure system is described.
Details are given of free radical polymerisation reactions in
aqueous solutions which produce latexes via both suspension and
emulsion polymerisation processes. Finally, ways of improving
the photosensitivity of poly(vinyl alcohol) modified with
styrylpyridinium groups utilising mixed [2+2]cycloaddition
reactions are described.

INTRODUCTION

Radiation curing refers to polymerisation induced by radition eg.
electron beam, visible or ultraviolet light. Of particular value is
the transformation of a liquid into a solid and this finds application
in the surface coatings industry, imaging and even dentistry [1]. The
most popular systems are totally solvent free although water borne
systems are increasing in importance. Polymerisation reactions
employed include free radical, cationic, anionic and cycloaddition
processes with the latter two processes being dealt with in more detail
by Professor J H J Frechet [3] and Dr A Reiser respectively.

## 1. A CATIONIC CURING SYSTEM: THE REMOTE CURE PROCESS

Photoinduced cationic curing of epoxides and vinyl ethers which involve
the photogeneration of Lewis/Bronsted acids is well documented [4].
The most popular photoinitiators are onium salts (iodonium and
sulfonium salts) although the recently introduced ferrocenium salt (η^5-
2,4-cyclopentadien-1-yl) [(1,2,3,4,5,6-η)-(methylethylbenzene)]-
iron(1^+) hexafluorophosphate (1^-)) is gaining popularity. Recent work
has shown that onium salts decompose homolytically [4] and
heterolytically [5,6]. Germane to our own work, was the finding that
iodonium salts can generate acid via an intramolecular process [6,7,8]
thereby eliminating the need to involve a solvent.
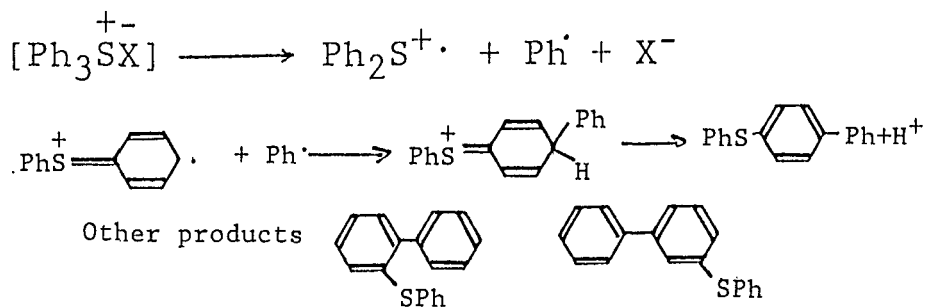
Figure 1

Light Baffle

Diepoxide

Photoinitiator

"Dry" nitrogen atmosphere
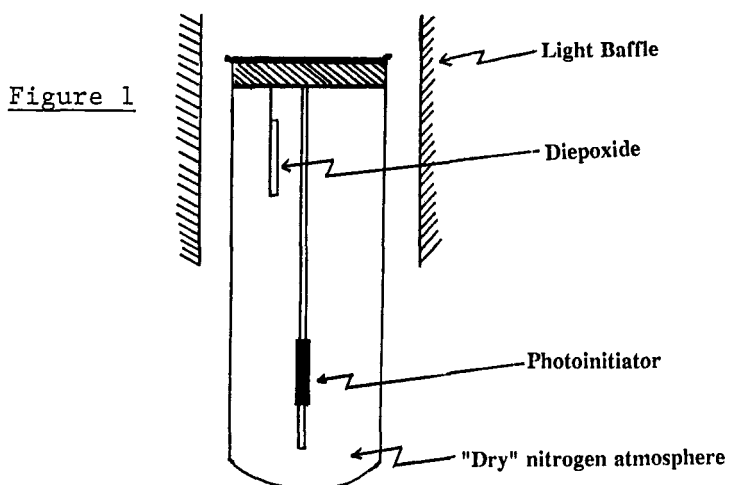
Hexafluorophosphate salts are commonly used and hexafluoro-phosphoric acid has been claimed to be the initiating species despite the fact that it is known to be unstable in organic media [9]. We have shown that electron beam and uv. induced fragmenta-tion of onium hexafluorphosphate leads to decomposition of the hexafluorophosphate anion and have proposed that this leads to the production of hydrogen fluoride [10]. By use of the equipment

$$HPF_6 \rightleftharpoons HF + PF_5$$
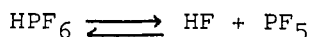
shown in Figure 1 we have demonstrated that onium salts, in the solid state photolyse to give a gas which induces polymerisation of the epoxide. Infrared studies confirm that hydrogen fluoride is evolved. These observations led us to design a "remote cure system" in which an onium, or ferrocenium hexafluorophosphate is irradiated to produce hydrogen fluoride which traverses a small gap to initiate polymerisation of an epoxide or vinyl ether [11] (Fig 2). Of the many factors which influence the efficiency of this process, the magnitude of the gap, the nature of the support and the surface density of the initiator are important. The ferrocenium salt is very efficient and we found this surprising since the accepted mechanism for its decomposition requires the involvement of the polymerisable monomer (epoxide) [12,13].

Photoinitiator

Paper initiator support

Purge Gas out

PTFE body

Ultraviolet source

Thin PTFE membrane window (clamped)

PTFE gauze

Resin monomer

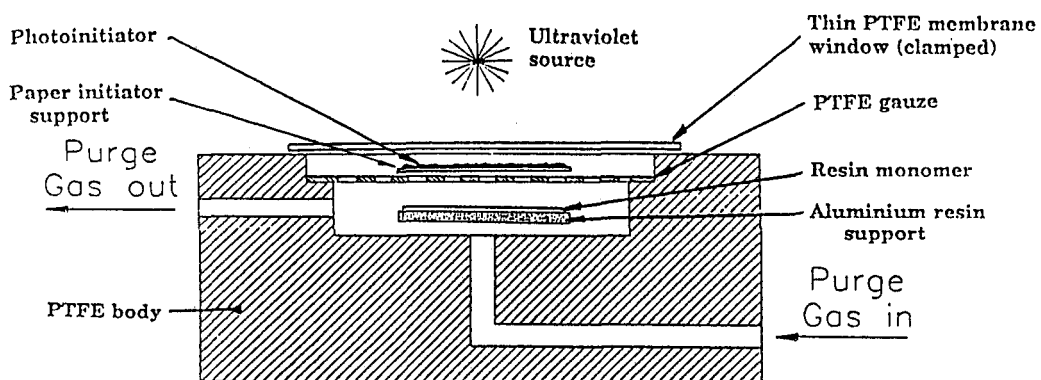Aluminium resin support

Purge Gas in

Figure 2   Remote Cure Equipment

An application of the remote cure system is to dual cure. Thus a mixture of an epoxide, an acrylate and a Type I free radical initiator on exposure to hydrogen fluoride in the remote cure process leads only to the polymerisation of the epoxide. If this is followed by exposure to light, the acrylate is then polymerised. This sequence of events may be reversed. The processes can be conveniently monitored by infrared spectroscopy (Fig 3).
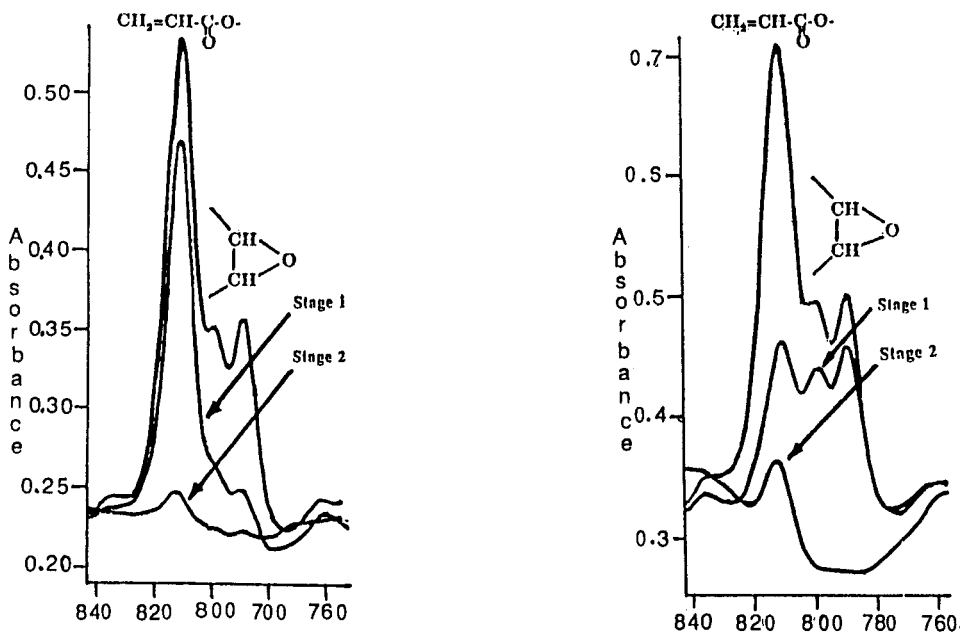
Dual Cure Type A
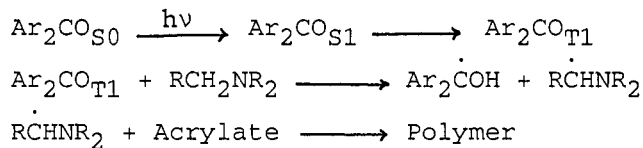Stage 1:Epoxy Polymerisation Indirect
Stage 2:Radical Polymerisation Direct

Dual Cure Type B
Stage 1:Radical Polymerisation Direct
Stage 2:Epoxy Polymerisation Indirect

Fig 3

2. FREE RADICAL POLYMERISATION IN AQUEOUS SOLUTION

Polymerisable monomer to be dispersed in the aqueous phase and in the case of emulsion polymerisation this is achieved by use of a surfactant. An important distinction between the two is that in suspension polymerisation several free radicals may be present in an oily droplet whereas in emulsion polymerisation only one radical is present in the growing latex particle. As a consequence suspension polymerisation leads to lower molecular weight polymers having a greater polydispersivity than those produced via emulsion polymerisation.

We have studied the heterogeneous photopolymerisation of acrylates by employing a whistle reactor (Fig 4) [16], which produces a suspension ultrasonically in combination with a conventional photochemical reactor. By use of oil soluble photoinitiators eg. benzoin methyl ether the products should be akin to those derived via a suspension process whereas with a water soluble photoinitiator system products similar to those produced by emulsion polymerisation may be obtained. Several water soluble ketones [2b] eg. sodium benzophenone-4-methyl sulphonate are available and these may be used in conjunction with an amine to provide an initiator system.

$$Ar_2CO_{S0} \xrightarrow{h\nu} Ar_2CO_{S1} \longrightarrow Ar_2CO_{T1}$$

$$Ar_2CO_{T1} + RCH_2NR_2 \longrightarrow Ar_2\dot{C}OH + R\dot{C}HNR_2$$

$$R\dot{C}HNR_2 + Acrylate \longrightarrow Polymer$$

The benzoin methyl ether initiated polymerisation of 2-ethylhexyl acrylate in water produced latexes having an average particle size of 3.5-4.0 m and a high polydispersivity. When sodium benzophenone-4-methyl sulphonate was used in conjunction with N-methyldiethanolamine as an initiator system a latex was obtained which showed a bimodal molecular weight distribution. Use of other amine synergists (Table 1) had a profound effect upon reaction time and the physical properties of the latexes, and of particular note was the molecular weight distribution (Fig 5).
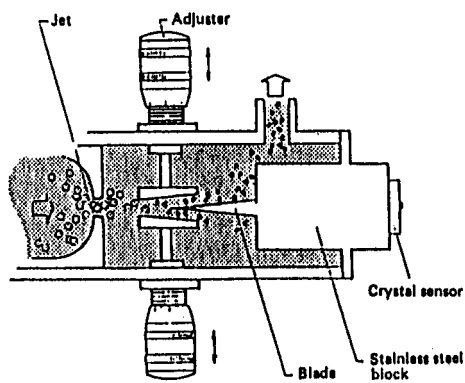
Fig 4

Diagram of a Whistle Reactor

1: N-methyldiethanolamine

2: N-n-butyldiethanolamine

3: triethanolamine

4: N-t-butyldiethanolamine

5: 2-(2-diethylamino-ethoxyl)-ethanol

6: N,N-dimethylethanolamine
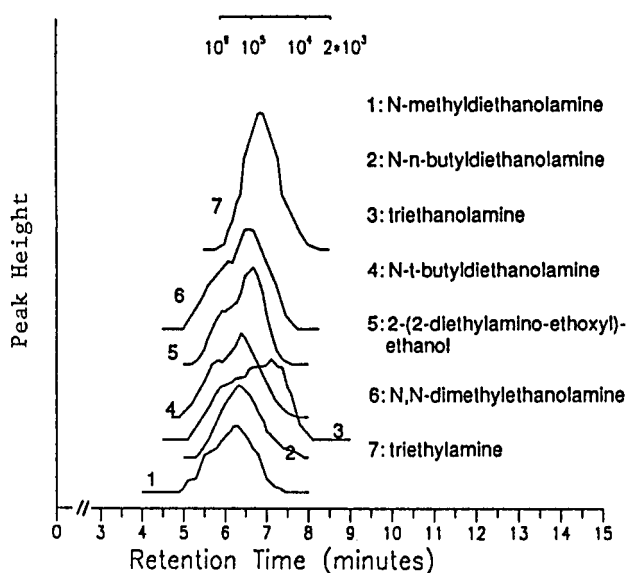
7: triethylamine

Fig 5   GPC Traces of Polymers Produced by Emulsion Polymerisation of 2-Ethylhexyl Acrylate With Various Amine Synergists

The hydrophilicity of the amine has an effect upon this distribution and the larger this is, the greater the proportion of high molecular weight species. We conclude that the use of the "water soluble" Type II photoinitiator system may lead to some emulsion polymerisation but the dominant process is still suspension polymerisation.

3. A WATER DEVELOPABLE IMAGING SYSTEM USING A [2+2] CYCLOADDITION

[2+2] Cycloaddition reactions have found application in imaging [17] with the cyclodimerisation of cinnamic acid and its derivatives being particularly favoured [18]. Styrylpyridinium compounds also undergo [2+2] cycloaddition reactions [19,20] and these have been used to make a photoresponsive poly(vinyl alcohol) [20]. A valuable feature of this system is that it is aqueous developable. For [2+2] cycloaddition processes to be effective, the reaction partners have to be sited close to each other. When poly(vinylalcohol) is modified with 1-methyl-4-[2-(4-formylphenyl) ethenyl] pyridinium methosulphate a photosensitive polymer is produced which exhibits excimeric fluorescence. Irradiation of the films led to the disappearance of this fluorescence. The observation of excimer emission points to aggregation of the pyridinium species in the film and we have suggested that reaction occurs via an

Table 1   Some Characteristics of the Polymers Produced by Emulsion Polymerisation Using Different Amine Synergists

AMINE	REACTION TIME (mins)	YIELD (%)	MEAN PRACTICE SIZE (m)	WEIGHT AVERAGE MOLECULAR WEIGHT
Triethylamine	60	83.0	3.47	140,000
2-(2-Diethylamino-ethoxy)-ethanol	50	50.0	2.36	558,000
N-n-Butyldiethanolamine	60	85.0	2.36	611,000
N-t-Butyldiethanolamine	80	62.3	2.87	1,094,000
N-n-Dimethylethanolamine	60	88.4	3.57	700,000
N-Methyldiethanolamine	60	78.0	3.64	1,460,000
Triethanolamine	60	80.7	5.80	539,000
N,N-Bis(2-hydroxyethyl)-p-toluidine	80	5.0	Unstable	
2-Diethylaminoethyl acrylate	80	18.0	Unstable	

excimer [21]. Thus, like the cycloaddition reaction of enones [22] the crosslinking is occurring via attack of an excited species upon a ground state species in which the latter provides a suitable double bond. We have therefore examined the possibility of carrying out mixed cycloadditions in which the poly(vinylalcohol) is functionalised with a styrylpyridinium group and an unsaturated aldehyde. A poly(vinylalcohol) carrying pendant styrylpyridinium groups was mixed with poly-(vinylalcohol) which had been reacted with 3-(2-furyl)acrolein. Films were prepared from the mixture and exposed to light. The presence of the acrolein increased the sensitivity of the film. Fluorescence spectra of such films showed emission from the styryl-pyridinium compound in its monomeric state and this emission decreased in intensity when the film was exposed to light. We concluded from these and other observations that a mixed cycloaddition process was leading to insolubilisation of the poly(vinylalcohol). That this process did not involve the furan ring [23] was shown by the finding that poly(vinylalcohol) modified with furfuraldehyde did not increase the sensitivity of the styrylpyridinium salt modified poly(vinylalcohol).

MIXED CYCLOADDITION
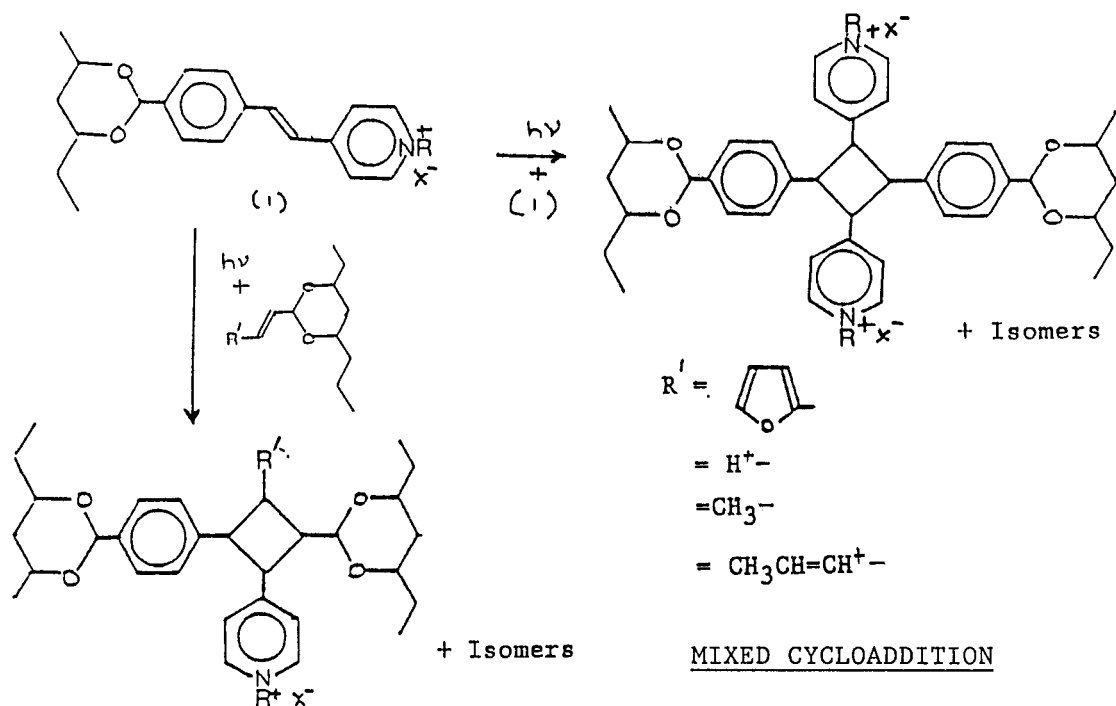
The scope of the mixed cycloaddition process has been extended by the use of acrolein, crotonaldehyde and 2,4-hexadienal in place of the furylacrolein. These findings open up further opportunity for producing photosensitive poly(vinylalcohols).

Acknowledgements

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