

Factors affecting the photoyellowing which occurs during the photoinitiated polymerization of acrylates

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Abstract

The influence of the type of photoinitiator, type of polymerizable reactive diluent and added amine synergist on the yellowing which occurs during the curing of clear films is examined. Type I photoinitiators based on acetophenone give rise to the least yellowing. The presence of amines, such as *N*-methyldiethanolamine, increases yellowing to a noticeable extent. Amino groups present in the initiator or the reactive diluent lead to marked yellowing. The chemistry responsible for the yellowing is explored.

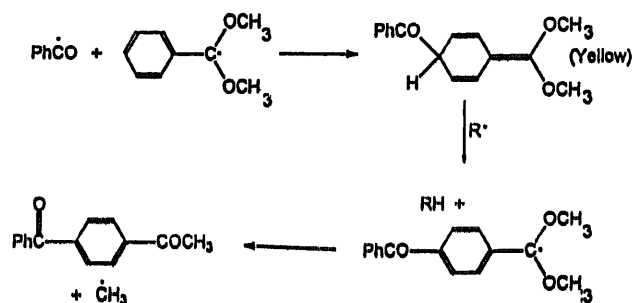
Keywords: Photoyellowing; Photoinitiated polymerization; Acrylates

1. Introduction

Photoinitiated radical polymerization processes are now widely used in many industries [1], e.g. printing [2], production of electronic components [3], coating of optical fibres [4], production of compact discs [5] and the production of three-dimensional objects [6]. A typical application in printing is to apply a UV-cured clear varnish over conventionally printed material to increase the aesthetic appeal of the product. Therefore it is of prime importance that the UV curing process produces an absolutely clear film and that the film should not age giving rise to discolouration or cracking.

In this paper, we examine some of the factors which can lead to yellowing during UV curing. The typical components of UV curing clear varnish formulations [7] include a photoinitiator, an acrylic monomer (reactive diluent), an acrylic oligomer (a prepolymer) and, in many cases, a tertiary amine (either as a synergist or to reduce the extent of oxygen inhibition [8]).

Some photoinitiators are known to promote photoyellowing to a greater extent than others [9]. The dimethylketal of benzil is such an example and, in this case, the coloured products are thought to be of structure "A" shown in Scheme 1. It is well known that the



Scheme 1.

photoreduction of benzophenone (a process which occurs when this compound is reduced by a tertiary amine) leads to the formation of coloured byproducts [10].

Prepolymers yield coatings which have a tendency to photoyellow on weathering. It has been shown that those containing an aromatic functionality or nitrogen are prone to yellowing [11]. Aromatic urethanes and aromatic epoxy-based compounds produce coloured compounds by undergoing a photo-Fries rearrangement [12]. It has also been suggested that aromatic urethanes based on MDI oxidize to give highly coloured quinone-imide products [13]. It appears that non-aromatic products are less prone to photoyellowing than their aromatic counterparts.

The amine component of the formulation can play a significant part in the yellowing during cure and after

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Table 1
Formulations used in the experiments

Number	Initiator	Reactive diluent	Prepolymer
A1	5% ITX	CL960	P3005
A2	5% BP	CL960	P3005
A3	5% 2	CL960	P3005
A4	5% 3	CL960	P3005
A5	5% 1	CL960	P3005
A6	5% ITX	TPGDA	-
A7	5% BP	TPGDA	-
A8	5% CPTX	TPGDA	-
A9	5% 3	TPGDA	-
A10	5% 1	TPGDA	-
A11	5% 1	TPGDA	P3005
A12	5% 1	CL959	P3005
A13	5% 1	HDDA	P3005
A14	5% 1	CL960	P3005
A15	2% 1	CL960	P3005
A16	3% 1	CL960	P3005
A17	4% 1	CL960	P3005
A18	5% 1	CL960	P3005
A19	2% 3	CL960	P3005
A20	2% BP	CL960	P3005
A21	2% CPTX	CL960	P3005
A22	2% ITX	CL960	P3005
A23	2% 1	CL960	P3005
A24	2% 2	CL960	P3005

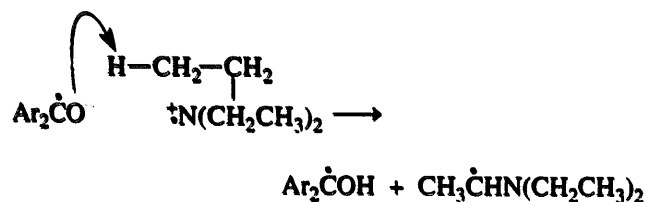
} + NMDEA (5%)

Ratio of diluent to prepolymer, 1:1 (v/v).

cure [8,14]. Tertiary amines, which act as excellent synergists and reducers of oxygen inhibition, have special features which give rise to these properties, namely a low ionization potential and reactive C-H bonds adjacent to the nitrogen atom. The low ionization potential facilitates the reaction of carbonyl compounds, singlet oxygen and other species with the amine via an electron transfer process



For chemical reaction to occur, the C-H bonds adjacent to the nitrogen have to be acidic, and generally the order of reactivity is $\text{CH}_3 > \text{CH}_3\text{CH}_2 > (\text{CH}_3)_2\text{CH}$.



The α -aminoalkyl radical so produced is an excellent initiator for acrylate polymerization and a good scavenger of oxygen. In the latter role, the amine becomes oxidized to give α -aminohydroperoxides which give rise to a variety of products, e.g. enamines, amides, dealkylation products. Most significantly, the photo-oxidation of amines produces a highly coloured poly-

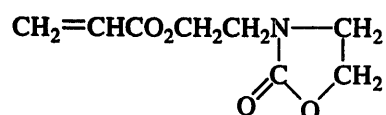
merization products, the identity of which remains unknown [15]. Consequently, it is not surprising that the presence of amines in formulations leads to yellowing and that the amines most prone to give rise to this effect are the best synergists and ameliorators of oxygen inhibition.

We report an investigation of the effect of the photoinitiator, polymerizable acrylate and *N*-methyldiethanolamine on the yellowing occurring during cure.

2. Experimental details

2.1. Chemicals

Benzophenone (BP) (Aldrich) was used as received. Isopropylthioxanthone (ITX) and 1-chloro-4-propoxylthioxanthone (CPTX) were kindly supplied by International Octel and used as received. Initiators 1 (Irgacure 907), 2 (Irgacure 369) and 3 (Irgacure 651) were kindly supplied by Ciba Geigy Ltd. (Basel, Switzerland). Tripropyleneglycol-diacrylate (TPGDA) (UCB Chemicals) hexanedioldiacrylate (HDDA), a monoacrylate of a cyclic carbamate (CL959) (SNPE) (see below)



a monoacrylate of a urethane (CL960, $\text{CH}_2=\text{CHCO}_2\text{CH}_2\text{CH}_2\text{NHCO}_2\text{CH}(\text{CH}_3)_2$ (SNPE) and Photomer 3005 (P3005) (an epoxyacrylate, Harcros Chemicals) were used as received. *N*-Methyldiethanolamine (NMDEA) (Aldrich) was dried over molecular sieves, distilled and stored under nitrogen.

2.2. Formulations

The formulations are shown in Table 1.

2.3. Techniques

The experimental set-up for real-time IR (RTIR) spectroscopy has been described previously [16]. Formulations were applied to a sodium chloride plate as a film (24 μm) and cured using a 100 W pressure lamp. The course of polymerization was monitored by following the decrease in the absorption band at 810 cm^{-1} .

For determining the extent of colouration during cure, films (24 μm) were applied to abraded aluminium panels and cured using a Fusion Systems UV cure unit equipped with a 300 W in^{-1} "H" lamp. Each panel was subjected to one pass at a belt speed of 5 m min^{-1} . The panels were stored in a dark, constant-temperature room for 48 h. Yellowness indices were determined using the standard test method (ASTM-E313-73) with a Spectrogard Colorimeter (Pacific Scientific). To ensure accuracy, five readings were recorded for each sample and the average value was used. The yellowness indices were calculated using the following equation:

$$\text{YI} = 100(1 - B/G)$$

where B is the blue reflectance (in per cent) and G is the green or luminous reflectance (in per cent).

3. Results

The rate of cure of a mixture of an epoxyacrylate containing a monoacrylate diluent by a range of type I and type II photoinitiators using RTIR spectroscopy is shown in Fig. 1. A similar experiment was carried out using TPGDA as the polymerizable species (Fig. 2). The type I photoinitiators 2-methyl-1-[4-(methylthio)-phenyl]-2-morpholinopropan-1-one (1) (Irgacure 907) and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one (2) showed excellent reactivity despite the lack of amine synergist in the formulation. This offered the opportunity of studying the cure initiated by 1 in which the reactive diluent was varied. The rate of cure was determined, using RTIR spectroscopy, for formulations containing the initiator (5% w/w) in an epoxyacrylate with monoacrylates, TPGDA and HDDA as diluents. As can be seen from Fig. 3, the rate of cure was highly dependent on the nature

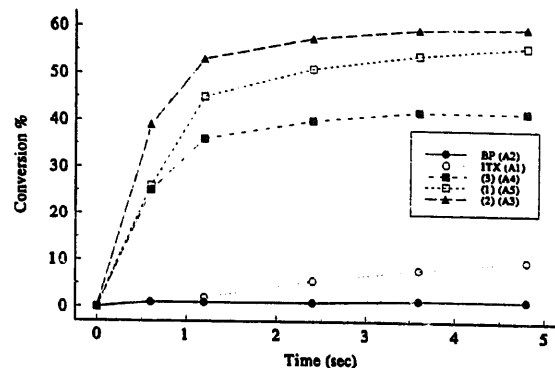


Fig. 1. Percentage conversion of acrylate double bonds as a function of time for the photopolymerization of CL960 and P3005 by various photoinitiators: ●, BP (A2); ○, ITX (A1); ■, 3 (A4); □, 1 (A5); ▲, 2 (A3).

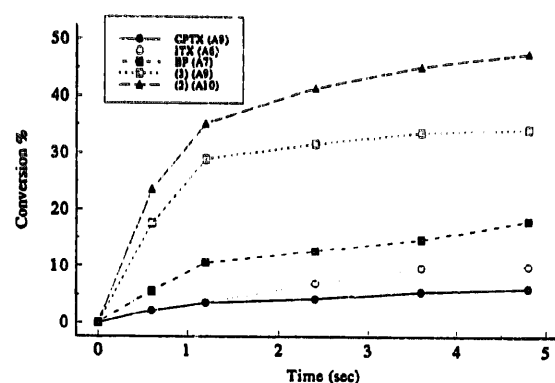


Fig. 2. Percentage conversion of acrylate double bonds as a function of time for the photopolymerization of TPGDA by various photoinitiators: ●, CPTX (A8); ○, ITX (A6); ■, BP (A7); □, 3 (A9); ▲, 2 (A10).

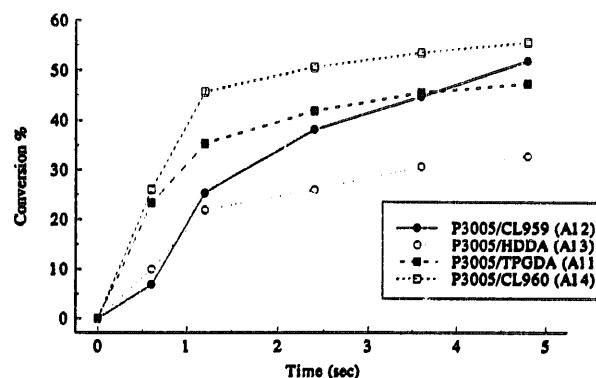


Fig. 3. Percentage conversion of acrylate double bonds as a function of time for the photopolymerization of various acrylate mixtures using 1 as photoinitiator (5% w/w): ●, P3005/CL959 (A12); ○, P3005/HDDA (A13); ■, P3005/TPGDA (A11); □, P3005/CL960 (A14).

of the formulation. Using the most reactive formulation, the effect of varying the concentration of 1, whilst keeping the light intensity constant, was studied. The results are shown in Fig. 4. Somewhat surprisingly, the lowest concentration of initiator was found to be the most effective over a 5 s irradiation period. Irradiation

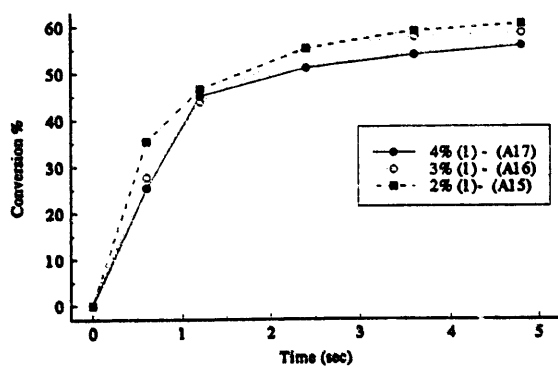


Fig. 4. Percentage conversion of acrylate double bonds as a function of time for the photopolymerization of a mixture of P3005 and CL960, initiated by various concentrations of 1: ●, 4% 1 (A17); ○, 3% 1 (A16); ■, 2% 1 (A15).

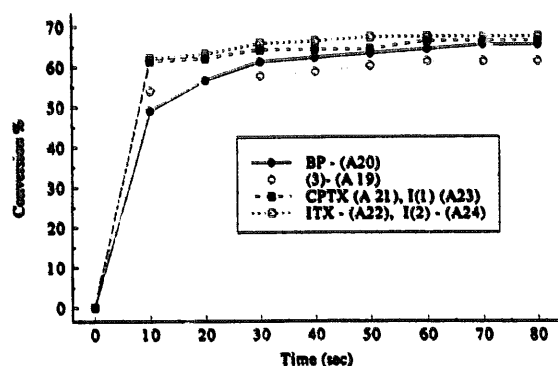


Fig. 5. Percentage conversion of acrylate double bonds as a function of time for the photopolymerization of a mixture of P3005 and CL960 by various photoinitiators (2% w/w) in the presence of *N*-methyl-diethanolamine: ○, 3 (A19); ●, BP (A20); ■, CPTX (A21), I (A23); □, ITX (A22), 2 (A24).

for more than 10 s led to conversions of 60%–70%, the highest conversion eventually being achieved by the formulation having the highest initiator concentration (4%).

The rate of cure of an epoxyacrylate containing a monoacrylate as a reactive diluent, using a variety of initiator types, in the presence of NMDEA was also studied by RTIR spectroscopy. As can be seen from Fig. 5 some differences in the rate of cure can be seen but, except for BP, very little further conversion of acrylate double bonds occurs after 10 s irradiation. In the case of BP, conversion of acrylate groups occurs steadily up to 70 s irradiation giving 60% conversion.

In order to assess the photoyellowing which occurs during cure, the formulations were coated onto abraded aluminium panels and cured (1 pass, 5 m/min⁻¹) using a high-intensity (300 W in⁻¹) "H" lamp. The spectral output of the latter is shown in Fig. 6. Yellowness indices for the cured films are shown in Table 2.

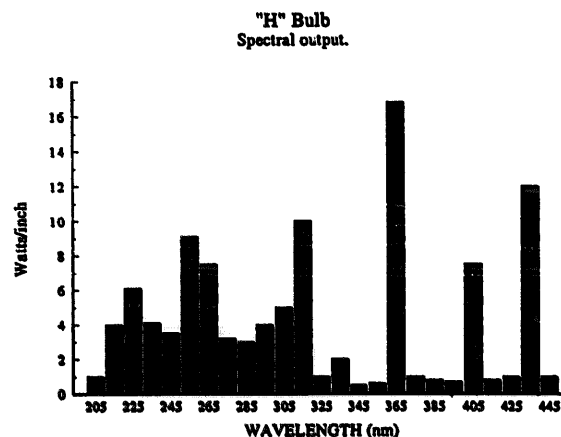


Fig. 6. Spectral output of the "H" bulb.

Table 2
Yellowness indices for a variety of cured films

Formulation	Yellowness index
A1	7.60
A2	7.40
A3	14.50
A4	5.80
A5	6.10
A12	8.40
A13	6.45
A14	6.12
A15	6.45
A16	6.45
A17	6.30
A18	6.45
A19	6.60
A20	6.10
A22	10.20
A23	7.74
A24	23.90

4. Discussion

The results shown in Fig. 1 demonstrate that simple aromatic ketones, such as BP and thioxanthone, are inefficient photoinitiators in the absence of a tertiary amine. Since some polymerization does occur, these initiators may perform better if curing is carried out in a nitrogen atmosphere (to reduce oxygen inhibition), although in such circumstances the ketone may be consumed via reduction, thereby reducing its efficiency. The observation that some cure occurs in air suggests that there are some reactive C–H bonds in the reactive diluent or prepolymer. Possible candidates include the CH₂ group adjacent to the nitrogen of the carbamate or CH₂ groups adjacent to oxygen present in the prepolymer. The relative reactivities of the initiators 1, 2 and benzil dimethylketal 3 show that the ability of 1 and 2 to utilize light in the 300–400 nm range leads them to perform better than 3. When TPGDA was

used as the polymerizable material, the performances of ITX and BP were improved (Fig. 2) with BP overtaking the thioxanthone. CPTX performed very poorly in this system. A factor that influences the performance of the thioxanthenes is the nature of their lowest triplet states. This depends on the polarity of the medium and becomes more and more marked (as judged by an increase in π - π^* character) as electron-donating substituents are introduced at positions in the nucleus where they can conjugate with the carbonyl group [17]. The relative reactivity of the two type I photoinitiators reflects the better absorbance properties of 1 and 2 compared with 3.

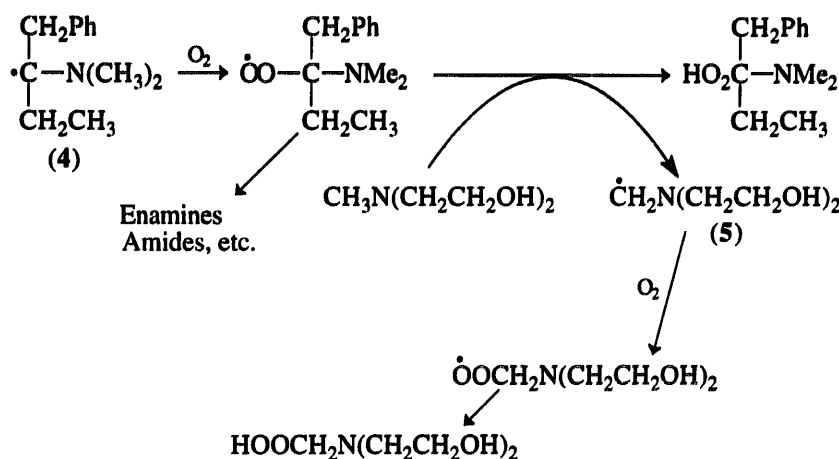
From Fig. 3, it can be seen that the performance of a particular initiator (in this case 1) is dependent on the type of monomer-prepolymer mix. An epoxy-acrylate (which is relatively unreactive) was used as the prepolymer and the reactive diluent was varied. HDDA was the least reactive, with a monoacrylate containing a cyclic carbamate group being only slightly more reactive. TPGDA is quite a reactive diluent and is only superseded by a monoacrylate containing a urethane group. The reasons for the different reactivities do not appear to be related to the concentration of acrylate groups, since the diacrylates do not produce the most reactive formulations. The reactivity, as measured by RTIR spectroscopy, probably reflects the changes in viscosity which occur during cure. The monoacrylates should keep the viscosity lower over a longer irradiation period than the diacrylates. This may well explain why the monoacrylate containing the cyclic carbamate leads, in the end, to a greater conversion of functional groups than TPGDA.

The effect of varying the concentration of initiator 1 on the rate of cure is interesting, since the most rapid and effective cure was obtained with the lowest concentration of initiator employed. This implies that the absorption of light by 1 when used at the 2% w/w level is highly efficient. However, the initiator is probably totally utilized after a relatively short period of irradiation and, consequently, higher levels of initiator become valuable if longer periods of irradiation have to be used to effect cure.

When NMDEA is included in the formulation, the type II photoinitiators perform well. BP, which in the absence of amine performs poorly, gives, after a reasonable irradiation period, 60% conversion of the acrylate double bonds. The thioxanthenes are extremely efficient, which is probably due to the reactivity of their triplet states towards the tertiary amine. The performance of the type I photoinitiators 1 and 2 is hardly affected by the addition of the amine (see Figs. 1 and 5), whereas for 3 there is an improvement. Since 3 is a less efficient initiator (producing radicals at a slower rate) than 1 or 2 (due to light absorption properties), its effectiveness will be more strongly influenced by oxygen inhibition, and since the amine helps to offset this effect, it will have a beneficial effect.

Table 2 shows that all the formulations exhibit yellowing under similar cure conditions. Undoubtedly, the natural colour of P3005 contributes, but, in the main, the colour derives from the photoreaction. When various initiators are used in similar formulations (samples A1–A5), it is immediately apparent that the type I initiator 2 leads to the greatest yellowing and this is exacerbated to an abnormal extent when it is employed in a formulation containing NMDEA (sample A24). This is probably due to α -scission of 2 producing the α -aminoalkyl radical 4, which can undergo a variety of oxidative reactions including triggering the oxidative decomposition of NMDEA.

ITX (sample A1) produces a yellow film, but much of this is due to the residual colour of the photoinitiator [18]. Further work has shown that type II photoinitiators, when used in systems containing oxygen, result in (after cure) at least 60% of unreduced ketone remaining. The presence of NMDEA (sample A22) leads to an increase in the observed yellowing. This can be attributed to the thioxanthone reacting with the amine to give the α -aminoalkyl radical (5), which do not only initiates



polymerization, but also reacts with oxygen, thereby ultimately producing an α -hydroperoxyamine.

Not surprisingly, BP, which is less coloured than ITX, leads to less yellowing (sample A2). Unusually, the addition of NMDEA leads to a slight reduction in yellowing when employed with this ketone. The reduction of BP is known to yield coloured products via the ketyl radical (6) and the presence of the amine may lead to the scavenging of such radicals with the regeneration of BP.

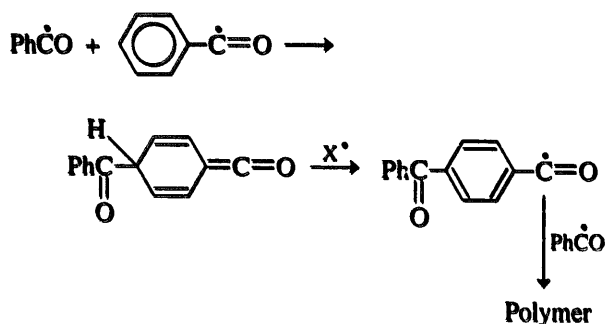
The type I photoinitiator 1 leads to some yellowing (sample A5), but this is far less marked than for initiator 2. Like 2, 1 produces an α -aminoalkyl radical on scission (radical 7) [19]



It is possible that this radical triggers the oxidation of NMDEA, thereby leading to the yellowing of formulation A23. Use of the type I photoinitiator 3 leads to the least amount of photoyellowing (formulation A4) and the increase in yellowing when NMDEA is added is minimal. It has been speculated that 3 forms coloured products derived from radical 8 [9]



It is possible, however, that in the case of 3 some of the yellowing is due to the benzoyl radical. It is known that the decomposition of initiators such as 3 in thin films leads to the production of benzil [20]. This presumably occurs via the dimerization of benzoyl radicals. It is conceivable that benzoyl radicals dimerize in other ways giving rise to polymeric carbonyl compounds



It is known that irradiation of benzaldehyde gives rise to a highly coloured polymer via the intervention of benzoyl radicals generated via hydrogen abstraction from the aldehyde group [21].

5. Conclusions

It has been shown that the choice of photoinitiator and reactive diluent plays an important part in determining the extent of yellowing that occurs on curing. The addition of *N*-methyldiethanolamine always leads to an increase in the extent of yellowing. Factors to be considered which will reduce the yellowing to a minimal degree include the avoidance of the use of tertiary amines and initiators containing tertiary amine groups, and the use of type I photoinitiators that do not produce radicals which can undergo radical coupling reactions to give products containing extended chromophores. These considerations, when used in conjunction with the previous observation that non-aromatic prepolymers give rise to less yellowing than those containing aromatic groups, should lead to formulations which will produce minimal yellowing on curing.

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