

Type II polymeric photoinitiators (polyetherimides) with built-in amine synergist

R. Stephen Davidson^a, Aylvin A. Dias^a, Derek R. Illsley^b

^a *The Chemical Laboratory, The University of Kent, Canterbury, Kent CT2 7NH, UK*

^b *Coates Lorrilleux Research, Cray Avenue, Orpington, Kent BR5 3PP, UK*

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Abstract

In this work, a photoinitiating system is described where both the benzophenone chromophore and the tertiary amine synergist are attached to a polymer backbone (i.e. amine-terminated polyetherimides).

Keywords: Polymeric photoinitiators; Built-in amine synergist; Benzophenone; Type II photoinitiators

1. Introduction

In recent years the effort to reduce the volatile migratable components in UV radiation cured coatings and inks has led to increased interest in polymeric photoinitiators. Polymeric photoinitiators are expected to offer certain advantages over their monomeric counterparts see Ref. [1].

(1) The use of polymeric photoinitiators provides a means of tying-in the photoinitiator-derived migratables that occur upon photolysis.

(2) Polymeric photoinitiators may display higher initiating efficiency owing to intramolecular energy migration. Energy migration may occur between adjacent chromophores (energy hopping) or between non-adjacent chromophores (in a loop).

(3) The use of a suitable polymer backbone or copolymer may provide a useful tool for tailoring the solubility properties of the polymer.

When considering the two types of photoinitiating systems, the Norrish type I (α -cleavage) photoinitiators would have to generate two or more macroradicals in order to fulfil the first criterion mentioned above, i.e. reduced migratables. Similarly, Norrish type II (hydrogen-abstracting) photoinitiators would require both the chromophore and the synergist component to be macromolecular.

Earlier we reported the use of benzophenone-based polyetherimides as a way of reducing the photoinitiator-based migratables [2]. However, the amine synergist was found to be the major extractable component of the cured films. We now describe a similar photoinitiating system where both the

benzophenone chromophore and the tertiary amine synergist are attached to a polymer backbone (i.e. amine-terminated polyetherimides).

Already, extensive work has been done on polymeric photoinitiators bearing photosensitive groups that generate free radicals or undergo H-abstraction [3–9].

Attaching benzophenone and tertiary amine (exciplex-based co-initiating) systems to polymeric carriers began in the mid-1970s [10]. However, much of the comprehensive work was undertaken in the early 1980s by Carlini and coworkers [11–14]. In a series of publications involving the study of polymeric photoinitiators bearing side-chain benzophenone and tertiary amine units, certain structure–activity relationships were brought to light.

Using a polymerizable benzophenone and a tertiary amine, e.g. acryloxybenzophenone and dimethylaminostyrene, homopolymers and copolymers were prepared that contained both synergist and chromophore pendant to the polymer backbone. The trend in initiating efficiency for the range of polymeric and monomeric components examined is shown below:

increasing	↑	poly(ABP) and DMAS
		poly(ABP) and poly(DMAS)
photoinitiating		ABP and DMA
efficiency		IBP and poly(DMAS)
		ABP–DMAS copolymer

where ABP is acryloxybenzophenone, IBP is isopropylbenzophenone, DMA is dimethylaniline and DMAS is dimethylaminostyrene.

Carlini and coworkers [11–14] indicated that the high initiating efficiency of the poly(ABP) and DMAS system was due to energy migration between the excited triplet states and ground state side-chain benzophenone chromophores. This hypothesis is supported by Kamachi et al. [15], who rationalized that energy migration would increase the effective collision area between excited benzophenone chromophores and hydrogen donors, thus improving the initiating efficiency. Carlini et al. also reported phosphorescence-quenching studies which have shown that increasing the mean distances between benzophenone chromophores in the copolymers causes a fall in efficiency of energy transfer to a naphthalene. The use of a polymeric synergist in conjunction with poly(ABP), i.e. poly(ABP) and poly(DMAS), displays a reduction of initiating efficiency which is probably due to the restricted mobility of the aminoalkyl macroradical and the reduced chance of triplet benzophenone reacting with the amine.

The copolymer ABP–DMAS, wherein the photoinitiator and synergist are in close proximity to each other, displayed the poorest performance. This is primarily because, whilst the forward hydrogen-abstrating step is much easier, the back reaction becomes equally favourable.

Another strategy for attaching both benzophenone and amine synergist to a polymer backbone is through the preparation of a polymeric analogue of Michlers ketone in the form of poly(*p*-dimethylaminobenzoylated styrene) [16–18]. However, this polymeric photoinitiator displayed poor photoreactivity owing to quenching of the triplet ketone by the tertiary amine. More recently, photosensitive siloxane polymers [19] containing benzophenone chromophore and/or synergistic tertiary amine and/or acrylic functionality, with varying compositions of one, two or three of the above groups, have been prepared. These products were prepared by reacting polysiloxanes with pendant 2,3-epoxypropyl groups, which reacted with one or more of the acid functional reagents. The results show that for the polymerization of acrylates the polysiloxane containing pendant benzophenone and acrylic moieties used with the free-amine synergist ethyl-*p*-dimethylaminobenzoate (EDB) displayed the highest photoinitiating efficiency.

Polysiloxane bearing both benzophenone and tertiary amine behaved poorly as a photoinitiating system when compared with the photoinitiating systems where polymer (polysiloxane) containing benzophenone was used with free-amine synergist (EDB) or when the photoinitiating system was a monomeric benzophenone (2-acetoxy-3-(2-ethylhexyloxy)propyl-2-benzoylbenzoate) and polysiloxane with pendant (dimethylaminobenzoate ester) moieties. These results are in accord with those obtained by Carlini et al. on carbon-based systems [14]. It is important to acknowledge that the greater photoinitiating efficiency of the polymeric Norrish type II photoinitiators, which was attributed to energy

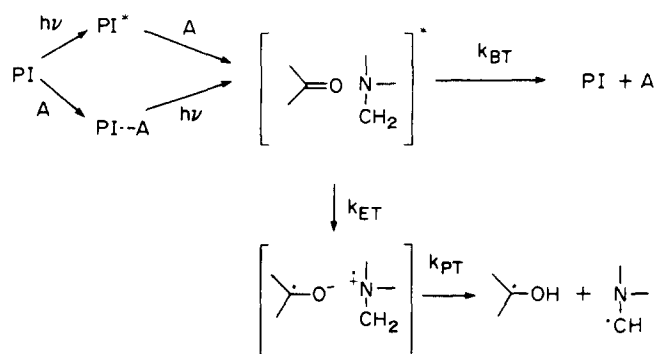


Fig. 1. Typical hydrogen-abstrating mechanism of a Norrish type II (benzophenone–tertiary amine) photoinitiating system: PI, pendant photoinitiator chromophore (aryl ketone); A, synergistic tertiary amine; k_{PT} , proton transfer process; k_{ET} , electron transfer process; k_{BT} , back electron transfer process.

migration down a polymer chain, is observed only when the benzophenone chromophore is in the polymer and not when the synergistic amine is used as a comonomer or indeed as a macromolecular synergist component.

Thus, the two effects which reduce the efficiency of fully polymeric systems are the back reaction of the hydrogen abstraction step that generates aminoalkyl initiating radicals and the presence of synergistic amine and benzophenone chromophores which will lead to interference with energy migration via an intramolecular exciplex, which leads to energy wastage.

Smets and coworkers [20,21] described the occurrence of energy migration when investigating the enhanced photocross-linking and electron donor–acceptor interactions in copolymers of vinylbenzophenone (VBP) and dimethylaminostyrene (DMAS).

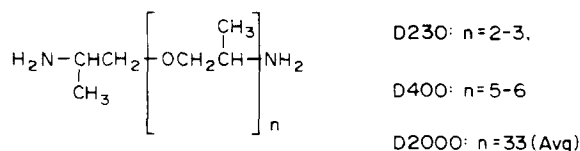
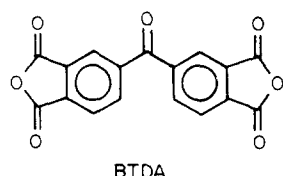
Yamamoto et al. [22] have prepared copolymers of vinylbenzophenone (VBP), dimethylaminostyrene (DMAS) or 2-*N,N*-dimethylaminoethylmethacrylate (DMAEMA) and methylmethacrylate. In investigating the cross-linking of the resultant polymer carrying pendant benzophenone and synergistic amine groups, they found that the photosensitive polymer containing the aliphatic amine (copolymer of DMAEMA) demonstrated a higher initiating cross-linking efficiency than the corresponding polymer containing pendant aromatic amine (copolymer of DMAS). However, absorption and emission spectral studies showed the aromatic amine to interact more strongly with the aryl ketone (benzophenone) in both the ground and excited states.

This was explained in the following manner. The generation of initiating cross-linking aminoalkyl radicals may follow one of the following routes:

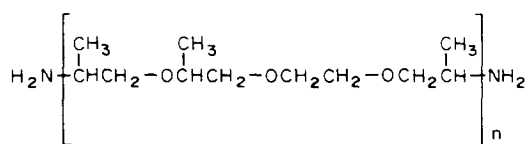
(1) via the excited triplet ketone $n-\pi^*$ state reacting with the ground state amine through charge transfer interaction and then undergoing hydrogen abstraction;

(2) photoexcitation of the ground state charge transfer complex (Fig. 1).

The photosensitive polymer containing pendant aliphatic amine synergist proceeds by only one route, i.e. via the



The ED6000 has, additionally, ethylene oxide in the backbone.



α ω POLYETHERDIAMINES

Fig. 2. α - ω -Polyetherdiamines used to prepare photosensitive polyetherimides.

excited triplet ketone. The polymer containing aromatic synergist proceeds via both routes. However, owing to the interaction of both the ground and excited states of this aromatic amine and aryl ketone, the back electron transfer (k_{BT}) process is able to compete more effectively with the proton transfer process that generates the ketyl radical and the aminoalkyl radicals.

The investigations reported so far have gravitated around polymeric photoinitiators that generate macroradicals pendant to the polymer backbone. Terminal macromolecular free radicals are likely to be far less sterically hindered and as such may perform better as initiating radicals than the corresponding pendant free radicals.

With a view to reducing the migratables associated with our previously described photoinitiating system [2], we prepared benzophenone-based polyetherimides with terminal synergistic amine functionality. The idea was to prepare a Norrish type II polymeric photoinitiating system with terminal tertiary amine.

2. Results

2.1. Synthesis

The photosensitive polyetherimides were prepared by reacting 3,3',4,4'-benzophenone tetracarboxylic dianhydride with polyetherdiamines of various molecular weights (molecular weights of 230, 400, 2000 and 6000, which are labelled as D230, D400, D2000 and ED6000 respectively; Fig. 2).

These photosensitive polyetherimides are labelled according to the parent polyetherdiamines from which they were synthesized. The polyetherimides were end capped with *N,N*-dimethylethylenediamine (DMED). The reaction is a typical condensation reaction as shown in Fig. 3. Since the dianhydride (BTDA) and the polyetherdiamine are difunctional whilst the synergistic terminal component (DMED) is effectively monofunctional, the reaction stoichiometry was adjusted to account for reactive functionality, i.e. X moles of the dianhydride (BTDA) was reacted with $X/2$ moles of the polyetherdiamine and X moles of the monofunctional terminator (DMED).

The polymers were characterized by gel permeation chromatography (GPC), UV, IR, ^1H and ^{13}C nuclear magnetic resonance (NMR). The molecular weight distributions were determined by GPC and are shown in Fig. 4. ^1H and ^{13}C NMR reveal the presence of trace amounts of acetic acid in the resultant polyetherimides.

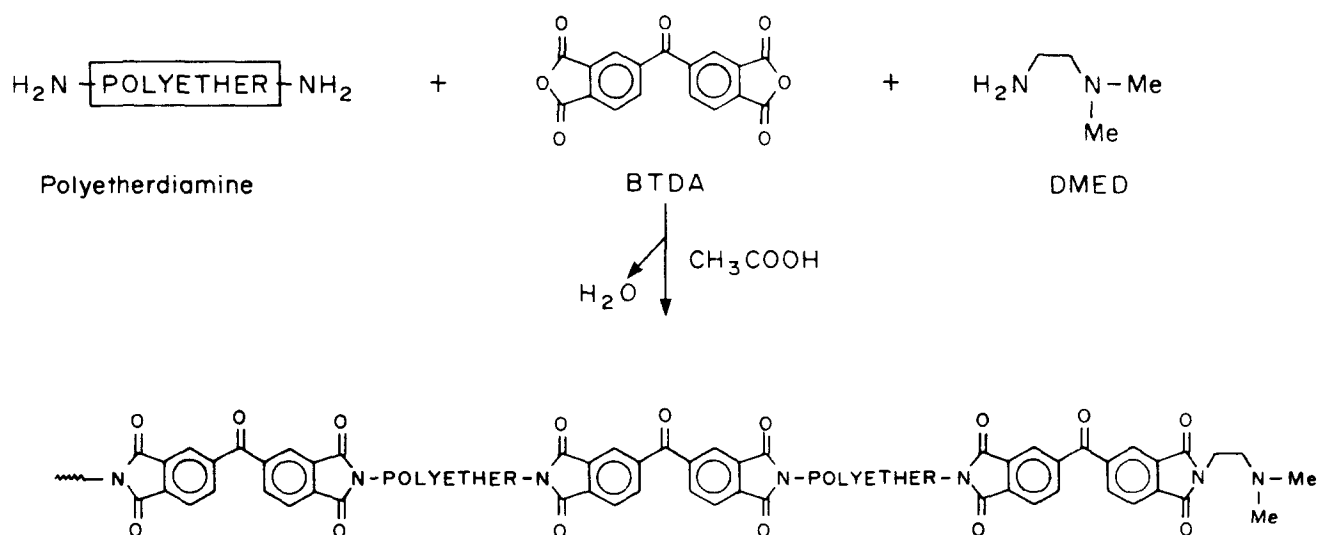


Fig. 3. Photosensitive polyetherimide with terminally built-in synergistic amine.

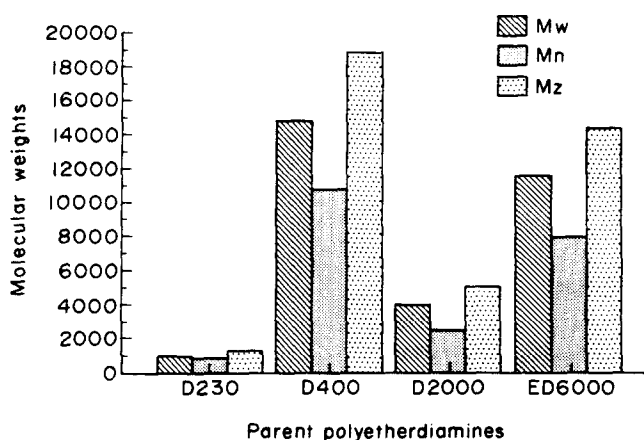


Fig. 4. Molecular weight distributions of photosensitive polyetherimides containing a terminal synergistic amine component.

Table 1
Physical appearance of photosensitive polyetherimides

Parent polyetherdiamine	Appearance
D230	Pale yellow solid
D400	Brown solid
D2000	Dark brown oil
ED6000	Light brown wax

Table 2
Rates of cure and induction times as determined by RT-IR on 2-hydroxyethylacrylate

Photoinitiator system	Induction time (s)	Rate of polymerization R_p (mol dm ⁻³ s ⁻¹)
Control BP-DME	5.1	0.28 ± 0.01
D230	7.5	0.14 ± 0.01
D400	10.5	0.16 ± 0.01
D2000	7.8	0.18 ± 0.01
ED6000	10.8	0.21 ± 0.01

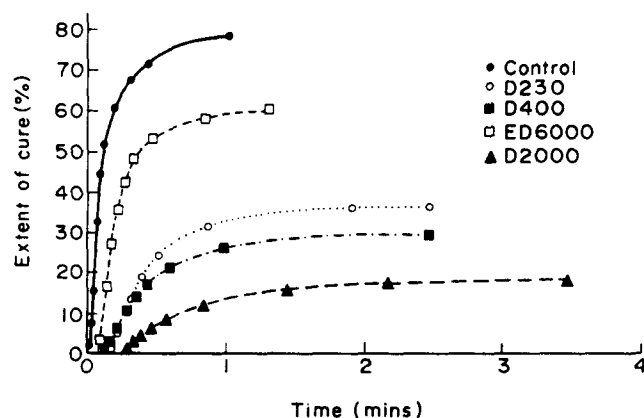


Fig. 5. Extents of cure in air as determined by photo-DSC on a urethane diacrylate formulation containing 6.0% of benzophenone chromophore and synergistic amine.

The appearance of the photosensitive polyetherimides varied with the length of the polyether chain used to join the benzophenone chromophores together (Table 1).

2.2. Performance of polyetherimides as polymeric photoinitiators

2.2.1. Real time IR (RT-IR) studies

These novel polymeric photoinitiators with terminal synergistic amine were dissolved in 2-hydroxyethylacrylate (HEA, 6% (w/w)). No additional synergistic amine was added to the acrylate formulation. The formulations were made up to contain molar equivalents of both benzophenone chromophore and polymer-bound synergistic amine (0.125 mmol). This was back calculated from the original reaction stoichiometry used in the preparation of the photosensitive polyetherimides and confirmed by UV spectroscopy (340 nm). The control formulation contained benzophenone (0.125 mmol) and *N,N*-dimethylethanolamine (DME, 0.125 mmol) which together constituted 6% (w/w) of the HEA formation.

From the results it was possible to calculate rates of polymerization (R_p). These rates along with the induction times are given in Table 2.

The polyetherimides with terminally built in amine synergist have a lower photoinitiation efficiency when compared with the analogous monomeric systems benzophenone (BP) and *N,N*-dimethylethanolamine (DME). The results show that R_p increases with increasing length of the polyetherdiamine used to link the chromophores together. It is also worth noting that with this HEA formulation there is a significant induction time (normally attributed to oxygen inhibition) despite the fact that the formulation is sandwiched between two NaCl plates as a 25 μ m film.

2.2.2. Photodifferential scanning calorimetry (photo-DSC)

This technique was employed to gauge the conversion of acrylate double bonds, i.e. the percentage polymerization, for each of the polymeric photoinitiators. Two series of experiments were conducted, one under nitrogen and the other in air, to assess the extent of oxygen inhibition and also to investigate the oxygen-scavenging ability of the tertiary amine when bound to a polymer. The formulations used were in similar stoichiometry to those for the RT-IR experiments, with the exception that the reactive diluent now used was a urethane diacrylate. The resulting formulations are much more viscous than the formulations used for the RT-IR experiments. Earlier work had shown that a viscous vehicle drastically reduced the performance of the polyetherimide photoinitiators [23]. The photo-DSC experiments were performed at 40 °C to overcome some of the retarding effect of viscosity upon photoinitiated photopolymerization.

The results displayed in Fig. 5 show that the rate of photoinitiated polymerization for formulations containing polymeric photoinitiators (i.e. where both benzophenone and tertiary amine are polymer bound) are much lower than for

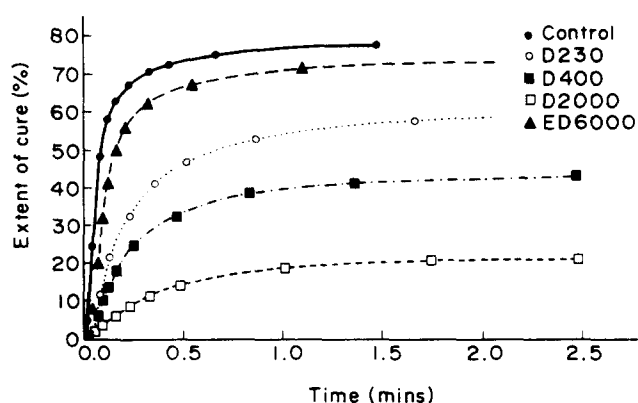


Fig. 6. Extents of cure under nitrogen as determined by photo-DSC on a urethane acrylate formulation–6% polyetherimide photoinitiator that contained 0.125 mmol of both benzophenone chromophore and synergistic amine.

Table 3
Viscosity measurements of urethane diacrylate formulations containing polymeric photoinitiators that were used for photo-DSC experiments

Formulation	Viscosity (P)
Vehicle + BP + DME (control)	11.12 ± 0.05
Vehicle + ED6000	20.8 ± 0.05
Vehicle + D2000	32 ± 0.05
Vehicle + D400	27.2 ± 0.05
Vehicle + D230	24 ± 0.05

Table 4
Assessment of crude cure and yellowing of polyetherimides

Photoinitiator system	Number of passes	Yellowness index (E313)
Control BP–DME	1	6.03
D230	4	26.49
D400	4	25.77
D2000	7	33.33
ED6000	7–8	13.55

the analogous monomeric photoinitiator systems (BP and DME). It is also worth noting that there was a significantly greater induction time for the polymeric photoinitiating systems than for the monomeric type II photoinitiating systems. The ED6000-based polyetherimides displayed the highest photoinitiation efficiency of all the polymeric photoinitiators. This agrees with the RT-IR results.

The results of photoinitiated polymerization under nitrogen are shown in Fig. 6. The most significant difference is the dramatic reduction in the induction time. The control monomeric benzophenone–dimethylethanolamine (BP–DME) photoinitiating system shows a 4% increase in the percentage acrylate double-bond conversion after 1 min when curing is performed under nitrogen. The polymeric systems show a 10% increase in acrylate double-bond conversion after 1 min upon curing under nitrogen.

2.2.3. Viscosity measurements of formulations used in photo-DSC experiments

To try to explain the photoinitiated photopolymerization characteristics of the various polymeric photoinitiators when a urethane diacrylate vehicle was used, the viscosities of the cure formulations used for photo-DSC experiments were measured. The results are given in Table 3. The trend in formulation viscosity is as follows:

control (BP–DME) < ED6000 < D230 < D400 < D2000

This trend agrees directly with the trend in photoinitiation efficiency as observed by photo-DSC:

control (BP–DME) > ED6000 > D230 > D400 > D2000

It is also worth noting that the solid polymeric photoinitiator D230 and D400 polyetherimides were formulated to give lower viscosity photoreactive formulations than the D2000 polyetherimide, which is an oil. (The oil was expected to solubilize more readily in a reactive diluent and give a lower viscosity formulation.)

2.2.4. Crude cure and colour measurements

The polymeric photoinitiators were empirically gauged on their ability to produce a hard film upon photocuring a mixture of multifunctional acrylate monomers. The appearance of the cured coating was also studied.

The polyetherimides with terminally built-in synergist were dissolved in an 85:15 (w/w) mixture of an epoxynov-alac acrylate and glycerol-propoxylated triacrylate (GPAT). This acrylic mixture gives a highly cross-linked, hard film upon photocuring and approximates to industrial systems already in use. The formulations were made up to contain molar equivalents of benzophenone chromophore (0.125 mmol) and synergistic tertiary amine (0.125 mmol) as 6% (w/w) of the acrylic reactive diluent. Films 25 μm thick were cured on a white test card under a UV Colordry rig set at a belt speed of 60 ft min⁻¹. The number of passes to pass the ‘‘thumbscrew test’’ was recorded. The cured films were then analysed spectrophotometrically to obtain a yellowness index. The (E313) yellowness index is a standard test method to assess the whiteness–yellowness of near-white opaque materials [24]. The procedures specified in this test method are designed to yield numbers correlating to visual estimates made under one set of typical observing conditions. The ability to produce a hard film and the yellowness index are given in Table 4.

Note that the most efficient polymeric photoinitiator as shown by RT-IR and photo-DSC, the ED6000-based polyetherimide, is now the poorest photoinitiator in terms of its ability to produce a hard film. The yellowness indices measured show the control BP–DME and the ED6000-based polyetherimide to have the least yellowing upon photocuring.

Table 5

Acid values of photosensitive polyetherimides with terminally built-in synergist

Photoinitiator	Acid value (mg KOH g ⁻¹)
D230	176
D400	142
D2000	296
ED6000	64

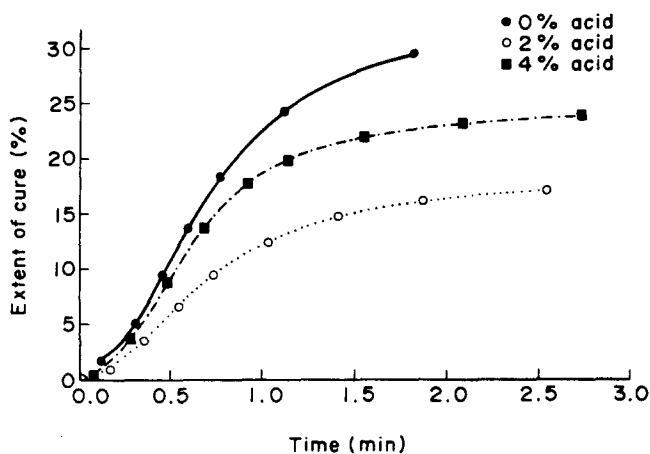


Fig. 7. Photo-DSC results (ED6000) displaying the effect of acetic acid on photoinitiated photopolymerization when polymeric photoinitiators are used.

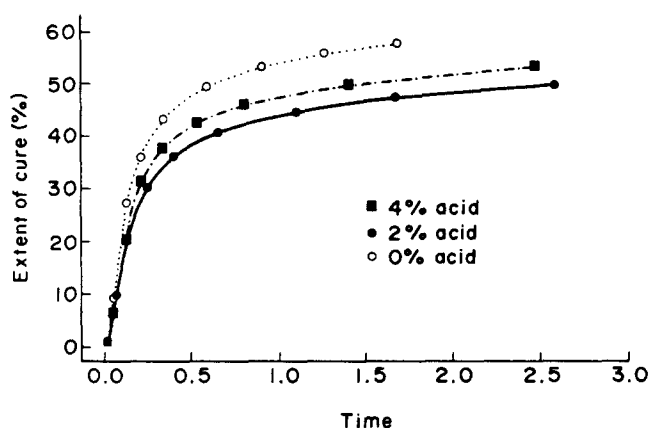


Fig. 8. Photo-DSC results (BP) displaying the effect of acetic acid on photoinitiated photopolymerization when monomeric photoinitiators are used.

2.3. Effect of acetic acid on photoinitiated photopolymerization: acid values of polyetherimides and effect of acid on rates of cure

During the handling of these benzophenone-containing polyetherimides with terminally built-in synergist, a faint odour of acetic acid was detected. Acetic acid was the medium (solvent) used for the preparation of the polyetherimides. The reason for this choice of solvent is given in an earlier

work [23]. Therefore the polyetherimides were titrated with aqueous KOH solution to determine their acid values. The results are given in Table 5.

Note that the polyetherimides with the highest and lowest acid values (the D2000 and D6000 products respectively) also have the lowest and highest photoreactivities respectively (compare Fig. 2 and Table 5).

The presence of acid in the polyetherimides prompted us to perform experiments to examine the effect of acetic acid on the photocuring efficiency of the polymeric photoinitiators (polyetherimides). The polymeric photoinitiator chosen for this study was the ED6000-based polyetherimide because of its inherently low acid value. The urethane diacrylate formulations used in the earlier photo-DSC experiments were doped with 0%, 2% and 4% acetic acid. The percentage conversion of acrylate double bonds was measured. The results are shown in Fig. 7 and indicate that there is a critical level of acetic acid, i.e. 2%. Above 2% the photoreactivity of the polymeric photoinitiators moves towards the ideal system with close to 0% acetic acid.

Similar experiments were performed on the monomeric photoinitiating system (BP-DME). Acetic acid was observed to have less of a retarding effect on the efficiency of photoinitiation when monomeric photoinitiators were used (see Fig. 8).

2.4. Gas chromatography-mass spectrometry (GC-MS) extraction results

A 25 cm² area of a cured coating comprising 6% polymeric photoinitiator and 94% 15:85 GPTA-epoxynovalac acrylate was immersed in CH₂Cl₂ for 48 h. GC-MS analysis revealed no photoinitiator-based extracts nor any acetic acid (Fig. 9). The only extractable component was uncured acrylate. The lack of any acetic acid may be due to evaporation under the high temperatures of the UV Colordry rig.

2.5. Hardness of cured films

These novel polymeric photoinitiators with terminal synergistic amine were dissolved in a mixture of GPTA and

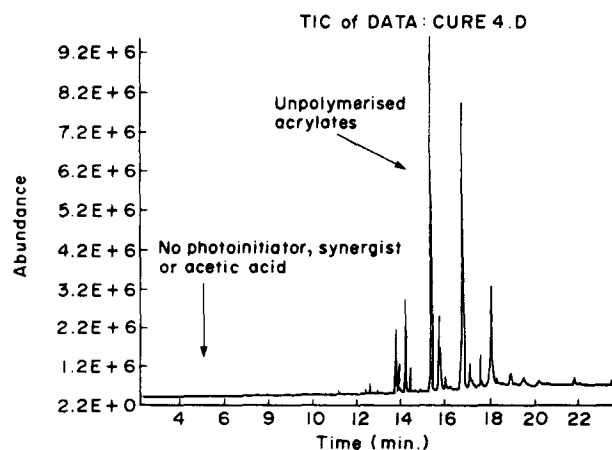


Fig. 9. Typical gas chromatogram of dichloromethane extracts of cured films.

Table 6
Pendulum hardness measurements of films cured with given photoinitiators

Photoinitiator system	Pendulum oscillations
Control glass	173
BP–DME	29
D230	20
D400	18
D2000	15
ED6000	12

epoxynovalac acrylate (15:85). No additional amine synergist was added. The formulations were made up to contain molar equivalents of benzophenone and polymer-bound synergistic amine (0.125 mmol).

In order to maintain equivalent amounts of chromophore in the formulations, the high molecular weight polyetherimides were needed in greater amounts. The formulations were then coated on to tin float glass and cured under a Colordry rig set at 20 ft min⁻¹ (10 passes gave a tack-free film), then subjected to the pendulum hardness test, where the number of oscillations of the pendulum was recorded. The results are given in Table 6.

The higher the number of pendulum oscillations, the harder is the film. On this basis the highest molecular weight polyetherimides gave rise to the softest films. This is attributed to the plasticizing effect of the polymeric photoinitiator. It is worth noting that the greater the amount of polymeric photoinitiator used (by weight), the softer is the film.

3. Discussion

The kinetic studies indicated that the polymeric photoinitiators bearing terminal synergistic amine suffer more acutely from oxygen inhibition relative to the monomeric analogues. This may be due to the reduced mobility of the tertiary amine now that it is polymer bound, thereby affecting the oxygen-scavenging ability and initiating efficiency of the photoinduced aminoalkyl radical. Since with exposed surface coatings, oxygen dissolves into thin films during photocure, it is important to ensure that the oxygen-scavenging ability of the polymer-bound synergist is greater than the diffusion of oxygen into the film during irradiation. The polymeric photoinitiators (polyetherimides) we have described may be of greater use in viscous formulations where oxygen diffusion into the films is significantly reduced.

The RT-IR experiments differ from photo-DSC in that the RT-IR formulations were sandwiched between two NaCl plates, which physically stops oxygen diffusion into the films. Despite this feature there is still a significant induction time as shown by RT-IR and this may be attributed partially to the presence of oxygen already dissolved in the formulation and in part to the reduced initiating efficiency of the polymer-bound aminoalkyl radicals.

The direct correlation between the extent of photoinitiated photopolymerization (as observed by photo-DSC) and the viscosity of the test formulations underlines the importance of viscosity as a factor influencing photoinitiated polymerization. The viscosity measurements themselves indicate that the different polymeric photoinitiators make varying contributions to the viscosity of the cure formulations. These contributions to viscosity are independent of the physical state, molecular weight or chromophore density of the polymeric photoinitiator.

The most efficient photoinitiator, the ED6000-based polyetherimide (as observed by RT-IR and photo-DSC), displayed the poorest performance in terms of ability to produce a hard cured film upon curing a mixture of multifunctional acrylates. This is because the polymeric photoinitiators with large chains (chemical components) between chromophores are added in larger weight-based amounts in order to ensure chromophore equivalent concentrations in the resultant formulations. This large addition of a polymer to the acrylate formulation can have a plasticizing effect, thereby affecting the ability to produce a hard film, as we have demonstrated.

Polymers bearing chromophore groups are known to undergo degradation (which can manifest itself as yellowing) by either thermal or photolytic processes [25].

The presence of the imide functionality, which has its own extensive photochemistry, provides another route to obtaining photolysis products which may be coloured [26]. Measurements of the yellowness index of the cured formulations indicated that polymeric photoinitiators of the type we have described (polyetherimides) give films of varying degrees of discoloration (yellowing). This yellowing is significantly greater than the yellowing observed with the monomeric photoinitiating system (BP–DME).

Scrutiny of the photosensitive polyetherimides prepared indicated the presence of trace amounts of acetic acid. Subsequent titration revealed relatively high acid values. This may be due to

- (1) protonation of the polymer-bound tertiary amine with trace amounts of acetic acid (used as reaction solvent) to give polymer-bound quaternary ammonium acetate and/or
- (2) a poor degree of imidization giving rise to the presence of amic acid.

Attempts to autotitrate these photosensitive polyetherimides to indicate the presence of the two acid groups (acetic acid and amic acid, which would have different p*K*_as) were unsuccessful.

Examining the effect of acetic acid on the extent of photoinitiated photopolymerization with the photosensitive polyetherimides, we observed that a level of 2% acetic acid markedly reduced the extent of polymerization. Below 2% the extent of cure tended towards the idealized system with no acetic acid. Acetic acid was found to have a more significant effect on the polymeric photoinitiators than on the analogous monomeric photoinitiating system (BP–DME).

4. Conclusions

The incorporation of both components of type II photoinitiating systems (benzophenone chromophore and amine synergist) does reduce the photoinitiator-based migratables in the cured coating. However, this benefit of reduced migratables has to be offset against the reduced photoinitiation efficiency, increased sensitivity to oxygen inhibition and yellowing of the cured films.

The importance of the viscosity of the cure formulations, the viscosity contribution of the polymeric photoinitiator and the effect of viscosity on the efficiency of polymeric photoinitiators have been hinted at before. We can now confirm the following:

(1) Polymeric photoinitiators can drastically affect the cure formulations into which they are put, which can in turn affect the initiation and propagation steps of the photoinitiated photopolymerization reaction.

(2) The viscosity of a formulation prior to the addition of a given photoinitiator is an important in affecting the photoinitiating efficiency of the polymeric photoinitiator.

Finally, the danger of using polymeric photoinitiators with low chromophore density (e.g. ED6000-based polyetherimide) is demonstrated in crude cure experiments where the large mass of polymeric photoinitiator added to an acrylic formulation resulted in a plasticizing effect which affected the film hardness.

Ironically, this same polymeric photoinitiator (ED6000-based polyetherimide) demonstrated the greatest photoinitiating efficiency by photo-DSC and RT-IR. This result emphasizes caution when extrapolating kinetic data acquired from idealized monomer systems to the applied area, where multifunctional monomers, film thickness, temperature, lamp spectral output and a host of other variables come into play.

5. Experimental details

UV spectra were recorded on a Perkin–Elmer Lambda 16 UV–visible spectrophotometer. IR spectra were recorded on a Biorad FTS-60 Fourier transform IR (FT-IR) spectrophotometer. GPC was carried out using Polymer Laboratories 500, 100 and 50 Å columns (each 300 mm long) on a Waters Maxima system fitted with an ACS 750/14 mass detector. Molecular weights were calculated based on polystyrene and polyethylene glycol standards from Polymer Laboratories. The samples were run using tetrahydrofuran as eluent at a flow rate of 1 ml min⁻¹. GC–MS was carried out using a 30 mm × 0.25 mm × 0.25 m (stationary phase thickness 0.25 μm) SE-30 non-polar column fitted with a Hewlett–Packard 5970 mass detector. ¹H NMR spectra were recorded on a Jeol FMX270 FT (270.05 MHz) spectrometer with tetramethylsilane as internal reference. ¹³C NMR spectra were recorded at 67.8 MHz on a Jeol FMX 270 FT spectrometer with tetramethylsilane as internal standard. Samples were run as CDCl₃ or DMSO-*d*₆ solutions. RT-IR was undertaken on a Perkin–

Elmer 599 IR spectrophotometer fitted with a Kratos medium pressure lamp. The Colordry UV rig was fitted with a medium pressure (100 W per linear inch) lamp. Photo-DSC was carried out using a Perkin–Elmer DPA 7 fitted with a 100 W Hg short arc lamp and a water filter. Runs were carried out at 25 °C.

5.1. Solvents, reagents and starting materials

Tetrahydrofuran (THF) was distilled from sodium and benzophenone under nitrogen. *n*-Butylamine and cyclohexylamine were distilled over KOH under nitrogen. The polyetherdiamines were obtained from Texaco. These products are supplied under the trade name Jeffamines. Lauryl acrylate was obtained from Lancaster MTM Research Chemicals. 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) and all other reagents and solvents were obtained from Aldrich Chemical Company and used without further purification.

The reactive diluent used in the photo-DSC experiments was a mixture of trimethylpropane triacrylate (TMPTA) and an aliphatic urethane diacrylate prepared from polypropylene glycol of molecular weight 550. This is a test formulation used for photo-DSC experiments at Coates Lorilleux Research (Kent). The ethoxylated phenol monoacrylate was obtained from Acros under the trade name Photomer 4039.

Colour measurements were undertaken with an ACS Spectrosensor 2 spectrometer at Coates Lorilleux Research (Kent).

5.2. Synthesis

5.2.1. Preparation of benzophenone-carrying polyetherimides terminated with a (synergistic) tertiary amine

BTDA (4 g, 12.4 mmol) was first dissolved in acetic acid (150 ml). To this, 6.2 mmol of the α - ω -polyetherdiamine (D230, D400, D2000 or ED6000) was added as an acetic acid solution (50 ml). The reaction mixture was refluxed for 2 h before being cooled in an ice bath. Upon cooling to 10 °C, 1.1 g (12.4 mmol) of *N,N*-dimethylethylenediamine (DMED) was added. The reaction mixture was left to reflux for a further 1.5 h.

Removal of acetic acid under reduced pressure gave orange and brown oils. These oils were left in a vacuum over (0.1 mmHg) at 25 °C over NaOH pellets for 2 weeks.

The D230 and D400 polyetherimides are oily products and therefore required an additional step in the work-up. They were stirred vigorously with 100 ml of Et₂O and then allowed to stand overnight. The ether layer was then decanted off and the samples put under vacuum (0.1 mmHg) once again. The products gradually gave rise to a solid foam over a period of 4–8 h. The reactions and subsequent work-up were performed with care not to expose the reaction mixtures and products to light.

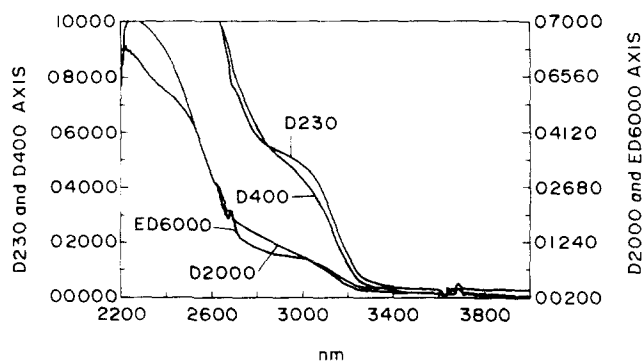


Fig. 10. UV spectra of polyetherimides with terminal tertiary amino groups, displaying benzophenone chromophore.

The UV spectra of the polyetherimides are shown in Fig. 10.

5.2.2. Amounts of polyetherdiamines used in polymer preparation

Parent polyetherdiamine	Mass used in reaction (12.4 mmol)
D230	1.43 g
D400	2.48 g
D2000	12.4 g
D6000	37.2 g

5.2.3. Characterization of polyetherimides containing terminal synergistic amine

Molecular weight determinations were carried out by gel permeation chromatography using polystyrene and polyethylene glycol standards. See Fig. 4.

IR ν (cm^{-1}): 1774 (C=O imide), 1715 (C=O imide), 1666 (C=O diaryl), 1391 (C–N aliphatic amine), 1365 (C–N imide), 1340 C–N (tertiary amine), 1106 (C–O ether), 727 (aromatic C–H def). $^1\text{H NMR}$ [27] (270 MHz, CDCl_3) δ : 1.10 (m, broad, CH_3 polypropylene glycol), 1.4 (d, CH_3 -CH–N), 1.8 (s, CH_3COOH residual amounts present in polymer), 2.4 (s, CH_3 -N), 2.8 (t, CH_2 -N(Me) $_2$), 7.9–8.1 (m, aromatic H benzophenone). $^{13}\text{C NMR}$ [28] (67.8 MHz, CDCl_3) δ : 194 (C=O benzophenone), 179 (C=O acetic acid), 167 (C=O imide), 138–120 (aromatic), 77.5 (CH_2O propylene glycol), 77 (CH–O propylene glycol), 56.4 (CH_2 -N(Me) $_2$), 45 (CH_3 -N), 17.5 (CH_3 propylene glycol).

All spectra described so far are typical of the polyetherimides prepared. As the polyether chain linking the chromophore groups together (e.g. D2000 and ED6000) gets larger, the spectral peaks of the benzophenone chromophore and the terminal synergistic amine become less prominent.

5.3. Photoreactivity experiments

Weight-based formulations comprising 94% 2-hydroxyethylacrylate (HEA) and 6% polymeric photoinitiator

(polyetherimide) were prepared. No additional tertiary amine was added, since the polyetherimides are terminated with amine synergist. The formulations were made up to contain equimolar amounts of both benzophenone chromophore and synergistic amine moieties (0.125 mmol). This was achieved by calculation based on the original reaction stoichiometry and was confirmed by UV analysis.

A control formulation which matches the molar concentrations of benzophenone and synergistic amine (0.125 mmol) was made up using 3% benzophenone, 3% *N,N*-dimethylethanolamine (DME) and 94% vehicle (HEA).

The formulations were sandwiched between two NaCl plates using polyethylene spacers designed to give a film 20 μm thick. RT-IR experiments on the sandwiched film were performed on a Perkin–Elmer 599 spectrophotometer specially fitted with a 200 W Hg–Xe lamp. This enabled the sample to be simultaneously irradiated by the UV lamp whilst spectral absorption changes in the IR region were recorded. The progress of polymerization was recorded by monitoring the disappearance of the acrylic double bond ($\text{CH}_2=\text{CH}$) twist at 810 cm^{-1} . Rates of polymerization were calculated using the equation

$$R_p = - \frac{M_0}{A_0} \left(\frac{A_2}{t_1} \times \frac{A_1}{t_2} \right)$$

where R_p ($\text{mol dm}^{-3}\text{ s}^{-1}$) is the rate of polymerization, M_0 (mol dm^{-3}) is the initial monomer concentration, A_0 is the initial absorbance, A_1 and A_2 are absorptions where DA changes linearly and t_1 and t_2 (s) are the times corresponding to absorptions A_1 and A_2 respectively.

The RT-IR results are given in Table 2.

5.3.1. Photodifferential scanning calorimetry

Experiments in air. Formulations consisting of 94% urethane diacrylate and 6% polymeric photoinitiator (polyetherimides with terminal synergistic amine) were prepared. These formulations were made to contain molar equivalent amounts of both polymer-bound benzophenone chromophore and terminal synergistic amine so as to enable a comparison of the different polymeric photoinitiators. A control formulation using 3% benzophenone, 3% *N,N*-dimethylethanolamine and 94% urethane diacrylate was also made up. This control formulation would match the molar concentrations of benzophenone chromophore and synergistic amine of the formulations containing polymeric photoinitiators (polyetherimides).

A mass of 0.8 mg of each urethane diacrylate formulation was added to the DSC pan. This approximates to a film 80 μm thick. Each of the 0.8 mg samples was irradiated for 4–5 min and the corresponding thermogram recorded. The percentage acrylate double-bond conversion was calculated based on a calorimetric value of 250 J g^{-1} as the heat of acrylate double-bond conversion. See Fig. 5.

Experiments under nitrogen. The same procedure as above was repeated after purging the DSC sample compartment

(fitted with a glove-box) with nitrogen for 30 min. See Fig. 6.

5.3.2. Viscosity measurements

The viscosities of the formulation used in the photo-DSC experiments were measured on a cone (size c) and plate viscometer. The samples were put on the heated stage of the viscometer and allowed to reach 65 °C. The reason for this elevated temperature is that at room temperature (25 °C) the viscosity of the reactive diluent was beyond the measuring capability of the instrument. See Table 3.

5.3.3. Crude cure and colour measurements

The polyetherimides with terminally built-in synergists were dissolved in an 85:15 (w/w) mixture of epoxynovalac acrylate and glycerol-propoxylated triacrylate (GPTA). This acrylic mixture gives a highly cross-linked hard film. These formulations were made up to contain the same amounts of benzophenone chromophore and synergistic amine (0.125 mmol) in order to enable the different polyetherimides to be compared.

Films 25 µm thick were applied with a K-bar on to a white test card. The test card was put under a UV Colordry rig set at a belt speed of 60 ft min⁻¹. The number of passes required before the coating passed the "thumbscrew" test was recorded.

The same coloured films were analysed with an ACS Spectrosensor 2 spectrometer with a "small area view" aperture. The data obtained from the spectrophotometer were analysed following procedures set up by ASTM Committee E-12. This is a standard method for indices for whiteness–yellowness of near-white opaque materials (E313 standard).

Results of both crude cure and colour measurements are given in Table 4.

5.3.4. Acid values of photosensitive polyetherimides

A mass of 0.2 g of each polyetherimide was dissolved in 50 ml of methylethyl ketone (2-butanone) and titrated against 0.156 M ethanolic KOH. Phenolphthalein was used as an indicator (colour change from clear to pink). Acid values were obtained from the equation

acid value =

$$\frac{\text{molar mass of KOH (g)} \times \text{molarity of KOH} \times \text{volume of titre (cm}^3\text{)}}{\text{mass of sample (g)}}$$

Results are given in Table 5.

5.3.5. Effect of acetic acid on photoinitiation efficiency

The polymeric photoinitiator chosen for this study was the ED6000-based polyetherimide because of its inherently low acid value. The urethane diacrylate formulation used in the earlier photo-DSC experiments were inoculated with 0%, 2% and 4% acetic acid. The percentage conversion of acrylate double bonds was determined by photo-DSC in the manner described earlier. The same procedure was followed for the

control (BP–DME) formulation. Results are shown in Figs. 7 and 8.

5.3.6. GC–MS extraction studies

A weight-based formulation of 6% polymeric photoinitiator (polyetherimide) and 94% vehicle comprising 15:85 (w/w) GPTA and epoxynovalac acrylate was coated on to tin float glass to give a film 25 µm thick. The film was passed under a Colordry rig at a belt speed of 20 ft min⁻¹ until a hard tack-free film was obtained. A fixed area of 25 cm² was detached from the glass and dissolved in dichloromethane (7 ml). The filtered dichloromethane extract was analysed by GC–MS. See Fig. 9.

5.3.7. Pendulum hardness test

Films 25 µm thick (on tin float glass) of the same formulations used for the extraction studies above were cured under the Colordry rig (10 passes, belt speed 20 ft min⁻¹). The films were analysed by the König pendulum hardness test. This method involves a pendulum fitted with a ball-bearing that scrapes along the surface of the coating. The softer the film, the fewer oscillations the pendulum will make across the film. See Table 6.

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