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Thioxanthones: their fate when used as photoinitiators

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It has been shown that when thioxanthones are used in conjunction with an amine synergist they initiate the polymerization of lauryl acrylate. Gel permeation chromatography (g.p.c.) showed that the polymer which is formed contains thioxanthone residues. It is suggested that the thioxanthyl ketyl radical acts as a chain terminator, with reactions occurring at the 2-, 4-, 5-, 7-, and 9-positions. Reactions at positions other than 9- can lead to incorporation of thioxanthone residues. When the aromatic amine synergist, ethyl *p*-dimethylaminobenzoate, is used the aromatic amine is also incorporated into the polymer. Copyright © 1996 Elsevier Science Ltd.

(Keywords: lauryl acrylate; thioxanthones; photoinitiators)

INTRODUCTION

Three decades ago it was found that aromatic ketones are photoreduced by aromatic[1] and aliphatic tertiary amines[2]. Of particular interest was the observation that many ketones possessing $\pi \rightarrow \pi^*$ triplet states were reactive, e.g. xanthone, thioxanthone[3] and fluorenone[4]. It was subsequently shown, using a variety of techniques, that reaction occurred via electron transfer from the amine ground state to the triplet ketone and that normally this was followed by rapid proton transfer reaction, thereby giving an aromatic ketyl radical and an α-aminoalkyl radical[5]. Following the discovery of this mechanistic pathway a number of substituted amines, e.g. 2-aminoalcohols[6] and α-amino acids[7] were found to react in this way, yielding α-aminoalkyl radicals via fragmentation processes (*Figure 1*).

These reactions have been in some cases the subject of much detailed investigation and this has shown that 1,2-diaminoethanes will also undergo fragmentation[8]. Paralleling the unravelling of the mechanism of the ketone–amine reactions was the development of free-radical radiation-curing reactions which were initiated by a ketone–amine system[9]. Having thus understood the ketone–amine reaction the possibility arose that one might be able to forecast which ketone–amine systems might be best for radiation-curing processes. This hope of linking theory with practice was subsequently dashed when it was found that there was little correlation between the rate of cure and the efficiency of the ketone–amine system[10].

Amines are not only used as synergists in free-radical-curing systems but also as agents for reducing the extent of oxygen inhibition[11,12]. In this process, α-aminoalkyl radicals play an important part (*Figure 2*).

It is also known that the triplet state of aromatic ketones is deactivated by ground state oxygen via an energy transfer process and this yields singlet oxygen[13]. This reactive oxygen species attacks appropriately substituted tertiary amines to give α-aminoalkyl radicals[12,14,15].

When amines are used as synergists they can give rise to α-aminoalkyl radicals via reaction with singlet oxygen and via hydrogen abstraction by radicals generated in the system.

In a Type II initiator system, which usually comprises an aromatic ketone and a tertiary amine, there are two potential initiating radicals, namely the ketyl radical and the α-aminoalkyl radical. Ketyl radicals are resonance-stabilized species and readily undergo coupling reactions, e.g. dimerization to give pinacols and combination with α-aminoalkyl radicals[16]. The dimerization of ketyl radicals and their reaction with other radicals can lead to the formation of coloured products, which is a positive nuisance when clear films are being produced. Structures for some of these products which are formed when alcohols and amines have been used as reductants have been elucidated[17] (*Figure 3*).

There is evidence to support the view that they are very inefficient initiating species and strong indications that they contribute to chain termination[16]. The prime candidate for initiating polymerization is the α-aminoalkyl radical. It has been shown that for a particular aromatic ketone, the rate of polymerization in bulk, in solution and in thin films, is strongly dependent upon the structure of the radical[10,18,19].

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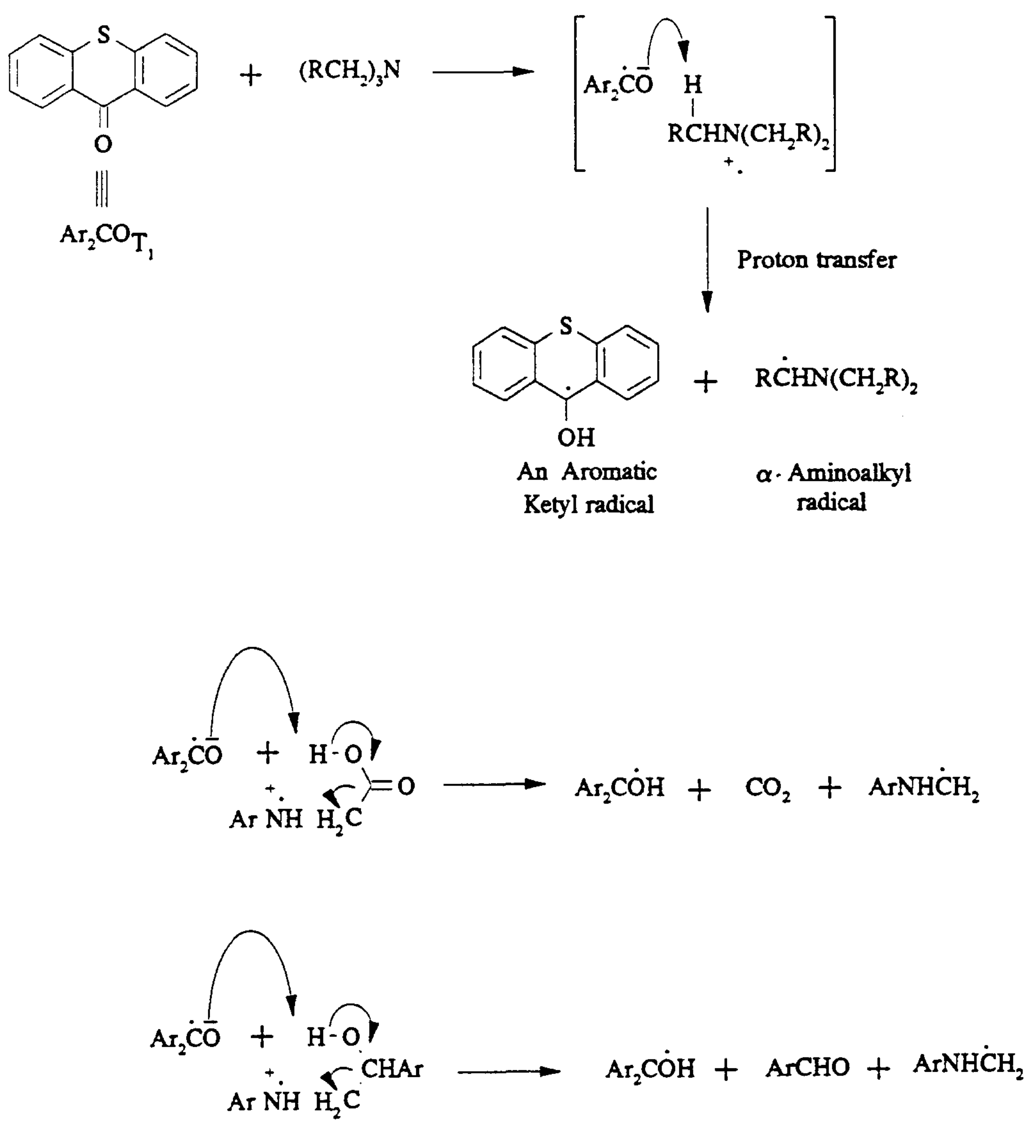

Figure 1 Reaction of a triplet aromatic ketone with a tertiary amine and substituted tertiary amines

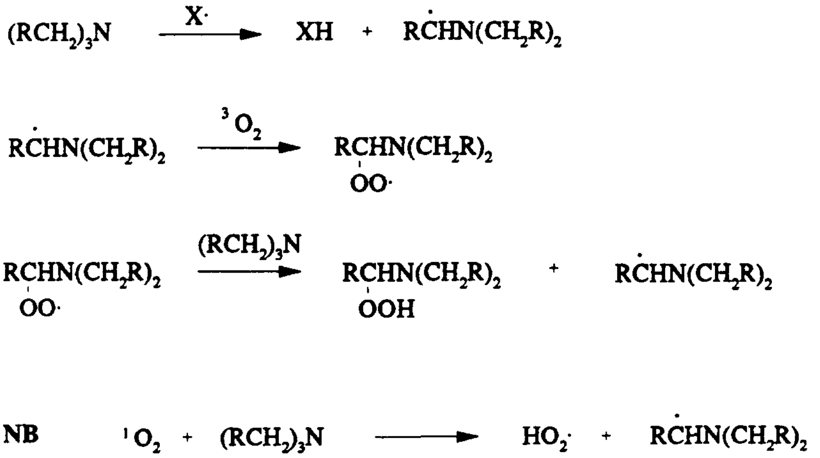

Figure 2 Oxygen-mediated generation of α-aminoalkyl radicals from tertiary amines

When a Type II system is used to initiate the polymerization of methyl methacrylate, the resulting polymer contains nitrogen, which implys initiation by the amine[9]. Other experiments which indicate that the α-aminoalkyl radicals initiate polymerization involve trapping the radicals by use of non-polymerizing model substrates for vinyl monomers, e.g. 1,1-ditolylethene (*Figure 4*)[20].

This method has the advantage that the products can be isolated and analysed by conventional procedures.

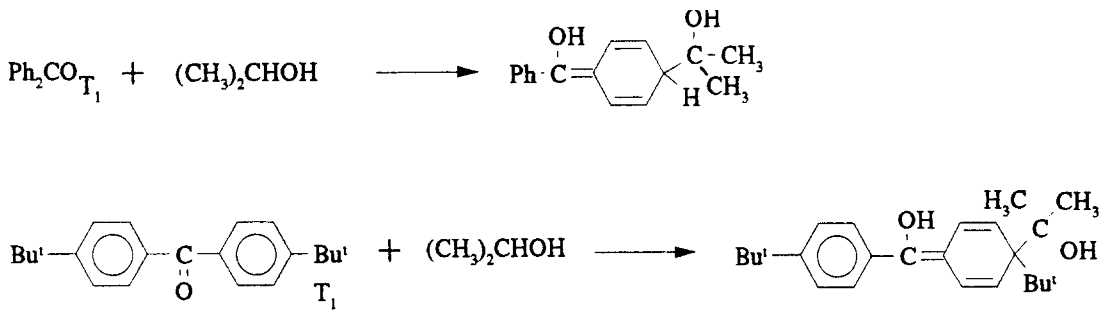

Figure 3 Formation of coloured products in the reduction of triplet carbonyl compounds

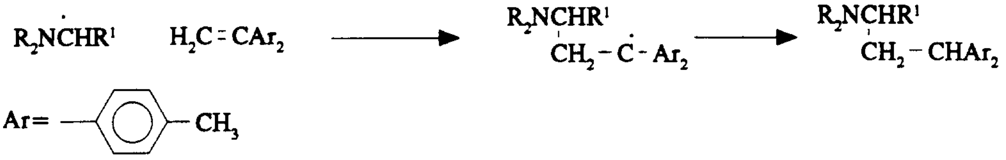

Figure 4 Trapping of α-aminoalkyl radicals by 1,1-ditolylethene

The α-aminoalkyl radicals can also be trapped by using nitroso compounds and the structure of the radical can then be deduced from the electron spin resonance (e.s.r.) spectra of the product of these reactions[19,21]. Some such radicals, derived from commonly used aliphatic amine synergists are shown in *Figure 5*.

Normally, N–CH_3 groups are more reactive than their substituted derivatives[1,22], and hence the radical, identified as being produced from *N*,*N*-dimethylethanolamine, is not the anticipated one.

N-methylated aromatic amines are effective reducing agents for triplet aromatic ketones[1]. A compound of this class, which finds extensive use in the radiation-curing industry is ethyl 4-dimethylaminobenzoate[11,23,24]. This compound is far more hydrophobic than the aliphatic amine synergists previously described and therefore finds extensive use in lithographic printing.

From the foregoing discussion it can be seen that α-aminoalkyl radicals probably act as initiating radicals, whereas the radicals derived from aromatic ketones act as chain terminators.

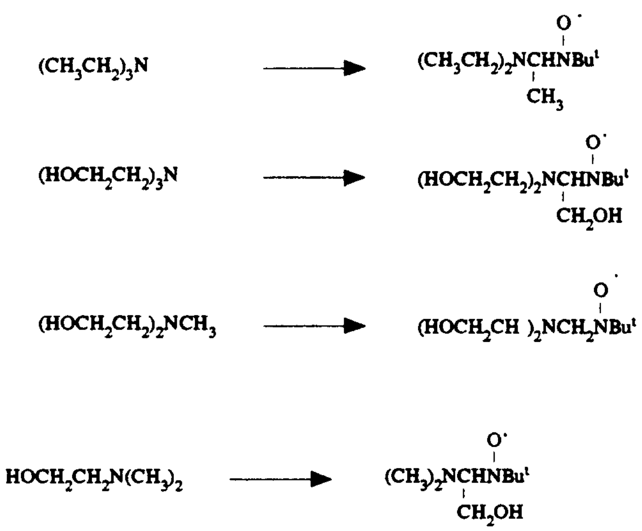

Figure 5 Radicals produced from aliphatic amine synergists, trapped by nitrosobutane

We report here upon an investigation of the thioxanthone–aromatic and aliphatic amine initiator systems in which the extent of incorporation of the initiator-derived species is investigated.

EXPERIMENTAL

All the equipment details and sources of materials have been given in an earlier publication[25].

Experimental plan

Solutions of the photoinitiator and amine synergist were made up in lauryl acrylate. Films of known thickness were spread on paper and then the films exposed to ultra-violet (u.v.) radiation by passing them underneath a medium-pressure lamp using a belt operating at a known speed. In this way, a controlled dose of radiation was delivered to the film. The films were dissolved in a fixed volume of tetrahydrofuran containing a known amount of toluene (as a marker for g.p.c.). These solutions were subjected to g.p.c. analysis by using the following detectors and conditions.

Detection by change in refractive index. By using this method the relative percentages of initiator, monomer and polymer could be determined for films subjected to various doses of radiation.

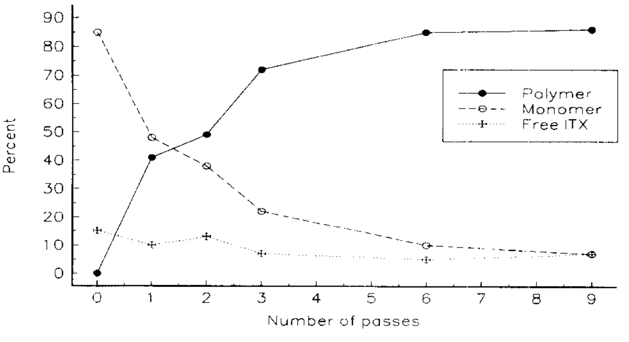

Figure 6 The fate of photoinitiator, monomer and polymer on curing ITX/NMDEA in lauryl acrylate

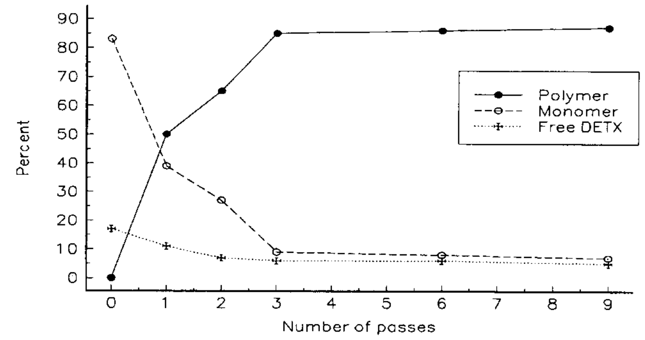

Figure 7 The fate of photoinitiator, monomer and polymer on curing DETX/NMDEA in lauryl acrylate

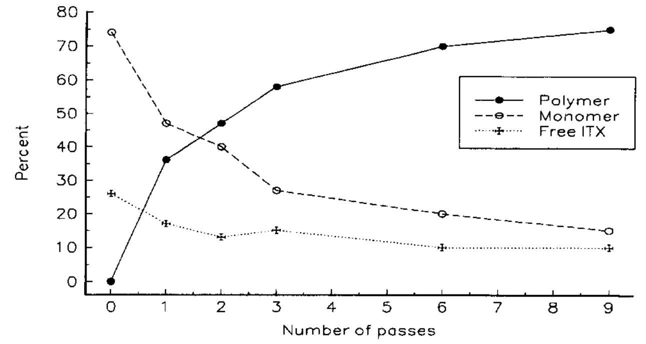

Figure 8 The fate of photoinitiator, monomer and polymer on curing ITX/EDB in lauryl acrylate

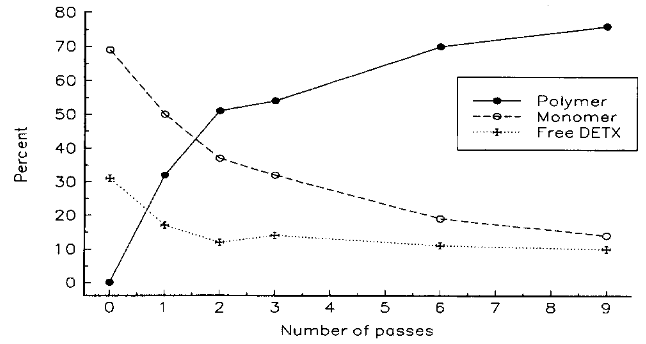

Figure 9 The fate of photoinitiator, monomer and polymer on curing DETX/EDB in lauryl acrylate

Table 1 Estimation of free and polymer-bound ITX present in films produced by polymerizing lauryl acrylate using an ITX/NMEDA initiating system

No. of passes	Free ITX (%) Unreduced	Free ITX (%) Reduced	Polymer-bound ITX (%) Unreduced	Polymer-bound ITX (%) Reduced	Total ITX (%)
0	100	0	0	0	100
1	81	5	8	2	96
2	73	7	11	5	96
3	70	8	13	7	98
6	66	9	15	9	99
9	62	9	19	8	98

Table 2 Estimation of free and polymer-bound DETX present in films produced by polymerizing lauryl acrylate using a DETX/NMEDA initiating system

No. of passes	Free DETX (%) Unreduced	Free DETX (%) Reduced	Polymer-bound DETX (%) Unreduced	Polymer-bound DETX (%) Reduced	Total DETX (%)
0	100	0	0	0	100
1	81	4	8	2	95
2	74	5	13	4	96
3	64	7	18	8	97
6	61	7	19	11	98
9	59	7	20	10	96

Table 3 Estimation of free and polymer-bound ITX present in films produced by polymerizing lauryl acrylate using an ITX/EDB initiating system

No. of passes	Free ITX (%) Unreduced	Free ITX (%) Reduced	Polymer-bound ITX (%) Unreduced	Polymer-bound ITX (%) Reduced	Total ITX (%)
0	100	0	0	0	100
1	84	7	5	5	101
2	84	4	10	2	100
3	78	7	10	5	100
6	77	6	12	6	101
9	72	7	14	7	100

Table 4 Estimation of free and polymer-bound DETX present in films produced by polymerizing lauryl acrylate using a DETX/EDB initiating system

No. of passes	Free DETX (%) Unreduced	Free DETX (%) Reduced	Polymer-bound DETX (%) Unreduced	Polymer-bound DETX (%) Reduced	Total DETX (%)
0	100	0	0	0	100
1	77	9	6	2	94
2	77	7	9	4	97
3	76	8	9	4	97
6	70	8	13	5	96
9	74	4	16	2	96

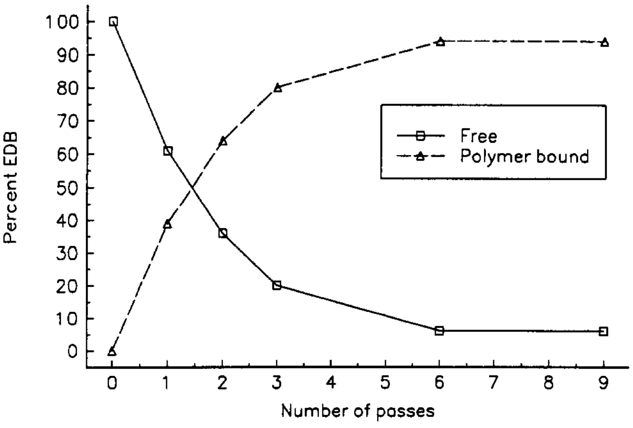

Figure 10 The fate of the synergist on curing ITX/EDB in lauryl acrylate

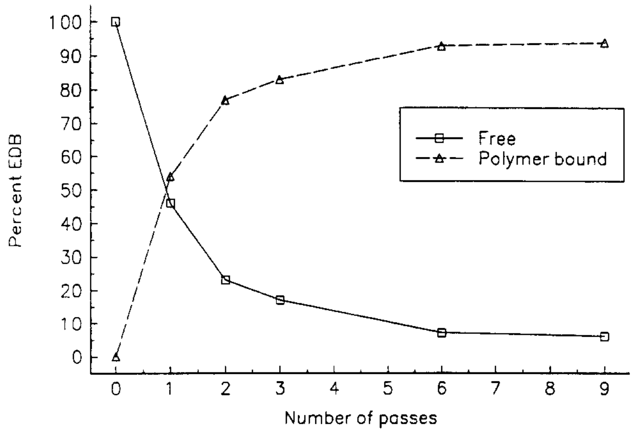

Figure 11 The fate of the synergist on curing DETX/EDB in lauryl acrylate

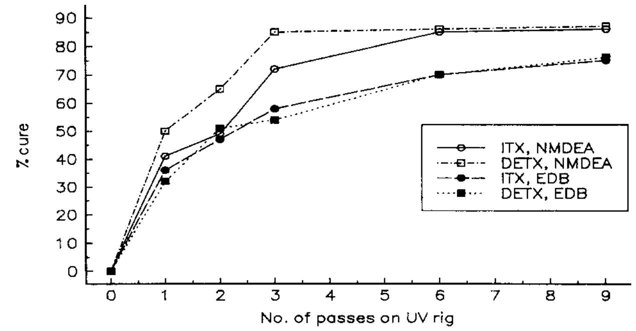

Figure 12 A comparison in cure for four different photoinitiating systems (in lauryl acrylate)

U.v. detector set at 254 nm. The use of 254 nm as the monitoring wavelength picks out the aromatic species—reduced and unreduced thioxanthones, aromatic amine synergist (if used), and to a much smaller extent, lauryl acrylate (or an impurity in lauryl acrylate). By monitoring at this wavelength, the extent to which aromatic

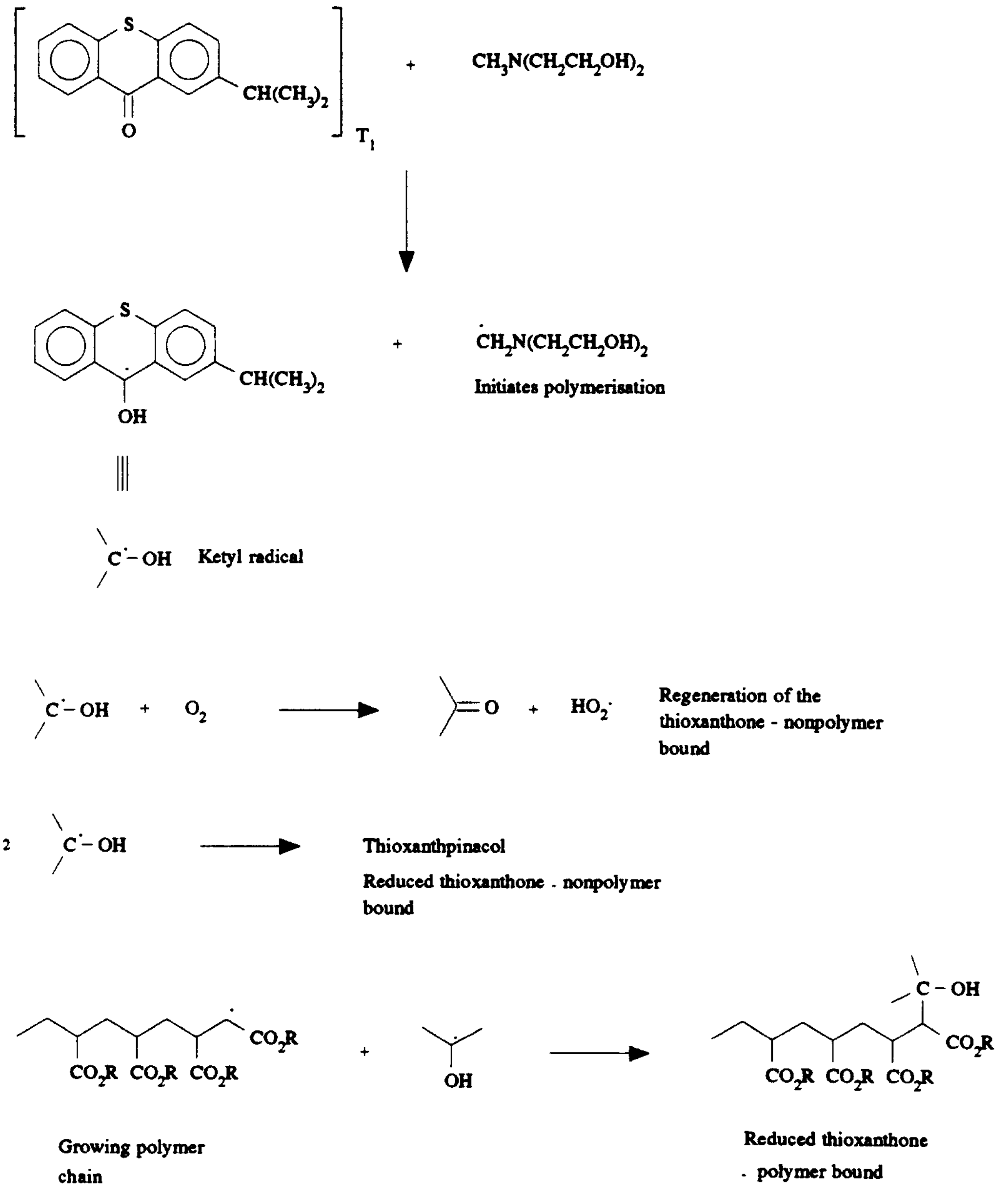

Figure 13 Origin of free thioxanthone and polymer-bound and free reduced thioxanthone in cured film

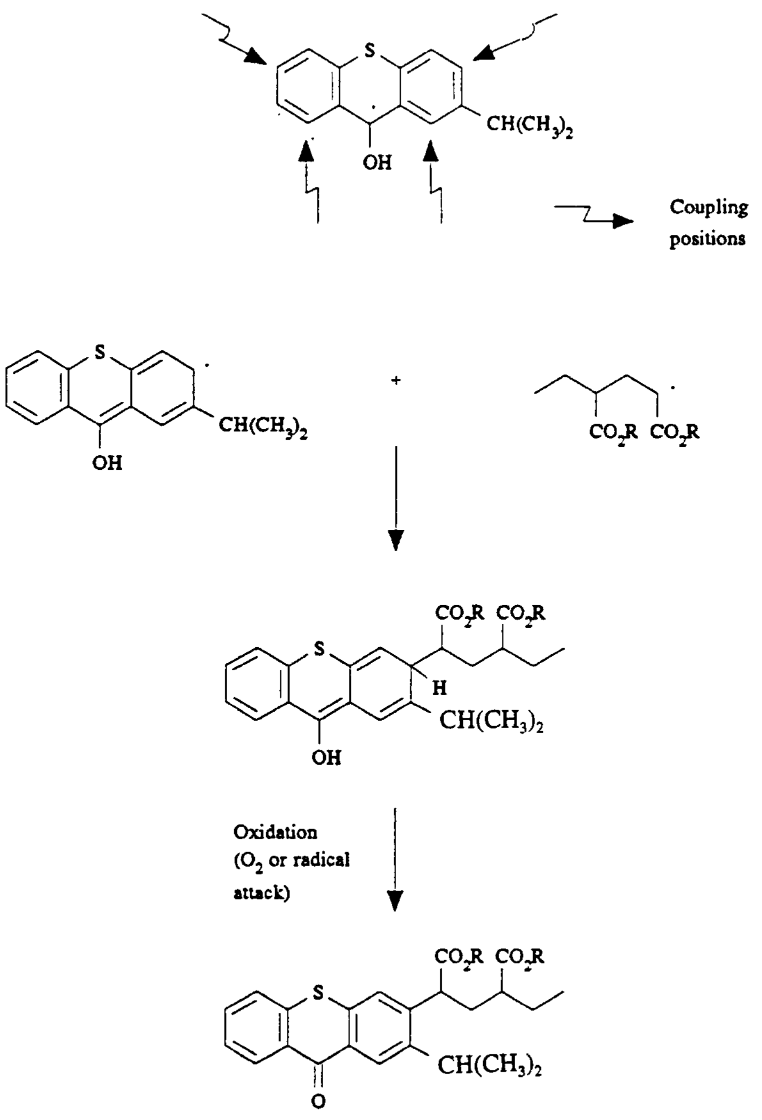

Figure 14 Origin of polymer-bound thioxanthone residues

units are incorporated into the polymer can be monitored.

U.v. detector set at 383 nm. The use of this wavelength enables the thioxanthone to be detected and to see if a polymer is produced which contains thioxanthone residues. Thus the percentage free and polymer-bound thioxanthone can be calculated. If the only aromatic residues present in the polymer and non-polymer-bound residues are thioxanthone, the percentage of aromatics detected at 383 and 254 nm should be the same. Differences are found, however and this is due to the thioxanthone undergoing reduction and to reduced thioxanthone being present as polymer-bound and polymer-free species.

U.v. detector at 310 nm. The aromatic amine synergist, ethyl 4-dimethylaminobenzoate, exhibits an absorption maximum at 310 nm. The thioxanthones used in this study absorb only weakly at this wavelength. Similarly, the lauryl acrylate employed exhibits a finite but very small absorption at this wavelength. Thus, by using a detector wavelength of 310 nm, the extent to which the aromatic amine is incorporated into the polymer can be ascertained.

RESULTS

Lauryl acrylate was polymerized by using photoinitiator systems consisting of the following: (a) isopropylthioxanthone (ITX) and *N*-methyl-diethanolamine (NMDEA), (b) ITX and ethyl 4-dimethylaminobenzoate (EDB), (c) 2,4-diethylthioxanthone (DETX) and NMDEA, and (d) DETX and EDB. The extent of polymerization as a function of radiation dose (i.e. number of passes under the lamp) was determined by g.p.c. and the results are shown in *Figures 6–9*. These figures also show how the concentration of the thioxanthones changes as a function of radiation dose. The systems using NMDEA as synergist were also analysed by g.p.c., using a u.v. detector set at 254 nm in one case, and at 383 nm in another, thereby enabling the extent of free and polymer-bound ITX and DETX and free and polymer-bound reduced thioxanthone to be determined. The results are shown in *Tables 1* and *2*. A similar analysis was carried out

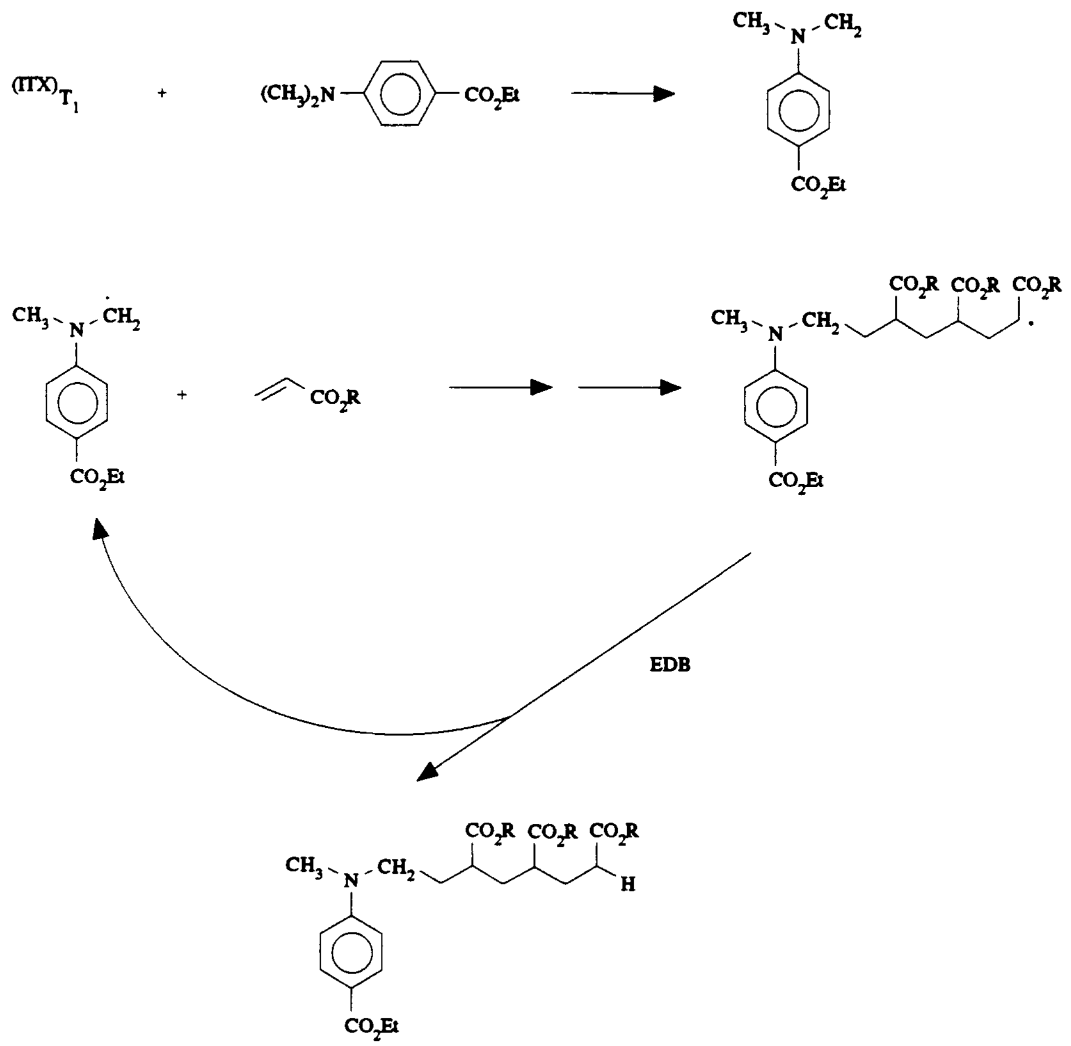

Figure 15 Role of EDB in the curing process

for those systems in which the aromatic amine (EDB) was used as synergist. *Tables 3* and *4* show these results. With these systems an analysis was made by using the u.v. detector set at a monitoring wavelength of 310 nm in order to determine the fate of the synergist. The results are shown in *Figures 10* and *11*. The rate at which the acrylate double bond is consumed as a function of irradiation dose for the various ketone synergist systems used was determined by infra-red spectroscopy, and the results are shown in *Figure 12*.

DISCUSSION

Figures 6 and *7* show that with NMDEA as the synergist, greater than 80% polymerization of lauryl acrylate occurs with DETX after three passes under the lamp, whereas ITX is a little slower and it is only after six passes that this level of curing is achieved. This result was confirmed by following the polymerization process by i.r. spectroscopy (*Figure 12*). The performance of the two initiators is similar when the aromatic amine EDB is used, and even after six passes under the lamp, the polymerization process is not complete. Thus, in the system being investigated, the aliphatic amine is the more efficient synergist. The absorption spectra of the two amines are very different, with the aromatic amine showing a strong absorption at around 300 nm. This absorption will effectively screen out some of the light that could be usefully absorbed by the thioxanthones[26].

When the polymerization process is followed by g.p.c. in association with a u.v. detector, the fate of the thioxanthones becomes more apparent than when change in refractive index is the source of measurement. *Table 1* shows that with NMDEA as the synergist, ITX undergoes some reduction, but this is not substantial. The g.p.c. results show that most of the ITX remains unreduced and that the thioxanthone chromophore is incorporated into the polymer. From a consideration of the reaction mechanism, we would expect some non-polymer-bound unreduced thioxanthone and some polymer-bound and non-polymer-bound reduced thioxanthone residues (*Figure 13*). What is the origin of the polymer-bound thioxanthone? Some years ago, the idea was put forward that part of the colour produced in films when a thioxanthone–amine synergist system was used could in part be attributed to adducts being formed via coupling with the ketyl radical[27]. From a consideration of the resonance structure of the thioxanthyl ketyl radical[28], the 2-, 4-, 5-, 7- and 9-positions of the radical can be identified for such coupling (*Figure 14*). There is plenty of precedent for the formation of coloured species in reactions of aromatic ketones with amines and other reducing agents. All of the evidence points to these species being formed via ketyl radicals.

DETX behaves in a similar way to ITX when NMDEA is used as the synergist (*Table 2*).

When the aromatic amine EDB is used as the synergist the results presented in *Tables 3* and *4* suggest that there is slightly more unreduced thioxanthone residues in the coating than when NMDEA is used as the synergist. However, the experimental uncertainty makes it difficult to make a precise judgement. It is proved very instructive to follow the utilization of the EDB as a function of percentage of cure (i.e. extent of acrylate double bonds consumed) (*Figures 10* and *11*). It is quite remarkable that so much amine is consumed in the curing process. The amine synergist fulfils two roles, i.e. that of a synergist and as a suppressor of oxygen inhibition. The g.p.c. results shown in *Figures 10* and *11* indicate that the amine is acting as a synergist. By extrapolation from work on related systems using a radical-trapping technique[20], we can be sure that the α-aminoalkyl radicals are acting as initiators. The high level of incorporation of EDB into the polymer suggests that the amine may also be acting as a chain-transfer agent (*Figure 15*).

Both of the aminoalkyl and ketyl radicals will act as oxygen scavengers. When the curing (using DETX) was carried out in a nitrogen atmosphere it was found that more reduced and unreduced thioxanthone and EDB was incorporated into the polymer. In the absence of oxygen the generation of ketyl radicals will be more efficient (due to the absence of quenching triplet DETX by ground-state oxygen), and they will not be removed by oxygen, and hence the steady-state concentration of ketyl radicals under these conditions will be higher. This higher concentration will favour incorporation of reduced and non-reduced thioxanthone residues in the polymer.

CONCLUSIONS

We have shown that the use of a thioxanthone in conjunction with an amine synergist to initiate the polymerization of lauryl acrylate leads to incorporation of thioxanthone residues into the polymer. This is rationalized as occurring via the growing polymer macro-radical reacting with the thioxanthyl ketyl radical at either the 2-, 4-, 5-, or 7-positions of the radical. When the aromatic amine synergist EDB is used, the amine is efficiently incorporated into the polymer. It is suggested that the radicals derived from the amine synergist initiate the polymerization and that the thioxanthone and reduced thioxanthyl residues are located at the tail of the polymer chain.

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