Photochemistry and photoinduced chemical crosslinking activity of type I & II co-reactive photoinitiators in acrylated prepolymers

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Abstract

The photoreactivity of Type I and II photointiators, namely, 4-(2-hydroxyethoxy)-phenyl-(2-hydroxy2-methylpropyl) ketone (Irgacure 2959, Ciba-Geigy) and 4-hydroxybenzophenone, respectively, have been examined in the free and bound form in melamine and urethane acrylate prepolymers. Co-reaction in the prepolymers was undertaken by partial replacement of the hydroxyacrylate components with the photoinitiators in the reaction with the isocyanate component. Both the photoinitiators were also converted into their corresponding acrylate derivatives for study. The free, bound and acrylated derivatives were then analysed by various spectroscopic techniques to evaluate the relationship between their photophysical properties and photoinitiation activity for photocrosslinking of commercial acrylated monomers and prepolymers. Photocuring studies using Hg sources (conveyor and RTIR) indicated that whilst binding the Type I photointiator reduced its efficiency in cure, the Type II photoinitiator was enhanced. The presence of an amine co-synergist, however, generally eliminated these differentials. Acrylation of the Irgacure 2959 also reduced photoactivity. Absorption spectroscopy indicated the presence of a strongly absorbing $n\pi^*$ transition in the far UV region for both chromophore types which undergoes a blue shift on binding to the prepolymer. Phosphorescence spectra, lifetimes and quantum yields also indicate the presence of low lying triplet $n\pi^*$ states for both types of chromophore. Binding appears to enhance the triplet lifetime and reduce the quantum yield of emission due to increased electron donation into the chromophore by the resin component and may in part account for their lower photoactivity. Microsecond flash photolysis identified the formation of benzoyl radicals in the case of the Type I system with a small enhancement in radical formation on binding. The Type II system gave ketyl radicals formed by hydrogen atom abstraction which were enhanced in the bound resin system. The latter would account for increased photoactivity for the bound Type II system. Nanosecond laser flash photolysis experiments identified the triplet–triplet absorption in the case of the Type II initiator. In the presence of a tertiary amine (triethylamine) the transient absorption and its lifetime were significantly enhanced due to exciplex formation. However, binding the benzophenone initiator to the resin significantly quenched the transient absorption and significantly reduced its lifetime. In the case of the Type I initiator the benzoyl radical was observed directly, confirming the microsecond flash photolysis data. Binding of the initiator to the melamine acrylate resin also reduced benzoyl radical formation and reduced the radical lifetime. This may account for the reduced photoactivity of the Type I bound initiator. Radical formation was also reduced when bound to the urethane acrylate but the lifetime was enhanced. For the initiator bound resin systems the presence of an amine co-synergist enhanced benzoyl radical formation. The implications of initiator co-reactions are discussed in terms of both the photochemical and commercial benefits. ©1999 Elsevier Science S.A. All rights reserved.

1. Introduction

The photochemical crosslinking of acrylated coatings by ultraviolet or visible light has become established technol-ogy for many industrial applications [1–11], including offset lithographic inks, flexographic inks, screen printing, metal decoration, basecoats for beverages cans [6], wood coatings [7], pigmented coatings for textile applications [8], coatings exhibiting a stereoscopic pattern [9], pigmented primary [10] and secondary optical fibre coatings [11].

Over the years, several types of photoinitiators have been developed to induce the photopolymerization or pho-

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tocrosslinking of acrylated systems. Free radical photoinitiators induce a free radical chain process in which low molecular weight monomers and prepolymers are converted by the absorption of UV/Visible light into highly crosslinked films. Measurements of the rates of curing or crosslinking vary from the simplistic, such as the thumb screw test, pencil and pendulum hardness methods to the more scientific methodologies involving real time infrared (RTIR) spectroscopy [12]. The basic mechanism for any photocurable free radical system involves the formation of free radical species through the absorption of light by the photoinitiator. The active initiating radical will then add to the monomer, inducing a chain growth polymerisation and eventually termination.

There are two basic categories of photoinitiators which meet the above requirements. The first group involves Type I photoinitiators which undergo a direct photofragmentation process (α or less common β cleavage) upon absorption of light and formation of initiating radicals capable of inducing polymerization [1,2,5]. The second group, known as Type II photoinitiators undergo a primary process of hydrogen atom abstraction from the environment, which may be the resin itself or a solvent, but usually a tertiary amine co-synergist is used for enhanced efficiency.

α–α-Dialkoxyacetophenones such as α–αDiethoxyacetophenone (DEAP) is one of the most frequently used photoinitiators of the Type I class [1,5]. The excited state undergoes two competitive reactions [4]. Norrish Type I cleavage gives a benzoyl radical and an alkyl radical. The alkyl radical fragments to give an alkyl ester of formic acid and an initiating alkyl radical. Both the benzoyl and the alkyl radicals initiate the polymerisation process. Norrish Type II intramolecular abstraction gives a 1,4 radical intermediate which decomposes to an oxetane by cyclisation, an acetophenone derivative and an aldehyde via elimination. The Norrish Type II reactions do not initiate polymerisation reactions. α-Hydroxyalkylphenones were introduced at the beginning of the 1980s as a new class of photoinitiators. α-Hydroxyalkylphenones are highly reactive, at the same time they possess high thermal stability and better colour characteristics in clear coatings. Upon irradiation benzoyl radicals are also formed (Fig. 1). As with other photoinitiators, the benzoyl radical is mainly responsible for the initiation of the polymerisation. The α-hydroxyalkyl radical can also participate in the initiation process.

Type II photoinitiators on the other hand undergo a primary bimolecular process of hydrogen atom abstraction from the environment, which may be the resin itself or a solvent. However, usually amine co-synergists are used for enhanced efficiency [1,2,5]. In this case, reaction usually occurs from the lowest excited state of the ketone, and depends on the intersystem crossing (ISC) rate, the configuration of the triplet state (n,π^* or π,π^*) and its corresponding energy. Here, the excited triplet state of the ketone forms an intermediate excited electron transfer complex (exciplex) with the tertiary amine. Electron transfer occurs with the

subsequent formation of radicals, the amino radical is then believed to be the main initiating radical (Fig. 2). Tertiary amines are mostly used as co-synergists, since they enhance the reactivity of Type II photoinitiators. Amines can also react as oxygen scavengers and thereby help to overcome oxygen inhibition.

The photochemical and photophysical properties of a wide range of benzophenone [13–16] and for that matter thioxanthone [17] photoinitiators (Type II photoinitiators) have been extensively studied and reviewed [18] in the literature. Benzophenone represents the most important bimolecular photoinitiator since the use of benzophenone combined with amines makes possible the formulation of cost effective UV inks and coatings. Benzophenone is frequently used in combination with unimolecular photoinitiators (Type I) as well as with tertiary amines for enhanced reactivity.

Modification of the structure of conventional photoinitiator chromophores for improved property requirements is a subject of much interest and activity [13–17]. In this context, structures based on the thioxanthone and benzophenone chromophores have attracted intensive academic and industrial interest [1–5]. Of particular interest is the development of polymeric photoinitiators [17]. Such systems are developed primarily to overcome the problems of initiator migration, lower volatiles and food contamination. However, much controversy has centred on the influence of polymer binding in terms of photoreactivity. This is often dependent upon the site of reaction, nature of the substrate and the nature of the initiator chromophore. In this study we have inter-compared the effect of co-reacting a Types I and II initiator in urethane and melamine acrylate prepolymers on their photochemical and photocuring activities. The structure of the co-reactive Type I initiator is based on 4-(2-hydroxyethoxy)-phenyl-(2-hydroxy2-methylpropyl) ketone (Irgacure 2959, Ciba-Geigy) while the Type II initiator is based on 4-hydroxybenzophenone. The structures of the initiators and their bound prepolymers are shown in A–H. An acrylated version of Iragcure 2959 was also prepared for comparison. The acrylated benzophenone equivalent was also prepared but found to be highly unstable and is, therefore, not mentioned further in the article.

2. Experimental

2.1. Materials

The chemical structures of the photoinitiators, their chemical names and suppliers are shown in Structures A–H. The solvents dichloromethane, pyridine, methylcyclohexane, acetonitrile, isopropanol and compounds used in the synthetic procedures below in this work were obtained from Aldrich Chemical, UK. All the solvents were of HPLC grade quality. The 4-(2-hydroxyethoxy)-phenyl-(2-hydroxy2-methylpropyl)ketone (Irgacure 2959) was obtained from
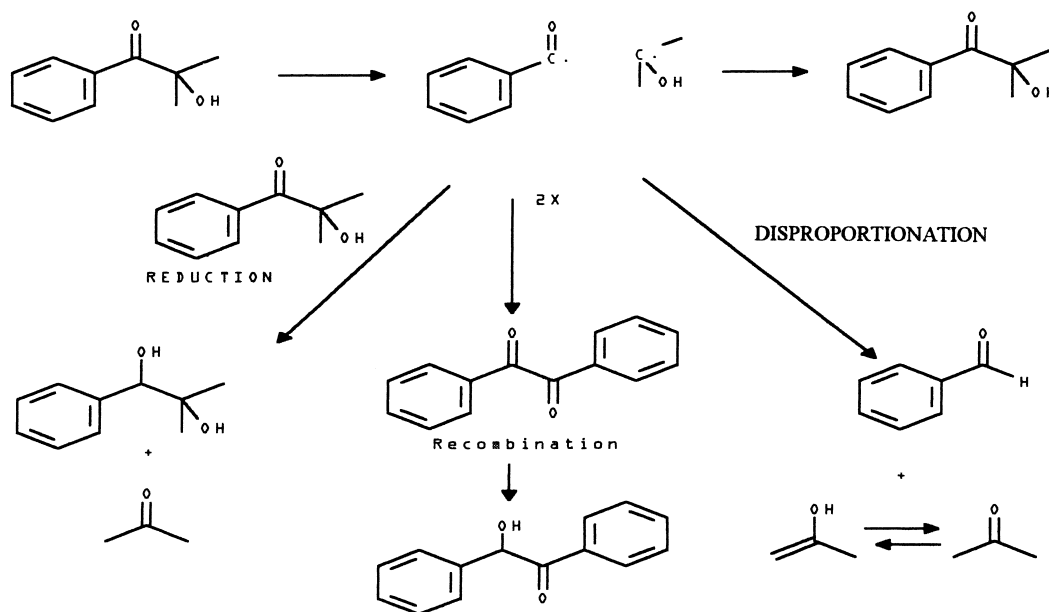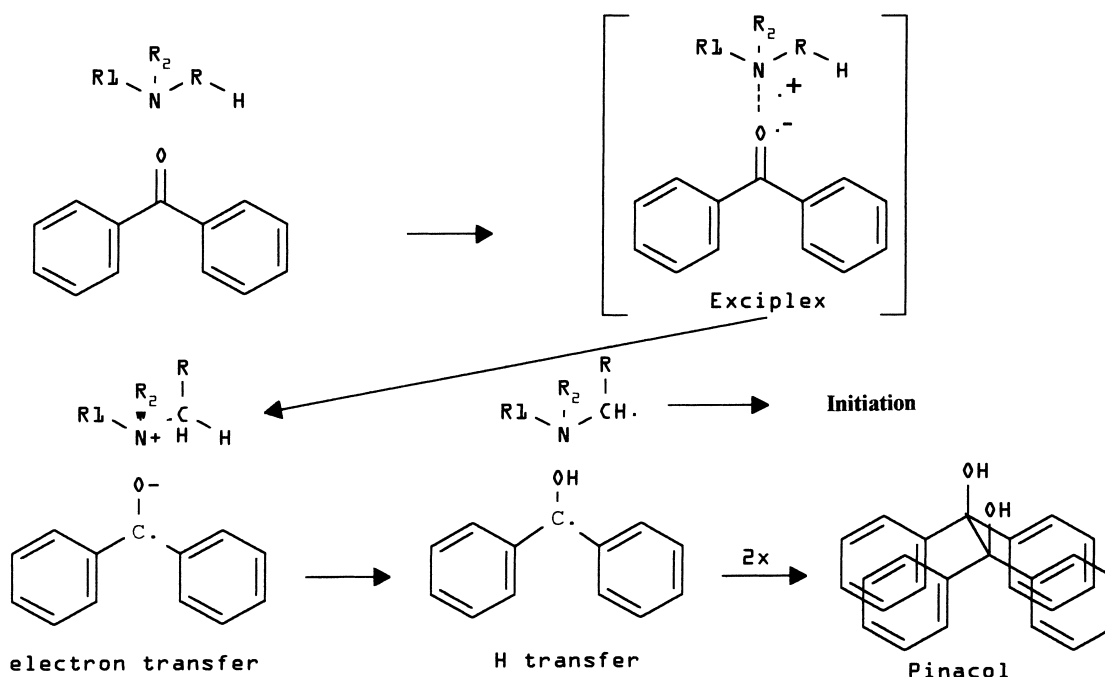
Fig. 1. Photoreactions of α-hydroxy alkylphenones in solution.

Fig. 2. Electron and hydrogen atom abstraction processes between benzophenone and an amine.

Ciba-Geigy, Switzerland. The 4-hydroxybenzophenone was also obtained from Aldrich. The prepolymer resins, water based urethane acrylate, Actilane 890 (melamine acrylate) and Actilane 430 (acrylated trimethylolpropane ethoxylate) were supplied by Akcros Chemicals, Manchester

2.2. Acrylated Irgacure 2959

There are a number of successful established routes to the synthesis of the acrylated Irgacure 2959 all of which gave relatively high yields of >80% depending upon the conditions. In one case the Irgacure 2959 (10 g; 0.045 mole) was dissolved in dichloromethane (50 cm^3) and pyridine (18 cm^3; 5 equivalents) for 30 min at 0°C. A solution of acry-loyl chloride (4.5 cm^3, 1.2 mole excess) in dichloromethane (50 cm^3) was then added dropwise over a period of 20 min keeping the temperature at 0°C. This was followed by the addition of dimethyl aminopyridine (0.054 g; catalyst) fol-lowed by stirring overnight for 18 h at room temperature. The solution was then diluted with water (10 cm^3) and then
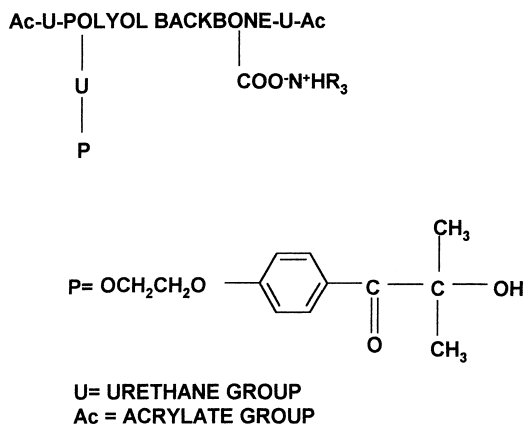
STRUCTURES A-F
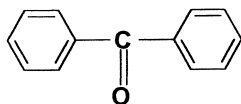
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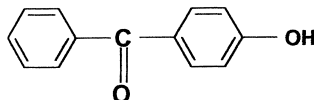
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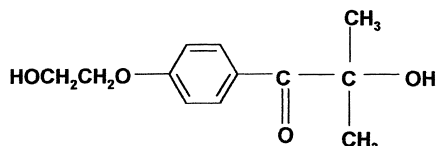
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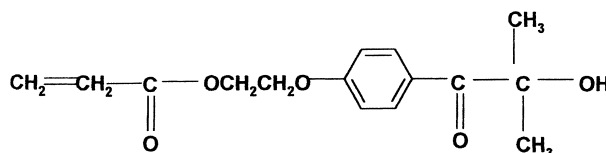
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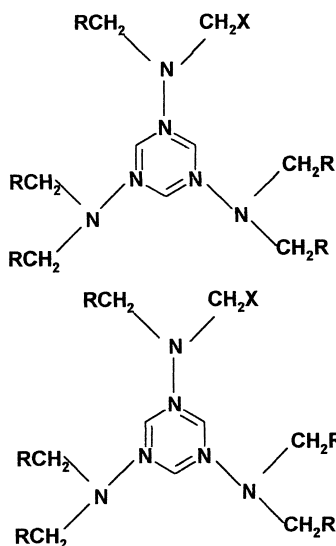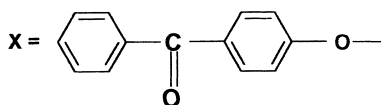
E: 4-HYDROXYBENZOPHENONE MODIFIED MELAMINE ACRYLATE
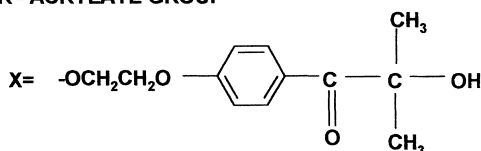
F: IRGACURE 2959 MODIFIED MELAMINE ACRYLATE ACTILANE 890

extracted with ether ($100 \, cm^3$). The extract was then washed with dilute hydrochloric acid ($2 \, M$; $100 \, cm^3$) and copper sulphate solution ($2 \, M$; $100 \, cm^3$) to remove all the pyridine. The product was then repeatedly washed with water ($2 \times 100 \, cm^3$) and dried over anhydrous $MgSO_4$. The solution was then filtered and the solvent removed by rotary evaporation to leave a yellow liquid.

2.3. Co-reactive initiator systems

Melamine acrylates are synthesised normally by a transetherification reaction of hexamethoxymethyl melamine with an appropriate hydroxyalkylacrylate or methacrylate using *p*-toluene sulphonic acid as a catalyst [2]. Here part of the hydroxyalkylacrylate is replaced by the Irgacure 2959 and 4-hydroxybenzophenone in the reaction to give E and F. In the case of the water based urethane polyol acrylate, the polyol is again partly replaced in the reaction by the Irgacure 2959 [2] to give G. Typical established synthetic procedures are already given in the literature for the prepolymers [2]. The amine co-synergist, diethylamine, was co-reacted with the acrylate functionalities on the resins and the acrylated 2959 via the standard Michael addition reaction already established in the literature [2].

STRUCTURES G AND H

Ac-U-POLYOL BACKBONE-U-Ac

U

P

COO⁻·N⁺HR₃

$P=OCH_2CH_2O$

CH₃

C

O

C

OH

CH₃

U= URETHANE GROUP
Ac = ACRYLATE GROUP

G: IRGACURE 2959 MODIFIED WATER BASED URETHANE

H : ACTILANE 890/ACTILANE 430 (ACRYLATED TRIMETHYLOLPROPANE
ETHOXYLATE) FREE IRGACURE 2959

2.4. UV spectroscopy

Absorption spectra were obtained using a Perkin–Elmer Lambda 7 absorption spectrometer on solutions of photoinitiators in three solvents of different polarity in order to study the effect of solvent polarity on the absorption properties of photoinitiators such as hyperchromic and hypochromic effects and hypsochromic and bathochromic shifts. Chloroform, acetonitrile and 2-propanol were the chosen solvents.

UV spectroscopic studies were conducted using quartz cells with a path length of 1 cm. The sample in the cell was subjected to ultraviolet light between 200 to 500 nm and the extinction coefficients were calculated using the Beer-Lambert's Law.

2.5. Phosphorescence measurements

Luminescence measurements are widely used by photochemists to study the photochemical processes occurring by a molecule upon the absorption of light. Phosphorescence measurements provide information related to the lowest lying excited triplet states of a molecule such as its energy, lifetime and phosphorescence quantum yield. Phosphorescence quantum yield measurements provide an idea of the relative number of molecules that emit phosphorescence following the absorption of light. Since the majority of the photochemical reactions are produced from the lowest excited triplet states of a molecule, quantum yield calculations have been extensively used to investigate the photophysical and photochemical characteristics of an extensive variety of chemical systems, such as photoinitiators.

The determination of phosphorescence quantum yields using optically dilute solutions is the most common method currently employed [19]. Phosphorescence quantum yields ($\phi_{phosphorescence X}$) can be calculated by the relative method with the following expression [20,21].

$$\phi_{phosphorescence\ X} = \phi_{phosphorescence\ R} \left(\frac{A_R}{A_X} \right) \left(\frac{\eta_X^2}{\eta_R^2} \right) \left(\frac{Area_X}{Area_R} \right)$$

where $\phi_{phosphorescence R}$ is the known quantum yield of the reference, A_R and A_X are the absorbance at the excitation wavelength of the reference and sample solution, respectively, η_X and η_R are the refractive indices of the solvents used in the reference and sample respectively, $Area_R$ and $Area_X$ are the integrated areas under the corrected emission spectra.

For sample and reference, it is assumed that the integrated luminescence intensity ($Area_R$ and $Area_X$) measured at 77 K is proportional to the fraction of light absorbed (A_R and A_X) measured at room temperature, all geometrical factors are identical, reabsorption and re-emission are negligible and isotropic light is emitted.

Linear proportionality between the phosphorescence emission intensities (area measurements) and the absorbance at the excitation wavelength $\lambda = 290$ nm has been examined over a range of optical densities. Similar low absorbance values around 0.05 at the excitation wavelength $\lambda = 290$ nm in methyl cyclohexane have been used in both reference and sample in order to avoid the need for any correction factor due to the systematic error created by the power series approximation (5% systematic error for $AL = 0.043$) [21].

Absorbance values were obtained from more concentrated solutions of known absorbance (absorbance around 1) by diluting the sample by a certain factor. This method presented

a higher accuracy than the direct spectroscopic measurement due to the error obtained when measuring low absorbance values (10% relative error is obtained when measuring the absorbance of a solution around 0.05 considering a detector sensitivity around ± 0.005) [19].The solvent selection is an important aspect, which should be considered when measuring phosphorescence quantum yields at 77 K since solvents of high purity are required for the formation of a transparent glass [20]. Traces of water should be avoided since they form non-transparent/cracked glasses. Absolute ethanol and methylcyclohexane form transparent glasses and provide reproducible results [21,22]. Triplet lifetimes can be calculated from the following first order rate equation:

$$\frac{\mathrm{d}I_t}{\mathrm{d}t} = kI_t \int \frac{\mathrm{d}I}{I} = \int k\,\mathrm{d}t \Rightarrow \ln I_t = \ln I_0 + k\,t$$

where I_t is the phosphorescence intensity at time t, I_0 is the phosphorescence intensity at time zero and k is kinetic constant. The triplet lifetime ι can be defined as the time required for the intensity to decrease to a value $I_\iota = 1/e\ I_0$. Substitution of $I_{I\iota} = 1/e\ I_0$ in the equation shows that the triplet lifetime is obtained from the inverse of the kinetic constant k.

$$\ln I_t = \ln I_0 + kt \Rightarrow I_t = I_0 e^{-kt} \text{ and at } t = \tau\ I_\tau = \frac{1}{e}I_0$$

$$= I_0 e^{-k\tau} \Rightarrow \tau = k^{-1}$$

Benzophenone has been used as the reference assuming a phosphorescence quantum yield of 0.74 in absolute ethanol at 77 K [19]. Phosphorescence quantum yields and triplet lifetimes were measured in ethanol with a Perkin–Elmer LS-5 luminescence spectrometer. All the spectra were corrected using a Perkin–Elmer IBM-compatible FL-WINLAB package with an appropriate file for this purpose.

2.6. Time resolved absorption spectroscopy set-ups

End-of-pulse transient absorption spectra on the millisecond time scale were obtained using a kinetic flash photolysis apparatus equipped with two xenon-filled flash lamps (operated at 10 kV) and a 150 W tungsten-halogen monitoring source. Transient decay profiles were stored using a Gould Model 1425 storage oscilloscope. Solutions were deoxygenated using white spot nitrogen gas (<5 ppm O_2).

Laser flash photolysis experiments were carried out using a frequency-quadrupled neodymium laser (J.K. Lasers Ltd.) which delivered 12 ns pulses of 266 nm radiation of energies up to 50–60 mJ. Transient absorption changes were measured by illuminating the quartz reaction cell (1 cm path-length) with light from a pulsed xenon lamp. Wavelength selection was achieved with a diffraction grating, high irradiance monochromator with a 5 nm band-width. Kinetic changes in the light signal at preselected wavelengths were detected and amplified using a Hamamatsu R1477 photo-multiplier prior to collection by a programmable digi-

tal oscilloscope (H P54510A). Solutions were deoxygenated using white spot nitrogen gas (<5 ppm O_2).

2.7. Real time infrared spectroscopy RTIR and photocuring

Different techniques have been used for measuring the reactivity and curing of UV systems. Both direct and indirect methods of analysis have been used in order to evaluate and compare the reactivity of photoinitiators. Real time infrared spectroscopy [11,12,23] (RTIR) is based on the decrease in the vinyl absorbance at 812 cm^{-1} during the polymerisation reaction. The sample is polymerised with UV radiation whilst the infrared beam measures the decrease of absorbance.

2.8. Photocuring

Coatings of 12 and 50 μm thickness were applied to 270 gsm of white-lined manilla paper board and cured under a medium pressure mercury vapour lamp (120 W/cm^2) [23–25]. Each pass under lamp on a conveyor belt corresponds to an energy output of 205 mJ/cm^2. The base formulation was a blend of 55/45 melamine acrylate (Actilane 890)/acrylated trimethylolpropane ethoxylate (Actilane 430). The photointiators were incorporated at such levels that the percentage added remained constant in terms of molar equivalents. The number of passes under the lamp required to achieve full cure was assessed by the thumb screw test i.e., application of ones thumb with mild pressure does not distort the coating.

2.9. RTIR

The irradiation source used was a Xenon lamp ILC 302UV(Laser Lines Ltd.) connected to a dispersive infrared spectrophotometer [26,27]. The lamp has a switched filter to irradiate with light above or below 400 nm using a fibre optic cable. A sample of the resin was positioned between two sodium chloride salt plates covered with two pieces of low density polyethylene film (50 μm) using a Teflon separator to give a film thickness of 12 μm. Two polyethylene films were placed in the reference beam in order to subtract the polyethylene absorption from the sample.

Plots of conversion percentage and polymerisation rate versus irradiation time with light <400 nm, were obtained. The polymerisation rates were calculated from the slope of % conversion versus time plots at short irradiation times.

3. Results and discussion

3.1. Photochemical crosslinking data

The photoactivities of the different photoinitiators free, acrylated and bound are examined in commercial urethane

Table 1
RTIR data from the photopolymerisation of Irgacure 2959 and 4-Hydroxybenzone structures 5% w/w in an Actilane 890/430 resin mixture (55/45 w/w)[a]

Actilane 890/430 (55/45 w/w)	Rp max (mol L^{-1} S^{-1})	% conversion at the rate of 35 s	% unsaturation at the rate of 35 s
Acrylated 2959 (12 μ)	2.46	52.7	47.3
Acrylated 2959 (50 μ)	3.45	58.5	41.5
Acrylated 2959 and amine Synergist (12 μ)	2.49	65.5	34.5
Acrylated 2959 and DEA (12 μ)	2.51	66.8	33.2
Free Irgacure 2959 (12 μ)	2.63	61.3	38.7
Free 2959 + Amine synergist (12 μ)	8.66	85.7	14.3
Built in Irgacure 2959 (12 μ)	2.1	37.5	62.5
Built in 2959 + Amine synergist (12 μ)	8.6	56.7	43.3
Free 4-OH Benzophenone (12 μ)	1.1	32.0	68.0
Free 4-OH Benzophenone + Amine Synergist (12 μ)	6.6	52.5	47.5
Built in 4-HO Benzophenone (12 μ)	0.4	13.3	86.7
Built in 4-HO Benzophenone+ amine synergist (12 μ)	5.6	64	36

[a] DEA: diethylamine added as a molar equivalence to the Acrylated 2959 via prior co-reaction with its acrylate group through the Michael Addition reaction. Amine synergist: 4.5% w/w of a diethylamine co-reacted acrylate monomer.

Table 2
Photocuring of Actilane 890 and 430 (55 45 w/w when mixed) with free and Acrylated Irgacure 2959[a]

Formulation	No. of passes 12 μ	No. of passes 50 μ
Act. 890/430 6.8% w/w free Irgacure 2959	1	1
Act. 890/430 8.4% w/w Acrylated Irgacure 2959	8	4
Act. 890/430 8.4% w/w Acrylated Irgacure 2959 4.5% w/w Amine synergist	1	1
Act. 890/430 8.4% w/w Acrylated Irgacure 2959 DEA	1	1
Act. 890 6.8% w/w free Irgacure 2959	1	1
Act. 890 8.4%% w/w Acrylated Irgacure 2959	3	2
Act. 430 6.8% w/w Acrylated Irgacure 2959	2	1
Act. 430 8.4% w/w Acrylated Irgacure 2959	13	5

[a] DEA: diethylamine added as a molar equivalence to the Acrylated 2959 via prior co-reaction with its acrylate group through the Michael Addition reaction. Amine synergist: 4.5% w/w of a diethylamine co-reacted acrylate monomer. Lamp energy: 205 mJ/cm^2.

and melamine acrylate formulations in such a way that the free initiator is compared at a molar equivalency of the bound system. Thus, bound initiator resins are mixed at the equimolar amounts with non-initiator containing unreacted resin. Two methods have been utilised in the analysis of photocuring behaviour. The first relates to RTIR spectroscopy where the rate of decrease in the vinyl absorption for the resins at 812 cm^{-1} is measured with real time upon irradiation. The second method simply relates to photocuring under a Hg lamp while the sample is moving on a conveyor belt at a set speed. The coating is then examined after each pass for softness by twisting the coating with the application of the operators thumb. It is a crude and highly subjective test but, is nevertheless, highly regarded in the field for industrial comparisons.

The complete set of RTIR data is shown in Table 1 for the rate of propagation (Rp), % conversion and % residual unsaturation. The Rp values provide useful information on the initial rate of cure which can often be a sharp rising slope within a short time period followed by a much slower gradual curvature. The latter is usual and normally associated with increasing viscosity of the cured resin restricting radical mobility. The film thickness effect was examined in the first instance for the acrylated 2959 resin systems where it is seen that the thicker coating at this level exhibits the faster cure speed. All comparisons were made at the 12 μ

thickness. For the Irgacure 2959, it is noted that the conversion rate for the free initiator is greater than that for either the acrylated or bound initiator molecules. In fact, the bound initiator was found to be the least effective system. The addition of an amine co-synergist, bound into the resins or acrylated 2959 via the Michael Addition, was interesting since it only appeared to slightly increase the efficiency of the acrylated initiator. However, when added to the free and bound initiator containing resins the rates of conversion were found to be enhanced to the same extent. Thus, addition of an amine co-synergist essentially removed the differential between the free and bound initiator in terms of curing efficiency.

The benzophenone chromophore was found to be much less effective than the Irgacure 2959 systems. Co-reaction of the 4-hydroxybenzophenone reduced photoactivity compared with that of the free initiator molecule. Again, the addition of the amine co-synergist significantly enhanced the rates of curing. In this case, while the Rp value for the free initiator was higher than that for the bound initiator the % conversion and unsaturation values were reversed. The bound benzophenone initiator with the amine co-synergist was more effective in terms of overall cure.

The overall commercial photocuring rates in terms of number of passes are compiled in Tables 2–4. A pass rate of 1 is the fastest cure. Table 2 shows the cure effects for free

Table 3
Photocuring of Actilane 890 : 430 (55 : 45) with free and bound Irgacure 2959 (2 μ)[a]

% Iragacure 2959 (w/w)	No. of passes free	No. of passes bound
2	11	13
3	7	8
4	7	3
5	2	2
7	1	2
8	1	1

[a] Lamp energy: 205 mJ/cm^2.

Table 4
Photocuring of Actilane 890 : 430 (55 : 45) with free and bound 4-Hydroxybenzophenone (12 μ)[a]

% 4-Hydroxybenzophenone (w/w)	No. of passed free	No. of passes bound
0.5	12	10
1	9	7
2	4	3
3	3	2
4	2	1
5	2	1

[a] Lamp energy: 205 mJ/cm^2.

Table 5
Effect of Benzophenone of the photocurring of a Actilane 890 : 430 (55 : 45) with Acrylated Irgacure 2959 (12 μ)[a]

% Benzophenone	No. of passes 4% w/w Irgacure 2959	No. of passes No Irgacure 2959
0	7	–
1	3	–
2	2	–
3	1	–
4	1	8
5	–	3

[a] Lamp energy: 205 mJ/cm^2.

and acrylated 2959 systems. Essentially, the data supports the RTIR analysis. The free Irgacure 2959 was found to be more effective than the acrylated 2959 system in mixed and separate resins based on Actlane 890 and 430. This differential is again, seen to be removed and efficiency enhanced in the presence of an amine co-synergist with the acrylated 2959. Table 3 illustrates the effect of bound and free Irgacure 2959 on the rate of photocuring with initiator concentration. Upto 8% w/w of photoinitiator is quite common in many coating systems, especially inks. The data shows that up to 4% w/w of initiator the bound system is less effective but becomes comparable at and above 5% w/w. Table 4 compares the free and bound forms of 4-hydroxybenzophenone. In this case, the bound systems give overall better cure at all concentration levels up to 5% w/w in contrast to the RTIR results.

Type I and Type II photoinitiators are often used in admixture in order to enhance cure characteristics where pigment systems are employed that block much of the incident irradiation. Table 5 illustrates the effect of increasing the addition of benzophenone on the photocuring activity of the acrylated 2959 in the Actilane 890/430 mixture. Benzophenone itself exhibits low activity in this system (without amine) until a 5% w/w concentration is achieved. However, with 4% w/w of the acrylated Irgacure 2959 the cure rate is significantly enhanced with 3% w/w of benzophenone effecting complete cure in one single pass. Here the benzophenone is believed to enhance cure through energy transfer to the Irgacure molecule enhancing the rate of scission to give benzoyl radicals.

3.2. UV spectroscopic results

The study of the spectral absorption shifts of the photoinitiators with solvents of varying polarities can help to identify the nature of the different absorption transitions occurring upon the absorption of light. Solvent shifts arise because of differences in the polarities of the ground and excited states. The polarity of an nπ excited state is less than that of the corresponding ground state - hence the blue shift in the absorption maximum of the n-π^* transition on increasing the solvent polarity. The reverse is the case for the π-π^* transition.

The absorption properties of the bound and acrylated initiators are shown in Table 6 at the absorption maxima. Essentially, for all the molecules studied here, there is a small blue shift in the absorption spectrum from chloroform to acetonitrile. This is indicative of an nπ^* transition but is undoubtedly mixed with a strongly absorbing main $\pi\pi^*$ transition owing to the intense nature of the extinction coefficient. There is also a weak electron withdrawing effect on binding both benzophenone and Irgacure 2959 chromophores to the resins. This would, in effect, reduce the absorption capacity of the molecules and reduce their activity which is what is observed in the absence of amine co-synergist in the RTIR analysis. Only in the case of the commercial curing does the benzophenone have an enhanced effect.

3.3. Phosphorescence results

Phosphorescence emission maxima, quantum yields and emission lifetimes in ethanol of the photoinitiator systems are compared in Table 7. The photoinitiators give rise to varying degrees of intersystem crossing ISC as reflected by their differing phosphorescence quantum yields. Substitution of benzophenone with the 4-hydroxy group reduces the emission quantum yield due to the partial electron donating effect of the oxygen atom, but also reduces the emission lifetime. The binding of 4-hydroxybenzophenone into the Actilane 890 reduces the emission quantum yield further but restores the emission lifetime to a value comparable to that of benzophenone. Enhanced electron donation into the chromophore by the resin units may increase the $\pi\pi^*$ character of the molecule. Alternatively, triplet energy transfer or intramolecular quenching by the bound resin units

Table 6
Absorption maxima and extinction coefficients of 4-Hydroxybenzophenone and Irgacure 2959 structures

Structures	Chloroform λ max (nm)	log ϵ	2-Propanol λ max (nm)	log ϵ	Acetonitrile λ max (nm)	log ϵ
A (Benzophenone)	252	4.2	252	4.0	246	4.3
B (4-Hydroxybenzophenone)	285	4.3	295	4.3	284	4.2
C (Irgacure 2959)	277	4.3	276	3.9	273	4.5
D (Acrylated 2959)	275	4.0	271	3.8	271	4.0
E (Bound 4-HHoBZ/ACT. 890)	272	3.7	279	3.2	272	4.2
F (Bound 2959/ACT. 890)	272	3.8	272	3.9	272	4.1
G (Bound 2959/Urethane)	276	4.2	272	3.7	271	3.8
H (Free 2959/ACT. 890 : 430)	277	3.6	273	3.7	273	3.5

Table 7
Phosphorescence Properties of 4-Hydroxybenzophenone and Irgacure 2959 structures (EX = 290 nm)

Structures	Emission λ max (nm)	Phosphorescence quantum yield ϕ_p	Emission lifetime τ (ms)
A (Benzophenone)	413 444 477 518	0.74	5.17
B (4-Hydroxybenzophenone)	417 446 478	0.42	2.67
C (Irgacure 2959)	406 434 466	0.05	6.38
D (Acrylated 2959)	406 434	0.06	2.18
E (Bound 4-HOBZ/ACT. 890)	417 447 478	0.16	6.15
F (Bound 2959/ACT.890)	407 436	0.02	21.87
G (Bound 2959/Urethane)	405 432	0.01	4.82

could quench the emission. Despite the substitutional effects the triplet lifetimes still remain relatively low consistent with the lowest triplet state remaining essentially $n\pi^*$ in character thus retaining the photoactivity of the benzophenone chromophore in terms of its hydrogen atom abstraction capability.

The Irgacure 2959 has a relatively low emission quantum yield which may be consistent with its photoreactivity via scission (Fig. 1). Previous studies using laser flash photolysis have shown that the triplet state is not the precursor to this reaction [28]. Binding the Irgacure 2959 to the Actilane 890 and the urethane acrylate reduces the emission quantum yields. In the former case the emission lifetime is significantly enhanced but reduced in the latter. Here different molecular rigidity and substitutional patterns may play a complex role. Acrylation of the Irgacure 2959 has little effect on the emission quantum yield but does reduce the emission lifetime.

3.4. Flash photolysis results

End of pulse transient absorption spectra of the photoinitiators in isopropanol are compared in Table 8 and in Fig. 3 where absorption spectra and maxima are compared and recorded in the UV region 300–400 nm. Bound 4-hydroxybenzophenone exhibits a higher maximum transient absorption spectrum than its free derivative, resulting from the formation of a high concentration of transient intermediates. The spectra of benzophenones are normally assigned to that of the ketyl radical formed by abstraction of a hydrogen atom by the excited triplet state of the chromophore from isopropanol as depicted in Fig. 2. Thus, the higher concentration of ketyl radicals in the case of the bound system suggests greater reactivity which is partly re-
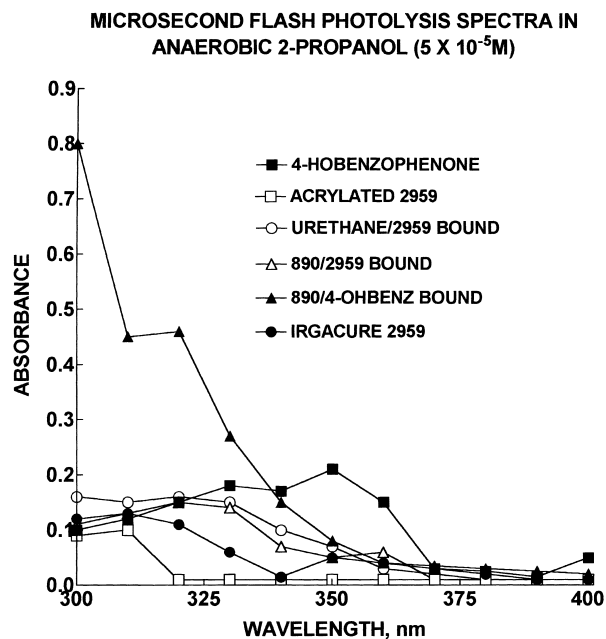

Fig. 3. End of pulse transient absorption spectra produced on microsecond flash photolysis in anaerobic 2-propanol (5×10^{-5} M) for (■) 4-hydroxybenzophenone, (▲) Actilane 890 bound 4-hydroxybenzophenone, (□) acrylated Irgacure 2959, (○) Urethane bound Irgacure 2959, (●) Irgacure 2959 and (△) Actilane 890 bound Irgacure 2959.

flected in the higher conversion data during photocuring (Table 4).

In the case of the Irgacure 2959 weakly absorbing benzoyl radicals are formed [28] with maxima at 310 nm. Binding or acrylation was found to have little influence on the transient absorption maximum and this is clearly reflected in the absence /reduction in photoactivity during photocuring.

Table 8
Microsecond flash properties of 4-Hydroxybenzophenone and Irgacure 2959 structures in nitrogen saturated 2-propanol

Strucures	λ max (nm)	Absorption max
B (4-Hydroxybenzophenone)	330	0.18
H (4-Hydroxybenzophenone bound ACT. 890)	315	0.48
C (Irgacure 2959)	310	0.13
D (Acrylated 2959)	310	0.11
F (2959 ACT. 890)	310	0.13
G (2959 Urethane)	315	0.17
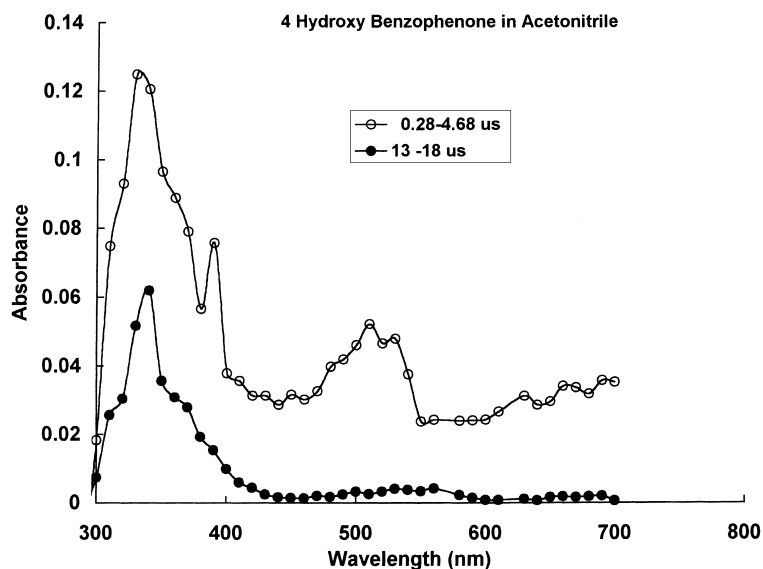
Fig. 4. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for 4-hydroxybenzophenone at (○) 0.28–4.68 ms and (●) 13–18 ms.
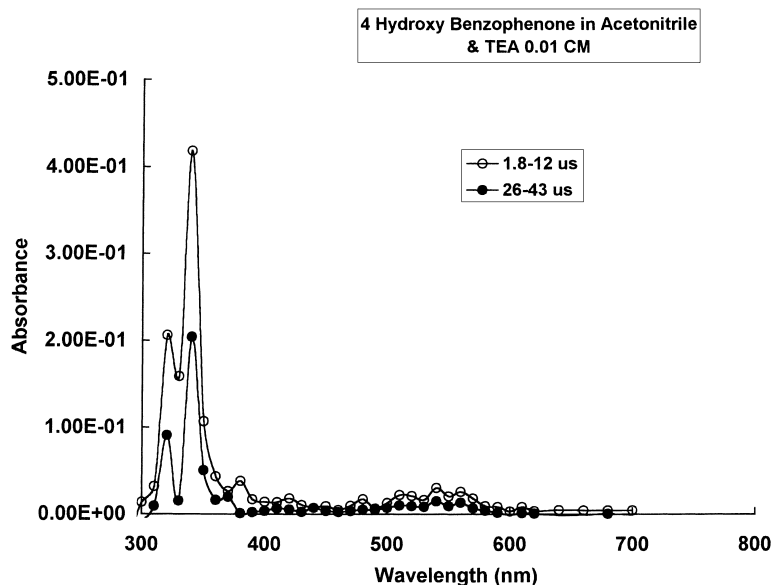
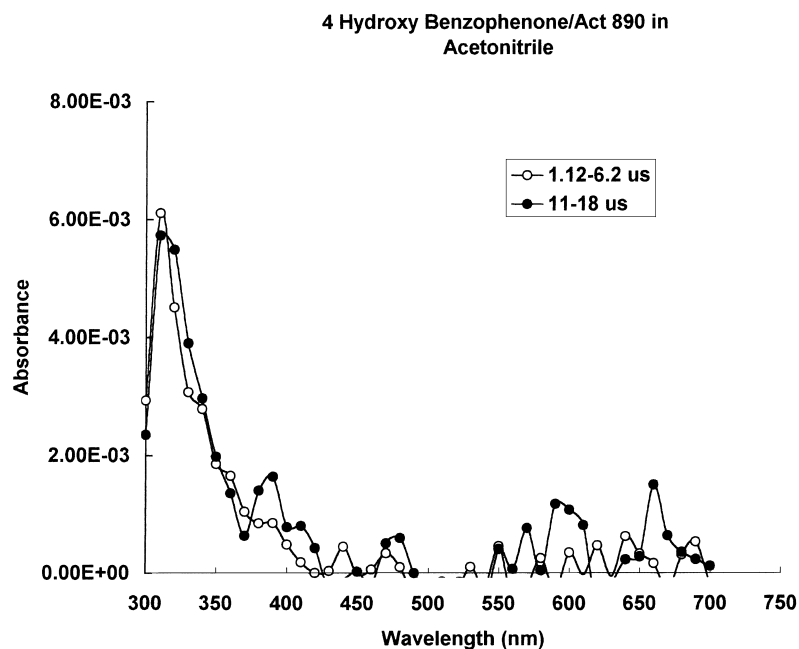

Fig. 5. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for 4-hydroxybenzophenone at (○) 1.8–12 μs and (●) 26–43 μs with 0.01 cm^3 of triethylamine.

4 Hydroxy Benzophenone/Act 890 in Acetonitrile

Fig. 6. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for 4-hydroxybenzophenone bound Actilane 890 at (○) 1.1–6.2 μs and (●) 11–18 μs.

Table 9
Nanosecond laser flash properties of 4-Hydroxybenzophenone and Irgacure 2959 structures in Acetonitrile

Structures	λ max (nm)	Absorption max	First order rate const. $10^5 \, s^{-1}$
B (4-Hydroxybenzophenone)	330	0.12	1.94
B 4-Hydroxybenzophenone+TEA ($0.01 \, cm^3$)	340	0.43	1.18
H (4-Hydroxybenzophenone bound ACT. 890)	310	0.006	11.7
H (4-Hydroxybenzophenone bound ACT. 890) + TEA ($0.01 \, cm^3$)	310	0.0062	2.14
C (Irgacure 2959)	310	0.042	1.25
C (Irgacure 2959) + TEA ($0.01 \, cm^3$)	310	0.028	1.39
D (Acrylated 2959)	310	0.0026	2.94
D (Acrylated 2959) + TEA ($0.01 \, cm^3$)	340	0.02	2.67
F (2959 ACT. 890)	320	0.0046	8.08
F (2959 ACT. 890) + TEA ($0.01 \, cm^3$)	310	0.011	2.63
G (2959 Urethane)	300	0.016	0.39
G (2959 Urethane) + TEA ($0.01 \, cm^3$)	300	0.024	0.29
H (Free 2959/ACT.890 : 430)	310	0.012	0.67
H (Free 2959/ACT.890 : 430) + TEA ($0.01 \, cm^3$)	320	0.012	0.26

3.5. Laser flash photolysis

End of pulse transient absorption spectra of the 4-hydroxybenzophenone systems on the nanosecond time scale are shown in Figs. 4–6 while those for the Irgacure 2959 systems are shown in Figs. 7–12. Spectra at two time delays are shown and all the absorption data and first order kinetic rate constants for the transient decays are compiled in Table 9. The kinetics of decay are primarily first order and these are quoted for comparative purposes in terms of transient decay and growth lifetimes. The transient absorption maximum of the 4-hydroxybenzopheone on nanosecond laser flash photolysis has two maxima at 330 and 500 nm coupled with a first order decay profile that

is typically associated with the triplet–triplet absorption [13,15,18]. In acetonitrile there appears to be little decay to give any residual product (Fig. 4). The addition of an amine co-synergist (triethylamine) gave rise to a significant enhancement in the transient absorption spectrum (Fig. 5) with a strong doublet at 320 and 340 nm and much weaker absorption at 550 nm. The lifetime of the transient is also increased and may, in part, be associated with the formation of the radical anion associated with triplet exciplex formation between the amine and aromatic ketone groups (Fig. 2). In radiation curing this reaction accounts, in the main, for the enhanced photoactivity of amine co-synergists. Binding the 4-hydroxybenzophenone to the Actilane 890 results in a marked quenching of the triplet-triplet absorption and is
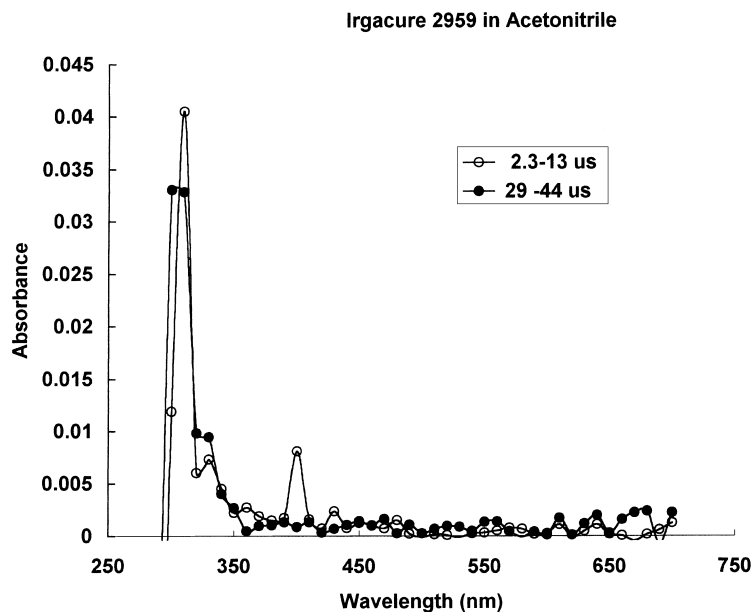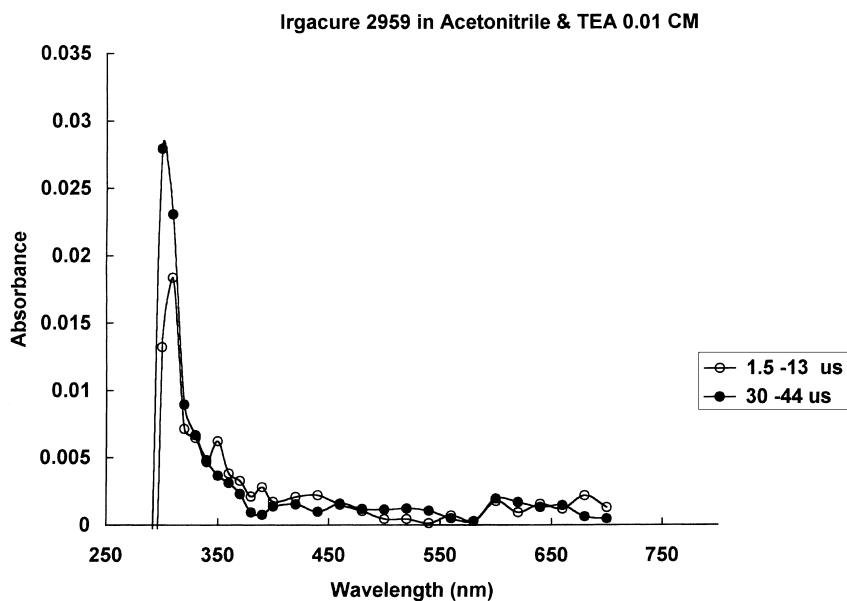
Irgacure 2959 in Acetonitrile

Fig. 7. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for Irgacure 2959 at (○) 2.3–13 μs and (●) 29–44 μs.

Irgacure 2959 in Acetonitrile & TEA 0.01 CM

Fig. 8. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for Irgacure 2959 at (○) 2.3–13 μs and (●) 29–44 μs with 0.01 cm^3 of triethylamine.

consistent with the lower phosphorescence emission quantum yields (Fig. 6). This triplet quenching also results in a significant enhancement in the triplet–triplet decay (Table 9). Quenching or possibly high photoreactivity may be operative. The addition of the triethylamine to the bound benzophenone-Actilane 890 had little influence on the transient absorption maximum. However, the amine did significantly enhance the triplet–triplet lifetime and restore it to the original value for the free molecule (Table 9). Exciplex formation, therefore, must still be operative for the

bound system where binding/association of the amine to the ketone is strong. Thus, strong intramolecular quenching in this case may reduce the triplet–triplet absorption possibly through intramolecular hydrogen atom abstraction giving rise to increased free radical formation as seen by microsecond flash photolysis.

Transient absorption spectra for the Irgacure 2959 are clearly different giving rise directly to the formation of the benzoyl radical which absorbs in the region 300–350 nm [28]. In fact, the absorption maxima in this laser study

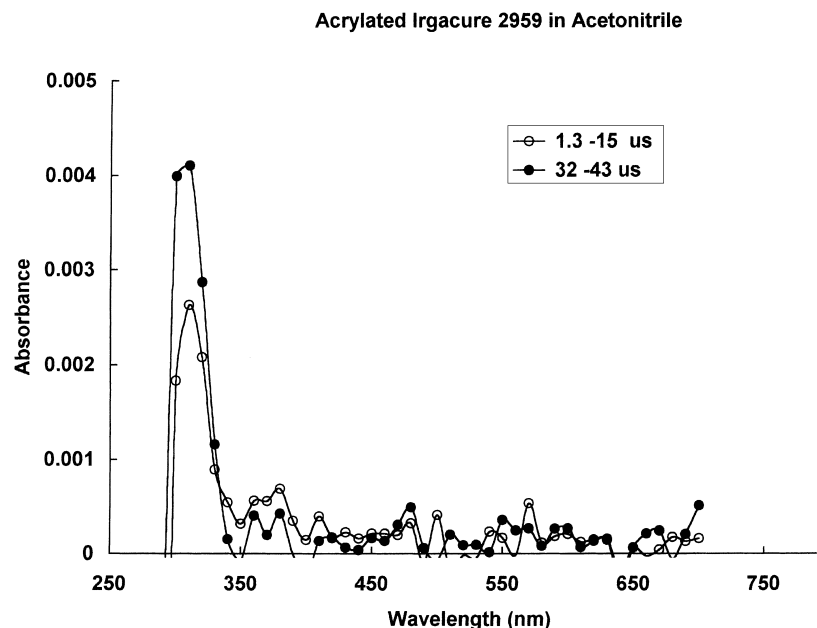**Acrylated Irgacure 2959 in Acetonitrile**

Fig. 9. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for acrylated Irgacure 2959 at (○) 1.3–15 μs and (●) 32–43 μs.
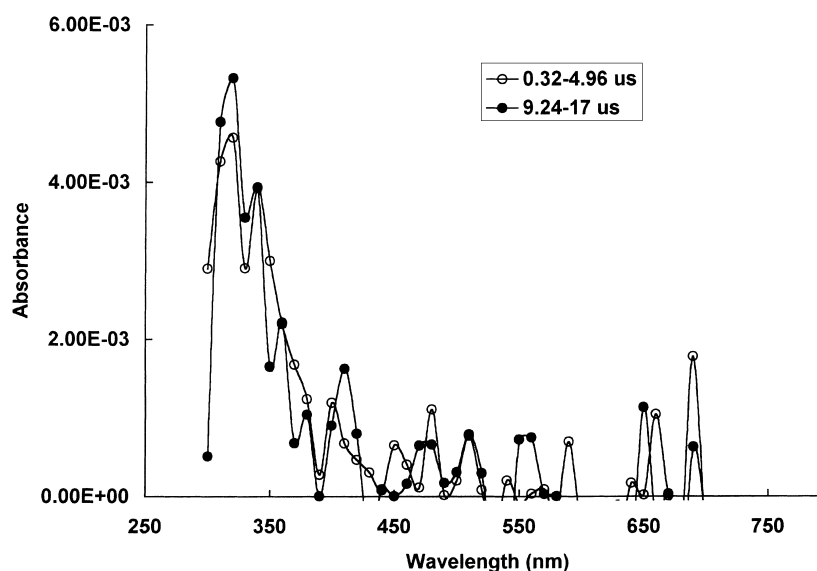

Fig. 10. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for Actilane 890 bound Irgacure 2959 at (○) 0.32–5.0 μs and (●) 9.2–17.0 μs.

matches that observed during microsecond flash photolysis. The sharp radical spectrum for the free molecule is shown in Fig. 7. The transient is also relatively long-lived and grows in following the laser pulse. The addition of the triethylamine reduced radical formation and increased the radical growth rate where an increase in transient was observed at longer time delays (Fig. 8). Acrylation of the Irgacure 2959 significantly quenched benzoyl radical formation and reduced photoactivity (Fig. 9). The first order growth rate was also enhanced. The addition of triethylamine to the acrylated 2959,

however, increased transient formation and its first order rate constant. The binding of Irgacure 2959 to Actilane 890 also quenched radical formation and markedly increased the rate constant (Fig. 10) showing a fast grow in after the initial pulse. Radical formation was also quenched (reduced) when bound to the urethane system (Fig. 11) and may account for reduced photoactivity on photocuring and RTIR. The addition of the triethylamine restored radical formation (Table 1) thus accounting for the increased photocuring rates. Of particular interest was the effect of adding the Actilane resins

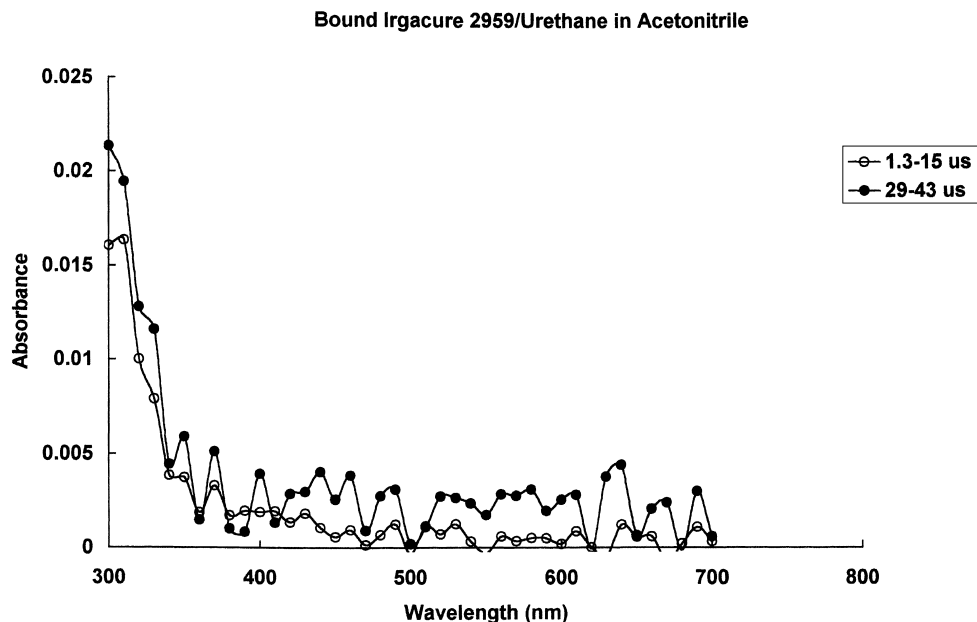**Bound Irgacure 2959/Urethane in Acetonitrile**

Fig. 11. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for a urethane bound Irgacure 2959 at (○) 1.3–15.0 μs and (●) 29–44 μs.

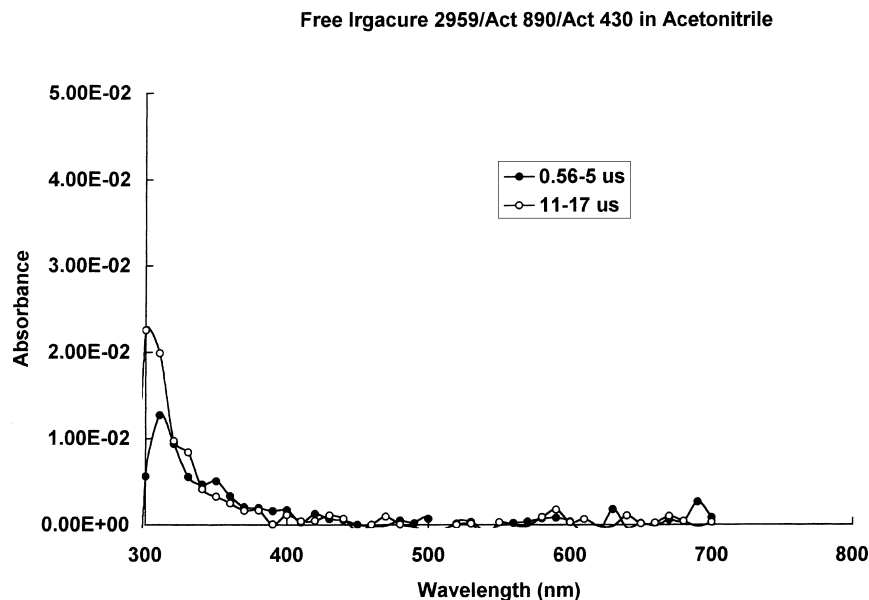**Free Irgacure 2959/Act 890/Act 430 in Acetonitrile**

Fig. 12. End of pulse transient absorption spectra produced on nanosecond laser flash photolysis in anaerobic acetonitrile for Free Irgacure 2959 with Actilane 890 and Actilane 430 mixture (55 : 45 w/w) at (○) 0.6–5 ms and (●) 11–17 ms.

to the free Iragcure 2959 on transient formation. The data in Table 9 and Fig. 12 show weak transient formation due to quenching although not as effective as binding coupled with a significant increase in radical lifetime; lowering of the first order rate constant. The addition of the triethylamine lowers the rate constant further.

Thus, quenching of the triplet in the case of the benzophenone chromophore may result in enhanced ketyl radical formation and hence reactivity whilst direct quenching of the benzoyl radical causes reduced photoactivity.

4. Conclusions

Photocuring studies indicate that whilst binding the Type I photointiator reduced its efficiency, the Type II photoinitiator was enhanced. The presence of an amine co-synergist however, generally eliminated these differentials. Acrylation of the Irgacure 2959 also reduced photoactivity. Absorption spectroscopy indicates the presence of a strongly absorbing $n\pi^*$ transition in the far UV region for both chromophore types which undergoes a blue shift on binding to the prepoly-

mer. Phosphorescence spectra, lifetimes and quantum yields also indicate the presence of low lying triplet $n\pi^*$ states for both types of chromophore. Microsecond flash photolysis identified the formation of benzoyl radicals in the case of the Type I system with a small enhancement in radical formation on binding. The Type II system gives ketyl radicals formed by hydrogen atom abstraction which are enhanced in the bound resin system. The latter accounts for increased photoactivity for the bound Type II system. Nanosecond laser flash photolysis experiments identified the triplet–triplet absorption in the case of the Type II initiator. In the presence of a tertiary amine (triethylamine), the transient absorption and lifetime are significantly enhanced due to exciplex formation. However, binding the benzophenone initiator to the resin significantly quenches the transient absorption and significantly reduces its lifetime. In the case of the Type I initiator the benzoyl radical was observed directly confirming the microsecond flash photolysis data. Binding of the initiator to the melamine acrylate resin also reduced benzoyl radical formation as well as the radical lifetime. This may account for the reduced photoactivity of the Type I bound initiator. Radical formation was also reduced when bound to the urethane acrylate but the lifetime was enhanced. For the initiator bound resin systems the presence of an amine co-synergist enhanced benzoyl radical formation.

Thus, the data suggests that whilst binding of a Type II photointiator may have benefits in photocuring, the binding of a Type I initiator has the opposite effect. However, grafting of the initiator chromophore has significant benefits in terms of lower migration rates and less volatiles following the curing process. From an environmental point of view such benefits out-weigh the obvious advantages of high cure rate. On the other-hand as the data indicates initiator blends may compensate for the reduced cure giving both the benefits of fast cure and less environmental concerns.

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