

A new series of type II (benzophenone) polymeric photoinitiators

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Abstract

Polyimides derived by the reaction of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with amino-terminated polyethers have been used as photoinitiators in conjunction with tertiary amine synergists for the polymerization of acrylates. The performance of the new, fully characterized materials was compared with that of benzophenone and BTDA. The performance of the novel photoinitiators was assessed by their ability to cure thin films of multifunctional acrylates. Real time IR spectroscopy and photo-differential scanning calorimetry were used to assess the cure rate and extent of photopolymerization. Cured films were subjected to solvent extraction to determine the level and nature of the extractable components and these were shown not to contain any of the photoinitiator. The polyimide photoinitiators were found to be absent in the extracts. The polymeric photoinitiators were shown to have lower reactivities than benzophenone and BTDA. The reactivity of the new photoinitiators is affected by such factors as the composition of the polyimide and molecular weight (which markedly changes the viscosities of the formulations).

Keywords: Benzophenone; Polymeric photoinitiators; Polyetherimides

1. Introduction

The recent surge of interest in polymeric photoinitiators has been a response in part to legislation that might be introduced requiring packaging materials and films to contain zero migrateables. Furthermore, polymeric photoinitiators might have a number of advantages over their monomeric counterparts, e.g. a greater reactivity due to effects such as energy transfer down a polymer chain in a mechanism similar to the antenna effect displayed by chlorophyll in plants [1].

The disadvantage of monomeric type I and type II systems is that their low molecular weight photolysis products are only "partially" trapped in the cured coating. These species may gradually migrate to the surface of the film and affect the film finish and appearance or, if the migrateables are odoriferous, give an unwanted odour to the film. In the case of food packaging, the quality of the product may be affected by these migrateables.

In using polymeric photoinitiators in curing formulations, certain factors have to be acknowledged.

(1) The polymeric photoinitiators will have a more drastic effect on the viscosity and hence alter the curing rate of the formulation relative to their monomeric analogues.

(2) They may need a higher molar percentage of chromophore owing to restricted mobility.

(3) These polymers will have different solubilities in comparison with their monomeric analogues. The moiety joining the chromophores will provide a useful handle for tailoring the solubility properties.

The incorporation of a photoinitiator moiety into a polymer may be accomplished by the following strategies:

(1) inclusion of the chromophore as a pendant or in a terminal position in a polymer;

(2) copolymerizing the chromophore so that it is present in the backbone of the polymer.

The types of polymeric photoinitiators may be broadly classified according to the two main types of free-radical photoinitiators, i.e. Norrish type I (cleavage) and type II (hydrogen-abstracting) photoinitiators.

1.1. Norrish type I (cleavage) polymeric photoinitiators

The typical examples of polymeric type I photoinitiators include a homopolymer of polybenzoin [2]. Ben-

zoin methyl ethers have been incorporated into a polycarbonate chain as a copolymer of 4,4'-isopropylidene diphenol (bisphenol A) [3].

Polymeric trichloroacetophenone [4], which undergoes β cleavage upon irradiation, generating a chlorine radical which initiates acrylate polymerization, has been described. The fate of the polymer-bound radical is as yet undecided. Oligomeric dibenzil ketals have been prepared by the reaction of benzil dimethyl ketal with triethylene glycol in the presence of toluene sulphonic acid [5].

The hydroxyl functionality on substituted acetophenones or benzoin has often been used to attach these type I photoinitiators to a polymer backbone. One favoured strategy has been to attach polymerizable moieties (e.g. acrylate or vinyl groups) to the free hydroxyl group. The subsequent polymerizable photoinitiators may be thermally or photochemically polymerized to give polymeric photoinitiators [6].

Modifications of this procedure have been used to prepare siloxanes [7,8] and even polymerizable urethane derivatives [9]. Type I polymeric photoinitiators pendant to a polymer backbone have been prepared by Friedel–Crafts acylations on to polystyrene to give polymer-bound alkylphenones. These materials exhibit good solubility in most monomers and UV-curing formulations. Efficient α cleavage has been shown to occur (by flash photolysis, etc.) [10] upon irradiation giving rise to the initiating radical on the polymer backbone. In addition, this polymeric photoinitiator was found to have a photoinitiating efficiency that matched that of the low molecular weight analogue. Coatings that were cured using the monomeric compound were found to give rise to odoriferous coatings, attributed to the benzaldehyde photolysis byproduct which is migrateable in the cured film. In the case where the polymeric photoinitiator was used, no odour was detected. This is probably because the benzaldehyde moieties are now covalently bound to the polymer backbone.

Polymeric acylated hydroxyacetophenones based on substituted cyclohexylphenyl ketones have also been prepared [11,12]. Acylations of the hydroxyl group have been shown to reduce the photoreactivity of three photoinitiators, whilst etherification or alkylation of the hydroxyl was shown not to reduce photoreactivity.

Benzoin has been derivatized via a substituent hydroxyl group carrying an acrylate function which can then be polymerized. The resulting polymer displayed a poor photoinitiating efficiency [13].

An interesting feature attributed to some polymeric photoinitiators is hyperchromism. This phenomenon describes the increased molar extinction coefficient of given chromophores in a polymer chain relative to an equivalent number of monomeric chromophores. Polymeric benzoin based on acrylated α -hydroxy methyl benzoin have been shown to display *hyperchromism* [14].

Hyperchromism is thought to arise owing to the polymer backbone adopting a conformation which allows the chromophores to interact or by the polymers associating to give localized high concentrations of chromophore.

The only commercially available polymeric photoinitiators are polymers bearing hydroxyalkylphenone moieties (KIP series [15]). This non-yellowing polymeric photoinitiator does not release benzaldehyde upon photolysis (since the benzoyl initiating radical is polymer bound), allowing for the production of low odour coatings.

1.2. Type II polymeric photoinitiators

Type II photoinitiators typically require the interaction of an aryl ketone or dye (the sensitizer) and a synergistic amine (the acceptor). Thus, in order to reduce the photoinitiator-based migrateables, both the photoinitiator and the synergist would have to be incorporated into a polymer. Alternatively, a polymeric type II photoinitiator could be used along with a polymeric or polymerizable amine synergist.

Polymeric sensitizers (which is what a type II polymeric photoinitiator effectively is) are already in use in other areas of applied photochemistry, e.g. oxygenation, harnessing solar power by valence bond isomerization [16,17] and imaging processes [18]. Most of the preparation of polymeric type II photoinitiators has gravitated around benzophenone, probably because of its relatively low cost. It still remains the most widely used photoinitiator in industry.

Analysis studies of copolymers of styrene or methyl methacrylate and 4-vinyl benzophenone in benzene solution have shown that hydrogen abstraction from the polymer backbone occurs [19,20].

Cross-linking and gel formation have also been displayed in poly(4-benzoylphenoxy methyl styrene) and in a heteroatomic polymer of benzophenone, poly(bis(4-benzoylphenoxy) phosphazene) [21].

Styrene-4-vinyl benzophenone copolymers have been shown not to polymerize styrene in the presence of hydrogen donors. This failure to polymerize styrene has been attributed to the benzophenone triplet energy in benzoylated styrene being higher than that of styrene, thereby enabling the styrene to function as a quencher [22].

The most extensive study of the influence of the chemical structure of benzophenone-containing polymers on the photoinitiating activity of mono- and bifunctional acrylates for use in UV-curable coatings has been performed by Carlini and coworkers [23–27]. Using acryloxy benzophenone and vinyl benzophenone, a variety of homo- and copolymers with synergistic amino acrylates and polymerizable naphthyl residues were prepared. From this study the following conclusions were drawn.

(1) Energy migration from interactions between neighbouring excited triplet state and ground state benzophenone moieties changes the efficiency of the polymeric photoinitiator.

(2) Energy migration would increase the effective collision distance between benzophenone chromophores and hydrogen donors, thus improving the photoinitiation efficiency.

(3) Comparison of poly(acryloxy benzophenone) and a copolymer of acryloxy benzophenone and methyl acrylate suggested that increasing the distance between benzophenone units reduced the photoinitiation efficiency of these polymeric photoinitiators, whilst copolymers of acryloxy benzophenone and methyl acrylate displayed a higher photoinitiating efficiency. This was attributed to the effectiveness of hydrogen-donating groups present as co-units. It was concluded that the properties of the co-units played a more important role in photoinitiation efficiency than did energy migration.

(4) Using polymers derived from a commercially available acrylated benzophenone (Uvecryl P36) and comparing them with polymers derived from 4-vinyl benzophenone and acryloxy benzophenone, Carlini was able to demonstrate that the rigidity of the main chain did not markedly affect the activity of the polymeric photoinitiators.

Investigations have not been restricted to benzophenone alone. One of the earliest reports on polymeric photoinitiators by Ledwith and coworkers was on copolymers of vinyl fluorenone and methyl methacrylate. These polymers were tested in combinations with tertiary amines and indol-3-yl acetic acid in benzene solution [28,29]. The polymers were found to display polymerization and photoreduction characteristics comparable with those of analogous monomeric systems.

Benzophenone has been inserted into the polymer backbone (with benzophenone tetracarboxylic dianhydride (BTDA)) en route to preparing benzophenone-containing polyester multiacrylate oligomers [30,31]. Predictably, these systems were found to cure readily on their own (autocurable, since they bear both the photoinitiator and the acrylate monomers) and in the presence of other reactive monomers without the use of an amine synergist. The physical properties of these polymeric photoinitiators were varied by changing the copolymer unit (polyol) that was initially condensation polymerized with BTDA.

Polymeric thioxanthenes have also been prepared, as copolymers of thioxanthone and methyl methacrylate [32,33]. A comprehensive study of the resulting copolymers revealed very short lifetimes of the triplet ketone, which were attributed to intramolecular hydrogen abstraction and self-quenching [34]. The low photoinitiating efficiency of these compounds was attributed to the polymer backbone shielding the carbonyl

group. These polymeric thioxanthenes nevertheless did polymerize acrylates.

We have prepared a benzophenone (type II) photoinitiating system by incorporating photoinitiator groups into the polymer backbones via a polycondensation reaction to give a polyimide. Predictably, these systems work in conjunction with the amine synergist in the curing process.

BTDA is a preferred starting material for incorporating benzophenone into polymer backbones and has been used to prepare polyester multiacrylate oligomers [30].

Incorporating benzophenone into a polyimide will confer certain benefits to the resultant photosensitive polymer.

(1) Polyimides are thermally stable and will display a good shelf-life stability.

(2) Their non-shrink properties should reduce the distortion of the coating upon photocuring.

The main disadvantage of polyimides is that they are generally insoluble. However, this solubility problem may be overcome by modifying the backbone as mentioned earlier.

Harris et al. [35] have discussed structural modifications necessary for attaining soluble, thermally stable polyimides. These modifications included the introduction of large substituents along the polymer backbone. Lee and Lee [36] have prepared soluble polyimides by using aromatic linkages and glycidyl ester pendant groups, whereas Jeong et al. [37] used tetraphenylpyrrole linkages to improve solubility.

Photosensitive polyimides which have already found applications in the microelectronics industry may be divided into two groups. The first class comprises precursors to polyimides, i.e. polyamic acids [38]. These are readily soluble and are first cured on to a film and then imidized after irradiation and development. However, they display a tendency to shrink in the imidization step. The second type comprises solvent-soluble photosensitive polyimides, which should be storage stable and non-shrinking [39,40].

We have prepared polyimide photoinitiators of the latter type. Solvent-soluble photosensitive polyimides have already been synthesized. For instance, Pfeifer and Rohde first reported autophotosensitive polyimides in 1985 [41]. They found that polyimides made by reacting BTDA and ortho-alkyl-substituted diamines can be directly photoimaged. Higuchi et al. have synthesized benzophenone-containing polyimides by polycondensing bis(amino-3-ethylphenyl) methane (DEDPM) with BTDA [42]. The resultant polymer BTDA–DEDPM shows good thermal stability up to 150 °C. Photoirradiation studies showed that cross-linking, possibly by benzophenone-initiated hydrogen abstraction, was most appreciable at temperatures above 100 °C.

In preparing the polyimides, we have reacted BTDA and α - ω polyether diamines of various molecular weights to produce solvent-soluble photosensitive polyimides. The polyether diamines have propylene oxide, ethylene oxide or both oxides in their backbone with primary amine end groups. They are given a number according to their approximate molecular weight. The letter D prefixing the molecular weight stands for diamine.

The α - ω polyether diamines used in our studies are the following, D230, D400, D2000 (with polypropylene oxide backbone) and ED6000 (polyethylene oxide-propylene oxide backbone). In all subsequent discussions the resultant photosensitive polyetherimides will be classed in terms of their parent polyether diamines.

2. Results

2.1. Preparation of polyimide photoinitiators

BTDA was found to readily condense with amines in acetic acid to give imides. Since the object was to prepare polymeric photoinitiators, α - ω -terminated oligomeric polyether diamines were used (Fig. 1).

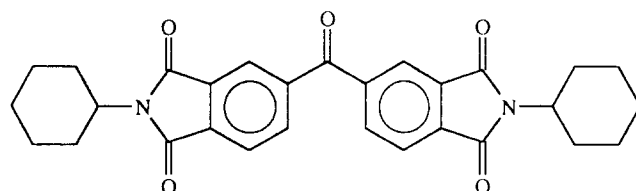
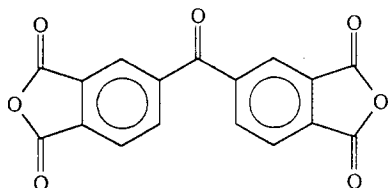
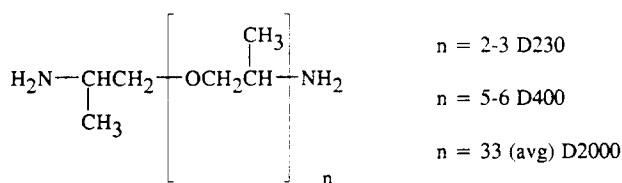


Fig. 2. Benzophenone tetracarboxylic di(cyclohexyl imide) (BDD), the control compound used to determine the extent of imidization.



The ED6000 has additionally, ethylene oxide in the backbone.

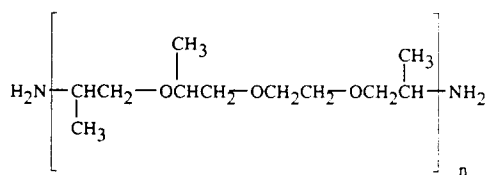


Fig. 1. Reactants used to prepare photosensitive polyetherimides.

These amines can be obtained in varying molecular weight and those utilized are shown in Fig. 1. Condensation of the dianhydride with these amines leads to a linear polymer. To control the molecular weight, *n*-butylamine (which would lead to end-capping of the polymer) was added in controlled amounts. An investigation as to the best method of preparing imides was carried out. The methods included reacting BTDA with the diamines (a) in acetic acid, (b) in formic acid, (c) in tetrahydrofuran (THF) with molecular sieves, (d) at room temperature in *N*-methyl pyrrolidinone followed by addition of cyclohexyl pyrrolidinone and heating to 120 °C and (e) at room temperature in *N*-methyl pyrrolidinone followed by heating in a microwave reactor. The degree of imidization was determined by IR spectroscopy using 3,3',4,4'-benzophenone tetracarboxylic di(cyclohexyl imide) as a reference compound (Fig. 2), which enabled comparison of the carbonyl imide stretch at 1778 cm^{-1} with the aromatic C-H deformation at 730 cm^{-1} .

Fig. 3 shows the degree of imidization achieved with each technique used as well as the molecular weights of the products. These results showed that heating the compounds in glacial acetic acid gave a good yield and a high percentage of imidization. Although the microwave method looked promising, reactions other than the imidization must have occurred, since the product obtained was a gel.

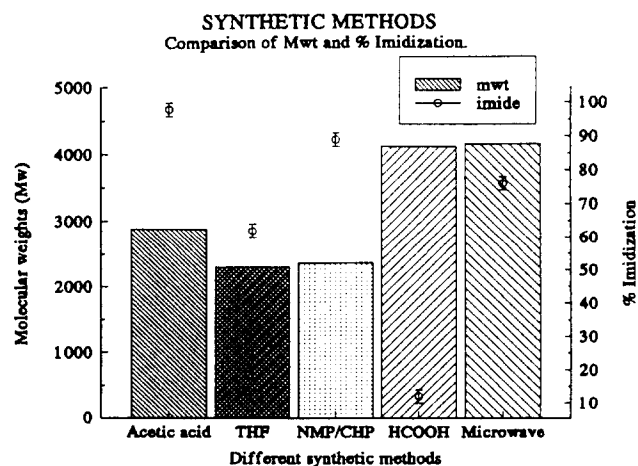


Fig. 3. Extent of imidization and polymerization for different synthetic routes.

Using glacial acetic acid as the reaction medium, a number of polyimides were prepared using α - ω diamino polyethers of varying molecular weights, either in a 1:1 ratio with *n*-butylamine or in a 9:1 ratio with *n*-butylamine (this is the amine molar ratio). Figs. 4 and 5 show the molecular weight distribution of the products obtained. The molecular weight distribution reflects not only the ratio of diamine to butylamine but also the time when the *n*-butylamine is added to the reaction mixture.

Appropriate experiments were carried out to determine the effect of the time of addition of the amine terminator. The results are shown in Fig. 6, from which it can be seen that the later the addition of *n*-butylamine, the higher are the molecular weight and polydispersity of the product.

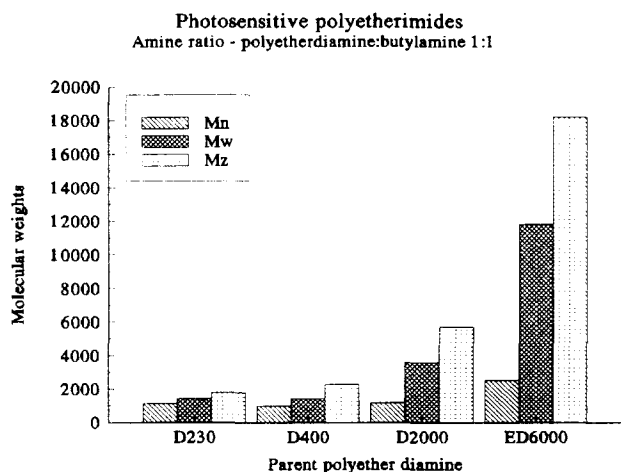


Fig. 4. Molecular weight distribution of the polyetherimides. Reaction BTDA + polyether diamine + butylamine (polyether diamine:butylamine 1:1 molar amine ratio).

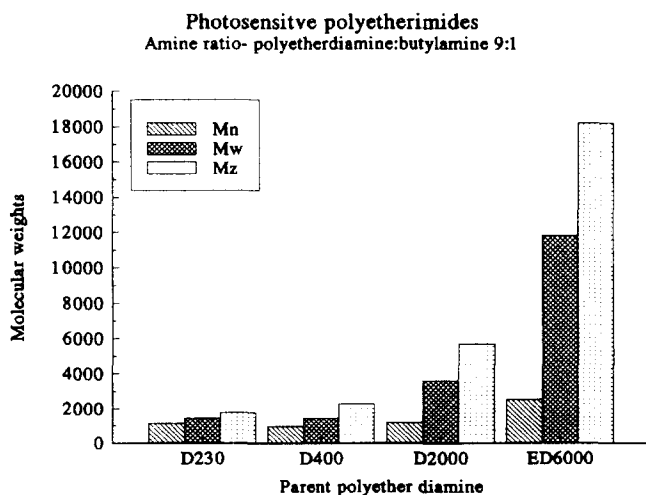


Fig. 5. Molecular weight distribution of the polyetherimides. Reaction BTDA + polyether diamine + butylamine (polyether diamine:butylamine 9:1 amine ratio).

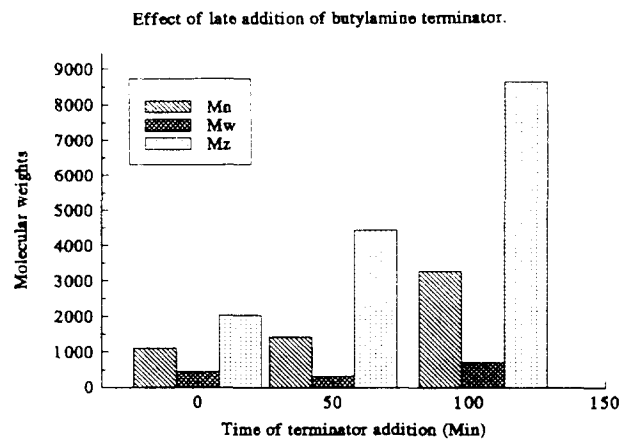


Fig. 6. Effect of terminator addition on molecular weight.

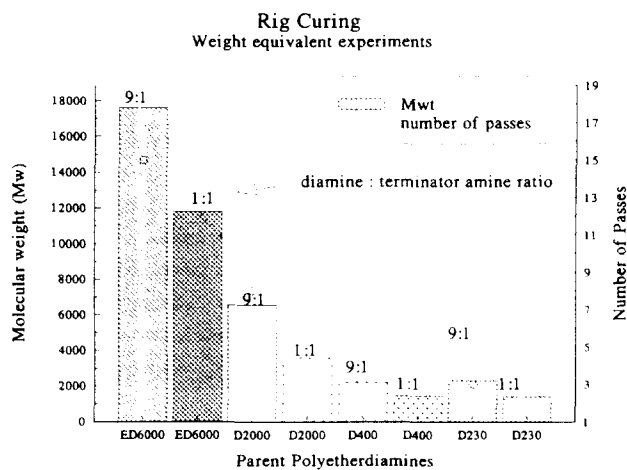


Fig. 7. Qualitative crude cure on a weight equivalent basis (5% of polymeric photoinitiator).

It was also found that carrying out the reaction at higher dilution did not significantly change the molecular weight of the polymer product.

2.2. Performance of polyimides as photoinitiators

2.2.1. Crude curing of thin films

The polyimides were found to dissolve in a range of acrylates and their ability to cure thin films was tested using a formulation containing *N,N*-dimethylethanolamine synergist (2% w/w) and a mixture of propoxylated glycerol triacrylate and epoxy acrylate (15/85 w/w). The polymeric photoinitiators were used on a weight-for-weight basis at the 5% level. Films of the mixture 20 μ m thick were laid on a glass plate, then passed under a UV lamp and the number of passes to give cure was recorded. The results are shown in Fig. 7.

The performance of the photoinitiators was compared with that of benzophenone. Not surprisingly, the reactivity of the polyimides was less than that of benzophenone and decreased as the percentage of the ben-

zophenone chromophore decreased. Films were assessed according to the thumbscrew test and then extracted using hexane and also dichloromethane. Hexane extracts displayed the amine synergist only. When dichloromethane was used, the amine synergist and low molecular weight oligomers containing acrylate groups were detected. Extracts were analysed by gas chromatography-mass spectrometry (GC-MS) (Fig. 8).

2.2.2. Real time IR (RT-IR) spectroscopic studies

The polymeric photoinitiators were dissolved in 2-hydroxyethyl acrylate containing either 5% *N,N*-dimethylethanolamine (DME) or ethyl *p*-dimethylaminobenzoate (EDB). Equimolar amounts of the photoinitiator were used so that each solution would absorb the same amount of radiation. From the results it was possible to calculate rates of photopolymerization (R_p). When DME was used as the synergist, it was found that for the polyimides with an average molecular weight (M_w) less than 8000 there was a clear distinction between the polyimides prepared using a 9:1 ratio of diamine to *n*-butylamine compared with where a 1:1 ratio was employed. For the polyetherimides with a molecular weight greater than 8000, cure was very slow. This is attributed to the high viscosity of the curing mix, which results from adding (on a weight basis as opposed to a molar basis) the same amount of photoinitiators (Fig. 9).

When the aromatic amine was used as the synergist, the R_p values were found to be much lower (Fig. 10) than for the aliphatic amine. We ascribe this to the screening effect of the amine, EDB, which has an absorption maximum at 315 nm which is within the excitation region of benzophenone.

The polyimide derived from the α - ω diamine ether of $M_w=2000$ was a liquid and therefore easy to formulate and furthermore showed reactivity similar to that of BTDA. This polyimide was used to study the

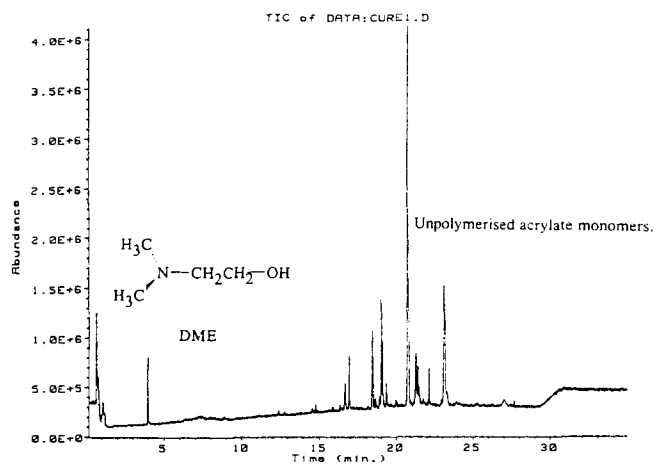


Fig. 8. GC-MS extraction results showing the synergist (DME) as a migratable component.

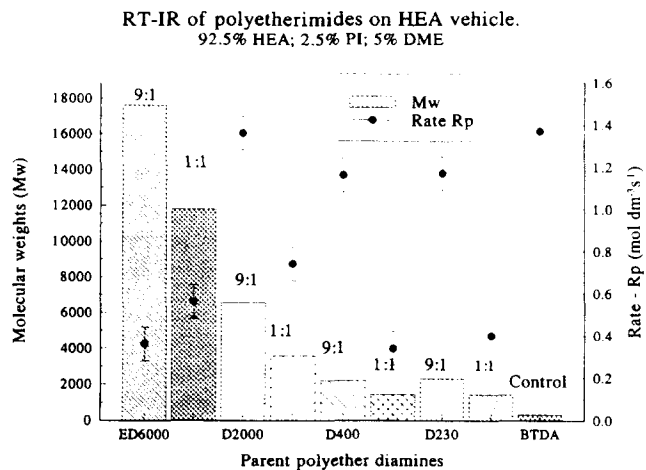


Fig. 9. RT-IR kinetic studies with aliphatic (DME) synergist.

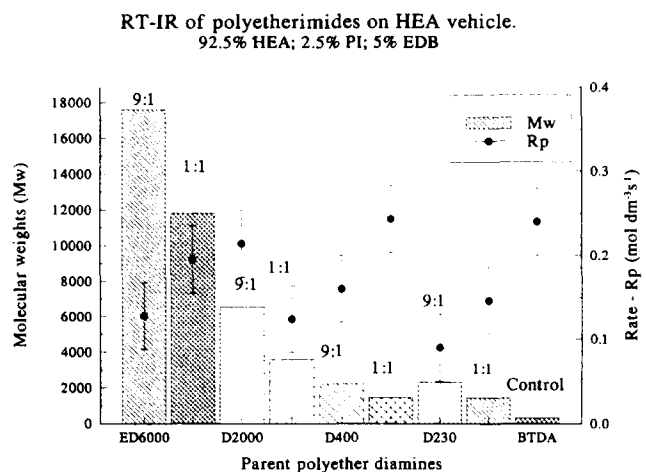


Fig. 10. RT-IR kinetic studies with aromatic (EDB) synergist.

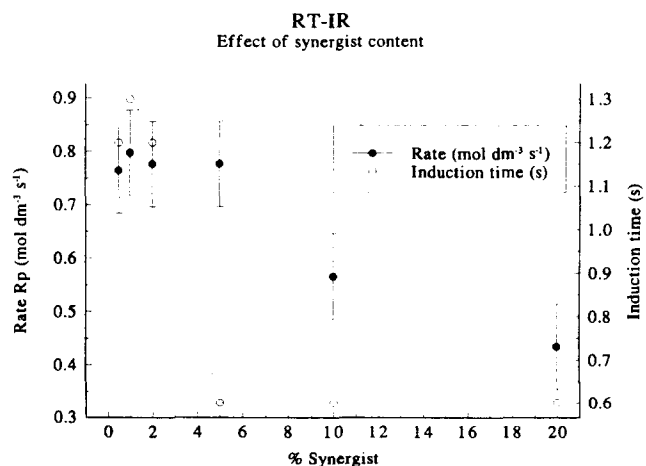


Fig. 11. Effect of synergist (DME) concentration on rate of polymerization (R_p) using the D2000 polyetherimide.

effect of varying the concentration of the aliphatic amine synergist (Fig. 11).

As can be seen from Fig. 11, increasing the concentration of amine above 2% leads to a decrease in

R_p , but this is offset by the higher concentration of amine leading to a reduced induction period.

We attribute the decrease in R_p to the amine acting as a chain transfer agent and the decrease in induction period as being due to the higher concentration of amine favouring oxygen scavenging.

2.2.3. Photo-differential scanning calorimetry (photo-DSC)

This technique was employed to assess the rate of cure for each of the photoinitiators. Two series of experiments were conducted: one under nitrogen and the other under oxygen to assess the extent of oxygen inhibition. The results shown in Figs. 12–14 relate to curing using the polyimides on a molar basis in the presence of *N,N*-dimethylethanolamine as synergist (2%). The vehicle is an acrylate mix composed of a urethane diacrylate and trimethylolpropane triacrylate. This particular mixture was used to overcome the creeping of the formulation up over the sides of the DSC sample pans, but it had the disadvantage of being viscous and thereby reducing the performance of the

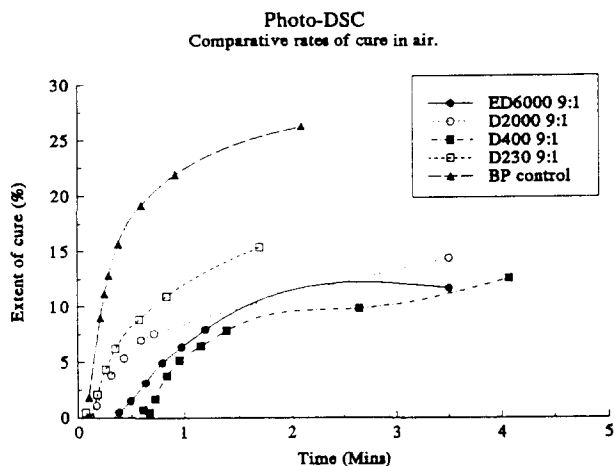


Fig. 12. Photoreactivity in air.

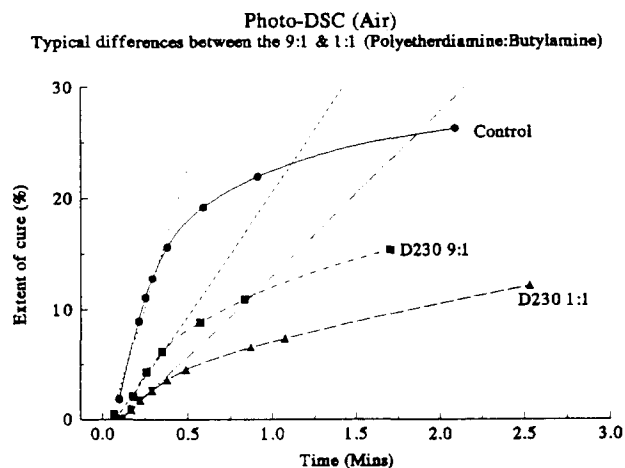


Fig. 13. Comparison of 9:1 and 1:1 (polyether diamine:butylamine) polyetherimide photoreactivity.

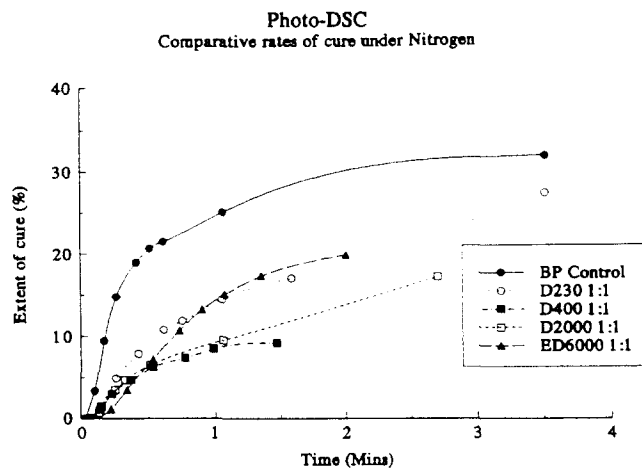


Fig. 14. Effect of nitrogen purging on photoreactivity.

polyimide photoinitiators. This viscosity effect is also reflected by the percentage conversion of acrylate double bonds.

The results confirm that polyimides made from a 1:1 mix (amine ratio) of the α - ω diamino ether and butylamine are less effective (in terms of cure rate) than those made from the 9:1 mix (Fig. 13).

The curing in the presence of air leads to relatively large induction periods for the poorer performing polyetherimides (Fig. 12), but under nitrogen these induction periods are eliminated (Fig. 14).

3. Discussion

Formation of the imides was found to occur smoothly when glacial acetic acid was used as the solvent. Other methods were investigated to determine the efficiency of imidization, the extent of polymerization and also, in the case of formic acid, whether a lower boiling point material could be used so as to aid its removal from the polyimide. The microwave method shows potential, but the occurrence of some gelling leads one to suspect that reactions other than the desired imidization are taking place.

By varying the proportion of the diamine to the monoamine terminator, the molecular weights could be controlled. Further control could be exercised by varying the rate of addition of the terminator and at what stage of the experiment the terminator was added. It was pleasing to find that the polyimide based on the diamine of molecular weight 2000 was liquid, since this aids formulation.

All the polyetherimides were used with an amine synergist (DME) to cure thin films composed of acrylate oligomer. When used on a weight-for-weight basis, the efficiency of the photoinitiator decreased with increasing molecular weight, because on a mole-for-mole basis the amount of benzophenone decreases as the molecular weight increases.

For a true comparison the materials should be used on a molar equivalent basis and this was done in the RT-IR and photo-DSC experiments. It was readily apparent that the use of high molecular weight photoinitiators has a distinct disadvantage: to obtain a comparable molarity, one has to use a much larger weight of the polymeric photoinitiator compared with the monomeric material.

Such a large addition can distort the results by leading to a marked increase in the viscosity of the curing mix. This effect is reflected in the RT-IR results, which also show that the amount of monoamine terminator used in the preparation is significant in determining the reactivity of the initiator.

This higher photoreactivity of polyetherimides prepared with less terminator may be ascribed to the polyether backbone providing some sites from which the triplet benzophenone can abstract hydrogen, thereby leading to incorporation of the polyimide into the polyacrylate.

The RT-IR study highlighted the point that care has to be taken in choosing the amine synergist and the concentration at which it is used. The aromatic synergist, which is excellent for thioxanthenes, performs less well with the polyimides, as shown in Fig. 6. This is due to the screening out of some light which would otherwise have been used for activating the benzophenone chromophore. With the aliphatic amine synergist a variation in performance with its concentration was found. This has implications for the potential use of such compounds, since if they can lead to chain transfer, film properties will be impaired owing to the presence of lower molecular weight acrylate oligomers. From these results it can also be seen that increasing the amine concentration significantly reduces the induction period but does not eliminate it. Obviously the curing formulation contains oxygen and its effect in retarding the cure cannot be completely eliminated by the addition of amine. The problem is exacerbated when the film is not covered as it is in RT-IR experiments, since during curing, process oxygen can diffuse into the film from the air.

To investigate the importance of this, such systems were examined using photo-DSC. These experiments confirmed the findings obtained using RT-IR spectroscopy. Furthermore, when curing was carried out under nitrogen, the percentage utilization of acrylate double bonds was higher than when acrylic curing was carried out in air. This suggests a diffusion of atmospheric oxygen into the film during curing and hence a lower percentage conversion of acrylate double bonds owing to the radical scavenging and triplet quenching nature of oxygen.

Given the drive to produce surface coatings with zero migrateables, we can say that the use of polymeric benzophenone anchors the benzophenone in the cure

films. The remaining problems are eliminating the occurrence of low molecular weight oligomers which contain acrylate groups and the design of systems which do not utilize low molecular weight amines.

We have described some polyimide photoinitiators possessing reasonable solubility in most acrylates. However, in the systems tested, their reactivity was somewhat lower than that of benzophenone. In some cases this may be attributed to the addition of the polyimide increasing the viscosity of the acrylate formulation, as a consequence of which the gel point is reached at an earlier stage, resulting in fewer acrylate double bonds being utilized.

These polyetherimides are of lower relative photoreactivity when compared with the commercially available hydroxyalkylphenones (KIP series [15]). The presence of another chromophore (i.e. imide functionality) as well as the benzophenone may result in competition for the UV radiation. The presence of imide functionality may also explain why the results we have obtained differ from the work on polymeric benzophenones by Carlini and coworkers [23–27].

4. Conclusions

Polymeric photoinitiators of the type described so far have displayed a need for careful formulation in order to overcome viscosity effects. Photo-DSC studies have shown how the polymeric photoinitiators (polyetherimides) are more prone to oxygen inhibition when compared with their monomeric counterparts.

Extraction studies indicate that the polymeric photoinitiator is not a migrateable component in the cured formulations. There is, however, the problem of eliminating the synergistic amine as a migrateable component. The elimination of the amine synergist will be the subject of further work.

5. Experimental details

5.1. General

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. Gel permeation chromatography (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. The samples were run using THF 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 nuclear magnetic resonance (NMR) spectra were recorded on a Jeol FMX 270 FT (270.05 MHz) spectrometer with tetramethylsilane as internal reference. ^{13}C NMR spectra were recorded at 67.8 MHz on a Jeol FMX 270 FT spectrometer with tetramethylsilane as internal standard. Samples were run as CDCl_3 or $\text{DMSO}-d_6$ solutions. RT-IR spectroscopy 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) Hg lamp. Photo-DSC was carried 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 $^\circ\text{C}$. Microwave experiments were carried out using a domestic Moulinex 650 W microwave oven and a 45 ml Parr microwave digestion bomb.

5.2. Solvents, reagents and starting materials

Tetrahydrofuran was distilled from sodium and benzophenone under nitrogen. Butylamine and cyclohexylamine were distilled over KOH under nitrogen. The α - ω polyether diamines 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 and all other reagents and solvents were obtained from the Aldrich Chemical Company and used without further purification.

5.3. Comparison of different synthetic routes

5.3.1. Preparation of control compound: synthesis of 3,3',4,4'-benzophenone tetracarboxylic di(cyclohexyl imide) (BDD)

4.00 g (12.4 mmol) of BTDA was dissolved in 50 ml of glacial acetic acid. To this, 2.46 g (24.8 mmol) of cyclohexylamine was added. The mixture was refluxed for 2 h. The resultant dark brown solution was subsequently cooled in a salt–ice bath to effect crystallization of the imide product. The crystals were collected by filtration and recrystallized from 1,4-dioxane to give 4.20 g (70.05% yield) of the white crystalline product.

Analysis. M.p. 310–314 $^\circ\text{C}$. Formula $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_5$ requires: C, 71.88; H, 5.82; N, 5.78. Found: C, 71.87; H, 5.69; N, 5.57. IR ν (cm^{-1}): 1774 (imide carbonyl), 1715 (imide), 1376 (C–H def. alkane), 716 (C–H def. aromatic or imide). ^1H NMR (270 MHz, CDCl_3) (ppm): 7.65–8.5 m (Ar–H); 4.05–4.17 t (HC–N); 2.29–1.19 m (C_6H_{10}). m/z : 483.9 (M^+), 402.8 ($\text{M}^+ - \text{C}_6\text{H}_{11}$), 321.8 ($\text{M}^+ - 2(\text{C}_6\text{H}_{11})$), 82 (C_6H_{10}).

5.3.2. Different preparative routes to achieving imidization

(a) *Acetic acid.* Based on a procedure by Vogel [43], 4.00 g (12.46 mmol) of BTDA and 24.92 g (12.46 mmol) of α - ω polyether diamine of molecular weight 2000 were refluxed in 100 ml of dry glacial acetic acid for 4 h. The product was isolated by removing the acetic acid in vacuo and then storing the resultant oil in vacuo over NaOH pellets for 1 week. The oil product was analysed by FT-IR and GPC to evaluate the percentage imidization and molecular weight as described below.

(b) *Formic acid.* The same procedure as in (a) was used except that the solvent was changed to formic acid (100 ml). The dark brown oil product was analysed by FT-IR and GPC as described below.

(c) *N-methyl pyrrolidinone (NMP) and cyclohexyl pyrrolidinone (CHP).* Using the same reaction stoichiometry as in (a) and a procedure similar to that described by Lewis et al. [44], the reactants were initially stirred with 120 ml of NMP for 3 h. 30 ml of CHP was added and the reaction mixture was heated to 120 $^\circ\text{C}$. The CHP was used to azeotrope the water that condenses from the imidization step. The reaction mixture was cooled after 3 h and the NMP solvent was evaporated off under reduced pressure (10 mmHg). The product, a golden-coloured oil, was analysed by GPC and FT-IR to evaluate the molecular weight and percentage imidization.

(d) *THF with molecular sieves.* The same reaction stoichiometry as in (a) was used except that the reaction medium was changed to dry, freshly distilled THF. The reaction flask was also charged with 4 g of molecular sieves. The reaction mixture was left to reflux for 3 h (following a procedure described by Scaiano et al. [45]). The THF solution was decanted from the reaction flask and dried further with anhydrous MgSO_4 . The dry THF solution was put under high vacuum to leave behind a golden oil. The sample was analysed by FT-IR and GPC to evaluate the percentage imidization and molecular weight as described below.

(e) *Microwave method.* This method differs from the rest in that the reaction was necessarily scaled down owing to the pressure built up in a microwave bomb when large amounts of reactant and solvent are used. 2 ml of an acetic acid solution prepared as in (a) was put into a 45 ml Teflon microwave cup. The Teflon cup was fitted with a lid and sealed in a Parr microwave digestion bomb. The sample was irradiated for a total of 500 s in five short bursts of 100 s separated by 5 min of cooling. The microwave bomb was allowed to cool to 30 $^\circ\text{C}$ and then opened. Upon opening the Teflon cup, most of the acetic acid escaped as vapour, leaving behind an oil at the bottom of the cup. The sample was analysed by FT-IR and GPC to evaluate the percentage imidization and molecular weight.

5.3.3. Comparison of percentage imidization by FT-IR

Using the control compound BDD, the C–H def. absorption at 730 cm^{-1} was compared with the carbonyl imide absorption at 1778 cm^{-1} . The ratio of the two absorptions was deemed to be indicative of 100% imidization. Similar absorption ratios were calculated for the various polyetherimides made by the five different routes. The ratios were compared with that of the control compound BDD and converted to a percentage accordingly. Molecular weight comparisons were made by GPC (see Fig. 3).

5.3.4. Effect of late addition of butylamine terminator

2.00 g (6.24 mmol) of BTDA was added to 50 ml of glacial acetic acid. To this, 0.713 g (3.1 mmol) of the α - ω polyether diamine of molecular weight 230 was added. The mixture was allowed to reflux for 50 min. The reaction mixture was then cooled to $25\text{ }^\circ\text{C}$ and 0.23 g (3.1 mmol) of butylamine was added. The mixture was now refluxed for a further 2 h. The acetic acid was then removed under reduced pressure, taking care not to heat the reaction flask above $30\text{ }^\circ\text{C}$. The resultant oil was stored at 25 – $30\text{ }^\circ\text{C}$ in vacuo in the dark over NaOH pellets for 1 week.

The same procedure was repeated again, except that the butylamine terminator was added after 100 min. Both products were analysed by GPC (see Fig. 6).

5.3.5. Synthesis of benzophenone-containing polyetherimides

These polyetherimides were prepared by condensation of BTDA and α - ω polyether diamines of varying molecular weights ($M_w = 250, 400, 2000, 6000$).

The ends of the resultant polymer were capped with *n*-butylamine to give a butylimide-terminated polymer. The ratios of *n*-butylamine and the α - ω polyether diamines were varied. Since the α - ω polyether diamines are difunctional whilst *n*-butylamine is monofunctional, the ratios described are in terms of molar equivalents of amine functionality. Two amine ratios were used: (a) polyether diamine: butylamine 9:1; (b) polyether diamine: butylamine 1:1 (see Table 1).

(a) *Preparation of polyetherimides with 9:1 polyether diamine:butylamine amine ratio.* 2.00 g (6.2 mmol) of

BTDA was dissolved in 100 ml of glacial acetic acid. To this, 5.58 mmol of appropriate α - ω polyether diamine was added. The mixture was refluxed for 1.5 h and then cooled to room temperature before the addition of 0.13 ml (1.2 mmol) of butylamine. The reaction mixture was refluxed for a further 1.5 h to give a clear brown solution. The acetic acid was then removed in vacuo, taking care not to allow the temperature of the water bath to rise above $40\text{ }^\circ\text{C}$.

The oil residues obtained from the α - ω polyether diamines of molecular weight 230 and 400, upon evaporation of acetic acid, were mixed with an equivalent volume of Na-dried diethyl ether and allowed to stand for up to 12 h. The ether layer was then decanted off and the residue put under high vacuum to give a foam solid after 30 min.

(b) *Preparation of polyetherimides with 1:1 polyether diamine:butylamine amine ratio.* The procedure is the same as in (a) except that 0.63 ml (6.3 mmol) of butylamine and 6.3 mmol of the polyether diamine were used.

5.3.6. Characterization of polyetherimides

Molecular weight determination was carried out by GPC using polystyrene and polyethylene glycol standards (see Figs. 4 and 5).

IR ν (cm^{-1}): 1775 (C=O imide), 1720 (C=O imide), 1665 (C=O diaryl), 1391 (C–N aliphatic amine), 1365 (C–N imide), 1106 (C–O ether), 727 (aromatic C–H def.). $^1\text{H NMR}$ (270 MHz, CDCl_3) (ppm): 1.09 (m) broad (CH_3 of polypropylene glycol also masking CH_3 of butylamine terminator), 3.4–3.6 broad (CH_2O), 3.9 m (Me –CH–N), 1.44 and 1.78 m (CH_2 of butyl terminator), 8.0–8.1 (m) (Ar–H benzophenone). $^{13}\text{C NMR}$ (67.8 MHz, $\text{DMSO-}D_6$) (ppm): 193 (C^{14}), 167 (C^7), 168 (C^6), 141 (C^8), 137 (C^9), 129 (C^{11}), 131 (C^{12}), 132 (C^{13}), 123 (C^{10}), 68.4 (C^{20} , C^{17}), 64.8 (C^{18} , C^{15}), 57.7 (C^{19}), 38.4 (C^{15}), 37.4 (C^4), 27.6 (C^3), 20.2 (C^2), 15 (C^1) (Fig. 15). (Not every carbon atom can be assigned owing to line broadening associated with polymers. The restricted rotation of the polymer allow the T_2 spin–spin relaxation time to dominate. Since T_2 is related to the linewidth, as T_2 decreases, i.e. the relaxation becomes quicker, the linewidth increases. Other line broadening may be due to the restricted rotation of the polymer which does not allow the dipolar interactions to average out. As well as this there is the effect of anisotropy broadening.)

UV spectra showing the benzophenone carbonyl are presented in Fig. 16.

5.4 Photoreactivity experiments

5.4.1. Crude cure

A weight-based formulation of 2% DME synergist, 5% polymeric photoinitiator (polyetherimide) and 93%

Table 1
Amounts of polyether diamines used in polymer preparation

Polyetherdiamines	Amount (g)	
	Polyether diamine:butylamine amine ratio	
	9:1	1:1
D230	1.29	0.71
D400	2.23	1.24
D2000	11.16	6.2
ED6000	33.48	18.6

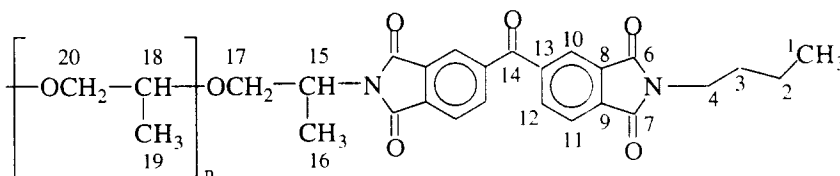


Fig. 15. Numbering system for polyetherimide.

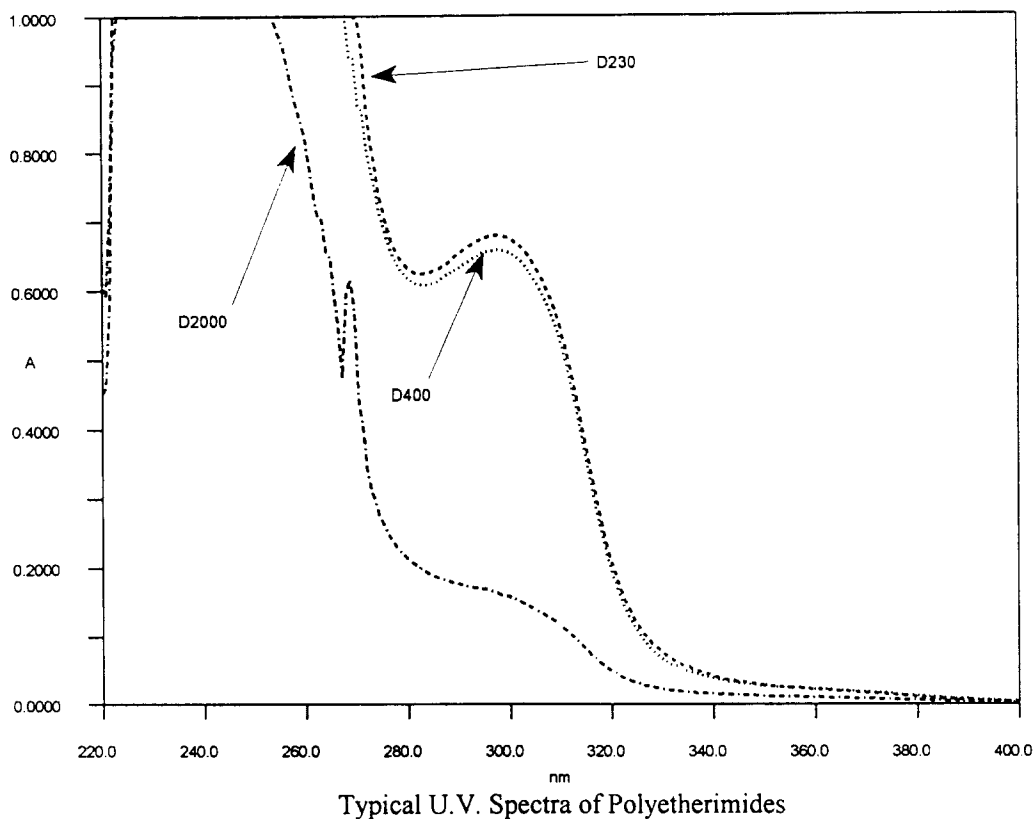


Fig. 16. Typical UV spectra of the polyetherimides: —, D230; ·····, D400; ---, D2000.

vehicle comprising 15:85 w/w propoxylated glycerol triacrylate (GPTA):epoxy acrylate was coated on to tin float glass to give a film 20 μm thick. The film was passed under a Colordry UV rig fitted with a medium pressure (100 W per linear inch) Hg lamp and set at a belt speed of 20 m min^{-1} . The number of passes required to give a hard film that would pass a “thumb-screw test” was recorded.

5.4.2. GC-MS analysis of extracts

A fixed area of 25 cm^3 of the above cured film was detached from the glass and soaked in 20 ml of hexane. The procedure was repeated using CH_2Cl_2 as solvent. After 24 h the hexane and CH_2Cl_2 extracts were analysed by GC-MS. The results of CH_2Cl_2 extraction are shown in Fig. 8.

5.4.3. RT-IR

(a) *DME as synergist*. Formulations comprising DME synergist, hydroxyethyl acrylate (HEA) and the

polyetherimide photoinitiators were prepared. 5% of synergist was used throughout and the polyetherimide photoinitiator concentrations (w/w) were adjusted to maintain equivalent molar concentrations of the benzophenone chromophore (25 mmol). The formulations were sandwiched between two NaCl plates using polyethylene spacers designed to give a film 25 μm thick.

RT-IR experiments on the sandwiched films were performed on a Perkin-Elmer 599 spectrophotometer specially fitted with a Kratos high pressure Hg 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 bond, which has a $\text{CH}_2=\text{CH}$ twist at 810 cm^{-1} .

Rates of polymerization were calculated using the equation

$$Rp = - \frac{M_0}{A_0} \times \frac{A_2 - A_1}{t_1 - t_2} \quad (1)$$

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

(b) *Aromatic synergist (EDB)*. The same experiments as in (a) were repeated, this time using EDB as synergist (see Fig. 10).

(c) *Effect of amine synergist*. Using the same procedure as in the previous RT-IR experiments, formulations containing 0.5%, 1%, 2%, 5%, 10% and 20% synergist (DME) and 97%, 96.5%, 95.5%, 92.5%, 87.5% and 77.5% vehicle (hydroxyethyl acrylate) respectively along with a fixed 2.5% photoinitiator (polyetherimide obtained from polyether diamine of molecular weight 2000 and where the polyether diamine:butylamine amine ratio was 9:1) were examined. The induction period before polymerization was also recorded. The results are shown in Fig. 11.

5.4.4. Photo-DSC in air

Formulations comprising DME synergist and polyetherimide photoinitiators in a urethane diacrylate were prepared. The photoinitiator concentration was adjusted to maintain a chromophore concentration of 25 mmol. The formulations contained 5% photoinitiator, 2% synergist and 93% vehicle (reactive diluent) made up of a urethane diacrylate. The reasons for the choice of vehicle are as follows.

(1) The vehicle is viscous and dense enough to prevent flow within the DSC pan and up the walls of the DSC pan, which would result in the loss of some thermal contact upon curing.

(2) The mixture approximates to industrially applied systems.

(3) The 0.8 mg weight of sample that is put into the DSC pan spreads to give a film 80 μm thick.

(4) The aliphatic urethane is transparent above 300 nm and the emission spectrum of the 100 W Hg short arc lamp is mostly above 300 nm.

Each of the 0.8 mg samples in the DSC pan was irradiated for 4.5 min and its thermogram recorded. The percentage conversion of acrylate was calculated using a value of 250 J g^{-1} as the heat of acrylate double-bond conversion. See Figs. 12 and 13 for the results.

5.4.5. Photo-DSC under nitrogen

Using the same formulations as above, the samples were irradiated after purging the DSC sample compartment (fitted with a glove-box) with nitrogen for 30 min (see Fig. 14).

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References

- [1] R.S. Davidson, *J. Photochem. Photobiol. A: Chem.*, 69 (1993) 263.
- [2] M.A. Abd-alla, *Makromol. Chem.*, 192 (1992) 277.
- [3] T. Doi and G. Smets, *Macromolecules*, 22 (1989) 25.
- [4] R.H. Heiter and G. Rosen, *US Patent 3 922 363*, 1976.
- [5] R. Hueiter, R. Kirchmayr, W. Rutsch and M. Rembold, *Eur. Patent EP 0 304 886*, 1989.
- [6] M. Koehler and J. Ohngemache, *Radcure Europe '87 Conf. Proc. Munich, 1987*, Society of Manufacturing Engineers, Conf. Proc. Chap. III, p. 1.
- [7] M. Koehler and J. Ohngemache, *Polym. Mater. Sci. Eng.*, 60 (1989) 1.
- [8] M. Koehler and J. Ohngemache, *ACS Symp. Ser.*, 417 (1990) 106.
- [9] K. Monami, M. Sato and M. Miimoto, *Jpn. Kokai Tokyo Koho JP 02 292 307*, 1990.
- [10] G. Li Bassi, *J. Radiat. Curing*, 16 (1987).
- [11] C. Carlini, S. Dal Canto, D. Donati and A. Moroni, *Pittura e Vernici*, 59 (1983) 73.
- [12] C. Carlini, *Br. Polym. J.*, 18 (1986) 2.
- [13] H. Hageman, *Prog. Org. Coat.*, 13 (1985) 123.
- [14] R.S. Davidson, H.J. Hageman and S. Lewis, *Radtech Europe '91 Conf. Proc.*, Radtech, Fribourg, 1991, p. 691.
- [15] G. Li Bassi, *Pittura e Vernici*, 62 (1986) 30.
- [16] E.C. Blossley, D.C. Neckers, A.L. Thayer and A.P. Schaap, *J. Am. Chem. Soc.*, 95 (1975) 5820.
- [17] A.P. Schaap, A.L. Thayer, E.C. Blossley and D.C. Neckers, *J. Am. Chem. Soc.*, 95 (1975) 3741.
- [18] H. Bottcher (ed.), *Technical Applications of Photochemistry*, Deutsche Verlag für Grandstoff Industrie, Leipzig, 1991.
- [19] C. David, W. Demarteau and G. Geuskens, *Polymer*, 10 (1969) 21.
- [20] G. Sanchez, G. Weill and R. Kuosel, *Makromol. Chem.*, 179 (1978) 131.
- [21] M. Gloria, F. Minto, F. Flamigni and P. Bartolus, *Macromolecules*, 20 (1987) 1766.
- [22] H.G. Heine, H.S. Rosen Krahtz and H. Rudolph, *Angew. Chem., Int. Edn. Engl.*, 11 (1972) 974.
- [23] C. Carlini, F. Ciardelli, C. Donati and F. Gurzani, *Polymer*, 24 (1983) 599.
- [24] C. Carlini, L. Toniolo, P.A. Rolla, F. Barigelletti, P. Bartolus and L. Flamigni, *New Polym. Mater.*, 1 (1987) 63.
- [25] C. Carlini, F. Ciardelli and P.A. Rolla, *Proc. XIII Int. Conf. on Organic Coatings in Science and Technology, Athens, Greece, 1987*, p. 79.
- [26] L. Flamigni, F. Barigelletti, P. Bartolus and C. Carlini, *Eur. Polym. J.*, 20 (1984) 171.
- [27] C. Carlini, *Br. Polym. J.*, 18(4) (1986) 236.
- [28] A. Ledwith, *Pure Appl. Chem.*, 49 (1977) 431.
- [29] A. Ledwith, J.A. Bosley and M.J. Purbrick, *J. Oil Col. Chem. Assoc.*, 61 (1978) 95.
- [30] W.Y. Chiang and S.S. Chan, *Angew. Makromol. Chem.*, 179 (1990) 57.
- [31] W.Y. Chiang and S.S. Chan, *J. Appl. Polym. Sci.*, 43 (1991) 1827.
- [32] F. Catalina, C. Peinado, R. Sastre, J.L. Mateo and N.S. Allen, *J. Photochem. Photobiol. A: Chem.*, 47 (1989) 365.

- [33] F. Catalina, C. Peinado, E.L. Madruga, R. Sastre and J.L. Mateo, *J. Polym. Sci. A: Polym. Chem.*, 28 (1990) 967.
- [34] N.S. Allen, C. Peinado, E. Lam, J.L. Kotecha, F. Catalina, S. Navaratnam and B.J. Parsons, *Eur. Polym. J.*, 26 (1990) 1237.
- [35] F.W. Harris, W.A. Feld and L.H. Hanier, *ACS Polym. Prepr.*, 17(2) (1976) 353.
- [36] H. Lee and Y. Lee, *J. Polym. Sci. A: Polym. Chem.*, 27 (1989) 1481–1497.
- [37] H. Jeong, M. Kakimoto and Y. Imai, *J. Polym. Sci. A: Polym. Chem.*, 29 (1991) 1691–1695.
- [38] H. Ahne, H. Eggers, W. Gross, N. Kokkotakis and R. Rubner, *Proc. 2nd. Int. Conf. on Polyimides, Ellenville, NY, 1985*, Society of Plastics Engineers Inc., Plenum, Ellenville, NY, p. 561.
- [39] N. Yoda and H. Hisato, *J. Macromol. Sci. Chem. A*, 21 (1984) 1641.
- [40] S. Kubota, S. Tanaka, N. Moriwaki and S. Etoh, *J. Photopolym. Sci. Technol.*, 2 (1989) 46.
- [41] J. Pfeifer and O. Rohde, *Proc. 2nd Int. Conf. on Polyimides, 1985, Ellenville, NY, 1985*. Society of Plastics Engineers Inc., Plenum, Ellenville, NY, p. 130.
- [42] H. Higuchi, T. Yamashita, K. Horie and I. Mita, *Chem. Mater.*, 3 (1991) 188–194.
- [43] A. Vogel, *Practical Organic Chemistry*. Longmans, London, 1978.
- [44] D.A. Lewis, J.D. Summers, T.C. Ward and J.E. McGrath, *J. Polym. Sci. A: Polym. Chem.*, 30 (1992) 1647–1653.
- [45] J.C. Scaiano, A.F. Brecknell and R.D. Small, *J. Photochem. Photobiol. A: Chem.*, 44 (1988) 99–110.