Preparation and Evaluation of Low Migration Oligomeric Photoinitiators with a Repeating Photoactive Site

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Abstract

UV-curing is an efficient, environmentally friendly technology used extensively for a variety of applications including food packaging. Its limitation is that small photoinitiator molecules may migrate into the foodstuff which, although not necessarily harmful, is undesirable and is subject to legislative requirements.

In order to meet these requirements a variety of oligomeric photoinitiators based on benzophenone have been prepared. To maximise their photoinitiating capability these have been prepared with a repeat photoinitiating unit and it has been attempted to minimise the non-photoinitiating portion of the molecule.

To evaluate migration a simple UV method of detecting and measuring migration has been developed and successfully validated.

Twenty four oligomers with a repeat photoinitiating unit have been prepared with six of these shown to be low-migrating with a seventh capable of being used as a low migrating oligomeric photoinitiator due to exhibiting a rapid speed of cure at low photoinitiator concentrations.

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Abbreviations

16HED	1,6-hexanediol ethoxylate diacrylate
BAED	bisphenol A ethoxylate diacrylate
BPTX	1-bromo-4-propoxythioxanthone
BTDA	3,3',4,4'-benzophenone tetracarboxylic dianhydride
CPTX	1-chloro-4-propoxythioxanthone
DBTDL	dibutyl tin dilaurate
DCM	dichloromethane
DMF	dimethylformamide
EDB	ethyl 4-dimethylaminobenzoate
FPTX	1-fluoro-4-propoxythioxanthone
GCMS	Gas Chromatography Mass Spectrometry
GPC	Gel Permeation Chromatography
HOMO	Highest Occupied Molecular Orbital
IR	Infrared
ISC	Inter System Crossing
ITX	2-isopropoxythioxanthone
LCMS	Liquid Chromatography Mass Spectroscopy
LED	Light Emitting Diode
LUMO	Lowest Unoccupied Molecular Orbital
UV	Ultraviolet
NMP	*N*-methyl pyrrolidone
PEEK	Poly Ether Ether Ketone
PEK	Poly Ether Ketone
ppb	parts per billion
ppm	parts per million
PVA	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
TBAB	tetrabutylammonium bromide
TDI	toluene-2,4-diisocyanate

TLC	Thin Layer Chromatography
TPGDA	tripropylene glycol diacrylate
VOC	Volatile Organic Compound
w/w	weight for weight

1.0 Introduction

1.1 Introduction to UV Curing

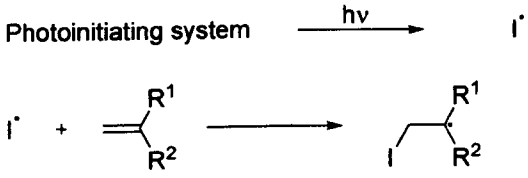
UV curing involves the exposure of a liquid monomer system to UV light which initiates a chain reaction resulting in the production of a solid polymeric system.[1] This has uses in applications as diverse as surface coatings, printing, electronics and dentistry.[2] The advantages over other methods, such as heat curing, is that it is energy efficient and environmentally friendly involving little or no Volatile Organic Compounds (VOCs).[3]

The curing process is started by the absorption of UV light by a photoinitiating system which, in turn, starts the polymerisation process. Two common methods of polymerisation are used, radical polymerisation of acrylates or cationic polymerisation of vinyl ethers and epoxides.[4] Of these the most common is the use of free radical polymerisation and this will from the basis for the photoinitiating systems used in this thesis.

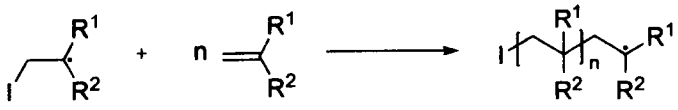
1.2 Radical Polymerisation

In radical polymerisation the activation of the photoinitiator by UV light produces a radical which can react with a double bond of a monomer by attaching to one end and forming a new radical at the other. This in turn can react with subsequent monomers to form a growing chain. Termination of the reaction may be by combination between two growing chains (or a growing chain and an initiator radical) or by disproportionation between two chains.[5] This is illustrated in Scheme 1.1.

Initiation

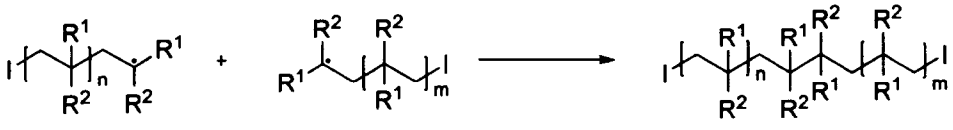


Propagation

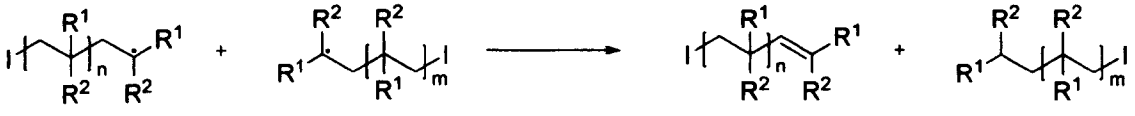


Termination

By combination



By chain transfer



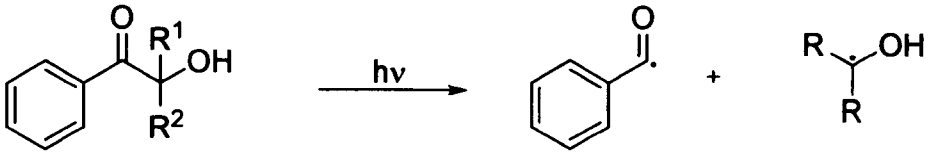
Scheme 1.1: Illustration of the steps involved in Radical Polymerisation[5]

The initiating radical is generally produced by one of two mechanisms which give rise to the two major classes of photoinitiator, type I and type II. Both types of photoinitiator contain an aromatic group with an adjacent carbonyl which forms the chromophore, or light-absorbing part of the molecule.[6] Type I photoinitiators are unimolecular systems which form radicals by a scission process which can occur in either the α or β position depending on the molecule.[2,4] Type II photoinitiators involve a chromophore which forms radicals by hydrogen abstraction which may be either intermolecular or intramolecular.[2]

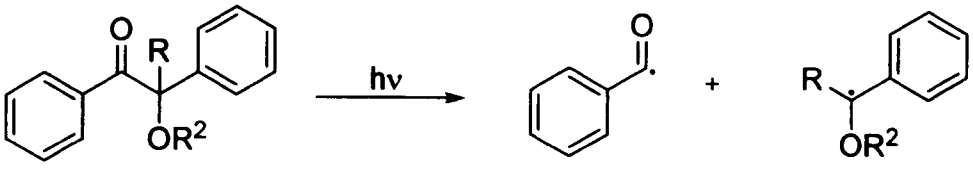
1.3 Type I photoinitiators

Type I photoinitiators form radicals by direct fragmentation of the initiator into two radical species. These are generally both highly reactive and both capable of initiating free radical polymerisation reactions.[6] Initially it was thought that this occurred through an intermediate triplet state of the carbonyl, however, experimental evidence has suggested that such an intermediate does not in fact exist, and the radicals are formed by direct fragmentation.[2] There are numerous different type I photoinitiators and a few of the common classes are shown in Scheme 1.2.

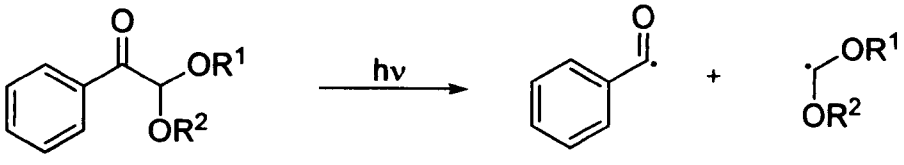
Hydroxyalkylphenones



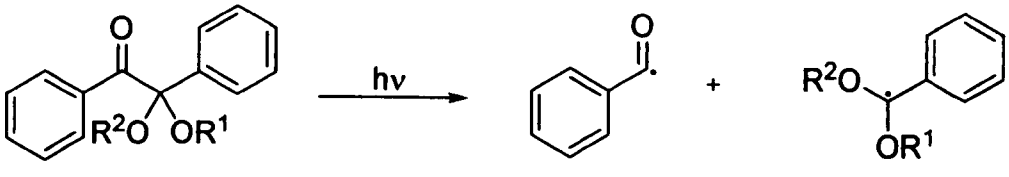
Benzoins



Acetophenones



Benzilketals

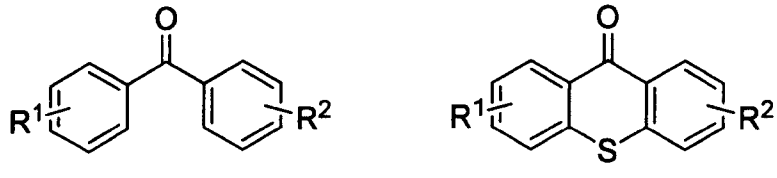


Scheme 1.2: Examples of Type I Photoinitiators[2,4]

The advantage of type I photoinitiators is that the lack of an intermediate triplet state avoids some problems such as oxygen inhibition. Oxygen inhibits free radical polymerisation by quenching the triplet state of the carbonyl. Since the triplet state in type I photoinitiators is quite short lived and is not responsible for their photocleavage this does not pose a problem. It is more of an issue with type II photoinitiators where the triplet state is more important to the formation of reactive radicals.[7] This, therefore, negates the need for the curing process to be undertaken in an inert atmosphere.[2] However, there are limitations as the cleavage process leads to the production of small fragment molecules which may be undesirable in the finished product.

1.4 Type II photoinitiator systems or hydrogen abstraction photoinitiators

In the most common type II photoinitiators a second aromatic group is attached to the carbonyl of the chromophore. Examples of these are benzophenones and thioxanthones shown in Figure 1.1.[6]



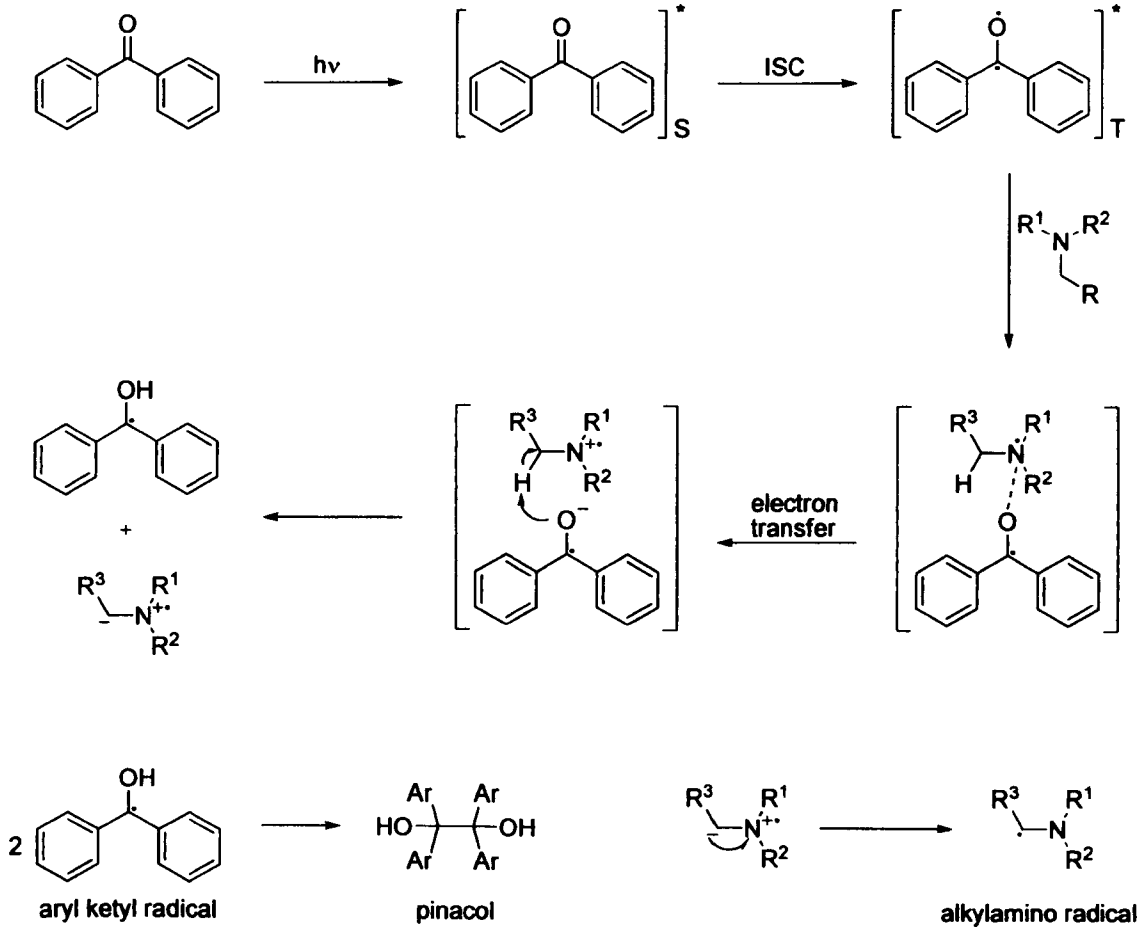
Benzophenones **Thioxanthones**

Figure 1.1: Type II Photoinitiators[6]

In the case of type II photoinitiators scission of the molecule does not occur but a low reactivity radical (intermediate triplet state) is formed on the ketone by UV absorption. This excited state intermediate then by interaction with an activated hydrogen containing function produces a highly active free radical by hydrogen abstraction.[6] The absorption of UV light by the chromophore causes an electron from the carbonyl to be raised into an excited singlet state. Inter system crossing (ISC) then takes the molecule into an excited triplet state.[2] The hydrogen abstraction takes place from a suitable donor, known as a synergist, via a charge transfer complex.[4] This is often a tertiary amine but may also be an

alcohol or other suitable donor. The abstraction is dependent on the triplet state energy of the exited ketone and the bond strength of the carbon-hydrogen bond to be broken.

This abstraction leads to the formation of two radicals. That formed from the chromophore is an aryl ketyl radical which generally has low reactivity while the amine forms a highly reactive alkylamino radical.[6] It is this alkylamino radical that initiates polymerization. The aryl ketyl radicals may combine together to form a pinacol type molecule or be photo-oxidised back to the ketone.[2] The two step mechanism for the initiation was confirmed in a study by Smeyers *et al* in 1995.[8] This is illustrated in Scheme 3.



Scheme 1.3: Activation of a Type II Photoinitiator[2,4]

1.5 What makes a good photoinitiator?

There are several factors that make up a good photoinitiator and as with most applications the aim is to maximise these factors in the best way possible. Often it may be that the improvement of one factor worsens another and in these cases a balance or trade-off between factors is necessary. The ideal for a good photoinitiator is that it should possess the following properties.[2,9]

1. High absorptivity in the region of activation
2. Capable of initiating efficient free radical formation
3. Solubility in the resin system
4. Odourless and non-yellowing
5. Stable for storage
6. Non-toxic
7. Low migration
8. Cost effective

The first three factors on this list are necessary for the effectiveness of any photoinitiator. If the initiator does not absorb in the UV region, does not form free radicals or cannot get into the resin system then they simply cannot function as an initiator. The other factors are undesirable and the aim would be to limit these factors. For example a photoinitiator can be very functional but also very expensive. This does not mean it does not work but it would not be much use in a commercial market. Alternatively, benzophenone does not have the best reactivity as a photoinitiator, but it is relatively cheap.[9] Current research into photoinitiators looks at those which can eliminate the negative characteristics and still maintain the best initiator performance.

1.6 Migration and toxicity

The aim of this project is to look at a solution to the problem of photoinitiator migration. Conventional initiators of both types tend to leave small residual molecules in the cured surface.[10] In the case of type I photoinitiators this is due to cleavage radicals reacting with other small fragments such as acidic protons or hydroxyl groups. This causes the

production of small molecules such as benzoic acid or methyl benzoate.[9] In the case of type II photoinitiators the initiator starts the polymerisation by hydrogen abstraction from another molecule and therefore remains itself as a small molecule.

Over time these small molecules can migrate through the resin to the surface. This can cause various undesirable effects such as yellowing of the surface, odour at the surface or migration into material in contact with the cured surface. This latter effect provides a particular problem with the use of photoinitiators in the production of food packaging.[10] One example of this has been the migration of 2-isopropylthioxanthone (ITX) from the ink on Tetrapak cartons into liquid baby milk in 2005. Although the European Food Safety Authority declared that this "is not likely to produce a health risk" it did conclude that it may "be considered undesirable".[11]

More recently in 2009 there has been an investigation by the European Food Safety Authority into the presence of methylbenzophenone in breakfast cereal.[12] They concluded that, based on the chemical similarity to benzophenone, there were no health concerns from short term consumption of low levels of methylbenzophenone. However the panel stated that continued use of methylbenzophenone would require a full risk assessment.

The guideline in 2005 from The Super Directive for multilayer Food Packaging sets the limit as 10 ppb for any non-evaluated substance and 50 ppb for the migration of any substance into foodstuff whether hazardous or not.[13] Since a study by Anderson and Castle in 2003 found levels of benzophenone above 50 ppb in 49 out of 350 foods tested there is obviously significant scope for the development of non-migrating photoinitiators.[14]

More recently Triantafyllou *et al* looked at migration of common organic contaminants into milk powder.[15] They reported on a variety of common organic contaminants and saw significant migration from all of them particularly acetophenone and benzophenone.

The most recent study is that by Sagratini *et al* who developed a new analytical method using gas chromatography-mass spectrometry (GCMS) and liquid chromatography-mass

spectrometry (LCMS) to gain accurate results on the migration of five different photoinitiator residues into forty samples of milk, fruit juices and wine.[16] Most significant in their results was that benzophenone was found in all forty samples in concentration ranges from 5-217 μg L^{-1} (equivalent to ppb), three of which were above the 50 ppb limit from the Super Directive above. The study also showed some migration of both 2-ethylhexyl-4-dimethylaminobenzoate and less significantly ITX.

Guidance in Europe is covered by a Commision Directive issued in 2002.[17,18] This sets a migration limit of 10 mg dm^{-2} for migration of any substance used in packaging into the foodstuff. This is equated by the directive to 60 mg kg^{-1} (60 ppm), similar to the requirements of the Super Directive. It goes on, however, to list specific limits for a number of known migrants. In this list benzophenone has the much tighter migration limit of 0.6 mg kg^{-1}. Hence the need for low-migration benzophenone based photoinitiators becomes even more significant.

This directive was further updated in 2008.[19] This sets the requirement for a set list of permitted migrants based on the list from 2002 with additions for any further migrants which have been submitted for inclusion. From January 2010, only substances included on this list will be permitted for use in packaging and their use must be within the migration limits set by the directive. This would be of particular relevance to the methylbenzophenone case outlined previously as it would not be acceptable to treat is as just being similar to benzophenone. The limit for benzophenone itself remains at 0.6 mg kg^{-1}.

Further details on the testing of migration and the significance of these migration limits can be found in section 4.0.

1.7 How to avoid migration

Migration occurs because small residual molecules from the photoinitiation process remain in the cured surface and are able to make their way though the surface over time and into

the product. One of the ways in which migration may therefore be reduced is by making the photoinitiator into a larger molecule.[20]

At first this may seem a simple case of adding large substituent groups to the initiator and hence making it bigger. This has been the method attempted in much of the research to date. The problem with this is that these additional groups will cause a decrease in the reactivity and solubility of the molecule and will also affect the final cured surface. However, if these additional groups also have photoinitiating properties then it could be possible to create a larger initiator which retained its reactivity. Indeed it may even be possible to increase reactivity as there will be a greater opportunity for electron transfer between adjacent groups on the same structure. While this has been achieved to some extent with various linking groups, these have in general been quite large and hence there are questions over the overall efficiency of the polymeric photoinitiator. The idea, therefore, of this thesis is to create a short oligomer with repeat photoinitiating units which will be large enough to prevent migration while still maintaining solubility and reactivity.

2.0 Advances in Photoinitiator Technology

2.1 Introduction

Photoinitiator technology has developed over the past 50 years from a small area of academic interest to a major commercial application. Research has moved from study of how and why initiators work to be driven by adaptations of known initiators to overcome problems which may restrict their use in a commercial marketplace. Some areas of research have led to interesting chemistry which has failed to gain commercial appeal while others have been developed for major industrial use. In the last 15 years developments have looked at various areas including faster cure rate, varying the absorption spectra and lowering migration.

In 1992, Davidson carried out a review into the recent development in photoinitiator technology at the time.[21] This highlighted three main areas of research. These were initiators which were effective at longer UV wavelengths extending into the visible, water soluble initiators and polymerisable and polymeric photoinitiators.

The first of these was necessary due to the use of pigmented coatings and had seen several developments, as will be discussed in Section 2.3. This research is still applicable today both for the continued use of pigmented coatings and also for the development of new technology with regard to the UV source. Modern photoinitiating systems use low energy LED arrays which produce radiation in the region of 390-410 nm as opposed to the older style mercury lamps which produce a strong emission around 254 nm.[22]

Water soluble photoinitiators were desirable due to many curing systems containing some water particularly with regard to inks. Again there were several developments in this area, which will be discussed later, but recent research has seen other photoinitiator characteristics take priority.

Development of polymerisable and polymeric photoinitiators was in its early stages but was being driven by the impending changes to food-packaging legislation. This has proved to

be the most researched area of photoinitiator design in recent times and will form the bulk of this review.

2.2 Early research

As stated previously, some areas of research led to commercial success while others gave rise to an academic interest but for various reasons were unable to find a niche in the modern marketplace.

As an example the production of photoinitiators from transition metals has been studied both with regard to carbonyl complexes and the use of metallocenes in the presence of molecules containing labile halogens.[23,24] In the case of the carbonyl complexes there is electron transfer from the excited carbonyl to the halide which is then cleaved from its parent molecule to leave an active radical. This radical can then initiate polymerisation having been shown to be successful with acrylate based systems.[20] With metallocenes the electron transfer is direct with the metal centre. An alternative to this is a complex with a benzyl ligand which is cleaved on irradiation to form a benzyl radical which can then initiate polymerisation.[24]

The advantage of these types of photoinitiator is that only a single radical species is produced which then attaches to the polymer chain thus eliminating residual products from the initiator. However, these complexes can be expensive and have their limitations. In the case of those requiring a halogen, undesirable halogen containing by-products have been shown to be formed such as hydrogen fluoride which limits their commercial appeal.[24] Also hydrogen transfer from the growing chain can occur, which can lead to low molecular weight polymers and hence a poorly cured surface. Due to this, interest in this area appears to have been carried out until the mid 1990s but there is very little evidence of continued research in recent literature.

By contrast other research has been developed into commercial products which are still in use today. In 1985, Encinas *et al.* carried out an investigation into the photochemistry of hydroxyalkanones.[25] Their work showed that α-hydroxyketones photodecompose by type I

bond cleavage adjacent to the carbonyl, β-hydroxyketones can react by both type I and type II mechanisms and γ-hydroxyketones may react by type II mechanisms. From these observations there has been developed several hydroxyketone type photoinitiators such as 2-hydroxy-2-methyl-1-phenylpropan-1-one which is commercially available as Speedcure 73® shown in Figure 2.1.[26]

Another example is the work by Allen *et al.* in 1994 looking at the use of 1-halogeno-4-propoxythioxanthones as photoinitiators.[27] They looked at 1-fluoro-4-propoxythioxanthone (FPTX), 1-chloro-4-propoxythioxanthone (CPTX) and 1-bromo-4-propoxythioxanthone (BPTX) comparing them with a similar initiator in current use 2-propoxythioxanthone (ITX). Their research found that there all three were effective as initiators but overall the most desirable properties were to be found in the CPTX. Again this is commercially available today as Speedcure CPTX® and it will be seen later that this has been taken further with the development of multiactive photoinitiators with the release of Speedcure 7010®.[23] Both of these molecules are shown in Figure 2.1.

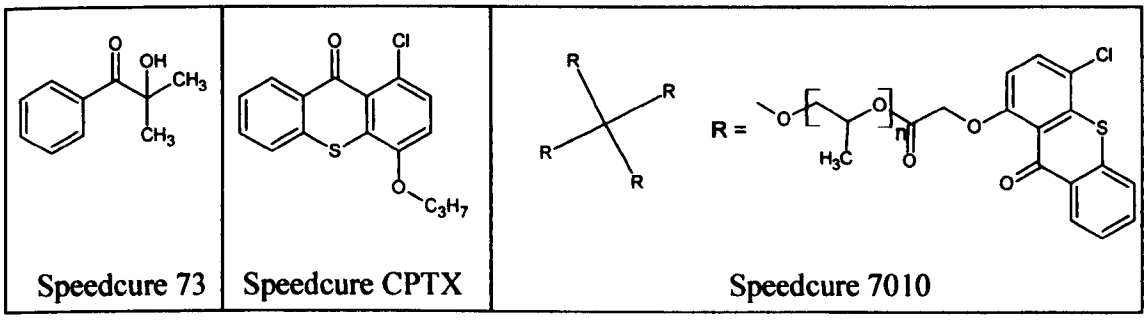


Figure 2.1: Examples of commercially available photoinitiators[26]

Further research has also been seen in the area of acylphosphine oxides. These are bleachable type I photoinitiators, that is the radicals formed by cleavage of the initiator do not absorb the incident UV light. Hence, once surface cure is achieved the UV light can penetrate deeper into the resin enabling far greater depths of cure to be achieved, up to a few cm.[28] More recently work has looked at the alternative of using germanium instead of phosphorus based photoinitiators. These acylgermanes exhibit a red shift in their UV

absorbance of around 50 nm compared with the acylphosphine oxides.[29] This is particularly useful for applications involving photoinitiators absorbing at longer wavelengths. This is discussed in more detail in Section 2.3. Examples of acylphosphine oxides and acylgermanes are shown in Figure 2.2.

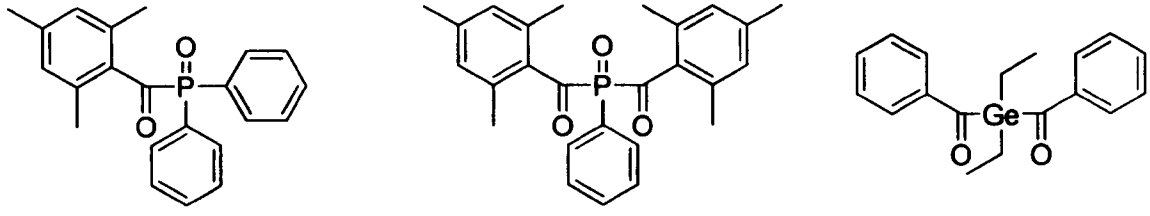


Figure 2.2: Acylphosphine oxides and acylgermanes[28,29]

2.3 Photoinitiators absorbing at longer wavelengths

As mentioned, in Section 2.1, one area which has been driven by commercial requirements is the development of initiators which absorb at higher UV wavelengths and wavelengths extending into the visible. These have use both with the requirement for initiators for be used in pigmented systems and the use of higher wavelength, lower energy radiation sources.

Initially this problem had been overcome by the use of sensitisers in a sensitiser/coinitiator system. Sensitisers are molecules which absorb at a higher wavelength and can then activate the initiator molecule by energy or electron transfer. This can be by donation of the excited electron to the lowest unoccupied molecular orbital (LUMO) of the coinitiator to create a radical or by accepting an electron from the highest occupied molecular orbital (HOMO) and hence creating a radical.[30]

In Davidson's review paper[21] there had already been the development of several novel initiators with significant absorption peaks at wavelengths greater than 350 nm. Two examples of novel type I initiators were given as shown in Figure 2.3. The paper also went on to discuss the increasing popularity of acylphosphonates as a type II photoinitiator.

These can be expensive but have the advantage of being extremely effective in the curing of thick coatings (50-100 μm).

Figure 2.3: Some novel type I initiators[21]

Further work looks at the effect of substituent groups on the chromophore of type I initiators. Electron donating groups on the aromatic ring have the effect of lowering the energy of the triplet state of the carbonyl hence increasing the wavelength of UV absorption. This however has to be balanced against the lowering of the yield of the α-cleavage product hence lowering the effectiveness as a photoinitiator. This may prove useful with altering the absorption characteristics of type II photoinitiators which do not undergo cleavage.[21]

An alternative to this was investigated in 2007 by Seidl *et al.*[31] Their work looked at inserting a double or triple bonded chain between the aromatic group and the carbonyl in the chromophore hence extending the conjugation in the molecule and shifting the UV absorption. They looked at several different possibilities and achieved success by shifting the absorption peak up to 50 nm towards the visible part of the spectrum. However, on testing these initiators the level of photopolymerisation activity was not as high as that of commercially equivalent analogues.

Davidson's paper also highlighted the growing development of thioxanthones both as sensitisers and as type II initiators in their own right. They have the advantage of having an absorption peak around 390 nm but it is difficult to shift this peak to more than 400 nm by the use of substituent groups.[21]

As can be seen from the work of Seidl *et al.*[31] there is still research into adjusting the absorption peak for photoinitiators particularly with the desire to use lower energy emission sources. However with the desire for low migration providing the more pressing concern more research time is being devoted to the development of non-migrating photoinitiators such as polymeric initiators rather than novel single molecule initiators. The absorption spectra of polymeric initiators are often affected by the polymer chain and so developments in the characteristics of the absorption spectra for polymeric photoinitiators are more likely to be fine tuned by adjusting the substituents on the finished polymer which may be significantly different from those seen from a single small molecule.

2.4 Water Soluble Photoinitiators

Another area of research which, although of significant value, has decreased in significance is that of water soluble photoinitiators. Again, although it would perhaps be desirable to have a water soluble initiator, the issue of migration is a more significant concern and hence it is this area of research which dominates.

Benzophenones and thioxanthones are often water soluble and so it is perhaps unsurprising that these have evolved as the major commercial type II photoinitiators. As will be seen later these have also had a significant role in the development of polymeric photoinitiators, perhaps in some hope of retaining some of their solubility characteristics. With these molecules seemingly providing the solution to a water soluble type II initiator little further research has been carried out in this area.

The only real development in the field is the synthesis of some type I water soluble initiators. These include Bunte salts in which β-cleavage gives rise the necessary radical and also some phosphinates which undergo α-cleavage to yield two reactive radicals both of which have been shown to initiate polymerisation. There has also been some research into adding substituent groups to the aromatic ring in the hydroxyalkylketone type initiators described earlier.[31]

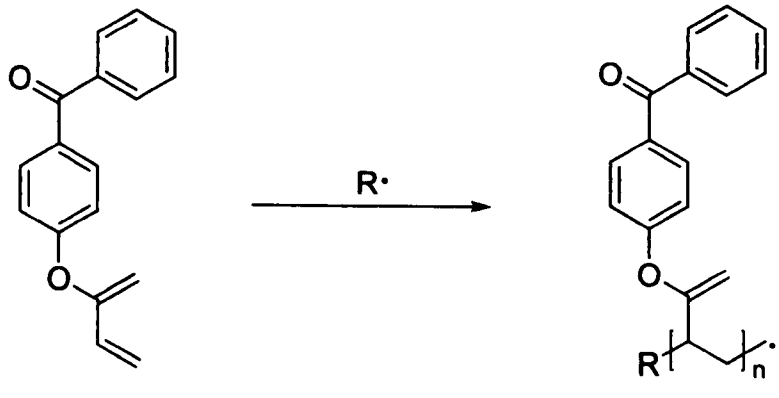
2.5 Polymerisable and Polymeric Photoinitiators

As discussed previously the major area of recent development in photoinitiator technology has been to look at producing photoinitiator systems which exhibit low migration characteristics. Ideally this will be with the minimum effect on the other desirable properties of the initiator. Two possibilities to achieve this are polymerisable and polymeric photoinitiators.

2.5.1 Polymerisable photoinitiators

With polymerisable initiators the initiator, synergist or sensitiser molecule contains a substituent group which is capable of undergoing polymerisation. When the initiator is used to cure a resin system the initiator itself also undergoes photopolymerisation and hence sees an increase in molecular weight which lowers its tendency to migrate. There is also the possibility that the initiator itself may become bound within the resin system.[32]

Most work in this area seems to have looked at using an acrylate substituent group as shown in the example in Scheme 2.1. This has been studied both with type I and type II initiators. Problems with type I initiators is that the initiator cleaves to form two separate radicals, hence there is the need to attach the polymerisable substituent to each radical fragment which may increase the difficulty of synthesis and affect the overall stability of the initiator prior to cure. It is possible that only one of the radicals needs to carry the polymerisable group as long as the other radical is the one that dominates the initiation of cure and hence can remain bound to the final cured surface.



Scheme 2.1: An example of the polymerisation of an acrylate photoinitiator

With type II initiators there is no cleavage so only one substituent group is needed on each molecule. This has been briefly studied by attaching an acrylate group to a benzophenone initiator but further investigation of this possibility is needed. With many resin systems being based around acrylate polymerisation it would seem useful to use this technology in the synthesis of polymerisable photoinitiators.[33]

It is also a possibility that the acrylate initiator monomer could be polymerised pre-cure to give a polymeric photoinitiator but again this has not been studied in depth. Inherent problems may be that acrylates polymerise very readily and that the polymeric form of the initiator may not be soluble in the resin system or in turn may affect the properties of the cured surface. Solutions to this could be the use of a chain stopper during polymerisation or to use a less readily polymerisable substituent such as an allylic group. The work on polymerisable photoinitiators covered in this thesis can be found in Section 4.3 with the pre-polymerised equivalents covered in Section 5.4.

2.5.2 Polymeric photoinitiators

Polymeric photoinitiators have been more extensively studied over the past 15 years although only recently are any becoming available on the market.

There are two main routes to the creation of a polymeric photoinitiator. The first is by the attachment of initiator molecules to existing polymer chains. A simple example of this may be the attachment of two initiators to either end of a polyether backbone thus increasing the molecular weight of the initiator as shown in Figure 2.4. However, the problem here is that the parent polymer does not act as an initiator and hence there will be a decrease in the reactivity of the overall system. This however is the simplest route to the creation of a polymeric initiator and has been used in several studies as will be seen later. This is also the basis for those polymeric initiators which are now on the market.

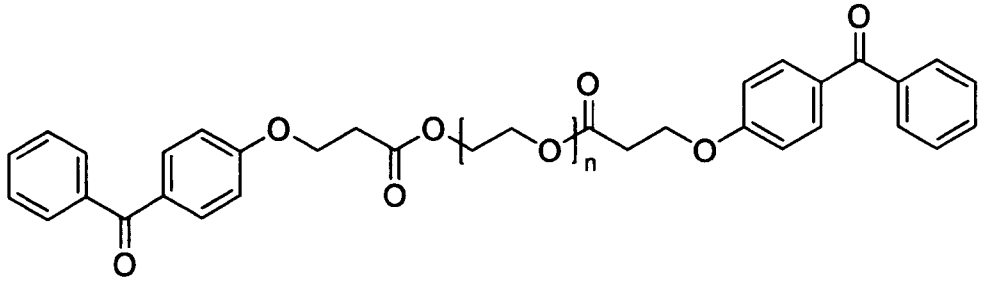


Figure 2.4: Simple polymeric photoinitiator with polyether backbone.

The second route would be to use the initiator as the base for the monomer unit in the polymeric initiator hence creating a polymeric initiator with a series of repeat active sites. Also, although this system causes some increase in molecular weight by the use of some non-photoreactive material, there may actually be an increase in the reactivity of the initiators due to the possibility of energy transfer between the initiator groups. Some studies in this area will be discussed and, although there has been some success in this area, these type of polymeric initiators are yet to be available on the market. Hence this is still a major area of interest for study and will form the bulk of the work for this thesis.

It should be noted that in 1999, Allen *et al.* published a study into the effectiveness towards polymerisation of free and polymer-bound type I and type II photoinitiators.[34] They found that although the activity of bound type I initiators was reduced compared with their free equivalents, the activity of the type II initiators was not. This would indicate that there is greater scope of the synthesis of type II polymeric photoinitiators.

2.5.3 Previous work on the synthesis of polymeric photoinitiators

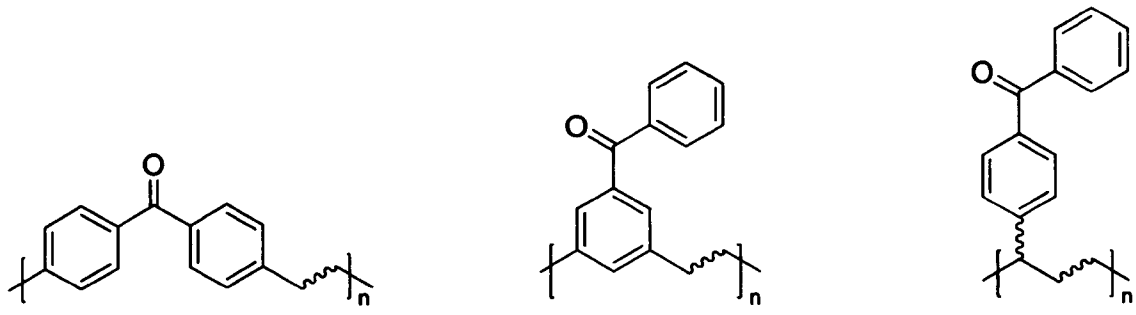
Following on from the 1992 review of developments in photoinitiator technology, Davidson wrote a further review on the possible options for the synthesis of polymeric photoinitiators. This review considered polymeric photoinitiators based on both type I and type II initiator systems.[32]

As with the polymerisable initiators, type I initiators provide inherent problems due the activation by a cleavage process. If these initiators lie within the polymer backbone then

initiator then activation will cause a splitting of the polymeric initiator into smaller fragments. Therefore, it is not possible to produce type I polymeric photoinitiators with adjacent repeating photoinitiator units. These would activate by fragmenting into small molecules and would defeat the object of using a polymeric initiator to prevent migration. The only way to achieve this would be to have a non-reactive polymer backbone between initiators which would have the negative effect of decreasing the reactivity of the molecule as described earlier. Another problem is that the initiating radical would have a polymeric backbone attached and as such would form a block copolymer with the cured resin which may decrease the quality of the final cured surface.

Alternatives would be to attach the type I initiator as a pendant molecule on a polymer backbone. This would cause small molecules to fragment from the polymer on initiation and as such it would be desirable that these were the more highly reactive radical. These type of initiators were looked at by Lewis and shown to be effective for the purposes of photoinitiation but the work did not look at migration data so did not give an indication if any of the fragments remained as small molecules.[33] This work looked, among other things, at a polymeric type I initiator with the chromophore as the pendant group.

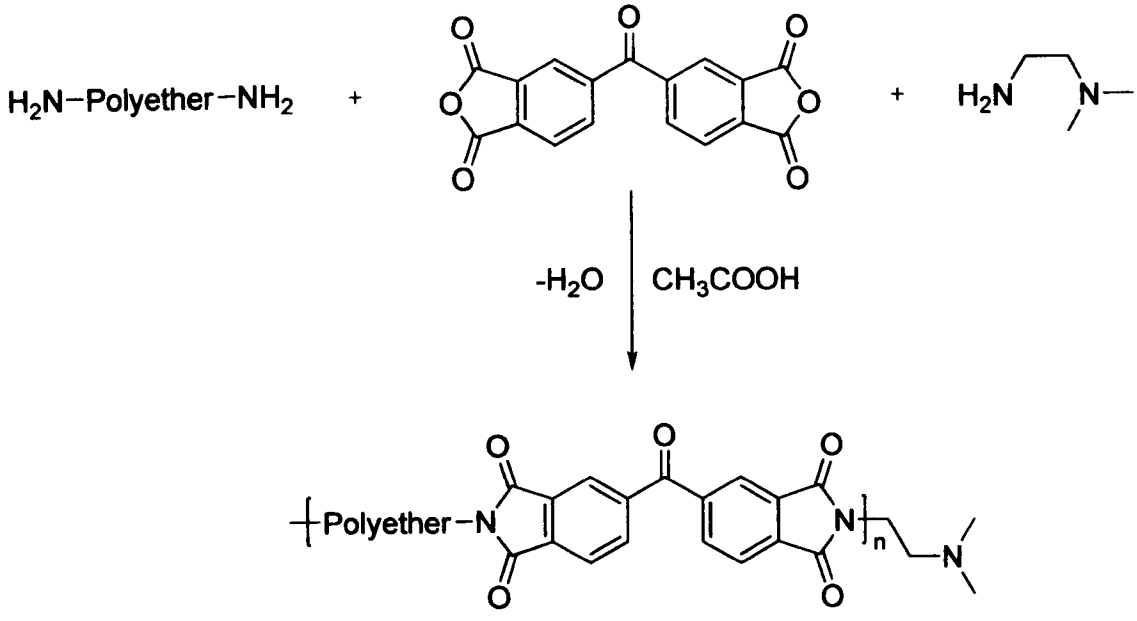
Type II initiators do not suffer from these problems since the activation is by hydrogen abstraction. Hence there is the possibility for polymers to be synthesised either with the polymer lying in the chain (with or without adjoining polymer groups) or with pendant groups. Examples of the different type of polymer using benzophenone as the photoinitiator are shown in Figure 2.5. The only problem with these systems is the need for a synergist. To avoid migration the synergist would also need to be polymeric. This could either be as a separate polymer or could be incorporated into the initiator polymer to form an initiator/synergist copolymer capable of activation by intra-molecular hydrogen abstraction. This possibility was used by Davidson for some of his first work on polymeric photoinitiators.[35]



a b c

Figure 2.5: Polymeric benzophenone photoinitiators showing a) an in-chain benzophenone linked by both rings, b) an in-chain benzophenone linked by one ring and c) a pendant benzophenone group on a polymer chain

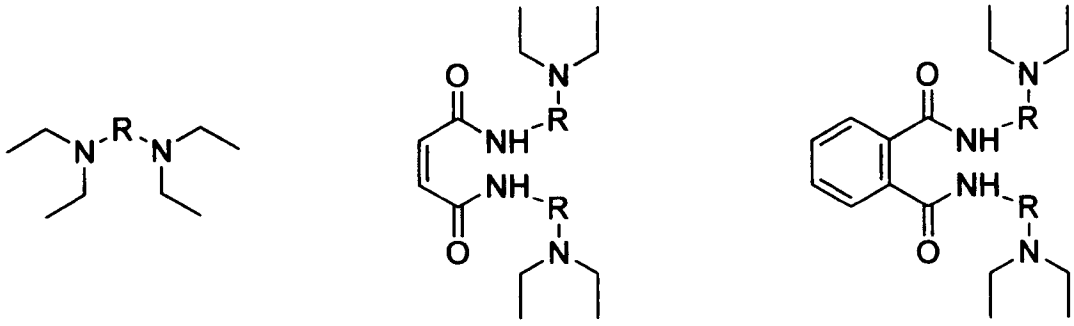
In 1994 Davidson *et al.* created a range of benzophenone containing photoinitiators from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and amino-terminated ethers shown in Scheme 2.2.[33] These polymers contained a benzophenone initiator along with an in-chain amine synergist linked together by polyether chains. Four ethers were used giving polymers with molecular weights between 2000 and 18000. The initiators worked but had lower reactivities than either benzophenone or BTDA itself possibly due to the length of the ether chain between repeat benzophenone groups. They did however show an improvement in migration characteristics with only the amine synergist being extracted into hexane and only the synergist and shorter chain oligomers extracted into dichloromethane. The problem encountered was the large molecular weight of the polymer led to a high viscosity of the pre-cure solution.[35] In 1995 they expanded on this to reveal that these molecules also showed increased oxygen inhibition and some yellowing effects.[36] This type of reaction was also studied by Xiao reacting BDTA with amino acids to produce alternative monomeric photoinitiators. This idea was patented in 2006 but since only monomers were looked at this would present no obstruction to further work in this area.[37]



Scheme 2.2: Synthesis by Davidson *et al*[35]

In 1997 Pasquale *et al* looked at the synthesis of alkyl-substituted poly(2,5-benzophenone).[38] This synthesis was based on the nickel catalysed coupling of aromatic dichlorides. The intended molecules were successfully synthesised with molecular weights in the region of 10000 which would be around 40-50 repeat units. They did not, however, carry out this synthesis with the intention of examining the photoinitiating properties so no data on this was reported.

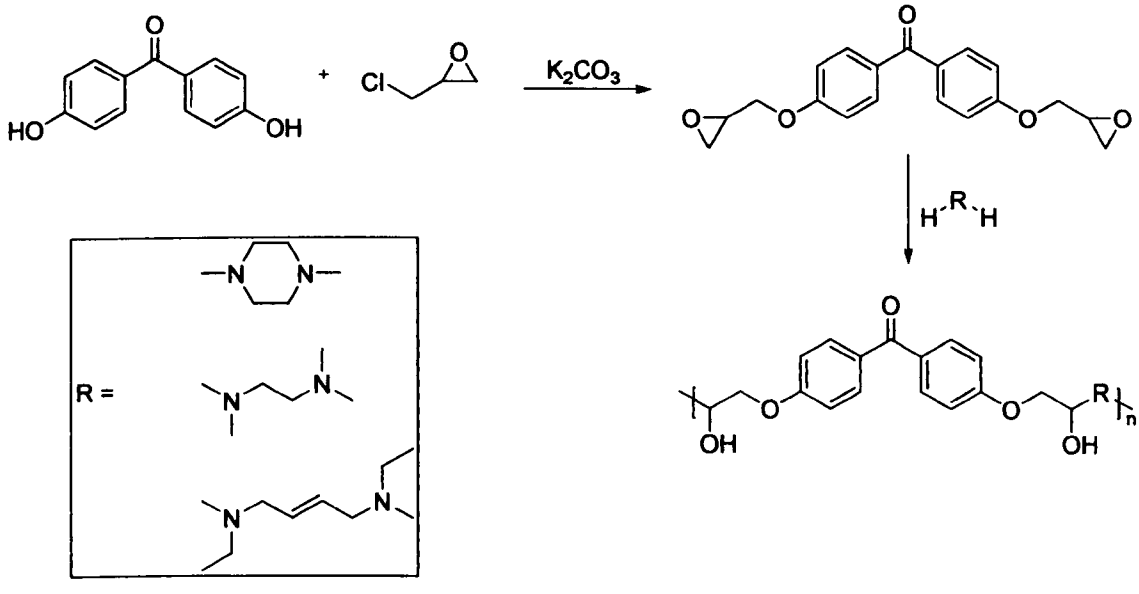
As well as the possibility of the photoinitiator being polymeric there is also the possibility of using an oligomeric amine synergist. Allen *et al* in 2001 looked at the synthesis of oligomeric amines for use as synergists in photoinitiating systems.[39] Their work looked at using terminal tertiary amine groups at either end of a polyether chain. These therefore contained two functional sites with an unreactive polymer in between. They created a range of oligomeric amines, shown in Scheme 2.3, with molecular weights ranging from 500 to 4250 and discovered that they were effective for use in a photoinitiating system although it appears from the results that the best polymerisation rates were for the shorter chains. They did not, however, report on the migration properties of these synergists.



R = $CH(CH_3)CH_2$-[$OCH_2CH(CH_3)$]$_x$-, x = 6 or 33

Scheme 2.3: Synergists synthesised by Allen *et al*[39]

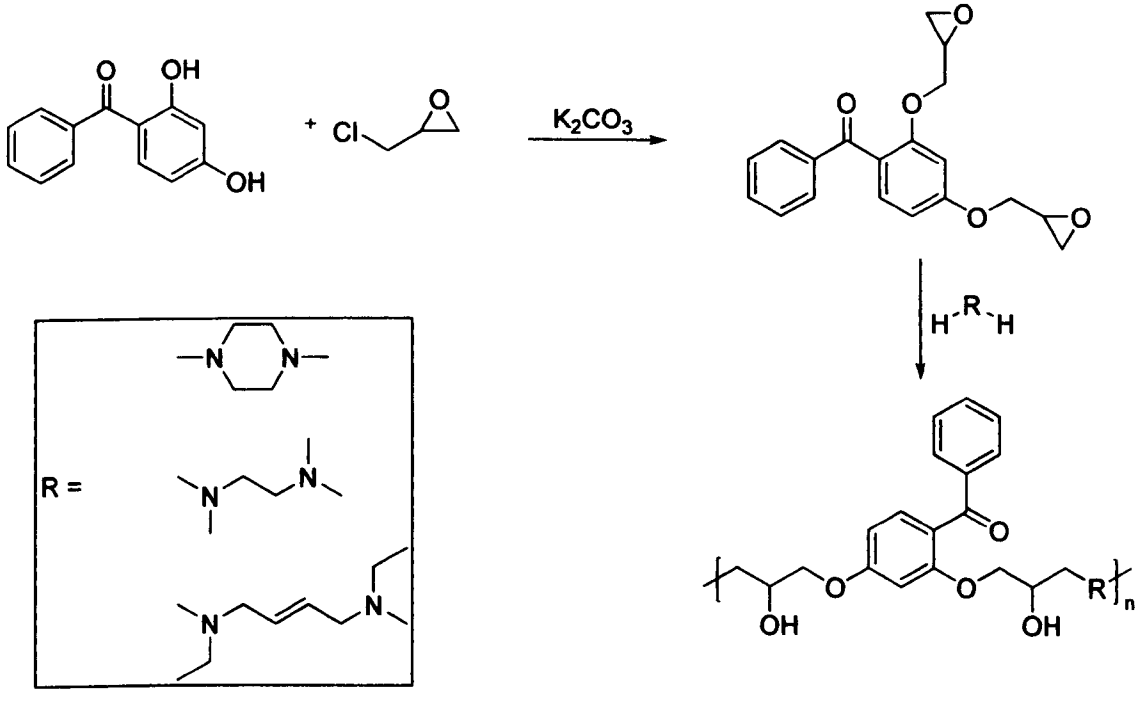
In 2004 Jiang *et al* continued working with the concept of synthesising polymeric photoinitiators containing an in-chain benzophenone and an amine synergist.[40] Their polymers had repeating units of benzophenone and amine synergist connected by short linking groups hence containing several photoactive sites. These were synthesised by reacting 4,4'-dihydroxybenzophenone with epichlorohydrin to form 4,4'-di-(2,3-epoxypropyloxy)benzophenone (DEBP). The epoxide groups could then be reacted with a diamine to form the polymer shown in Scheme 2.4.



Scheme 2.4: Polymer Synthesis of Jiang *et al*[40]

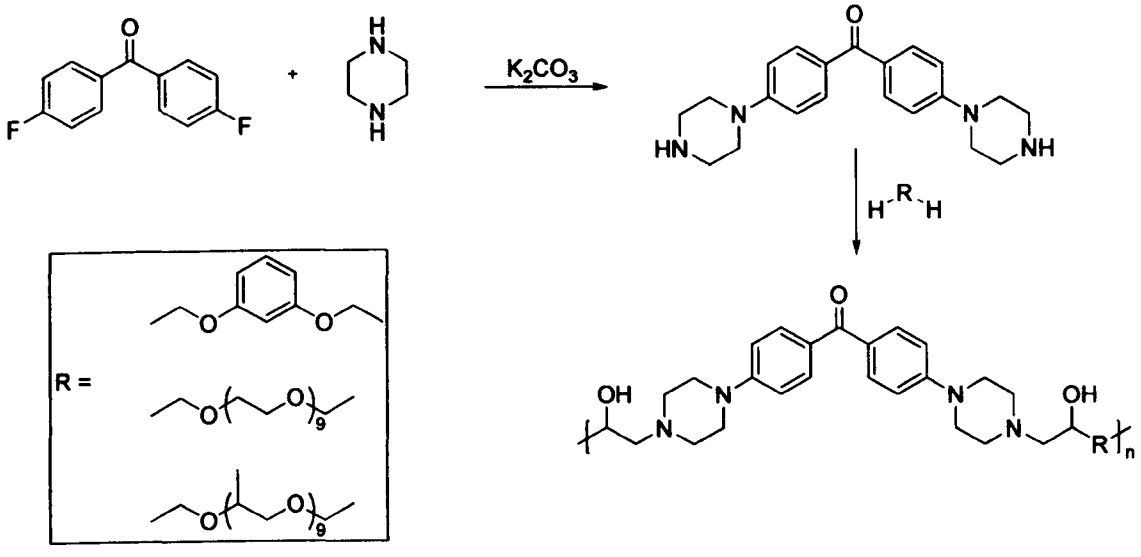
The molecular weights of their polymers were in the region of 4000-5000. They looked at polymers synthesised using three different amines and discovered that the reactivity was dependent on the amine type and the monomer system of the resin. This would indicate that even though there may be success in creating one particular type of polymeric initiator there is still considerable scope for further development due to the variety of resin systems available on the market. They did report that the new initiators showed similar UV spectra to that of benzophenone but, although they did not report on how the new initiators compared with each other, they did not report on how they compared with benzophenone for reactivity. Neither did they report on any migration characteristics of the polymers.

Jiang went on to work with Wang *et al* in 2008 looking at the same synthesis with 2,4-disubstituted benzophenone in place of 4,4'-disubstituted, shown in Scheme 2.5.[41] These polymers provided more efficient photoinitiation than both the 4,4'-disubstituted polymers or the monomeric benzophenone equivalent. Again, though this study was only carried out to look at the synthesis of the polymers and their functionality as an initiator, they did not include any data on the migration properties of these photoinitiators.



Scheme 2.5: Polymer Synthesis of Wang *et al*[41]

Jiang also collaborated with Wen *et al* on a similar reaction involving a diamine containing photoinitiator, Michler's ketone, and epoxides as shown in Scheme 2.6.[42] These again proved successful as polymeric photoinitiators with inbuilt synergist and good rates of photopolymerisation were reported. However, whereas the previous work had compared the rate of photoinitiation with that of the monomeric equivalent, this study made no comparison with monomeric Michler's ketone. Also there was again no migration data reported. This development has also been granted a patent in 2008.[43]

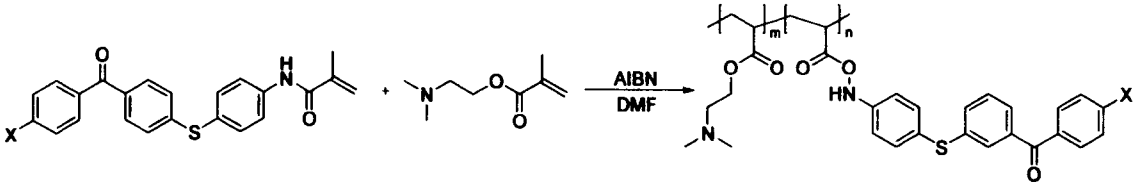


Scheme 2.6: Polymer Synthesis of Wen *et al*[42]

All of these syntheses had one common factor. The linking group had an effect on UV curing dependent on the resin used. It appears therefore that different photoinitiators behave differently with different resin systems even if the difference is only slight. As such with the development of any new polymeric photoinitiators it would be better to design a type of structure which can be shown to have desirable photoinitiation and low migration properties and then tailor this development to individual resin applications as required.

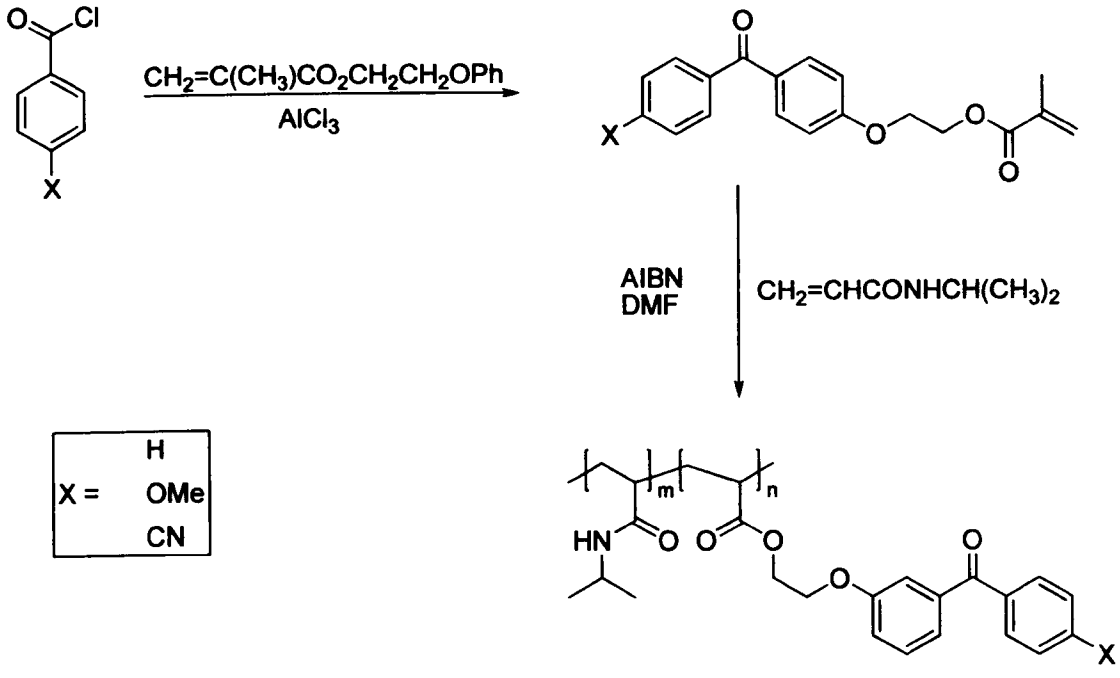
In 2006 Wang *et al* went on to look at the alternative of polymeric photoinitiators with side chain benzophenone and amine synergist.[44] These are of the type where the functional

groups are attached as pendant groups on a polymer backbone. In this case the photoinitiator and amine synergist both have attached groups with methacrylate moieties. These methacrylate groups are subsequently polymerised to form the polymer backbone with the photoactive sites attached to the backbone by short linker groups as shown in Scheme 2.7. Three homopolymers were synthesised including two with different repeat initiator units and one with repeat synergist units. There were also two copolymers synthesised from the amine synergist and the two different initiators. These were synthesised with molecular weights ranging from 14000-300000. They report that these initiators show surprisingly high efficiency compared with standard benzophenone and also an increased rate of polymerisation. Again, however, they do not report on the migration properties of the polymeric material in the final cured surface.



Scheme 2.7: Polymer synthesis of Wang *et al*[44]

Another study with pendant photoinitiator and amine synergist was carried out in 2008 by Rufs *et al.*[45] They copolymerised a benzophenone with attached methacrylate group and an acrylamide, as shown in Scheme 2.8 to form polymers with molecular weights in the range 44000-50000. They report on the rates of polymerisation in their chosen resin being comparable with that of the equivalent monomer, and that polymerisation rates are improved by electron donating groups on the benzophenone. However, as with many studies although the synthesis was carried out to provide a low migrating photoinitiator they did not carry out any migration testing on their synthesised material.

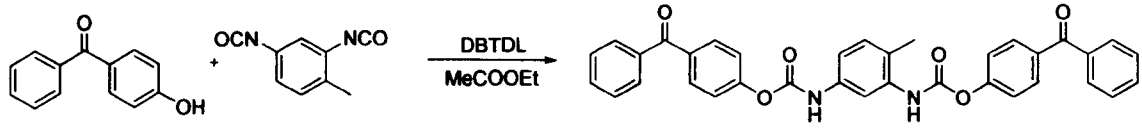


Scheme 2.8: Synthesis of Rufs *et al.*[45]

More recently Xiao *et al* continued with a variation on the work of Jiang *et al* from 2004. In their case instead of synthesising compounds using the epoxide they used acryloyl chloride to form the diacrylate and then reacted this with the amine.[46,47] This was done using both 4-hydroxybenzophenone and piperazine to form a single molecule containing two initiator and two synergist groups[46] and with 4,4'-dihydroxybenzophenone to form a polymer.[47] Testing of both of these novel initiators showed improved rates of polymerisation and final conversion compared with a benzophenone/amine system, however they did not go on to report on the migration characteristics of either material. It is also perhaps surprising that they did not run a comparison of the single molecule type initiator with the polymer, which may have given an indication as to whether the improvement in the reaction kinetics was due to energy transfer between initiator components on the chain or just between the adjacent initiator and synergist.

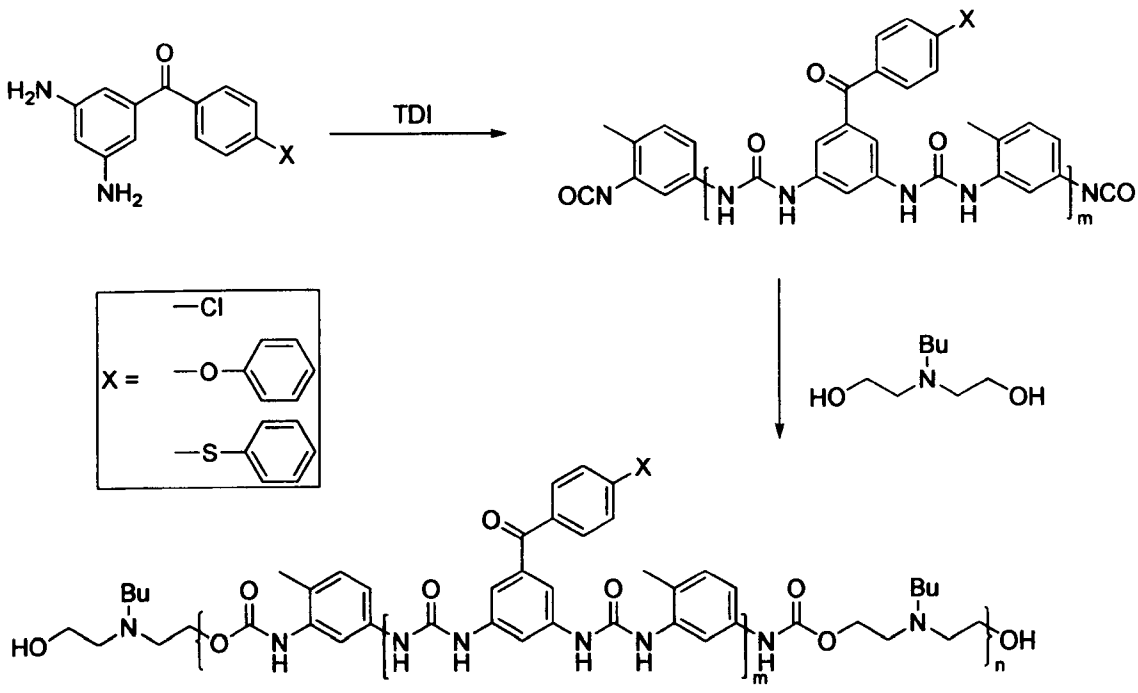
Xiao along with two colleagues from the previous work also looked at reacting 4-hydroxybenzophenone with toluene-2,4-diisocyanate (TDI) using a dibutyl tin dilaurate (DBTDL) catalyst to form a different type of molecule containing two initiator/synergist

groups shown in Scheme 2.9.[48] This molecule also showed improved rate of polymerisation compared with a standard benzophenone system. However, once again there was no investigation of migration characteristics and no comparison with other initiators of the same type. It is worth noting that, since several of the novel initiators discussed seem to have shown improved kinetics compared with existing initiator systems, it may be a worthwhile study to carry out a comparison of the properties of all these initiators to establish which seem to be the most promising.



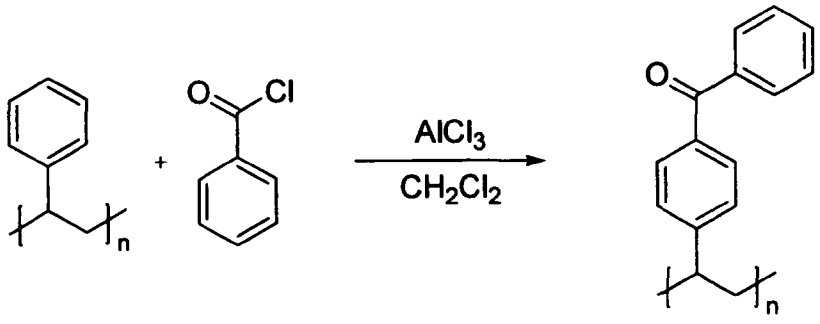
Scheme 2.9: Synthesis by Xiao *et al*[48]

Wei *et al* also used TDI in the synthesis of their benzophenone containing polymeric photoinitiators reacting three different 3,5-diaminobenzophenones with the TDI to form a short polymer chain and then reacting this with another amine, N-butyldiethanolamine to form a PU-type polymer as shown in Scheme 2.10.[49] They then looked at how the substituent groups on the photosensitive part of the polymer affected the UV/Vis spectrum and hence the ability of the initiator to generate radicals. This revealed that the substituent groups had a significant effect on the UV/Vis maxima and hence showed that adjusting the wavelength of the UV absorption may not be so simple as just changing the functional groups on the chromophore. The comparison of initiators in this study was confined to those polymeric initiators created for the study and no comparison was made with existing initiators.



Scheme 2.10: Synthesis by Wei *et al*[49]

The work discussed so far has looked at producing a polymer from monomers which include a photoinitiator unit. An alternative would be to create a polymer or use an existing polymer which could undergo further synthesis to form an initiator. One example of this would be to undertake a Friedel-Crafts reaction using polystyrene and benzoyl chloride to form a polymer with pendant benzophenone groups, a polyvinylbenzophenone. This polymer was successfully synthesised by Hong and Sun in 2007, as shown in Scheme 2.11, but this was to use its UV absorbing and radical forming properties as an antibacterial agent rather than as a photoinitiator.[50] They also in 2008 varied the concentration of benzoyl chloride in the reaction to form polystyrene/polyvinylbenzophenone copolymers for the same use.[51] The author understands that further work has been carried out looking at the use of this type of polymer as a photoinitiator but there have been problems with solubility in the resin system.[52] The photoinitiator is, however, quite active and could be suitable for use in low concentrations. No migration testing has yet been performed on this type of photoinitiator and as yet the work done is unpublished.[52]



Scheme 2.11: Synthesis of Hong and Sun[50]

Another similar possibility would be to graft 4-hydroxybenzophenone onto polyvinylchloride (PVC). This type of chemistry has been investigated for medical purposes but only onto high molecular weight PVC that would again have solubility problems if it were to be used as a photoinitiator.[53] It could be possible to use a low molecular weight PVC but this is expensive and so cost could prove a restriction to its commercial appeal.

Also looking at grafting onto existing polymers, Chen et al. saw success with grafting onto hyperbranched polyglycerols.[54] Making use of the multiple free hydroxyl groups available they were able to attach benzophenone, as an initiator, 4-dimethylamino benzoate or 1-piperidinepropionate, as a synergist, and 2-[2-(2-methoxyethoxy)ethoxy] acetate, to aid with solubility. An example of the type of structure seen by one of their products is shown in Figure 2.6. The polyglycerols used had between 17 and 179 free hydroxyl groups and resulted in polymers of molecular weight up to 44000. In each case every hydroxyl end group was substituted with either photoinitiator, synergist or solubility agent. They reported that the resulting initiators showed good solubility in the resin system and compared favourably with (4-benzoylphenoxy) acetate, a benzophenone type initiator, in terms of performance. Finally they also reported that the new initiators showed low migration with no extractable low molecular weight residues in the final cured surface. This then is one example of a polymeric photoinitiator that has been fully tested as a low migration photoinitiator. However it does not yet seem to have appeared on the market.

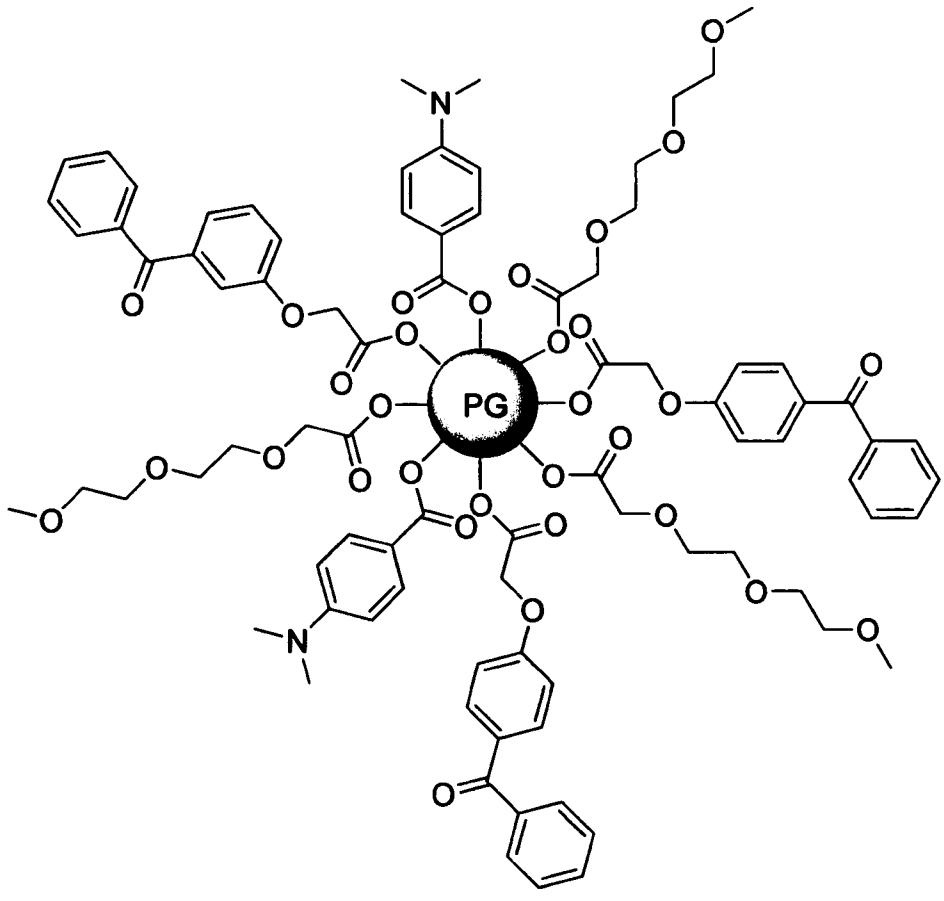


Figure 2.6: An example of the polymers synthesised by Chen *et al*[54]

As a final note Lambson Group Limited have released three new products for use in photoinitiation using polymeric photoinitiators to achieve low migration. These use pentaertythritol centre with polypropylene glycol chains terminating in the initiator group hence forming a four armed star polymer. The terminal groups available are benzophenone, ethyl 4-dimethylaminobenzoate (EDB) or CPTX which was discussed earlier and shown in Figure 2.1. Those with benzophenone and EDB also include in their formulation some polymeric material which is just a polyethylene glycol chain terminated with the initiator groups. These have obviously proved successful as low migration initiators but do not perhaps perform as well as a chain of repeat initiator units could if the desired solubility in the resin system could be achieved.[26]

2.6 Patents

Some of the patented literature on polymeric photoinitiators has been discussed in section 2.5. Further to this a patent search was carried out ensure that work to be carried out in this thesis was not duplicating other research. A worldwide search was carried out via the European patent agency database esp@cenet. The search is summarised in table 2.1. All searches included the term "photoinitiator".

Search Terms (+ "Photoinitiator)	**Hits**
Low Migration	6
Non Migration	0
Polymeric	447
Low Migration + Polymeric	1
Benzophenone	167
Low Migration + Benzophenone	3
Benzophenone + Polymeric	4
Low Migration + Benzophenone + Polymeric	0
Polymerisable	172
Polymerisable + Benzophenone	8

Table 2.1: Patent Search

Although the search revealed a large number of patents for polymeric or benzophenone photoinitiators very little had been patented with low migration in mind. The earliest patent to consider migration was submitted in 1991 by Bonham *et al* and photoinitiators with a halomethyl-1,3,5-triazine moiety.[55] They discovered that the bulking out of their photoinitiators reduced migration which provides the basis for this work. However their patent was not concerned with oligomeric photoinitiators such as those covered in this thesis.

As mentioned a patent was submitted in 1997 by Anderson *et al* to cover the work of the polypropylene glycol photoinitiators which have now reached the market as Speedcure

7004, 7010 and 7040.[56] This does not clash with the work in this thesis which was looking at improving on these products by developing an oligomeric photoinitiator with a repeating active unit.

The only other relevant patent found prior to the commencement of this thesis was by Speer *et al* in 2002.[57] They had looked at oxygen scavenging compositions and inadvertently discovered that their composition also exhibited low migration. This composition utilised transition metals which were not involved in the syntheses covered in this thesis so therefore there is no clash of interests with this patent.

Recently there are six patents filed which are of interest with regard to the subject of this thesis. Two of these are that for the BDTA and Michler's ketone syntheses mentioned previously.[37,43] The others look at photoinitiators based on polystyrene and polymerisable photoinitiators.

The two dealing with polystyrene based photoinitiators were submitted by Xue in 2007 and Liu *et al* in 2008.[58,59] The first looked at attaching acyl groups to polystyrene by a Friedel-Crafts reaction.[58] This was one alternative considered for this thesis but since the author was aware of work already being studied in this field other alternatives took priority. The latter patent was for iodonium salts of polystyrene for use as a low migrating cationic photoinitiator.[59] This thesis is concerned with free radical photoinitiators so there is no issue with this patent.

The two patents concerning polymerisable photoinitiators were both submitted by Wei, one in 2006 and the other in 2008.[60,61] Both involved introducing an amino group to benzophenone and then subsequently reacting with an allyl chloride[60] or acryloyl chloride[61] to provide a polymerisable portion of the molecule. This is similar to the work covered in Sections 4.3 and 5.4 of this thesis which also looks at polymerisable allyl and acryloyl groups. However the work in this thesis is concerned with attaching the polymerisable group to hydroxybenzophenones via an oxygen link as opposed to a nitrogen link so they are sufficiently different to the molecules covered by this patent.

In addition to this search the author has been made aware of a couple of other relevant patents termed as multi-functional photoinitators.[62,63] The first submitted by Burrows *et al* in 2003 concerns benzophenone groups attached by short linker chains to polyhydroxy compounds having 2-6 hydroxy groups.[62] One of the ideas for this thesis was possibly to attempt grafting of halobenzophenones onto PVA. While this would be a similar idea this type of molecule would not be covered by this patent. As it was this idea was not fully explored therefore issues with this patent are not relevant.

The other patent submitted by Herlihy, also in 2003, concerns the same type of molecule with thioxanthone in place of benzophenone.[63] Again this is not of relevance to work carried out in this thesis.

Further to the initial search each proposed oligomeric photoinitiator synthesis was first checked with the patent database to see if a current patent existed. Although occasionally there were similarities between the molecules synthesised and some patents, in these cases the patents were for a very different use and so there would not be a problem as any work developed to patent stage from this thesis would be submitted under a different application.

2.7 Aims of this research

It has been seen that research has been done into the possibility of creating a polymeric photoinitiator and the first of these are now becoming commercially available. Others have potentially been effective although there are problems with solubility, viscosity and cost which can limit their commercial appeal. It has also been seen that differing requirements can call for differing initiators so, therefore, there is a lot of scope for development of polymeric initiators which may offer either a particular characteristic or an improvement in those available at present.

The aim of the thesis, therefore, will be to create simple oligomeric photoinitiators which are as close as possible to the reactivity of their own monomer unit and display low

migration characteristics. Beyond this it will be attempted to optimise these oligomers to provide the best characteristics of all that makes a good photoinitiator.

This thesis will look not only at creating the oligomers but also ensuring that they are tested to show that they are able to be functional as an initiator. One point which has been clear from the literature review is that much of the research shows only the synthesis of a polymer which could potentially be used as a photoinitiator. Often no report is made of how the newly developed photoinitiator performs and whether is does indeed a) initiate cure and b) not migrate. The aim of this thesis will be to include complete performance testing any new material deemed suitable for use as a photoinitiator.

Finally, given the wide scope for development of photoinitiators, this thesis will be directed by attempting to produce an oligomeric photoinitiator where as much of the molecular weight as possible is taken up by the photoinitiating group.

3.0 Testing of Photoinitiators

3.1 Introduction

Once a new photoinitiator has been created it needs to be tested so that its properties may be compared with existing products. As seen earlier a good photoinitiator should possess certain characteristics. These are repeated here for clarity.

1. High absorptivity in the region of activation
2. High quantum yield for free radical formation
3. Solubility in the resin system
4. Odourless and non-yellowing
5. Stable for storage
6. Non-toxic
7. Low migration
8. Cost effective

The first property, high absorptivity, can be assessed by the UV extinction coefficient. This should be assessed both at the required wavelength for the particular UV source to be used as well as looking at the UV maxima for a particular initiator. The extinction coefficient at the required wavelength allows for a direct comparison of photoinitiators for a particular lamp whilst knowing the UV maxima can be useful if an initiator has other desirable properties and an alternative light source can be used.

Typical mercury UV lamps have a series of emission peaks between 250 and 400nm. Low pressure lamps predominantly emit at 254 nm while higher pressure lamps show more emission peaks at higher wavelengths. Typical emission spectra for low, medium and high pressure UV lamps are shown in Figure 3.1.[64] Modern systems are now looking at LED technology for UV curing due to its lower energy consumption, optical stability and durability of the lamp.[65] LED emissions are typically a very narrow band at around 380-390 nm, a typical example is shown in Figure 3.2. For the purposes of this thesis UV extinction coefficients for any successful photoinitiators have been reported at 254 nm (Hg Lamp), 385 nm (LED) and also at any maxima between 220 and 400 nm.

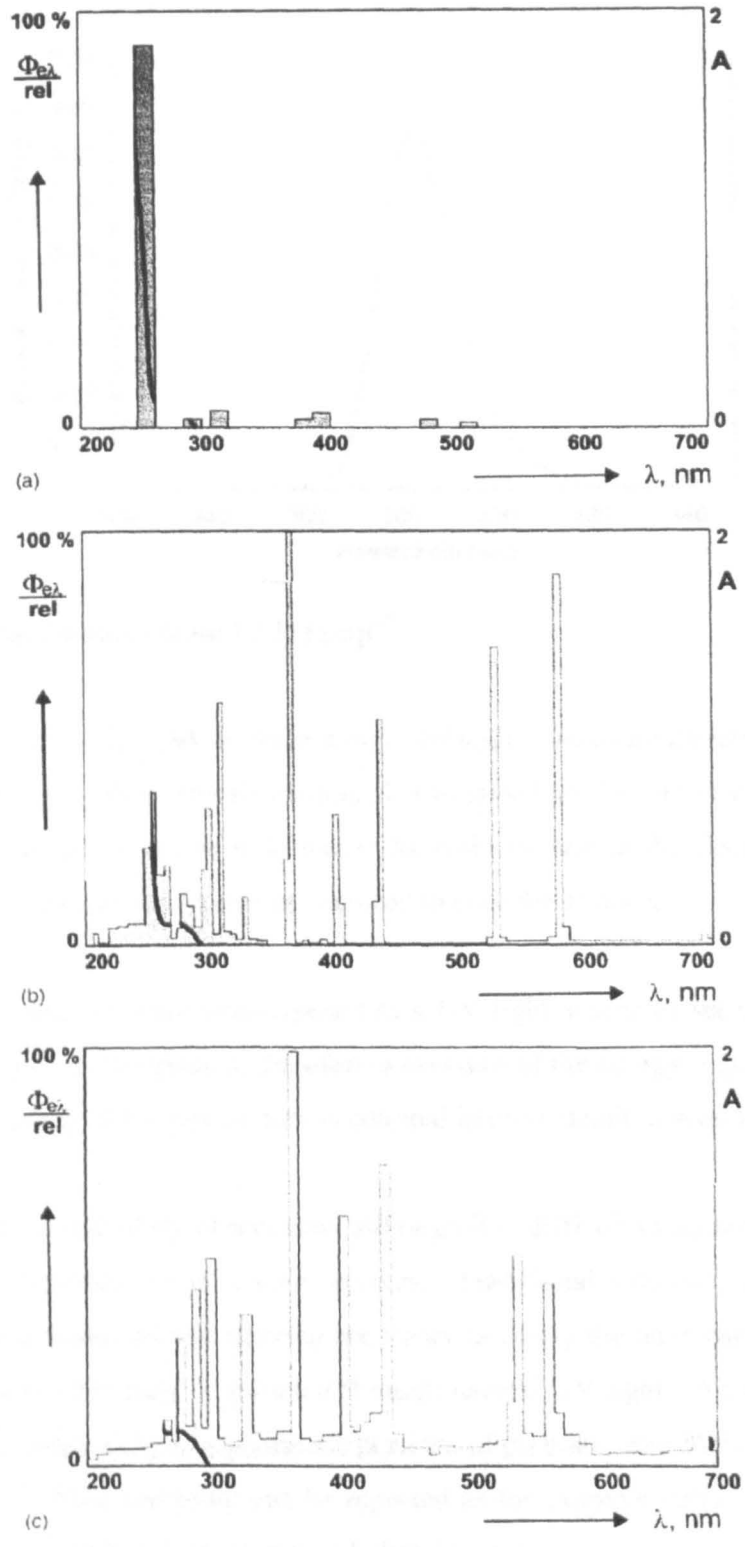


Figure 3.1: Typical output spectra for a) low-pressure, b) medium pressure and c) high pressure mercury UV lamps[64]

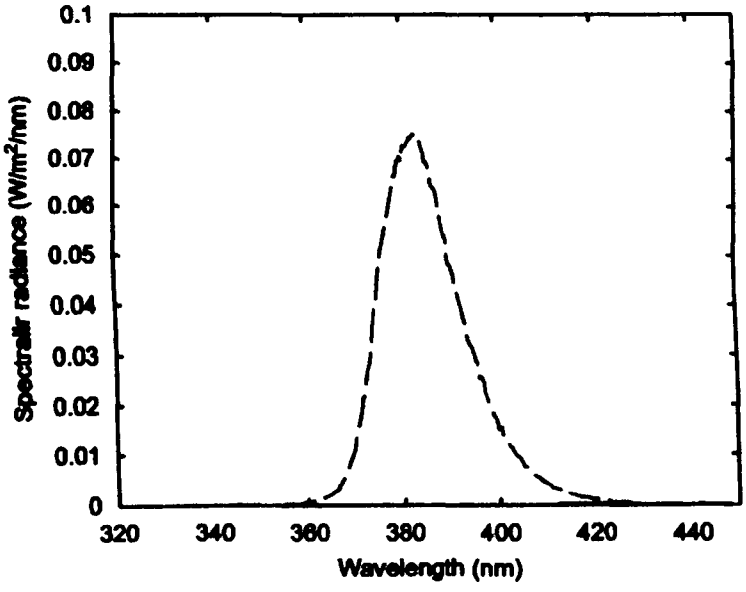


Figure 3.2: Typical output from LED lamp[65]

High quantum yield for free radical formation is difficult to measure directly. However, the effect of the number of free radicals generated is to speed up the rate of cure. The overall aim of maximising this property is to cause the resin to cure in the fastest possible time hence minimising the amount of energy required to cure the surface.

To carry out this test the resin was exposed to a UV light source of set power. The time taken for the cure to be complete is therefore a measure of the energy required to fully cure the resin. This testing of the rate of cure is covered in more detail in section 3.2.

Solubility can be estimated by observation although it is difficult to accurately quantify the solubility of a photoinitiator in a resin system. Traditional solubility methods such as forming a saturated solution and filtering are tricky as firstly the resin can be quite viscous and secondly some cure may be initiated through natural UV light. An approximation of solubility can be obtained by dissolving set portions of photoinitiator in the resin until loose solid is observed. Then solubility can be reported as for example <5%. This is generally sufficient information for industrial users of photoinitiators.

Photoinitiator concentrations in resins are usually around 2-4% w/w. Therefore it is desirable for the solubility of the photoinitiator to be at least 4%. However, should the solubility be less than 4% it may still be suitable for use as long as it can provide an effective cure at a lower concentration. It should be noted that this concentration applies to single molecule photoinitiators, for oligomeric photoinitiators the weight of initiator to obtain the desired concentration has been calculated with respect to the molecular weight of the photoactive portion of the oligomer such that the concentration is 2% w/w photoinitiator, not 2% w/w oligomer.

The odour and yellowing of the cured resin was not the priority issue in this thesis. Any significant observations have been reported but in general refinement of the photoinitiator structure would provide a further development after any migration issues have been dealt with. Similarly stability and toxicology studies would provide further work in developing the synthesis of the initiators from laboratory scale preparations to industrial applications. Those photoinitiators which were successfully synthesised had their characterisation repeated after six months as a form of initial stability test.

Low migration can be shown by carrying out migration testing methods using HPLC or GC. These are discussed further in section 3.3. These methods often involve development work for each initiator so it would be better if a generic method could be found to enable a quick and simple determination of the migration properties of an initiator in a cured resin. As a solution to this a method was developed whereby a simple UV spectrum of a solution which had been in contact with the cured resin showed the migration of the photoinitiator from the resin. The development of this method is covered in detail in section 4.0.

Finally cost obviously does not require a testing method, merely a calculation of the raw materials and energy processes involved. However, as with many developments the key is firstly to make it work then to worry about the cost. For this thesis as long as the cost of a particular chemical was not seen as being overly expensive it was considered suitable for use. Improving the cost effectiveness would again be an exercise for the industrial

development of the synthesis. As it was, all the chemicals used were relatively cheap to buy.

Overall the two significant issues for testing were "How well does it work?" and "Does it migrate?". The first was answered by measuring the rate of cure while the second by migration testing. The oligomeric photoinitiators which were found to work as well, or close to as well, as industry standards whilst exhibiting low migration characteristics were then recommended as possibilities for further development. For each successfully synthesised photoinitiator results have been reported against the eight criteria of "What makes a good photoinitiator?".

3.2 Testing for Rate of Cure

To get an idea of the rate of cure it was necessary to expose the resin to a UV source of set power and measure the time taken to achieve completeness of cure. Exposing resins containing different photoinitiator systems to the same lamp enables a comparison of the cure times, and hence the cure rates, to be determined. From this comparisons can be made between different photoinitiator systems. Alteration of the system may involve changing the type and/or concentration of the initiator.

Completeness of cure can be measured in a number of ways. Probably the most analytical is to simultaneously measure the IR spectra of the resin to observe changes in the resin's structure during cure. For example, acrylate resins show an IR peak at 1634 cm^{-1} due to the acrylate carbon-carbon double bond. This double bond breaks during polymerisation and hence a reduction in the intensity of the IR peak is seen. Changes in the intensity of this peak can be plotted against time to establish a profile of the cure and the time for complete cure can be read from this graph.

Limitations to this method are that it can be expensive, is resin specific and may show inaccuracies to interfering absorbencies from other molecule in the photoinitiating system. Further to this IR scans of solid substances are often difficult to obtain showing little detail and broad peaks.

Alternatives involve simple tests which can be carried out on the resin by hand to "feel" for the cure. Since exposure of the skin to UV light sources is undesirable the resin is removed from the UV light at periodic intervals for testing until the cure is complete. Typically this is achieved by the use of a conveyor belt system. A conveyor running at a set speed carries the supported resin under a UV lamp hence exposing it for a set time and therefore a set amount of energy. Simple tests may be performed on the resin after each pass to check whether cure has been achieved. The number of passes under the lamp to achieve cure is therefore a measure of the time, and hence the energy, required to cure the resin. This was the method applied for this thesis.

The speed of the conveyor belt was adjustable so that a suitable number of passes is required for the cure to enable a comparison between photoinitiators to be made. Shown in Figure 3.3 is the DYMAX UVC-5 curing system used. The belt speed was set at 16.5 m min^{-1} giving an energy output of 110 mJ cm^{-2}.

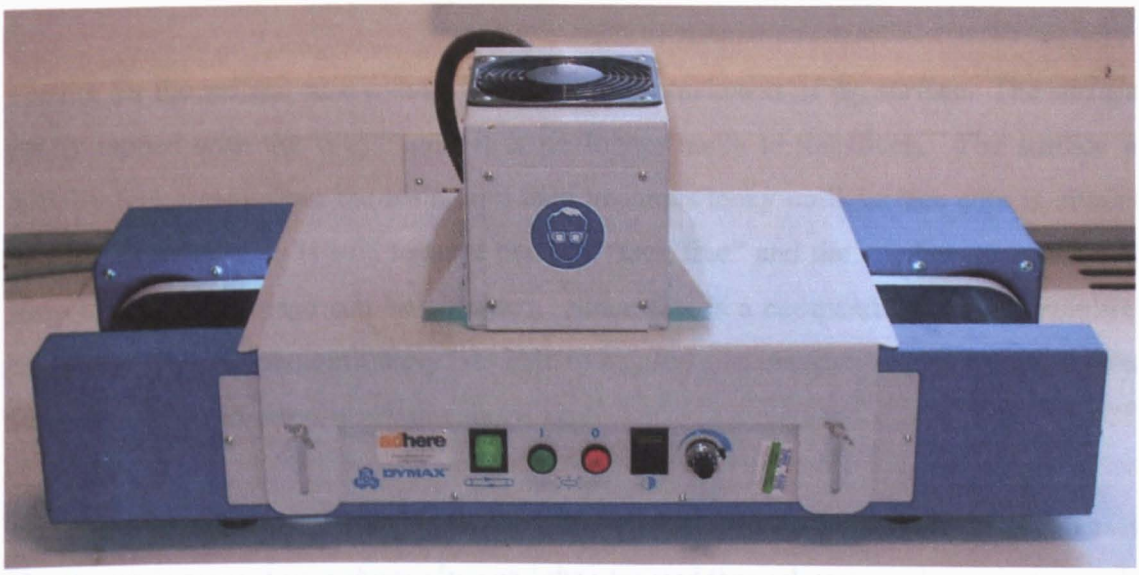


Figure 3.3: DYMAX UVC-5 Curing Conveyor System

The resin was prepared to a set thickness for consistency of testing. The exposure of the surface is uniform so surface area is not important but depth can be. Oxygen inhibition occurs at the surface and so is more of a consideration for thin films than thick ones.

Constant thickness was achieved by applying a portion of resin to a suitable support and then dragging a threaded bar to spread the film. The threads on these bars, known as K-bars, are designed to give a film of set thickness. Two different thicknesses of film were tested, K0 (4μm) and K3 (24μm). The bars are shown in Figure 3.4.

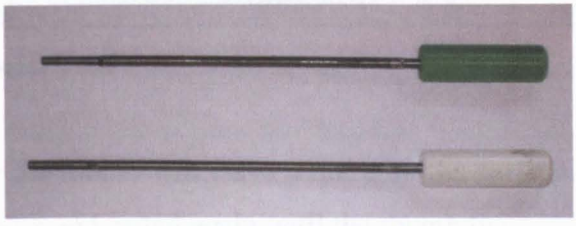


Figure 3.4: K-bars. Green (K3, 24μm) and White (K0, 4μm)

There are two stages reached during resin curing. The first is a surface cure where the exposed surface has become cured although there may not be complete curing of the resin underneath. The second is a complete cure when then entirety of the resin has been cured such that no monomer remains. This takes longer as energy from the UV lamp is lost as it passes through the resin such that the resin deeper in the surface takes longer to cure.

Testing for the surface cure is done by checking for tackiness of the surface. The surface is gently tapped with the finger until it is no longer tacky to the touch. The surface will initially feel greasy from the resin, and then becomes tacky until surface cure is obtained. At this point the resin is said to have become "tack free" and the number of passes of the lamp to reach this stage can be recorded. Since this is a comparative test the number of passes for different photoinitiators was able to be used as a measure of performance without the need to convert into the actual energy used.

Testing for complete cure is most easily carried out by a method known as a "thumb twist". The thumb is pressed onto the surface and then twisted through 90°, as shown in figure 3.5.

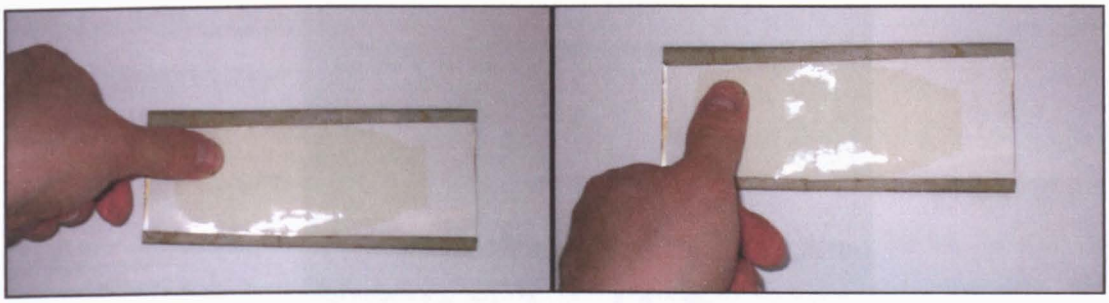


Figure 3.5: Thumb Twist Test

If curing is incomplete the thumb will leave a mark on the surface and so the resin can be passed under the UV lamp and tested again until the thumb twist test does not leave a mark. Again the number of passes of the lamp was recorded and used as a comparison of the relative effectiveness of different photoinitiators. Figures 3.6 to 3.8 show the appearance of the resin through testing.

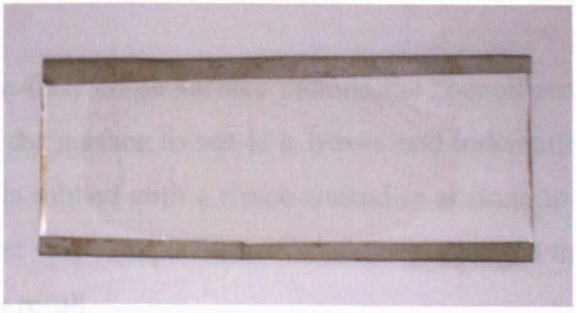


Figure 3.6: Uncured resin film. Film shown is a 24 µm film using 2% w/w benzophenone photoinitiator

Figure 3.7: Surface cured resin (Tack Free). Note also slight yellowing on cure.

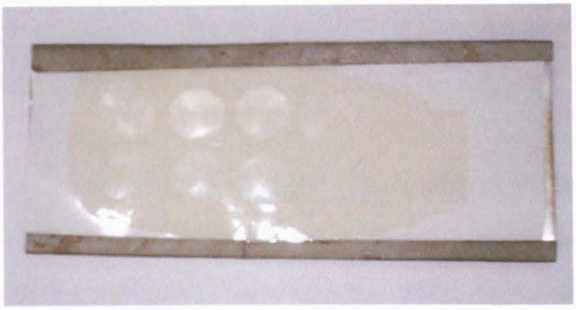


Figure 3.8: Fully cured resin showing thumb twists. Top row passes 8-11, bottom row passes 12-15. Note marks getting fainter until no mark from pass 15. This resin was fully cured after 15 passes of the lamp.

Although both of these tests are subjective, repeat testing by the same user can give a quick and effective comparison of the cure rates of different photoinitiators. For the purposes of this thesis each test was repeated three times with the results averaged and rounded to a whole number.

Alternative tests for the fully cured surface include the "pencil scratch" test where a hard pencil is drawn across the surface to see if it leaves and indentation or the "acetone rub" test where the surface is rubbed with a tissue soaked in acetone to see if it leaves a mark. The "pencil scratch" test was also performed when it was judged that curing was complete as a confirmation of the result.

3.3 Migration Testing

For this thesis the primary design concern for the photoinitiators was that they show low or preferably no migration so that they may be considered suitable for use in food packaging. Therefore, it was necessary to have some sort of test to determine whether any migration of the photoinitiator occurs and, if so, the amount of migration.

The simplest way to determine migration is to place the photoinitiated resin in contact with the foodstuff in question for a period of time then analyse the foodstuff to determine if any migration has occurred. In order to separate the photoinitiator from the foodstuff HPLC or GC methods are used either directly on the foodstuff or following an extraction procedure.

The level of migration must be determined for every foodstuff which will use the photoinitiated resin in its packaging.

This however presents a problem in the design of new photoinitiators. Each photoinitiator in question will show a different retention time whether analysed by HPLC or GC. Also in the case of oligomeric photoinitiators there may be different retention times for different chain lengths of the oligomer. This can affect the resolution of the peaks shown for the photoinitiator from those of the different components of the foodstuff. Overall this can involve a lengthy process of method development for a particular photoinitiator in a particular foodstuff which may be a waste of time and effort if the new photoinitiator were still to migrate.

This problem was evident in a study by Silva *et al* in 2006.[66] They conducted a summary of different techniques used to analyse the migration of 8 known migrants. Overall the best method for a particular migrant varied between HPLC and GC and then which particular column, solvent, temperature program, etc, would provide the best result. They concluded that it would not be possible to reliably draw up an analytical protocol to cover all possibilities. Accurate method development for migration testing is only possible once the migrant/foodstuff combination is known.

Therefore it would be preferable to have a simple method of determining whether a photoinitiator is likely to migrate that could be used for trial purposes before going on to full method development only for those photoinitiators which have shown low migration at the trial stage. Since photoinitiators obviously absorb UV light then it was thought to develop a method whereby the initiator is extracted into a suitable solvent and then, after a suitable period of time, the solvent may be examined by UV spectroscopy to observe if there had been any migration of the photoinitiator into the solvent. Work carried out during this thesis looked at the development of this UV method and then used the method to test the migration properties of the newly developed photoinitiators.

4.0 Development of UV Method for Migration Testing

4.1 Introduction

As seen previously determination of the migration characteristics of a photoinitiator can involve lengthy method development which is generally specific to each individual photoinitiator and each contact substance. When developing new photoinitiators it would be useful to have a quick and simple method to evaluate whether the photoinitiator is likely to show low migration characteristics or not. With regard to this a method was developed using a simple UV spectroscopy test.

The method involved cutting a set area of cured resin of known thickness and then immersing it in a set volume of solvent for a suitable time to allow full migration to occur. The solution was then examined by UV spectroscopy. Since photoinitiators are intended to absorb UV light then any migration of a photoinitiator was able to be shown by peaks in a UV spectrum. This method was both qualitative with regard to the tendency to migrate as well as being quantitative for those photoinitiators which do migrate. The method was firstly validated by using benzophenone as the photoinitiator.

As discussed in Section 3.3, migration testing methods are usually developed to determine the migration of a photoinitiator into a particular foodstuff. Since this method was developed to easily determine whether a photoinitiator migrated then suitable common solvents were used to simulate typical foodstuffs. The solvents used were 85% ethanol, to simulate migration into aqueous and alcoholic food products, glacial acetic acid, to simulate food products where an acidic environment may be present such as vinegar, and diethyl ether, which simulated for those photoinitiators likely to migrate into a fatty or oily environment. These three solvents were used for the method validation and subsequently for the testing of the new oligomeric photoinitiators.

It should be noted that, since the sample was immersed in the solution, this method accounted for migration both from the surface of the resin and through the paper support. While usually contamination of any foodstuff will normally only occur from migration through the packaging material it was thought that, if a photoinitiator showed low

migration from both sides then it will certainly show low migration through the support. Since this was developed as a quick method to establish those photoinitiators which may show low migration then allowing migration from both sides would not be detrimental to establishing the tendency of a particular photoinitiator to migrate.

Figure 4.1 shows the general method for a 24 μm thick resin. Initially the size of the piece of resin cut out was 4 cm^2 and the volume of solvent was 25 ml. This was determined so that 100% migration of a sample with an initial benzophenone concentration of 2% would give a UV absorbance maximum of about 1.0 while a sample with 4% concentration would give a value of about 2.0. However preliminary investigations showed a UV absorbance maximum for a sample with 2% initial benzophenone concentration of only about 0.16 and that for a 4% sample as 0.60 suggesting migration was far from 100%. Therefore the size of the resin piece was increased to 8 cm^2 and the volume of solvent changed to 20 cm^3. This gave absorbencies at 2% and 4% initial benzophenone concentration as about 0.36 and 1.25 respectively. For future use of the method it would also be necessary to adjust these amounts if the photoinitiator under test had a UV extinction coefficient or migration profile considerably different to that of benzophenone.

Finally, it is preferable that the migration of the photoinitiator is examined when migration is complete. Since preliminary studies had indicated that the method was likely to be successful in identifying migrants it was then used to look at the migration of benzophenone over time. Figures 4.2 to 4.4 show the absorbance data for benzophenone in the three test solvents over a series of time points. These show that the majority of the migration occurred rapidly in the first 24 hours but then continued slowly over the next few days. Migration appeared to reach completion, or as near to completion as experimental accuracy allows, around day 4-5. Therefore it was decided that testing of the solutions after 7 days would allow for near complete migration and therefore reliability of results.

1. Weigh 7.0 g* of tripropylene glycol diacrylate (TPGDA)* into a weighing boat.
2. Add 3.0 g* of bisphenol A ethoxylate diacrylate (BAED)* to the weighing boat.
3. Add 0.2 g* of benzophenone* and 0.2 g* of ethyl dimethylamino benzoate*.
4. Mix until all solids have dissolved (gentle warming may be necessary).
5. Apply a small quantity of the prepared resin to the support and smooth with a number 3 K-bar (24μm).
6. Pass resin under UV curing lamp and determine number of passes for total cure.
7. Pass cured resin under lamp again for the same number of passes determined in step 3 to ensure completeness of cure.
8. Cut out $8cm^2$ of cured resin, weigh, cut into 4 equal sized pieces and place in labelled sample vial.
9. Cut out $8cm^2$ of resin support, cut into 4 equal sized pieces and place in vial labelled blank.
8. Pipette 20.0 cm^3 of 85% v/v ethanol* into each vial, seal and shake.
9. Shake periodically over the next 7 days.
10. Obtain UV spectra between 200 nm and 400 nm for each sample solution using the blank sample as the UV blank.
11. Note any peaks in UV spectra and compare with UV absorbance maxima of the photoinitiator under test

Note: This method is for testing the migration of benzophenone at an initial photoinitiator concentration of 2% w/w from a 70:30 TPGDA:BEAD resin to a solution of 85% v/v ethanol. Quantities and substances marked * may be varied according to the required test.

Figure 4.1: UV method for determination of migration

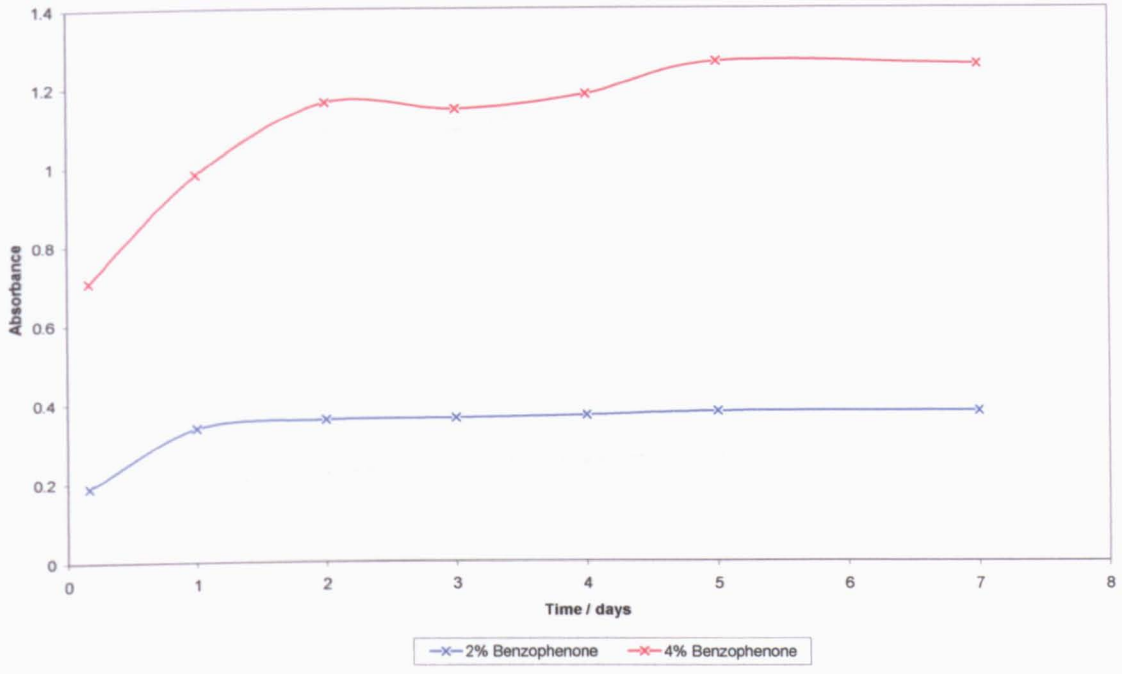


Figure 4.2: Migration of benzophenone into 85% v/v ethanol over time

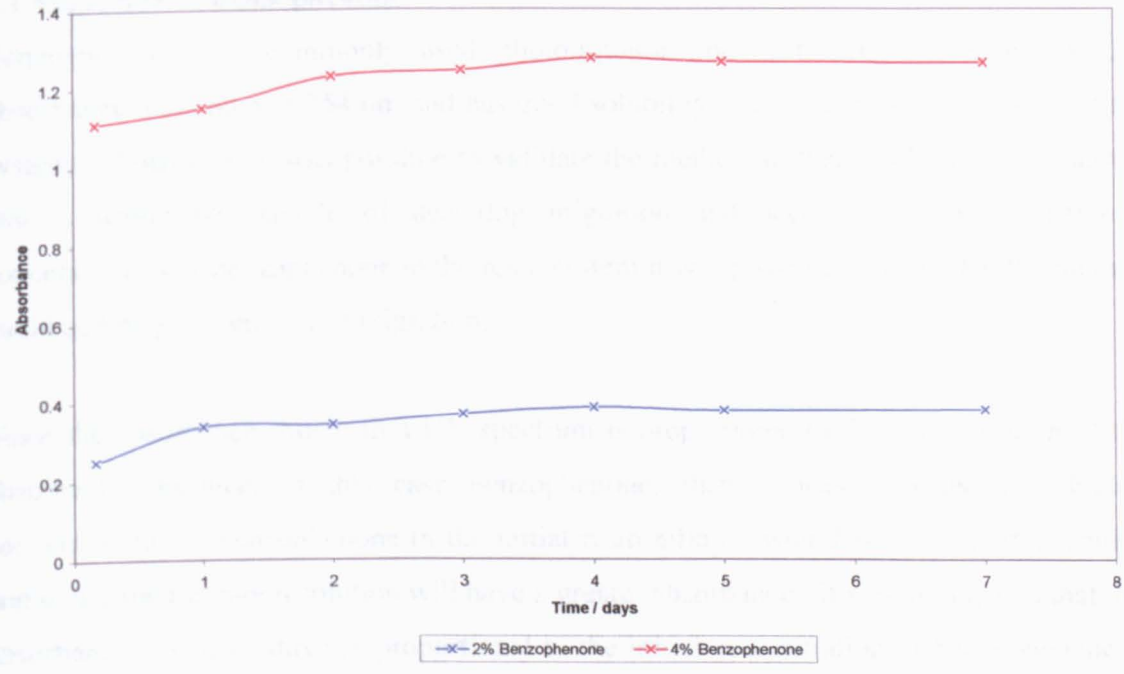


Figure 4.3: Migration of benzophenone into glacial acetic acid over time

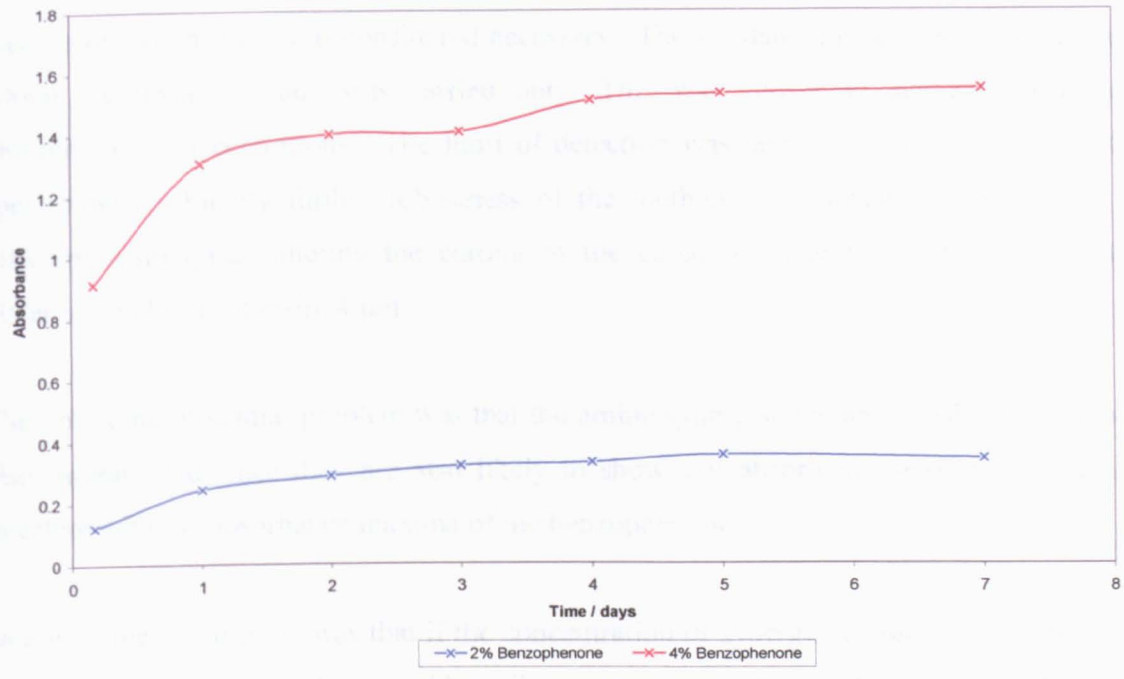


Figure 4.4: Migration of benzophenone into diethyl ether over time

4.2 Migration of Benzophenone

Benzophenone is a commonly used photoinitiator known to migrate. It has a UV absorbance maximum at 254 nm and has good solubility in a number of solvents and resin systems. Therefore, it was possible to validate the method so that firstly it can be shown that it would be capable of detecting migration and secondly by using different concentrations of benzophenone in the resin system it was possible to show that the method could quantify the amount of migration.

Since the absorbance shown in a UV spectrum is proportional to the concentration of the absorbent substance, in this case benzophenone, then it was expected that higher concentrations of benzophenone in the initial resin mixture would show greater migration and hence the migration solution will have a greater absorbance. It was anticipated that this absorbance would be directly proportional to the initial concentration of benzophenone in the resin mixture.

The validation looked at the accuracy, or repeatability, of the results and also the linearity of absorbance at different concentrations. Since UV spectroscopy is known to be precise then no precision study was considered necessary. The validated range was taken that over which the linearity study was carried out. This was chosen to account for typical photoinitiator concentrations. The limit of detection was taken as being the limit of the spectrometer. Finally further robustness of the method was carried out by looking at different resin types, altering the cutting of the cured resin, and also by looking at a different thickness of resin, 4 μm.

The only other potential problem was that the amine synergist and any sensitiser used may also migrate and since they are also likely to show UV absorbance maxima they could interfere with the absorbance maxima of the benzophenone.

One possible assumption was that if the concentration of synergist or sensitiser in the resin were kept constant then they would exhibit constant migration and hence have the same effect on the UV spectrum for each sample. Therefore since the method proved accurate and linear then a measure of the migration could be determined by looking at the difference in absorbance at two concentrations negating any effect of the synergist or sensitiser.

This assumption was simultaneously tested by looking at the synergist used, ethyl 4-dimethylaminobenzoate (EDB). EDB shows a UV absorption maximum at 310 nm with zero absorption at 254 nm. Since benzophenone has a UV absorption maximum at 254 nm and shows zero absorption at 310 nm then there was to be no interference from either migrant on the other. The validation of benzophenone was therefore able to be carried out reliably, as the absorbance measured at 254 nm was an accurate quantification of the benzophenone concentration in the migration solvent, while the spectra were also examined to see that any peak at 310 nm was constant thus implying constant migration of the synergist. To reduce further complication no sensitiser was used.

4.2.1 Accuracy

Determination of the accuracy of the method was simply a matter of repeating the method to see if the same results are obtained. Concentrations of benzophenone in the initial resin were prepared at 2%, 3% and 4% w/w with respect to the resin. $8cm^2$ of cured resin was then extracted with $20.0cm^3$ of either 85% ethanol, acetic acid or diethyl ether. Each resin sample for test was prepared and examined six times.

In order to ensure consistency all tests were carried out on a resin mixture consisting of 70% tripropylene glycol diacrylate and 30% bisphenol A ethoxylate diacrylate. The concentration of EDB was 2% w/w with respect to the resin. The resin was spread to a thickness of 24μm, using a No. 3 K-bar, on a paper support and was cured using a Dymax UVC-5 conveyor curing system. The resin was passed under the lamp for twice the number of passes required to obtain total cure so that there would be no likelihood of free resin monomer remaining which might affect the UV result.

The solutions were examined after 7 days using a Perkin Elmer Lambda 25 UV spectrometer. Scans were carried out between 200 nm and 400 nm. With acetic acid and diethyl ether there was some deterioration of the signal below 230 nm so scans were carried out between 230 nm and 400 nm. The blank for the spectrometer was a 7 day extraction from an $8cm^2$ piece of the paper support into the appropriate solvent.

Figure 4.5 shows the output spectra for migration of benzophenone into 85% ethanol for initial concentrations of 2%, 3% and 4%. All six spectra are shown for each concentration and by visual inspection there seems to be good agreement between samples at the same concentration. At 254 nm the absorbance increases with increasing initial benzophenone concentration as expected showing an increase in migration of the photoinitiators. There is a consistent shoulder peak at 310 nm suggesting that there is a consistent migration of the EDB. This is useful as when photoinitiators are examined which may have absorbance maxima coinciding with that of EDB then the absorbance due to the migration of the EDB can simply be subtracted as a constant.

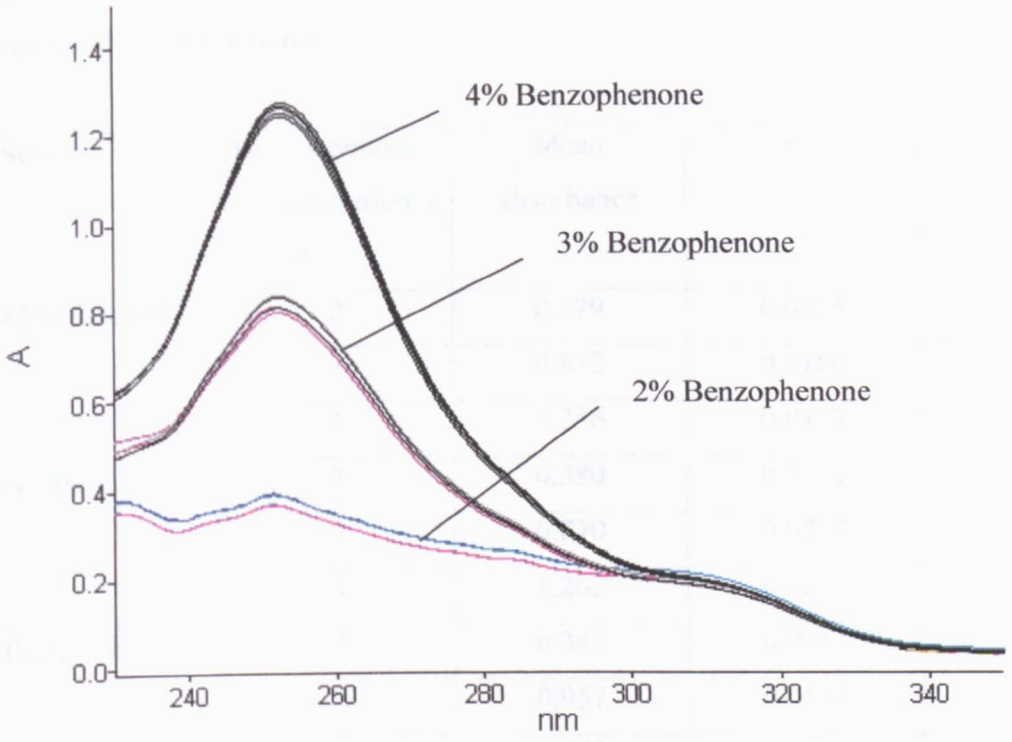


Figure 4.5: Migration of Benzophenone into 85% Ethanol

This pattern was repeated with the samples for migration into the acetic acid and the diethyl ether although with slight variation of the wavelength and value of the absorbance maximum due to solvent effects. UV absorbance data for benzophenone in the solvents used is shown in Table 4.1.

Solvent	λ_{max} / nm	ε / L mol^{-1} cm^{-1}
85% Ethanol	254	19 400
Acetic Acid	254	16 300
Diethyl Ether	249	20 200

Table 4.1: Benzophenone absorbance data

Statistical analysis was now be carried out on the maximum UV absorbance in order to establish the accuracy of the method. Mean, standard deviation (SD) and relative standard

deviation (%RSD) have been calculated for each initial benzophenone concentration in each of the three solvents.

Solvent	Benzophenone Concentration / %w/w	Mean absorbance	SD	%RSD
85% Ethanol	2	0.379	0.0085	2.24
	3	0.812	0.0160	1.97
	4	1.256	0.0127	1.01
Acetic Acid	2	0.380	0.0131	3.43
	3	0.870	0.0220	2.53
	4	1.262	0.0243	1.93
Diethyl Ether	2	0.341	0.0151	4.43
	3	0.957	0.0544	5.69
	4	1.543	0.0718	4.65

Table 4.2: Statistical analysis of accuracy results

The results show a high degree of accuracy with the relative standard deviation in most cases being less than 5%. The greatest variation of results is seen with the diethyl ether possibly due to the relative volatility of this solvent. There is, of course, some error to be taken into account with the preparing of the samples, particularly when cutting out the resin, but in general it seems there can be confidence that if a particular result is obtained for the migration of benzophenone from a sample resin then this can be taken as indicative of a certain initial concentration in that resin.

Of course the intention of this method was not to quantify an unknown migrant but rather to determine whether a potential migrant of known absorbance does indeed migrate. These results indicate that if a migrant is present in a set quantity then it will give the same absorbance each time the test is run. In this way there is confidence that a UV absorbance at the wavelength of a migrant substance which changes if the initial amount of that

substance is changed is indicative that that substance does indeed migrate. The level of this absorbance was then able to be used to accurately calculate the amount of migration which has occurred.

A further part of this accuracy test was to look at whether the cutting of the resin had any effect. There is a possibility that some migration may occur from deeper in the resin via the cut edges. Therefore, if more cuts were to be made greater migration might occur resulting in doubt of the integrity of the results. Typically the cured resins under test were cut into four pieces before immersion in the solvent. The test was also performed with the resin cut into many small pieces to see if this made any difference to the results. Table 4.3 shows that the migration does not appear to depend upon the number of pieces cut.

Solvent	Benzophenone Concentration / %w/w	Absorbance (Four Pieces)	Absorbance (Many Pieces)
85% Ethanol	2	0.379	0.368
	4	1.256	1.252
Acetic Acid	2	0.380	0.392
	4	1.262	1.268
Diethyl Ether	2	0.341	0.346
	4	1.543	1.533

Table 4.3: Effect of cutting of the resin

Overall the method has good accuracy in the three solvents over the desired initial concentrations establishing reliability in the repeatability of the results. With precision assumed from the UV spectrometer the result can then be taken as a true indication of the amount of migration of the photoinitiator into the solvent. Linearity tests were then carried out to determine if the migration is proportional to the initial photoinitiator concentration.

4.2.2 Linearity

Linearity was determined by looking at the absorbance at different initial concentrations of photoinitiator in the resin mixture and then evaluating the results for any statistically significant correlation. Industrially photoinitiator concentrations vary between about 2-4% so linearity was determined in this range. The absorbencies at 2%, 3% and 4% were already known from the accuracy study in Section 4.2.1. For the linearity study absorbance at 2.5% and 3.5% initial photoinitiator concentration were also examined. The samples were prepared for analysis in the same way as those in the accuracy study.

Figures 4.6 to 4.8 show a graphical representation of the results of the linearity study. They also show the theoretical line that would be observed if all of the benzophenone in the initial resin were to migrate into the solvent. As can be seen from these figures, although there is significant migration it is much less than 100%.

From visual observation it can be seen that the migration of the benzophenone shows a linear response with respect to the initial concentration of benzophenone in the resin. Linear regression analysis of the data for migration into 85% ethanol, acetic acid and diethyl ether gives correlation coefficients of 0.999, 0.997 and 0.995 respectively. From this confidence intervals can be calculated as 125.5, 52.3 and 43.5 which show that there is significant confidence in the correlation even at the 1% level.

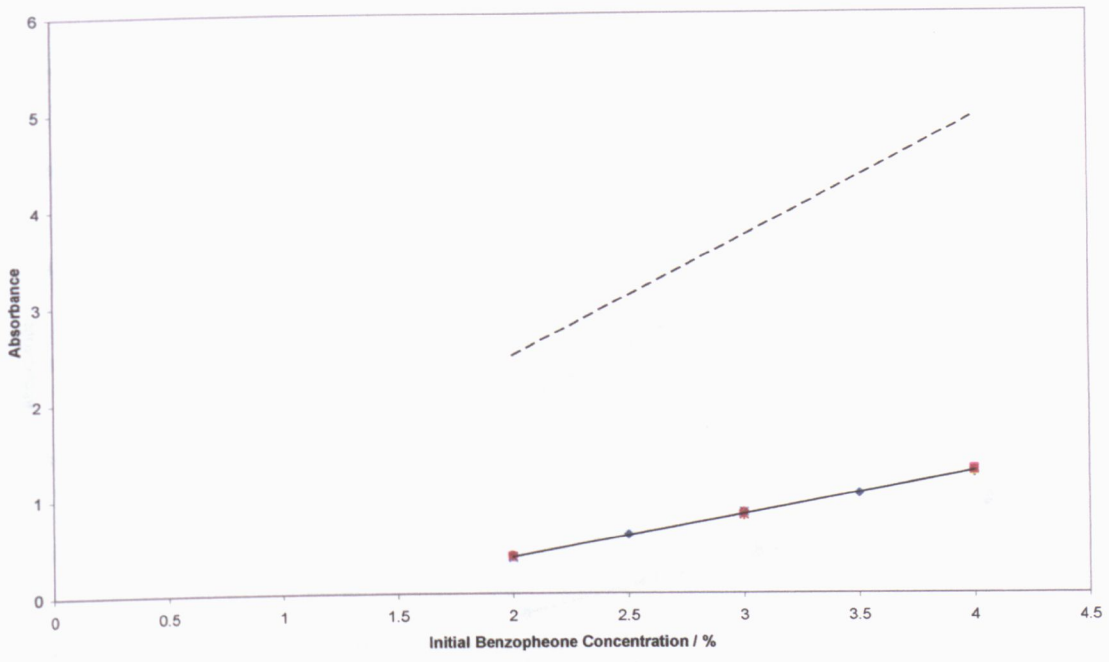


Figure 4.6: Linearity data for migration of benzophenone into 85% ethanol at 254 nm

(_____ Best fit line ---------- Theoretical line for 100% migration)

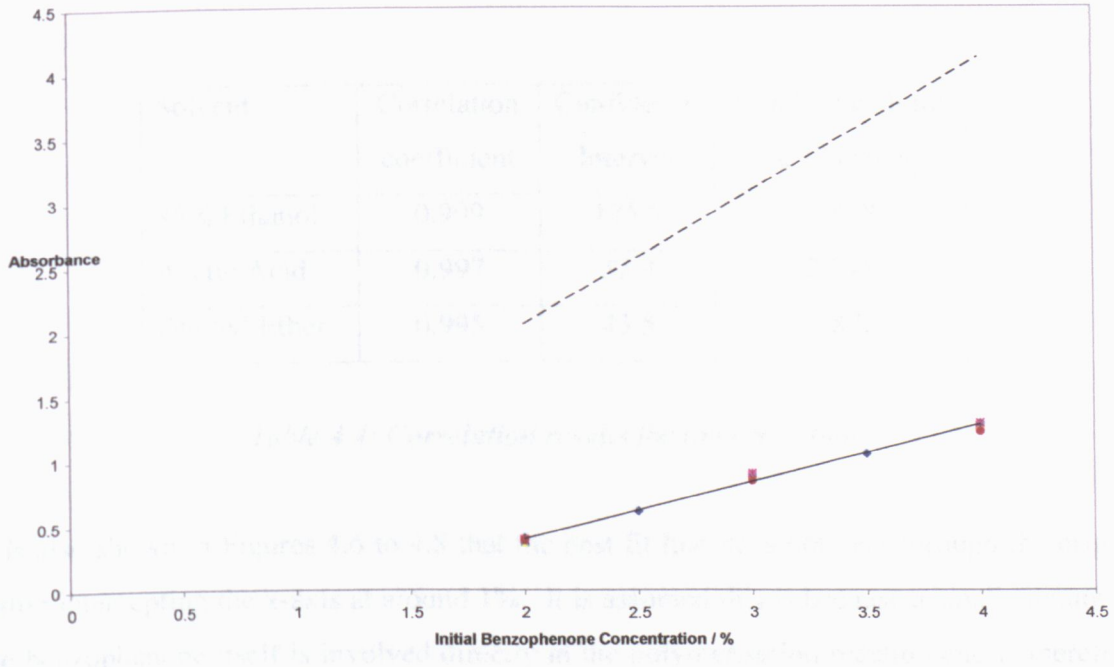


Figure 4.7: Linearity data for migration of benzophenone into acetic acid at 254 nm

(_____ Best fit line ---------- Theoretical line for 100% migration)

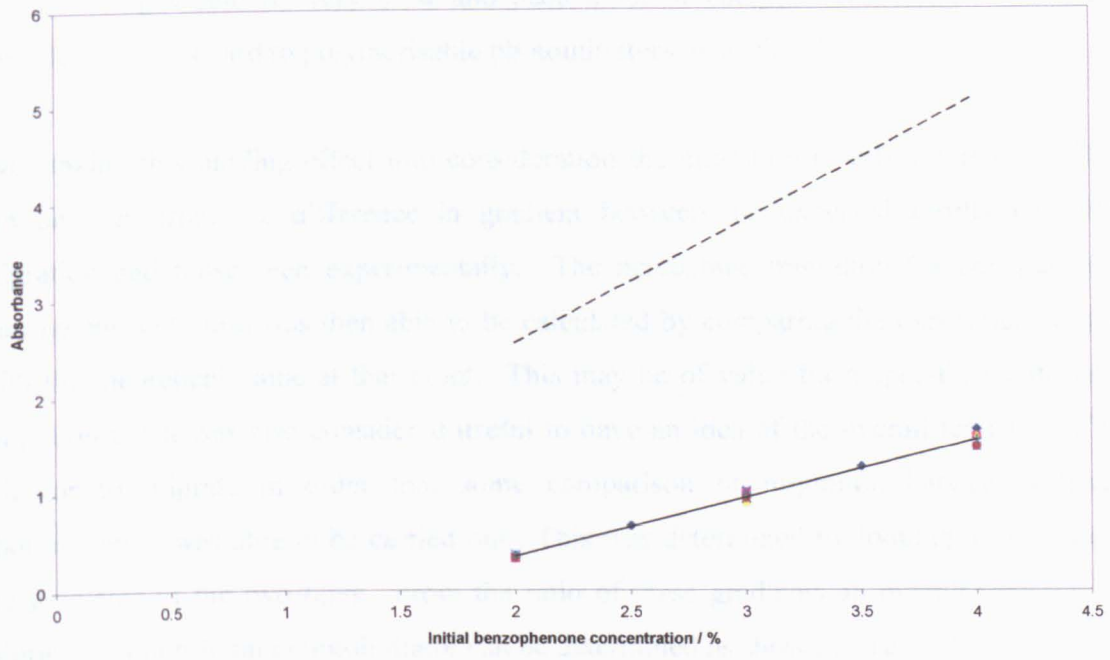


Figure 4.8: Linearity data for migration of benzophenone into diethyl ether at 254 nm (_____ Best fit line ---------- Theoretical line for 100% migration)

Solvent	Correlation coefficient	Confidence Interval	Confidence limit at 1% level
85% Ethanol	0.999	125.5	2.878
Acetic Acid	0.997	52.3	2.878
Diethyl Ether	0.995	43.5	2.878

Table 4.4: Correlation results for linearity study

It is also shown in Figures 4.6 to 4.8 that the best fit line does not pass through the origin, rather intercepting the x-axis at around 1%. It is assumed this is because a small amount of the benzophenone itself is involved directly in the polymerisation reaction and is therefore kept entirely bound to the resin. It could be asked why not use a small initiator concentration and hence avoid migration that way. The reason for this is that those

molecules which become bound are no longer able to initiate further polymerisation. Due to this curing would be very slow and need a lot of energy. This effect was further considered with regard to polymerisable photoinitiators in section 4.3.

Even taking this binding effect into consideration the migration is still less than 100% as can be seen from the difference in gradient between the expected results for 100% migration and those seen experimentally. The percentage migration for any particular starting concentration was then able to be calculated by comparing the experimental value with the theoretical value at that point. This may be of value for a specific incidence of migration but it was also considered useful to have an idea of the overall tendency of the initiator to migrate in order that some comparison of migration between different photoinitiators was able to be carried out. This was determined by looking at the ratio of the gradients of the two lines. From the ratio of these gradients an overall tendency for migration of non-bound photoinitiator can be determined as shown in Table 4.5.

Solvent	Experimental Gradient	Theoretical Gradient	Tendency to migrate / %
85% Ethanol	0.438	1.228	36
Acetic Acid	0.441	1.031	43
Diethyl Ether	0.601	1.273	47

Table 4.5: Tendency to migrate for benzophenone

Overall from these results it has been seen that there is a statistically significant confidence that the migration of a photoinitiator shows a linear response with respect to the initial concentration of photoinitiator in the resin mixture. It has also been seen that there is an effect whereby some of the initiator does not migrate due to binding to the resin.

Finally an evaluation of the tendency for an initiator to migrate was determined by looking at the ratio of the gradients of the theoretical and experimental data. This use of a ratio is particularly useful as it allows for the determination of tendency to migrate even if the

photoinitiator exhibited an absorption maximum overlapping with other migrants or with anything else which may be present in the migration mixture.

4.2.3 Synergist Migration

One of the objectives of the validation was to establish that the amine synergist used showed constant migration and hence could be discounted, or have its effect incorporated into the calculation, when looking at the migration of a photoinitiator. This was evaluated by looking at the UV absorbance data for the migration solutions at the value of the absorbance maximum for EDB. Table 4.6 shows the mean, standard deviation (SD) and relative standard deviation (%RSD) for the UV absorption of the amine synergist.

Solvent	Mean Absorbance	SD	%RSD
85% Ethanol	0.190	0.0071	3.8
Acetic Acid	0.070	0.0082	11.5
Diethyl Ether	0.141	0.0118	8.5

Table 4.6: Statistical analysis of EDB migration

From this it can be seen that the UV absorbance due to migration of the synergist is relatively constant and therefore does not have an effect on any evaluation of the migration of a photoinitiator. Again the migration data for 85% ethanol showed the greatest accuracy with the lowest %RSD at 3.8%. It is interesting to note that the expected absorbance due to the synergist would be around 1.7 whereas the observed values are less than 0.2 suggesting that as little as 10% of the synergist migrates.

It was originally thought that it may be necessary to eliminate any effects of synergist migration by using a non-migrating polymeric synergist. With regards to this some cured resins were prepared using a commercially available polymeric amine synergist based on EDB, Speedcure 7040. Samples of these resins with initial benzophenone concentrations of 2%, 3% and 3% were analysed for migration. Table 4.7 shows a comparison of the migration results for benzophenone with EDB and Speedcure 7040.

Solvent	Benzophenone Concentration / %w/w	Absorbance	
		EDB	Speedcure 7040
85% Ethanol (254 nm)	2	0.379	0.388
	3	0.812	0.806
	4	1.256	1.249
Acetic Acid (254 nm)	2	0.380	0.384
	3	0.870	0.905
	4	1.262	1.226
Diethyl Ether (249 nm)	2	0.341	0.411
	3	0.957	0.925
	4	1.543	1.523

Table 4.7: Comparison of results with non-polymeric (EDB) and polymeric (Speedcure 7040) amine synergist

There was little difference seen between the migration data with the use of non-polymeric or polymeric synergist. The only difference in the UV spectra was the elimination of the synergist migration peak at 310 nm when the non-migrating synergist was used. Since it was already been determined that the method can take into consideration any peak from the synergist it was decided, from a cost point of view, to continue to use EDB as the synergist for the testing of new photoinitiators.

4.2.4 Limit of detection

Obviously this method was not developed specifically to quantify photoinitiator migration, although it has been shown to do this and this in itself may prove a useful tool. Rather the requirement was to show that a photoinitiator shows low migration. It was therefore necessary to determine what exactly low migration is.

As mentioned in Section 1.6, current legislation sets migration limits specific to each migrant. Therefore it is not possible to know the limit that will be set for a new

photoinitiator. Since this thesis looked at oligomeric photoinitiators based on benzophenone it was decided that the aim of this thesis would be to develop a photoinitiator which would meet the benzophenone requirement limits of <0.6 mg kg^{-1} of foodstuff.[19]

If the assumption is made that our 1 kg of foodstuff is kept in a 1 dm^3 cube coated with 24 μm of resin then the total volume of resin would be 1.44 cm^3. Taking a resin density of approximately 1.2 g cm^{-3} makes the mass of resin 1.73 g. A 2% w/w initial photoinitiator concentration would then give a mass of photoinitiator of 35 mg. Therefore the legislation allows for approximately 2% of photoinitiator to migrate into the foodstuff.

Assuming a photoinitiator has a similar extinction coefficient to benzophenone then it was necessary for the UV method to show an absorption maximum of less than 0.05 for an initial photoinitiator concentration of 2% and less then 0.1 for 4%. From the accuracy of the data and the assumed precision of the UV spectrometer this was observed but is close to the limits of reliability for the method.

Also other photoinitiators may show interference from migration of the synergist. This was eliminated by using the gradient of the linearity graph as an approximation of the tendency to migrate. To meet the legislative requirements the tendency to migrate should be less than 2%. Again, assuming the new photoinitiator has an extinction coefficient similar to that of benzophenone, then this required a gradient of less than 0.025 or a difference between the absorbance at 2% and 4% initial photoinitiator concentration of less than 0.05.

Again this was rather close to the limits of reliability for this method and so it was decided that low migration would be taken as a gradient of less than 0.05 or a tendency to migrate of less than 4%. This proved sufficient to deem that a new photoinitiator is suitable to be taken on for further development as a low migrating photoinitiator.

It was previously noted, in Section 4.1, that this testing method gave an overestimation of the migration into a foodstuff. Since the resin and support were immersed in the migration solution then the result is a measure of the total migration both for the resin surface and

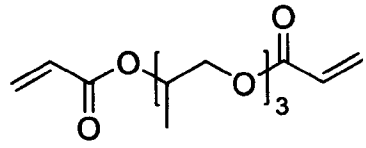
through the support. This is why observed migration of benzophenone is much higher than that seen in other migration studies. This built in overestimation means that where a new photoinitiator showed a tendency to migrate of less 4% then it would be likely to meet legislative requirements when progressed to detailed development.

For the purposes of low migration the difference in absorbance between 2% and 4% initial photoinitiator concentration was measured and a tendency to migrate of less than 4% was taken as low migration and has been reported as <4%. Tendency to migrate of greater than 4% has been reported as a percentage and the photoinitiator was not considered suitable for development as a low migrating photoinitiator.

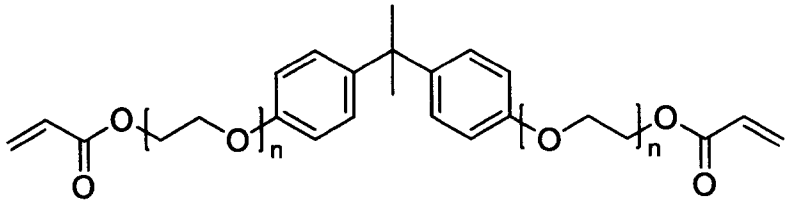
4.2.5 Different resins

The validation work described in Sections 4.2.1 to 4.2.4 was carried out on the same resin mixture, 70% tripropylene glycol diacrylate (TPGDA) and 30% bisphenol A ethoxylate diacrylate (BAED). This was the resin mixture that was used throughout the performance and migration testing of the new photoinitiators. However, as a robustness test on the validity of the new migration testing method the migration of benzophenone from other resin mixtures was also considered. This was to see if migration was resin dependent or whether low migration from the test resin could be taken as likely low migration from all resins.

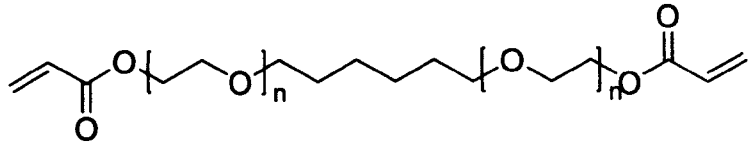
Migration testing was carried out on the TPGDA/BAED resin in proportions of 50/50 and 30/70 and also on mixtures of TPGDA with 1,6-hexanediol ethoxylate diacrylate (16HED) in proportions of 70/30, 50/50 and 30/70. Structures of these resins are shown in Figure 4.9. The UV absorbance data from testing on different resins is shown in tables 4.8 and 4.9.



tripropylene glycol diacrylate (TPGDA)



bisphenol A ethoxylate diacrylate



1,6-hexanediol ethoxylate diacrylate

Figure 4.9: Resins used for migration testing

Resin A	Resin B	% Resin A	% Resin B	Absorbance		
				Ethanol	Acetic acid	Diethyl ether
TPGDA	BAED	70	30	0.379	0.380	0.341
		50	50	0.409	0.427	0.375
		30	70	0.443	0.607	0.461
16HED	BAED	70	30	0.104	0.132	0.037
		50	50	0.164	0.302	0.164
		30	70	0.172	0.382	0.293

Table 4.8: Testing of different resin mixtures, initial benzophenone concentration 2%

Resin A	Resin B	% Resin A	% Resin B	Absorbance		
				Ethanol	Acetic acid	Diethyl ether
TPGDA	BAED	70	30	1.256	1.262	1.543
		50	50	1.297	1.274	1.247
		30	70	1.188	1.300	1.449
16HED	BAED	70	30	0.402	0.931	0.498
		50	50	0.746	1.170	1.369
		30	70	0.786	1.253	1.297

Table 4.9: Testing of different resin mixtures, initial benzophenone concentration 4%

From these results it appeared that migration was dependent on the resin mixture used. There was variation in the absorbencies recorded both when the resin composition and resin type are changed. It was hypothesised that this was due to both the amount of the photoinitiator bound during cure and also the relative affinity for the photoinitiator to remain in the resin system or migrate to the solvent.

The 16HED/BAED system showed much lower migration than the TPGDA/BEAD system for all three solvents when an initial photoinitiator concentration of 2% was used but migration was only significantly lowered for the 4% initial photoinitiator concentration when a 70:30 mixture is used.

It was also noted that in general migration is greater when there is more BAED in the resin system. However, this trend becomes far less evident in the TPGDA/BEAD system when 4% initial photoinitiator concentration was used.

These trends suggest that benzophenone has a greater tendency to become bound to the linear resins rather than the bulkier aromatic resin. The greater amount of the linear resin used the more benzophenone was bound on cure and hence migration was less.

Benzophenone also seemed to have a greater affinity to stay within resins containing 16HED as opposed to those containing TPGDA. At the larger initial photoinitiator concentration migration was much the same for all TPGDA/BAED resin compositions suggesting that the small binding effect of the TPGDA had become insignificant and that the photoinitiator had much the same affinity for all resin compositions. With 16HED/BAED resins there was both the binding effect of the 16HED and the affinity effect hence a trend was seen in the degree of migration at different resin compositions.

Overall the resin type and composition does have an effect on the tendency to migrate. Hence, proof of low migration in one resin system is not necessarily indicative of low migration in another. However, since the general trends seen in one resin system do seem to be evident in all resins systems testing then a general likelihood of low migration may be obtained by carrying out migration testing in a particular resin system.

Since the aim of developing this method was to provide a simple method for establishing a likely low migration, it was deemed satisfactory to carry out the migration test in a particular resin system. Those photoinitiators which showed a tendency to migrate were then rejected while any which showed low migration could be put forward for further detailed investigation. Since different applications where photoinitiators are used have different resin systems then detailed development work often involves selection of a photoinitiator due to its properties in a particular resin system. It is therefore more financially prudent to have a range of photoinitiators which generally show low migration and then fit one to a specific application rather than attempt to establish low migration in every resin system a customer could conceivably require.

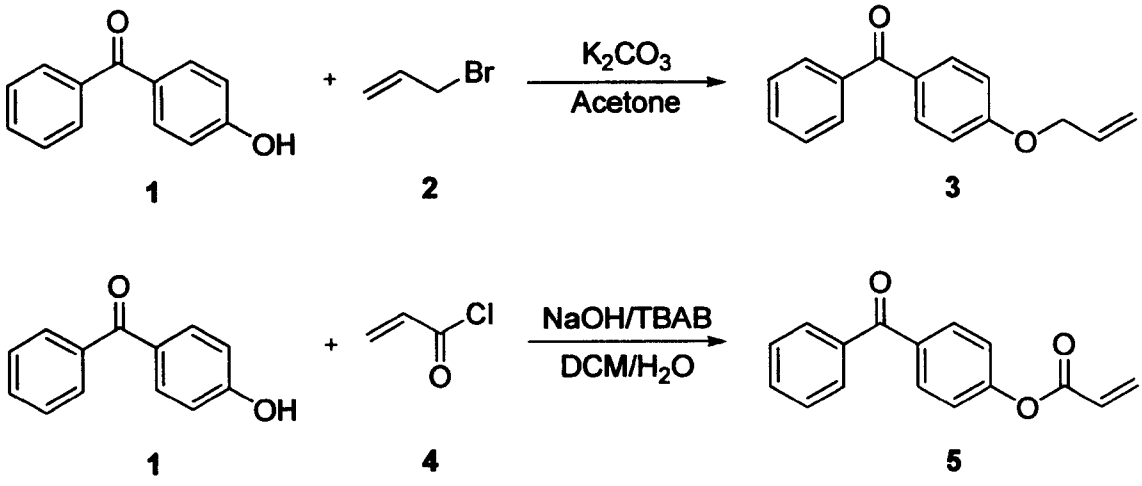
Since the 70:30 TPGDA/BEAD resin has been used throughout the validation and works well at showing migration of benzophenone then it was also considered suitable for use for migration testing of the benzophenone type oligomeric photoinitiators developed in this thesis.

4.3 Polymerisable Photoinitiators

Previous work has touched on the possibility of using a photoinitiator containing a polymerisable group.[32,33] The idea behind this is that during cure the photoinitiator itself may polymerise and hence this may restrict its movement in the resin and limit its tendency to migrate. There is also the possibility that the polymerisable part of the photoinitiator may become incorporated within the resin during cure and hence the photoinitiator will remain bound to the cured surface.

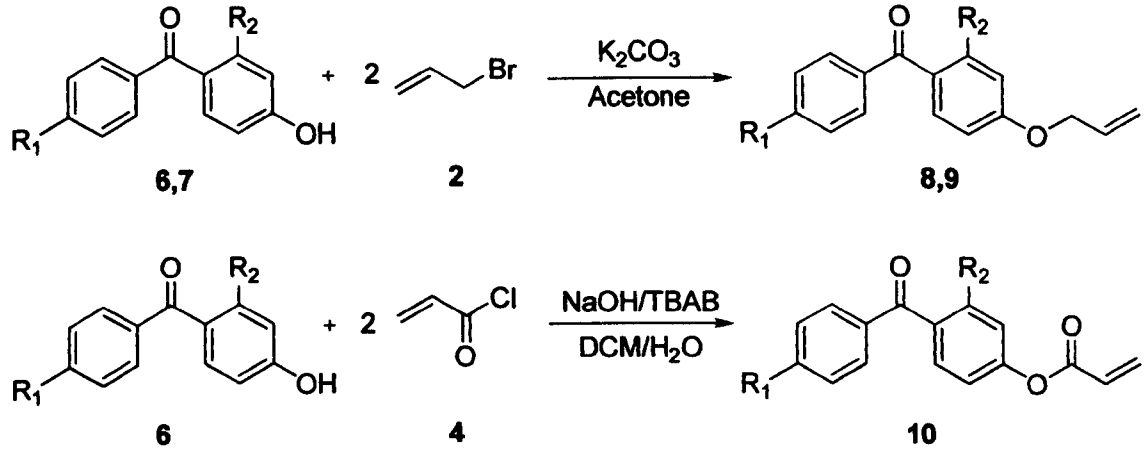
With regard to this photoinitiators containing one of two potentially polymerisable functional groups, either an allyl group or an acryloyl group, were investigated. The allyl group, it was expected, would be less likely to polymerise and hence more likely to migrate. Therefore, as well as a general investigation into the potential of these molecules as low migrating photoinitiators, this was also used as further validation of the migration testing method.

4-acryloyloxybenzophenone (**3**) has been considered previously for use as a photoinitiator and has been seen to bind to the cured resin although there may be questions over its long term stability. 4-allyloxybenzophenone (**5**) may provide a more stable alternative but also may bind or polymerise less readily increasing the possibility of migration. The synthesis of these two molecules from 4-hydroxybenzophenone (**1**) and allyl bromide (**2**) or acryloyl chloride (**4**) is shown in Scheme 4.1.



Scheme 4.1: Synthesis of 4-allyloxybenzophenone and 4-acryloyloxybenzophenone

As well as further studying the photoinitiating characteristics of these two molecules, the synthesis of diallyloxy or diacryloyloxy benzophenones starting from dihydroxybenzophenones was also considered. 4,4'-dihydroxybenzophenone (**6**) and 2,4-dihydroxybenzophenone (**7**) are both commercially available so these were used with the same method to synthesise the respective diallyloxy (**8,9**) and diacryloyloxy (**10**) derivatives for investigation as shown in Scheme 4.2.



6; R_1 = OH, R_2 = H
7; R_1 = H, R_2 = OH
8; R_1 = $OCH_2CH{=}CH_2$, R_2 = H
9; R_1 = H, R_2 = $OCH_2CH{=}CH_2$
10; R_1 = $OCOCH{=}CH_2$, R_2 = H

Scheme 4.2: Synthesis of diallyloxy and diacryloyloxy benzophenones

All five photoinitiators proved to be soluble in the resin system and, when coupled with an amine synergist (4-ethyl dimethylamino benzoate), successfully cured the resin on exposure to UV light. Tables 4.10 and 4.11 show the curing data in terms of the number of passes of the lamp for surface cure (Tack Free) and depth cure (Thumb Twist) for the potentially polymerisable photoinitiators at 2% and 4% initial photoinitiator concentration. The data for standard benzophenone is included as a comparison.

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone	7	10
4-allyloxybenzophenone **(3)**	8	14
4,4'-diallyloxybenzophenone **(8)**	10	16
2,4-diallyloxybenzophenone **(9)**	6	12
4-acryloyloxybenzophenone **(5)**	16	29
4,4'-diacryloyloxybenzophenone **(10)**	19	33

Table 4.10: Testing for speed of cure for potentially polymerisable photoinitiators, 2% initial photoinitiator concentration

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone	4	8
4-allyloxybenzophenone **(3)**	5	11
4,4'-diallyloxybenzophenone **(8)**	6	12
2,4-diallyloxybenzophenone **(9)**	4	8
4-acryloyloxybenzophenone **(5)**	9	13
4,4'-diacryloyloxybenzophenone **(10)**	12	25

Table 4.11: Testing for speed of cure for potentially polymerisable photoinitiators, 4% initial photoinitiator concentration

The allyloxybenzophenones **(3,8,9)** showed cure times comparable with that of benzophenone while the acryloyloxybenzophenones **(5,10)** seemed to cure at a much slower rate. This suggested that the acryloyloxybenzophenones either self polymerise or

else bind to the curing resin thus restricting their movement within the resin and hence their ability to initiate polymerisation. Also 4-acryloyloxybenzophenone **(5)** showed a higher cure rate than 4,4'-diacryloyloxybenzophenone **(10)** possibly due to the fact that the photoinitiating part of the molecule is less hindered when bound to other molecules, either the resin or other photoinitiators. This is particularly evident at the higher concentration when total cure times for the 4-acryloyloxybenzophenone are not far behind those seen for the allyloxybenzophenones.

The suggestion from this is that the allyloxybenzophenones do not either self polymerise or bind to the resin and behave rather as a single molecule photoinitiator similar to benzophenone. This suggested they would migrate and this was useful as an extension to the validation of the migration testing method. Since the acryloyloxybenzophenones seemed to either self polymerise or bind to the resin they were also useful for validation by demonstrating that a theoretically non-migrating photoinitiator indeed shows no migration when tested as per the UV migration testing method.

Further evidence of the self polymerising ability shown by the acryloyloxybenzophenones which was not evident in the allyloxybenzophenones was obtained by attempting a self polymerisation with EDB in toluene. Mass spectrometry analysis showed molecular ion peaks corresponding to a range of different chain lengths for the acryloyloxybenzophenones while that for the allyloxybenzophenones did not. This also opened up the possibility of pre-polymerising the acryloyloxybenzophenones for use as an oligomeric photoinitiator. This work is covered in section 5.4.

Migration testing was carried out on the samples using the same method as used for the benzophenone. UV absorbance data is shown in Table 4.12. Since extinction coefficients are similar to those for benzophenone then no alteration of the sample size or solvent volume was necessary.

Solvent	Sample	λ_{max} / nm	ε / L mol^{-1} cm^{-1}
85% Ethanol	4-allyloxybenzophenone **(3)**	224, 292	9 840, 16 640
	4,4'-diallyloxybenzophenone **(8)**	225, 296	10 930, 18 320
	2,4-diallyloxybenzophenone **(9)**	246, 281	12720, 6 630
	4-acryloyloxybenzophenone **(5)**	258	18 510
	4,4'-diacryloyloxybenzophenone **(10)**	264	16 660
Glacial acetic acid	4-allyloxybenzophenone **(3)**	290	15 950
	4,4'-diallyloxybenzophenone **(8)**	295	19 680
	2,4-diallyloxybenzophenone **(9)**	281	6450
	4-acryloyloxybenzophenone **(5)**	257	17 300
	4,4'-diacryloyloxybenzophenone **(10)**	262	18 202
Diethyl ether	4-allyloxybenzophenone **(3)**	283	18 500
	4,4'-diallyloxybenzophenone **(8)**	284	23 940
	2,4-diallyloxybenzophenone **(9)**	241, 276	17 820, 7 880
	4-acryloyloxybenzophenone **(5)**	253	20 540
	4,4'-diacryloyloxybenzophenone **(10)**	260	16 630

Table 4.12: UV absorption data for allyloxy and acryloyloxy benzophenones

Since the allyloxy benzophenones were expected to migrate 4-allyloxybenzophenone was tested at initial concentrations of 2%, 2.5%, 3%, 3.5% and 4% so as to see if the method would show a similar response to that of the benzophenone and hence help to confirm the validity of the method. Testing was carried out as per the method on page 46 with of 4-allyloxybenzophenone in place of the benzophenone and the weight of photoinitiator adjusted accordingly.

The remaining samples were tested at only 2% and 4% initial concentration to use the method to show the tendency either to migrate or not depending on the sample. As mentioned in section 4.2.4 tendency to migrate can be calculated by looking at the difference in absorbance maximum when 2% and 4% initial photoinitiator concentrations

are used. For samples with more than 1 maximum absorbance the migration data was evaluated at each maximum.

Figures 4.10 to 4.12 show the migration data for the migration of 4-allyloxybenzphenone into 85% ethanol and diethyl ether. For the migration in 85% ethanol the results have been plotted for the absorbance at both maxima, 224 nm and 292 nm. The UV spectra for migration into acetic acid did not show any migration of the photoinitiator. In each case the pattern of migration seen is similar to that of the benzophenone in the previous validation work. Again a linear response is seen visually and correlation figures can be calculated to support the visual evidence.

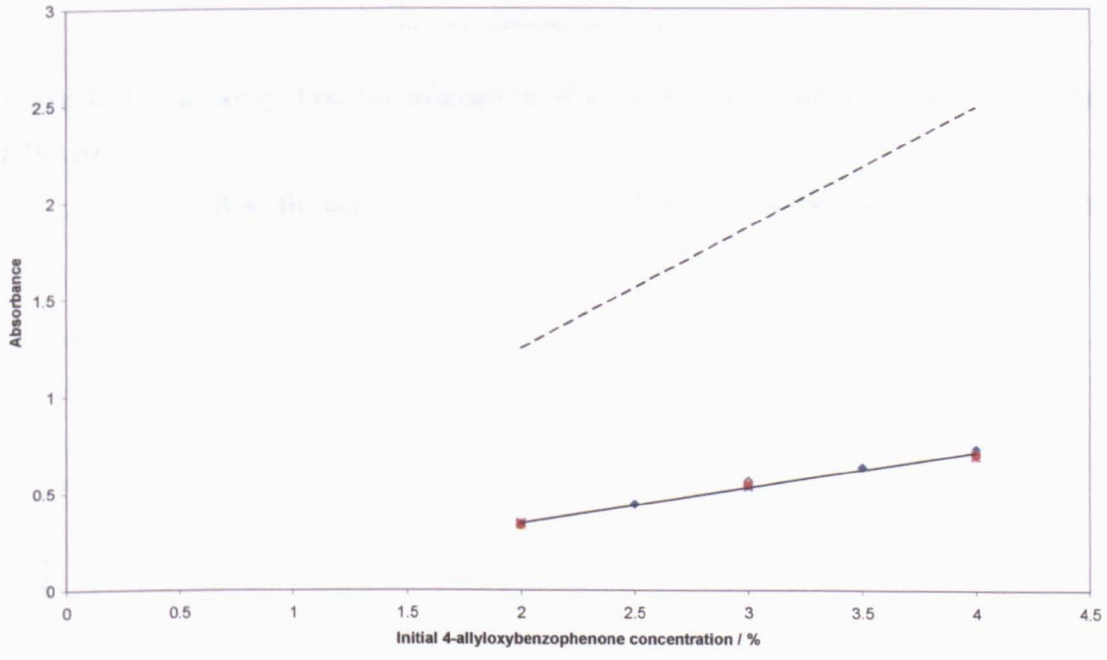


Figure 4.10: Linearity data for migration of 4-allyloxybenzophenone into 85% ethanol at 224 nm

(_____ Best fit line ---------- Theoretical line for 100% migration)

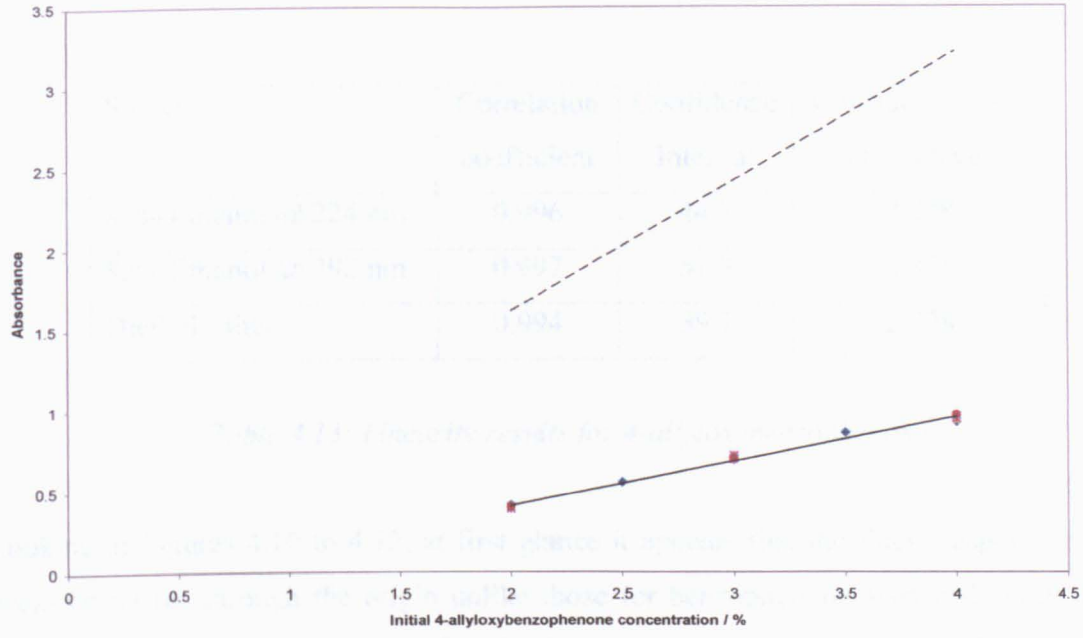


Figure 4.11: Linearity data for migration of 4-allyloxybenzophenone into 85% ethanol at 292 nm

(_____ Best fit line ---------- Theoretical line for 100% migration)

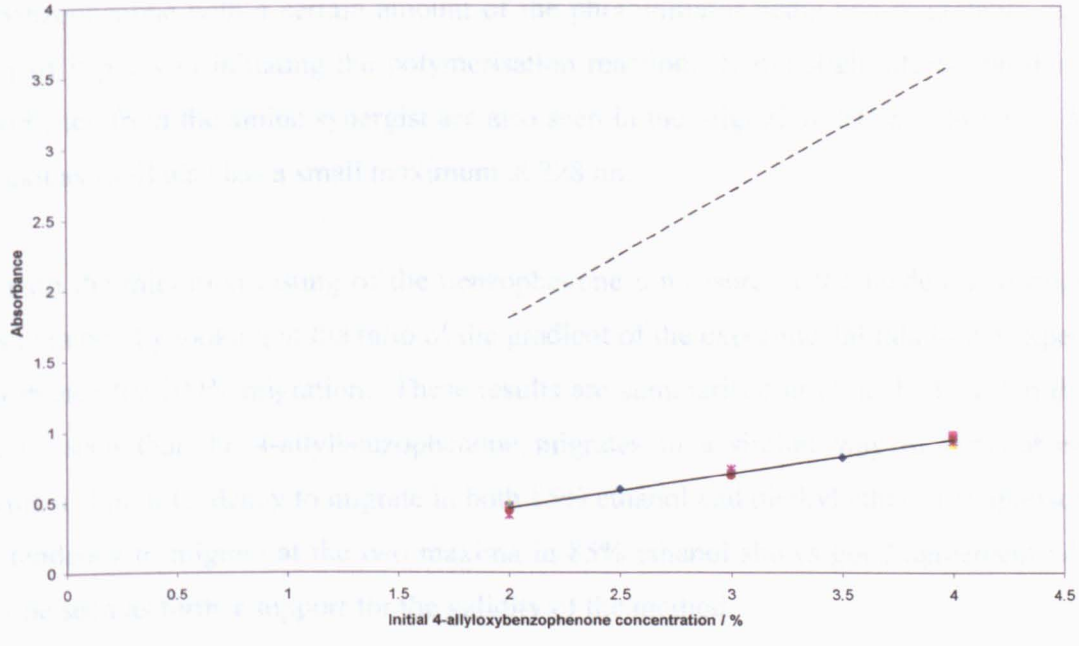


Figure 4.12: Linearity data for migration of 4-allyloxybenzophenone into diethyl ether at 283 nm

(_____ Best fit line ---------- Theoretical line for 100% migration)

Solvent	Correlation coefficient	Confidence Interval	Confidence limit at 1% level
85% Ethanol @ 224 nm	0.996	44.7	2.878
85% Ethanol @ 292 nm	0.997	51.2	2.878
Diethyl Ether	0.994	39.7	2.878

Table 4.13: Linearity results for 4-allyloxybenzophenone

Looking at Figures 4.10 to 4.12, at first glance it appears that the linear response on this occasion passes through the origin unlike those for benzophenone seen in Figures 4.6 to 4.8. This is the case for both maxima in the case of migration into 85% ethanol and the diethyl ether. However, it must be noted that since 4-allyloxybenzophenone has a UV maximum around 290 nm there is also a contributing factor from the migration of the amine synergist. Taking this into account would give a similar pattern of migration to that of benzophenone with a certain amount of the photoinitiator being non-migratable due to the part it plays in initiating the polymerisation reaction. Some slight effects on the UV absorbance from the amine synergist are also seen in the migration data at 224 nm in 85% ethanol as EDB also has a small maximum at 228 nm.

As with the migration testing of the benzophenone a measure of the tendency to migrate was obtained by looking at the ratio of the gradient of the experimental rata to the expected absorbance for 100% migration. These results are summarised in table 4.14. From this it can be seen that the 4-allylbenzophenone migrates in a similar way to benzophenone having a similar tendency to migrate in both 85% ethanol and diethyl ether. Comparison of the tendency to migrate at the two maxima in 85% ethanol shows good agreement which may be seen as further support for the validity of the method.

Solvent	Experimental Gradient	Theoretical Gradient	Tendency to migrate / %
85% Ethanol (224 nm)	0.183	0.623	29
85% Ethanol (292 nm)	0.275	0.806	34
Diethyl Ether	0.243	0.896	27

Table 4.14: Tendency to migrate for 4-allyloxybenzophenone

2,4-diallyloxybenzophenone and 4,4'-diallyloxybenzophenone also showed a tendency to migrate. Peaks were observed at the UV maximum in the migration spectra which increased as the initial photoinitiator concentration was increased from 2% to 4% as shown in Table 4.15. Using these two results an approximation of the tendency to migrate can be determined and this is also shown in Table 4.15.

Sample	Solvent	Absorbance		Tendency to migrate / %
		2%	4%	
2,4-diallyloxybenzophenone	85% Ethanol	0.135	0.366	23
	Acetic acid	-	-	-
	Diethyl ether	0.222	0.535	22
4,4'-diallyloxybenzophenone	85% Ethanol	0.290	0.619	22
	Acetic acid	-	-	-
	Diethyl ether	0.345	0.760	21

Table 4.15: Migration data for diallyloxybenzophenones

Again no migration was seen with acetic acid as the solvent suggesting that allyloxybenzopheones may have a much higher affinity for the resin than the solvent. Migration into 85% ethanol or diethyl ether is similar, as was seen with the 4-allyloxybenzophenone, although the tendency to migrate is lower for the diallyl species

than the monoallyl. This is likely to be due to the bulkier molecule showing greater affinity for the resin over the solvent so its migration is restricted.

UV spectra for the migration of 4-acryloyloxybenzophenone and 4,4'-diacryloyloxybenzophenone showed only small peaks corresponding to the migration of the amine synergist. These peaks were the same at both initial concentrations of photoinitiator in the resin suggesting that there was no migration of the photoinitiator. This was true for all solvents supporting the theory that the acryloyloxybenzophenones are either self-polymerised or incorporated into the resin on curing and hence are unable to migrate. The results of the testing of the polymerisable photoinitiators are summarised in Table 4.16.

Sample		**4-allyloxy-**	**4,4'-diallyloxy-**	**2,4-diallyloxy**	**4-acyloyloxy-**	**4,4'-diacryloyloxy-**
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	9 080	2 160	11 100	17 860	7 220
	λ_{max}	16 640	18 320	12 720	18 510	16 660
	395 nm	0	0	0	0	0
Rate of Cure @ 2% Concentration	Tack Free	8	10	6	16	19
	Thumb Twist	14	16	12	29	33
Solubility in Resin		>4%	>4%	>4%	>4%	>4%
Odour and Yellowing		Slight Yellowing	Slight Yellowing	Slight Yellowing	Slight Yellowing	Slight Yellowing
Stability/Months		>6	>6	>6	>6	>6
Toxicity		To be determined	To be determined	To be determined	To be determined	To be determined
Migration (Tendency to Migrate)		30%	22%	23%	<4%	<4%

Table 4.16: Summary of results for polymerisable photoinitiators

In conclusion it has been seen that allyloxybenzophenones are able to initiate UV curing with similar rates to those observed with benzophenone. This suggests that they are not able either to be self-polymerised or incorporate with the resin but initiate as a single small molecule. As such they are still able to migrate. This migration was observed following a similar pattern to that seen with benzophenone supporting the validity of the UV migration testing method in being able to evaluate migrating photoinitiators.

Conversely, acryloyloxybenzophenones while also initiating UV curing work at a much slower rate than benzophenone as they are either self-polymerised or incorporated into the resin, thus limiting their ability to move freely in the curing resin and further initiate polymerisation. This also does not leave them free to migrate and hence they show no UV absorbance in migration solvents further supporting the validity of the UV migration testing method to highlight potential low migrating or non-migrating photoinitiators.

4.4 Conclusion

The method has proved successful in observing the migration of a known migrating photoinitiator. The results were able to be repeated accurately at different initial photoinitiator concentrations typical of those used in industry. The method was further able to show this reproducibility of results in three different solvents, 85% ethanol, glacial acetic acid and diethyl ether. The precision of these results has been assumed to be of an acceptable level from the known precision of UV spectroscopy in determining the concentration of a UV active substance in a solution.

It has also been shown that a linear response is observed in the migration of the photoinitiator with respect to varying initial concentrations of that photoinitiator in the resin system. This has been seen both for the photoinitiator chosen for the validation and also a photoinitiator, 4-allyloxybenzophenone, synthesised with the possibility of it being non-migrating, although on testing it was shown to migrate.

This further revealed that there appears to be two reasons why a photoinitiator may not totally migrate, (1) a set amount from a binding with the resin on cure and (2) a variable proportionate amount due to affinity with the resin over the migration solvent. Therefore, although a specific measure of photoinitiator migration may be determined for a particular initial concentration, it is also possible to calculate a general tendency to migrate by looking at the gradient of the linear response. This tendency to migrate provides a better measure for comparison between different photoinitiators.

In terms of limits of detection, to meet legislative requirements for migration a photoinitiator with an extinction coefficient similar to that of benzophenone would need to show a UV absorbance peak of less than 0.05. If looking at the gradient as an indication of tendency to migrate then the difference between the absorbance maxima at 2% and 4% initial photoinitiator concentration would need to be less than 0.05, representative of a tendency to migrate of less then 2%. This is bordering on the limits of detection for the method but, since this method is to determine a general tendency not to migrate, a photoinitiator showing a tendency to migrate of less than 4% has been reported as low migrating and tendency to migrate has been reported as <4%.

The validation work also showed the degree of migration to be resin specific. This would mean some tailoring of a photoinitiator to a resin system as required for a particular application. However, for the purpose of this thesis, where a photoinitiator was shown to be low migrating in a certain resin system then it was assumed to be likely to show low migration in other resin systems and therefore was considered as suitable for further development as a low migrating photoinitiator.

Investigating the cure rates of some potentially polymerisable photoinitiators, allyloxybenzophenones and acryloyloxybenzophenones, showed differences between the two groups in that, while allyloxybenzophenones cured similarly to benzophenone, acryloyloxybenzophenones cure much slower suggestive of potential self-polymerisation or incorporation into the resin. This would suggest they may be low migrating and evaluation with the new migration testing method supported this theory with allyloxybenzophenones showing tendency to migrate similar to benzophenone at around 30% while acryloyloxybenzophenones showed tendency to migrate <4%. This also backs up the validity of the method to identify new photoinitiators as low migrating.

Overall the new UV migration testing method was considered suitable for obtaining an approximation of the tendency to migrate of a photoinitiator and hence the identification of low migrating photoinitiators which could then be suitable for further development for use in the photoinitiation industry.

5.0 Polymeric Photoinitiators

5.1 Introduction

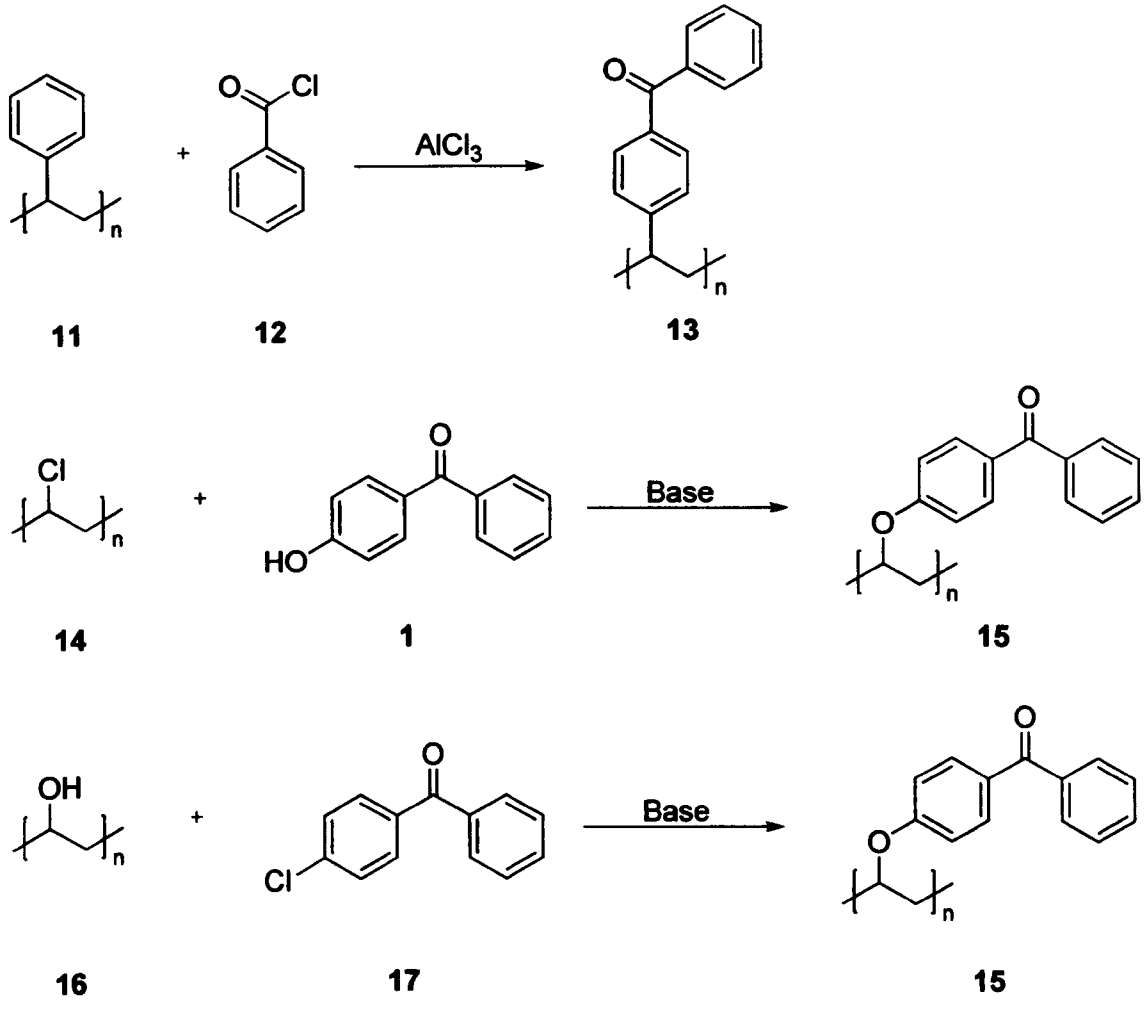
Development of polymeric photoinitiators, as with any photoinitiators, is done to meet with the criteria discussed earlier in Section 3.1. In particular, the purpose of creating the polymeric photoinitiator is to limit migration but, while doing so, the polymeric photoinitiator must maintain its functionality, i.e. it must be soluble in the resin and initiate curing on exposure to UV light.

Previous work on this discussed in Chapter 2.0 has been successful in creating polymers with a repeat photoinitiating unit but these have involved the addition of a significant amount of extra material in the form of linking chains and pendant groups. In the syntheses reviewed earlier the photoinitiating groups in the polymer account for less than 50% of the molecular weight of that polymer. The aim of this thesis was to look at limiting the amount of extra material hence creating a polymer where the bulk of the polymer is the photoinitiating group. In this way the amount of photoinitiator used in curing could be minimised with beneficial implications for the quality of the finish and the overall cost. To gain a comparison of this the molecular weight average of the polymer and the molecular weight of the photoinitiator on which it is based were used to estimate a percentage of photoinitiator in the polymer.

In order to synthesise these polymeric photoinitiators two routes were initially considered. One was to synthesise a new polymer which would contain the photoinitiating groups, the other was to attach photoinitiating groups to an existing polymer. It was also decided that in order to focus the research, the photoinitiating groups incorporated into the polymer would be based on benzophenone.

With regard to the latter route, options included a Friedel-Crafts type attachment of benzoyl chloride (**12**) to polystyrene (**11**), attaching hydroxybenzophenone (**1**) to poly(vinyl chloride) (**14**) or attaching a halobenzopheone (**17**) to poly(vinyl alcohol) (**16**). These all had the same issue, obtaining the base polymer as a suitable low molecular weight material at a reasonable cost. With the addition of the fact that the polystyrene synthesis was being

researched by other groups it was decided to concentrate on synthesising new polymers containing the repeat photoinitiating unit.



Scheme 5.1: Attachment of photoinitiating groups to existing polymers

When looking at the synthesis of a polymer containing a benzophenone repeat unit, there are two options for the orientation of the benzophenone group. One is that the group may lie entirely within the chain with both aromatic groups linked in to the polymer chain, the second is that the polymer may incorporate one ring with the other attached to the polymer backbone as a pendant group. The first obviously needs to involve some benzophenone type molecule in its synthesis while the second could involve the synthesis of an aromatic polymer and then undergo subsequent derivitisation to form the benzophenone group or involve direct synthesis from a benzophenone type molecule.

The advantage of direct synthesis is that the newly synthesised polymer is able to be used as a photoinitiator. This is useful because derivitisations of polymers can be difficult, particularly with regard to solubility of the polymer in the solvent required for the derivitisation process. Direct polymerisation makes the monomer to polymer reaction the final step in the synthesis avoiding the need for the awkward derivitisation reaction. Limitations are that the polymerisation involves a specific benzophenone type molecule. Subsequent variation of the structure for different applications would then involve a variety of different reactions on the polymer chain with the aforementioned difficulties about reactions of polymers.

Conversely, derivitising an aromatic polymer to form the photoinitiating group allows for easy variation of the photoinitiator structure. A wide variety of incoming groups could be used leading to a variety of substituted benzophenones or even other photoinitiator types which opens the window for the use of that synthetic route for a range of applications. Of course, this involves finding a successful route for the derivitisation step.

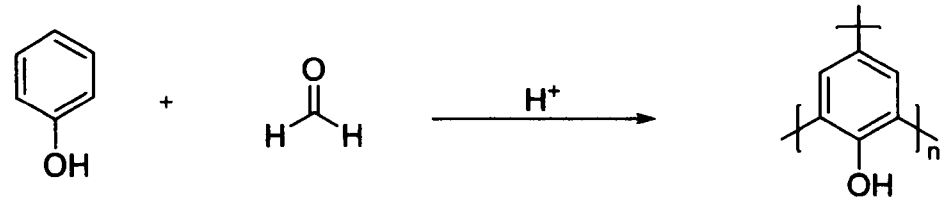
The syntheses looked at in this thesis included both options. Different synthetic routes were attempted and where there was successful synthesis of a polymer with any photoinitiating portion then these were taken on for further performance testing.

The polymers, once synthesised would need naming. These names were based on the IUPAC system last updated in 2002 for naming regular single strand polymers.[67] There is, however, no literature to cover when a substance should be considered an oligomer or a polymer. Since the molecules synthesised in this thesis were in general quite short chains it was thought more appropriate to use the term oligomer rather than polymer. Therefore, all synthesised polymeric material will be referred to as oligomers and the prefix oligo- will be used for naming purposes.

5.2 Formaldehyde polymers

5.2.1 Introduction

A known polymerisation reaction is that of phenol (**18**) and formaldehyde (**19**) to form a cross-linked resin (**20**). This is typical of the polymer structure found in Bakelite. As seen in Scheme 5.2 it involves linking of aromatic groups with methylene bridging groups. Due to the ortho/para directing effect of the phenolic hydroxyl group the links are formed at the 2, 4 and 6 positions forming the high-molecular weight three dimensional structure.



18 **19** **20**

Scheme 5.2: Phenol/formaldehyde polymerisation

It was thought that if the 4-position were to be in some way protected then a linear two dimensional polymer might be formed with aromatic rings linked by methylene groups. If these aromatic groups could be converted to benzophenone groups then a polymeric photoinitiator with the active sites separated only be methylene bridges would be produced.

This protection of the 4-position has been seen many times before and is quite a common strategy in phenol-formaldehyde chemistry. However, rather than producing linear oligomers, cyclic oligomers are formed known as calixarenes. These molecules have a basket-like structure with a narrow bottom rim consisting of the phenolic –OH groups and a wider upper rim consisting of the para-substituents.[68] Most commonly these cyclic products result as tetramers, or calix(4)arenas, although calixarenes may contain any number of repeat units. A typical example of a calixarene structure is shown in Figure 5.1.

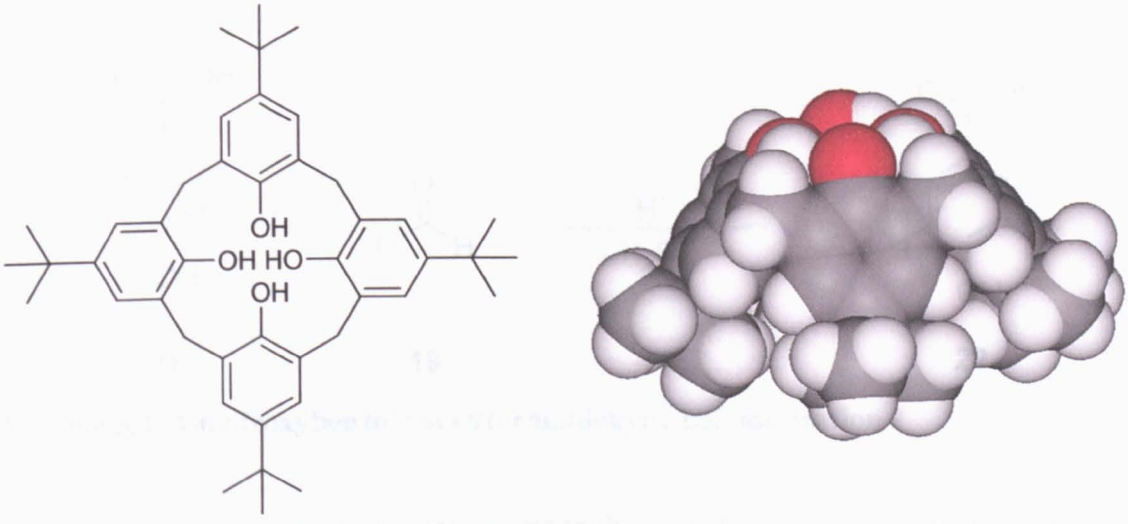
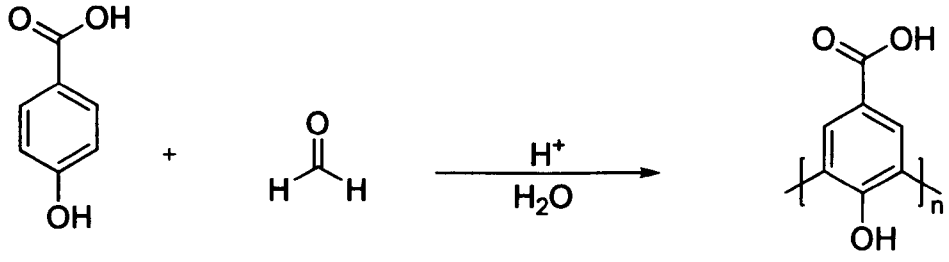


Figure 5.1: Calixarene based on 4-*tert*-butylphenol[68]

It was thought likely, therefore, that the syntheses in this thesis may show the production of cyclic oligomers. This was not a significant problem since the intention of this project was to create oligomeric photoinitiators which do not migrate. Therefore, it did not matter whether these were cyclic or linear oligomers. Indeed, as will be seen later, the production of cyclic oligomers was a key feature of this work.

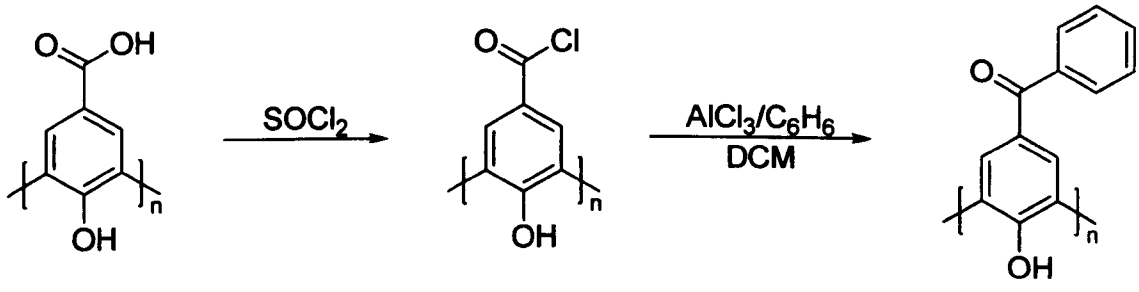
It was therefore necessary to choose a suitable para substituent as the basis for creating an oligomeric photoinitiator. Since it is desirable when synthesising a photoinitiator to include a carbonyl group adjacent to the aromatic group, in order to form the chromophore, it was thought to use a carbonyl group to obstruct the 4-position during the polymerisation. It was decided to attempt the polymerisation using 4-hydroxybenzoic acid (**21**) to obtain the polymer (**22**) shown in Scheme 5.3.



21 19 22

Scheme 5.3: 4-hydroxybenzoic acid/formaldehyde polymerisation

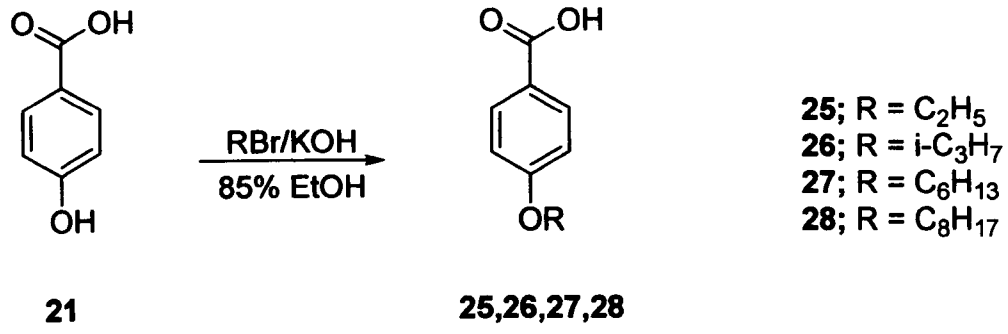
The intention was to convert the acid group to the acid chloride (**23**) and then use a Friedel-Crafts type reaction to attach an aromatic ring, e.g. benzene, forming a benzophenone polymer (**24**) as illustrated in scheme 5.4.



22 23 24

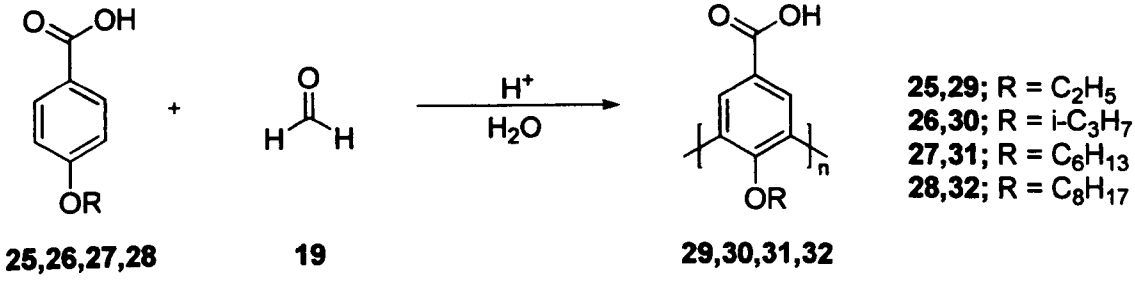
Scheme 5.4: Derivitisation of 4-hydroxybenzophenone polymer

The synthesis was also attempted by first forming the ether of the phenolic group and then polymerising. It was thought this would improve the solubility of the molecule both for the polymerisation and the subsequent derivitisation step. It would also prevent competing reactions of the phenolic group during the Friedel-Crafts reaction step. This ether synthesis was carried out using bromoalkanes and a one-pot Williamson type synthesis.[66] Chain lengths used were C_2H_5, i-C_3H_7, n-C_6H_{13} and n-C_8H_{17} to form 4-ethoxybenzoic acid (**25**), 4-isopropoxybenzoicacid (**26**), 4-hexyloxybenzoic acid (**27**) and 4-octyloxybenzoic acid (**28**) as shown in Scheme 5.5.



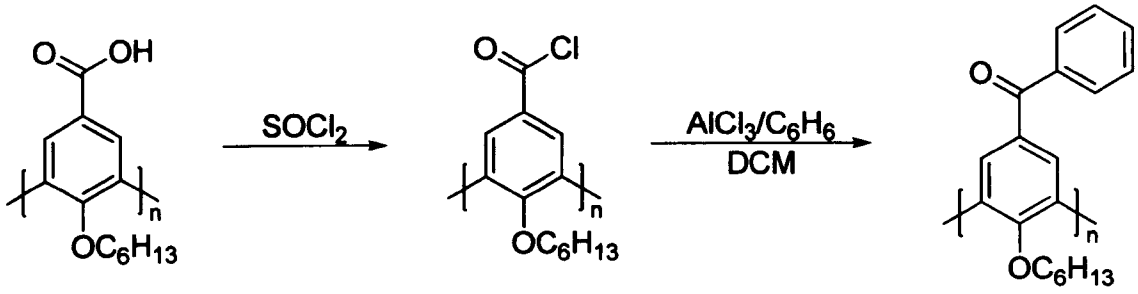
Scheme 5.5: Etherification of 4-hydroxybenzoic acid

The 4-alkoxybenzoic acids (**25,26,27,28**) then underwent the same polymerisation with formaldehyde (**19**) as the 4-hydroxybenzoic acid (**21**) as shown in Scheme 5.6. It was then intended to carry out the same derivitisation step as with the 4-hydroxybenzoic acid polymer (**22**).



Scheme 5.6: Polymerisation of 4-alkoxybenzoic acids

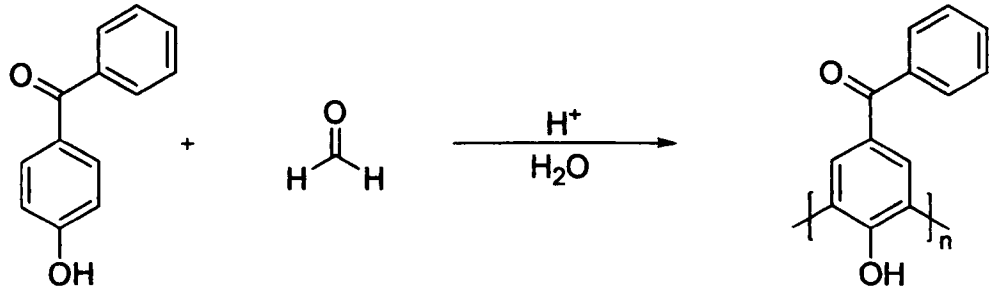
An alternative to this synthesis was to first form the 4-hydroxybenzoic acid polymer (**23**) then form the ether (**29,30,31,32**) before undergoing the derivitisation step. This route was carried out by forming the hexyl ether of the polymer (**31**) and then attempting to convert to the acid chloride (**33**) and subsequently the polymeric photoinitiator (**34**) as described in Scheme 5.7.



32 **33** **34**

Scheme 5.7: Derivitisation of 4-hexyloxybenzoic acid

Another possibility was to avoid the derivitisation step by directly synthesising a polymer containing the photoinitiating unit. As described earlier the formation of the linear polymer involves obstruction of the 4-position form the phenol polymerisation. Since this position remains blocked throughout the derivitisation to the photoinitiator it was also thought possible to use a photoinitiator molecule with a para-substituted phenolic group such as 4-hydroxybenzophenone (**1**). This underwent the same polymerisation reaction as before to form the polymeric photoinitiator (**24**) directly as shown in scheme 5.8.



1 **19** **24**

Scheme 5.8: Polymerisation of 4-hydroxybenzophenone

5.2.2 Results and Discussion

Polymerisation of 4-hydroxybenzoic acid **(21)** was successfully carried out with the polymer **22** precipitating from the reaction mixture as the reaction progressed. This suggested limited solubility of the growing polymer chain in the reaction solution. Typically most of the material observed in the precipitated polymer was between trimer to pentamer length although there was some higher molecular weight material up to octamer length with an overall molecular weight range of 500-1300. NMR spectroscopy confirmed the presence of the bridging methylene groups as well as indicating an aromatic structure similar to 4-hydroxybenzoic acid.

Further investigation of this reaction revealed that indeed the polymer seemed able to grow to a certain length at which point it would precipitate from the solvent and polymer growth would stop. Analysis of the reaction solvent post reaction showed no polymeric material and TLC analysis showed an absence of the 4-hydroxybenzoic acid starting material indicating that the reaction was complete. Alternatives such as adding excess formaldehyde or using more solvent gave polymers with similar molecular weight distribution.

The synthesis was also attempted in a variety of different solvents including ethanol, various concentrations of glacial acetic acid and dimethyl sulphoxide. Of these the most successful was the acetic acid. Low concentrations of acetic acid up to 40% produce similar looking polymers to those with water. These also showed a similar molecular weight distribution to those synthesised using water as the solvent. Higher concentrations of acetic acid, 60-80% also produced successful polymers although they had a green colour which could not readily be explained. Since they also showed a molecular weight distribution similar to that of the products from the polymerisation in water it was decided not to pursue the reasons for this colour but to bear this solvent in mind for later synthesis.

The problem with all these polymers was an issue of solubility. The polymers showed very limited solubility in acetone and some degree of solubility in tetrahydrofuran, which was useful for analysis purposes but neither solvent would be an option for the subsequent

derivitisation steps to form the photoinitiator. Various attempts were made to produce the acid chloride **24** including the use of pure thionyl chloride or thionyl chloride in xylene, diethyl ether, dicholormethane and dimethylformamdide. However, although the polymer was soluble in the hot solvents, conversion of the acid to the acid chloride could not be achieved. This was taken to be down to the solubility of the polymeric material so it was decided to attempt alternative synthesis looking at the possibility of polymerising alkoxybenzoic acids.

As mentioned in the introduction to this chapter, and shown in schemes 5.5 and 5.6, polymerisation using 4-alkoxybenzoic acids **(25-28)** was hoped not only to improve solubility by addition of a flexible "tail" to the molecule but also the protection of the phenolic group could be useful during the derivitisation procedure. 4-ethoxybenzoic acid **(25)**, 4-isopropoxybenzoic acid **(26)**, 4-hexyloxybenzoic acid **(27)** and 4-octyloxybenzoic acid **(28)** were all synthesised and then the polymerisation step was attempted as before.

Unfortunately the alkoxybenzoic acids did not polymerise. In each case the alkoxybenzoic acid dissolved into the reaction mixture on heating but no precipitated polymer was formed. On cooling solid material precipitated which analysis showed to be the unreacted 4-alkoxybenzoic acid. This was tried in all the solvents used for the 4-hydroxybenzoic acid polymerisation but none proved successful.

Although both the hydroxyl group in 4-hydroxybenzoic acid and the alkoxy group in 4-alkoxybenzoic acid are activating towards the ortho position on the ring, the hydroxyl group has a greater activating effect. Since the carboxylic acid deactivates the ring it seems that the effect of the hydroxyl group is powerful enough to facilitate polymerisation whereas the alkoxy group is not.

The alternative to this synthetic route was to form the ether of the hydroxybenzoic acid polymer. The synthesis was attempted to form the hexyl ether and proved successful with analysis showing trimer to pentamer length of the 4-hexyloxybenzoic acid polymer **(32)**. However, solubility had not been greatly improved and conversion to the acid chloride **(33)**

again proved impossible. Since the polymerisation step had been successful, while the derivitisation had not, it was decided move on to attempting the synthetic route involving direct polymerisation of the photoinitiator based on 4-hydroxybenzophenone.

Polymerisation of 4-hydroxybenzophenone was successful. The benzoyl group is less deactivating than the carboxyl group and the activating effect of the hydroxyl group allowed for ready formation of the precipitated oligomer **(24)**. As with the 4-hydroxybenzoic acids polymers the chains were relatively short, typically dimer to tetramer length although chains of up to octomer length were also observed. Overall the molecular weight range was 400-1800 of which 87% was due to the photoinitiator group. Again NMR spectroscopy was used to confirm the presence of the methylene bridges and to show the structural integrity of the hydroxybenzophenone group.

Again, as with the 4-hydroxybenzoic acid, the polymerisation was investigated in different solvents and using excess formaldehyde and extra solvent. As with the 4-hydroxybenzoic acid this did not have a significant effect on the molecular weight distribution of the oligomer.

This successfully synthesised oligomeric photoinitiator, oligo[(5-benzoyl-2-hydroxy-1,3-phenylene)methylene] **(24)** could now be assessed against the eight performance criteria the results of which are shown in Table 5.1.

Sample		Oligomer 24
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	4 860
	λ_{max} = 298 nm	14 520
	395 nm	0
Rate of Cure		N/A
Solubility in Resin		Insoluble
Odour and Yellowing		N/A
Stability		> 6 Months
Toxicity		To be determined
Migration		N/A
Cost		N/A

Table 5.1: Performance data for oligomer 24

Although oligomer **24** had good UV absorptivity it unfortunately proved insoluble in the resin system. As such it could not initiate cure in the resin and no further testing could be carried out. Therefore, while it may be an oligomer containing repeat photoinitiator units it is not suitable for use as a photoinitiator. The relative proportion of photoinitiator material to non-photoinitiator in the oligomer has been reduced but this has come at a compromise of solubility. If it is not possible to dissolve the photoinitiator in the resin then it is not suitable for industrial use.

One possible forward step for this synthetic route would be to react the hydroxyl group with a suitable molecule which may aid solubility. This has been briefly investigated by trying the hexyl etherification reaction but due to the insolubility of the molecule, the reaction proved unsuccessful. Reacting the hydroxyl group prior to polymerisation would cause the same problems of deactivating the ring and restricting polymerisation so this was not considered a viable alternative.

With other alternative polymer syntheses showing greater promise as a viable polymeric photoinitiator, this synthetic route has been left at this point. The formaldehyde oligomer with a repeat benzophenone unit has been synthesised but not to the point at which it is suitable for use as a polymeric photoinitiator.

5.2.3 Conclusion

While it is possible to polymerise 4-hydroxybenzoic acid with formaldehyde, the polymer produced has poor solubility in a number of solvents such that it is not possible to further derivatise the polymer to form the necessary photoinitiating units. Some form of improvement in solubility is necessary to make this synthesis viable. Reacting the hydroxyl group prior to polymerisation prevents the polymerisation reaction occurring and while post-polymerisation reaction of the hydroxyl group is possible it has so far not caused an improvement in solubility.

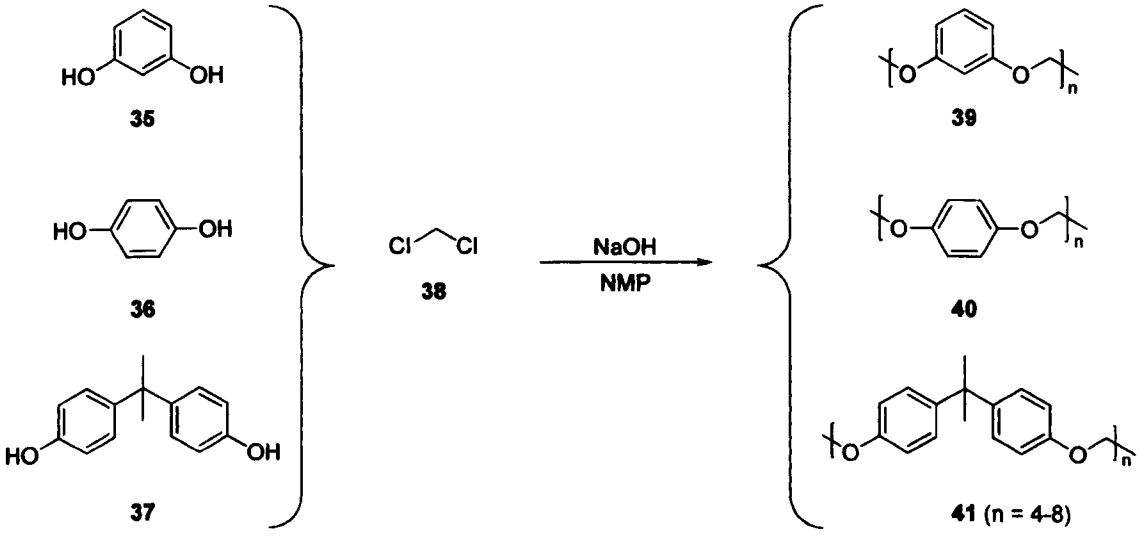
It is also possible to polymerise 4-hydroxybenzophenone to directly synthesise an oligomeric photoinitiator. The molecule produced has a molecular weight range of 400-1800 containing 2-8 repeat units with very little of the oligomer not being part of the photoinitiating unit. However, this oligomer also has poor solubility and therefore does not dissolve in the resin system. This means that it cannot initiate curing and so the oligomer is not suitable for use as a photoinitiator.

5.3 Aryl/alkyl polyethers

5.3.1 Introduction

Following on from the work on the formaldehyde polymers it was thought to use the success of the etherification reactions to create a polyether with linked aromatic groups and then convert these aromatic groups into benzophenone groups using a Friedel-Crafts reaction.

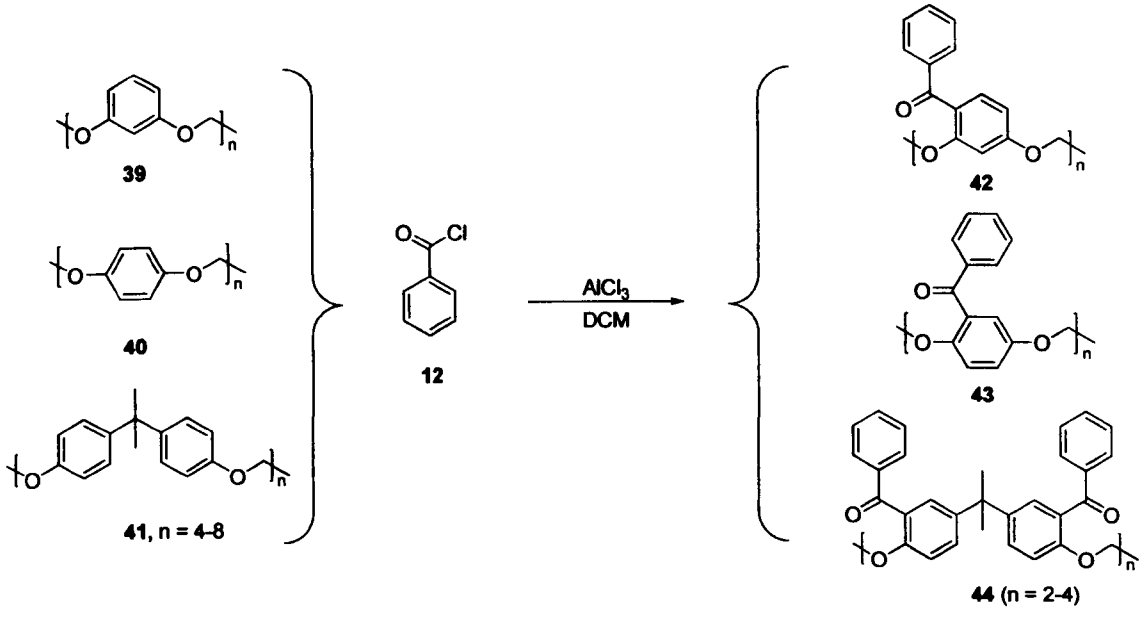
To create the polymer an aromatic diol was reacted with a dihaloalkane. The diols used for this were resorcinol (**35**), hydroquinone (**36**) and bisphenol A (**37**). Since the intention was to minimise the size of the non-photoinitiating part of the molecule, then dichloromethane (**38**) was used as the dihaloalkane which would give a dioxymethylene linking group as shown in Scheme 5.9.[70]



Scheme 5.9: Synthesis of aryl/alkyl polyethers[70]

Derivitisation to the photoinitiator was intended to be carried out by a Friedel-Crafts acylation using benzoyl chloride (**12**). It was suspected that this would be most easily achieved with the resorcinol polymer (**39**). The two alkoxy groups are both activating to the ring and both ortho/para directing. This should facilitate substitution at the 2,4 and 6 positions on the ring with the 4 and 6 positions being favoured due to steric effects. In the

hydroquinone polymer (**40**) there is competing reactions for substitution at the 2 and 3 positions so substitution was expected to be more difficult. The bisphenol A polymer (**41**) also has competing groups but the alkyl substituent is less activating than the alkoxy group so it was suspected any substitution would ortho to the alkoxy group. These reactions are summarised in Scheme 5.10.

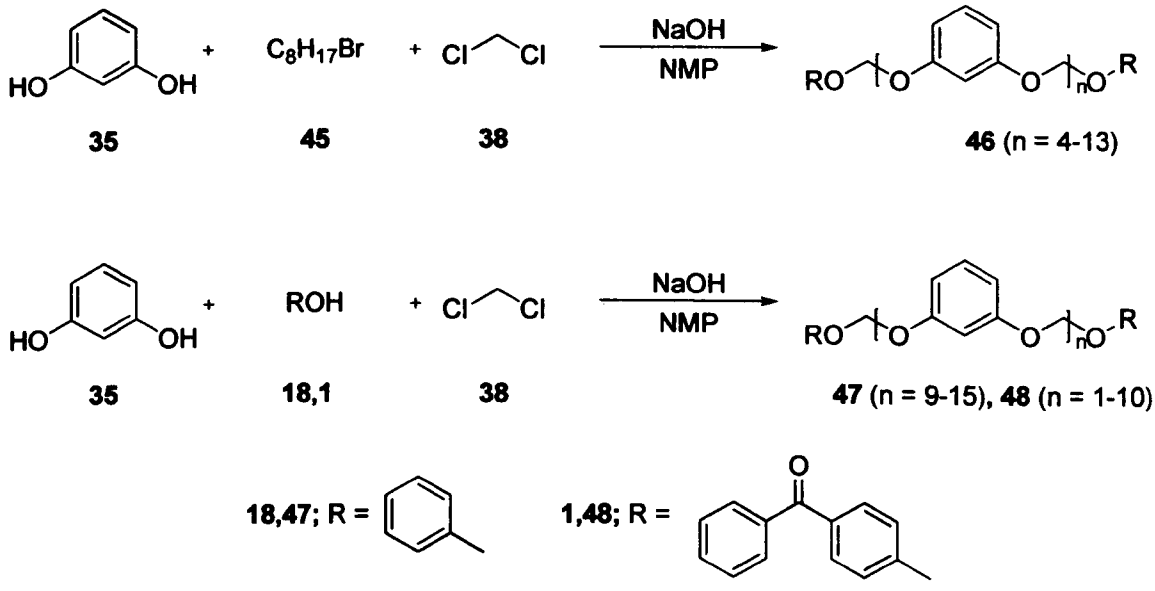


Scheme 5.10: Derivitisation of aryl/alkyl polyethers

These polymers would also have a good ratio of the photoinitiator part of the molecule to the non-photoinitiating part. Although there is the addition of two oxygen atoms into the bridging group, compared with the methylene bridge seen previously, this group is still relatively small when compared to the molecular weight of the photoinitiating group easily achieving the aim of the photoinitiating group representing over 50% of the molecule.

Firstly the resorcinol oligomers were investigated. Since the polymerisation reaction proceeded rapidly to form a high molecular weight insoluble oligomer it was decide to introduce a chain stopping molecule to limit the degree of polymerisation and make the product easier to work with for the subsequent derivitisation. This was done both by using alkyl chain stopper, octyl bromide (**45**) and an aromatic chain stopper, phenol (**18**). Also 4-hydroxybenzophenone (**1**) was used, since the aim is to create a polymeric photoinitiator it

made sense to use a photoinitiator as chain stopper such as to maximise the functionality of the polymer. For completeness, these 4-hydroxybenzophenone chain stoppered oligomers (**48**) were also tested for their performance as a photoinitiator. The chain stoppered polymer syntheses are shown in Scheme 5.11.

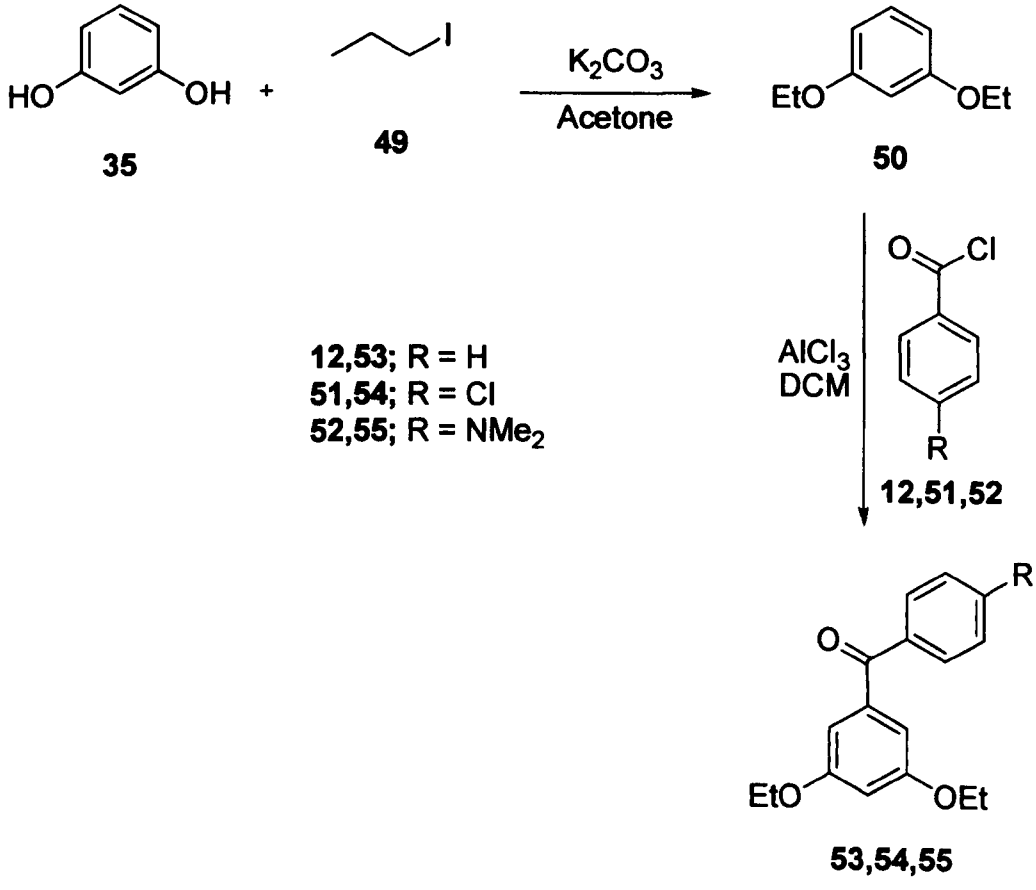


Scheme 5.11: Chain stoppered resorcinol polymers

One of the benefits of this synthesis is that during the derivitisation step the incoming benzoyl chloride may itself contain substituents. This can be used to affect the properties of the photoinitiating group such as the UV absorbance which can be useful when tailoring the polymer for different applications. With regard to this a short side study was carried to see how different substituents might affect the UV absorbance. To simulate the polymer, resorcinol (**35**) was reacted with ethyl iodide (**49**) to form 1,3-diethoxybenzene (**50**).[71] This would both represent a molecule with alkoxy substituents but would also protect the phenolic groups during the subsequent Friedel-Crafts reaction as would be seen with the polymer.

The diethoxybenzene (**50**) then underwent the acylation reaction with benzoyl chloride (**12**), 4-chlorobenzoyl chloride (**51**) and 4-dimethylaminobenzoyl chloride (**52**). This gave

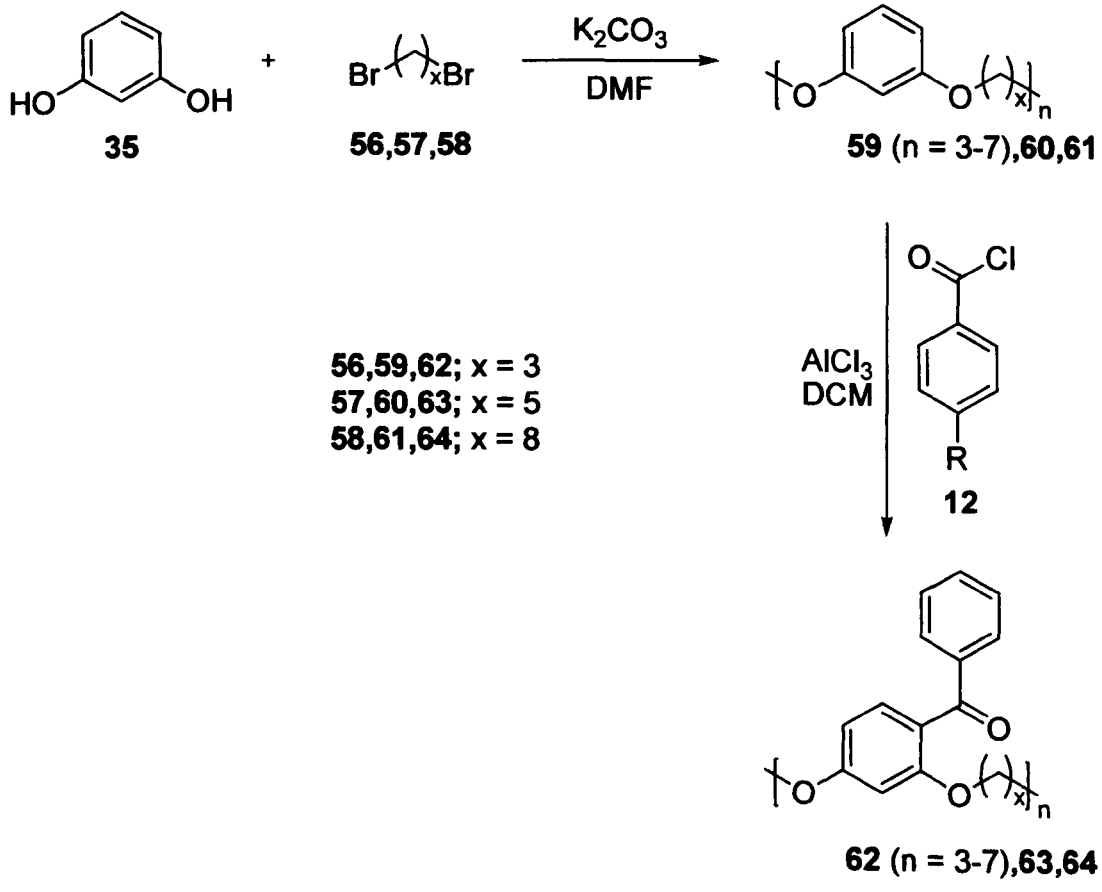
an unsubstituted diethoxybenzophenone (**53**) representative of the typical derivitisation step, a chloro-substituted diethoxybenzophenone (**54**), which would show the effect of a substituent as well as providing a potential site for conversion to other functional groups, and a dimethylamino-substituted diethoxybenzophenone (**55**) which could potentially incorporate a synergist group into the photoinitiator. This side study is illustrated in Scheme 5.12.



Scheme 5.12: Side study of substituted diethoxybenzophenones

When applying the derivitisation step to the oligomers solubility again was an issue. To attempt to overcome this it was thought to introduce more flexibility to the polymer by use of a longer linking group. Although this would be increasing the amount of no-photoinitiating material in the polymer, it would still give, on derivitisation, a polymer with

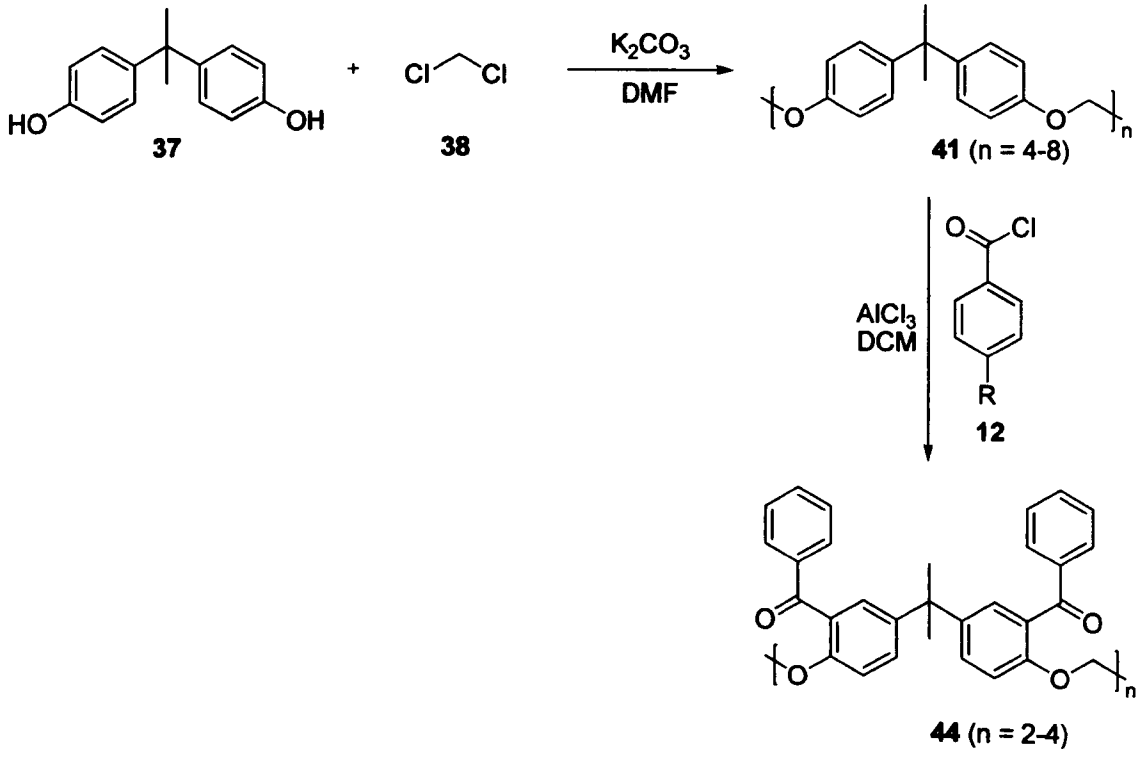
more than 50% of the molecular weight being the photoinitiating group. 1,3-dibromopropane (**56**), 1,5-dibromopentane (**57**) and 1,8-dibromooctane (**58**) were used as linking groups and no chain stopper was used.[72] The improved solubility allowed attempts at conversion to the photoinitiator with benzoyl chloride (**12**) to be carried out as shown in Scheme 5.13.



Scheme 5.13: Synthesis and derivitisation of resorcinol polymers with longer linking groups

The synthesis of these aryl/alkyl polyethers with hydroquinone was not so successful and, since it was also expected that the derivitisation step would be less successful, then it was decided not to investigate this polymer further.

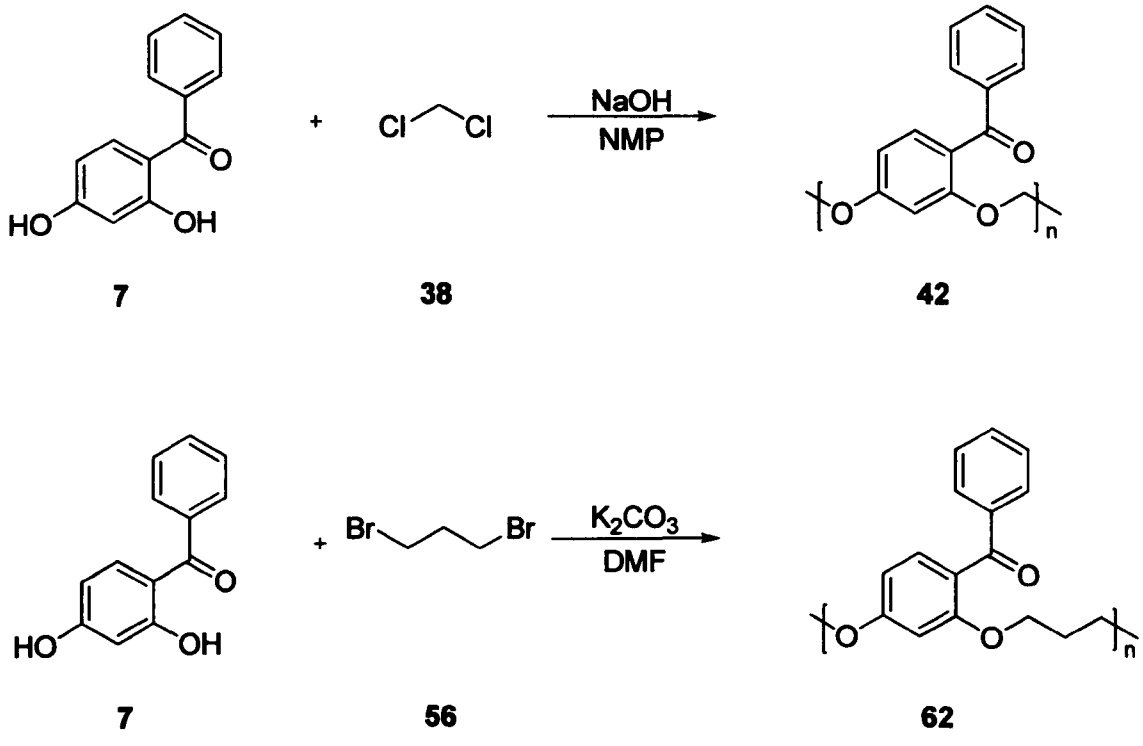
The synthetic route with bisphenol A (**37**) was pursued in a similar manner to the resorcinol polymers using dichloromethane (**38**). A non-chain stoppered oligomer **41** was synthesised and underwent the derivitisation reaction as shown in Scheme 5.14 to give the polymeric photoinitiator (**44**). A chain stoppered version (**65**) was also synthesised using 4-hydroxybenzophenone (**1**) as a chain stopper.



Scheme 5.14: Synthesis of polymeric photoinitiator from bisphenol A

Since the bisphenol A oligomers showed better solubility than the resorcinol oligomers it was not attempted to increase the size of the linking group. However, a note should be made that colleagues at Lambson Ltd have use this synthesis to develop oligomers based on bisphenol A with propylene linking groups. They have also succeeded in carrying out the Friedel-Crafts reaction with 2-chloroisopropanoyl chloride to synthesise a type 1 polymeric photoinitiator based on this synthetic route.

A final option that was considered was to use the commercially available 2,4-dihydroxybenzophenone (7) and form polyethers (42,62) using the same synthetic routes as those for the resorcinol. This would result in an oligomeric photoinitiator similar to that observed with the derivitisation of the resorcinol oligomer. This synthesis is illustrated in Scheme 5.15.



Scheme 5.15: Polymerisation of 2,4-dihydroxybenzophenone

5.3.2 Results and Discussion

Polymerisation using resorcinol and dichloromethane was carried out as shown in scheme 5.9 however, as mentioned in the introduction, the resultant polymer appeared to proceed rapidly to produce a high molecular weight material which proved insoluble and therefore difficult to analyse. Hence, it was necessary to introduce chain stoppers in order to give a degree of control over the reaction. The octyl bromide chain stopper gave an oligomer (46) with 4-13 repeat units and a molecular weight range of 700-1800, the phenol gave an oligomer (47) with 9-15 repeat units and molecular weight range of 1300-2000 and the 4-

hydroxybenzophenone gave an oligomer **(48)** with 1-10 repeat units and molecular weight range of 550-1650. Of course this last polymer already includes 2 photoinitiating groups as the end groups.

The substituted photoinitiators in the side study had also been successfully synthesised. 2,4-diethoxybenzophenone **(53)**, 4-chloro-2',4'-diethoxybenzophenone **(54)** and 4-dimethylamino-2',4'-diethoxybenzophenone **(55)** were all synthesised as shown in Scheme 5.12 and characterised in reasonable yields (40-50%). As expected acylation of the 1,3-diethoxybenzene occurred in the 4-position and it seemed likely that this would prove successful for derivitisation of the oligomers so long as solubility could be achieved.

The purpose of this side study was also to look at the effects of some substituents on the UV spectra of the photoinitiator. These are summarised in Table 5.2 with data for benzophenone included as a comparison.

Sample	λ_{max} / nm	ε / L mol^{-1} cm^{-1}
Benzophenone	254	17 800
2,4-diethoxybenzophenone **(53)**	244, 284	16 540, 9 250
4-chloro-2',4'-diethoxybenzophenone **(54)**	254	4 960
4-dimethylamino-2',4'-diethoxybenzophenone **(55)**	228, 345	26 490, 19 690

Table 5.2: UV data for substituted benzophenones

The table shows that there is a significant effect on the UV absorption maxima dependent on the nature of the substituent group. This would prove useful for further development work as the polymer chain is effectively a substituent group on the benzophenone and hence will cause a change in the UV spectra. If this was to be an unsatisfactory change due to the application the photoinitiator was being designed for then it could be countered by the introduction of a substituent group on the incoming acyl group. For example, as seen in the data above the ethoxy groups cause a shift in the main UV maximum to a lower wavelength. The addition of a chloride brings this maximum back to 254 nm, albeit with a

reduction in the extinction coefficient. On the other hand the introduction of the amine group causes a UV maximum at the longer wavelength of 345 nm. This is getting close to the emission wavelengths of LED sources as discussed earlier. It is interesting to note that a minor modification might make this photoinitiator suitable for use with both mercury lamps and LEDs.

With both steps of the synthesis complete the challenge now was to put them together. However, the problem now, as with the formaldehyde type oligomers, was solubility. The resorcinol oligomers also had poor solubility and it was not possible to find a suitable solvent in which to carry out the derivitisation step. To aid solubility it would be necessary to use a larger bridging group. This solubility issue also applied to solubility of the 4-hydroxybenzophenone chain stoppered oligomer in the resin mixture. It had been intended to performance test these oligomers as a comparison despite them not containing repeat photoinitiating units. However, the lack of solubility meant that this was not possible. Due to the fact that although they are oligomeric photoinitiators they do not meet the brief for this thesis their performance against the "good photoinitiator" criteria are not reported here.

It should be noted at this point that one of the major difficulties faced when working with these oligomers is solubility. This not only presented a problem with achieving the necessary solubility in the resin for curing, but also presented a problem with analysis. While the formaldehyde based oligomers in section 5.2 had been characterised by mass spectrometry and NMR to give structural information and end group analysis, the rest of the oligomers proved difficult to analyse.

Solubility issues meant that NMR data was very difficult to obtain and even when this was possible ^{1}H-NMR data was often confused and difficult to interpret. ^{13}C-NMR data was obtained for some oligomers and was supportive of the structure being suggested by MALDI-TOF mass spectrometry.

All this meant that, while it would have been preferable also to obtain mass spectrometry data by gel permeation chromatography (GPC), solubility issues meant that it was decided

to rely on the MALDI-TOF data and leave more detailed analysis to be carried out on any of the new photoinitiators which may be suitable for commercial use.

MALDI-TOF data was, however, good enough to suggest that the desired oligomer had been formed. The difference in mass between peaks corresponded exactly to the repeat unit of the oligomer and the overall mass values could be fitted to whether the oligomer was linear or cyclic.

The polymerisation reaction with the longer dihaloalkanes was successful but proceeded rather less readily than the reaction with dichloromethane. This gave more limited chain lengths and the polymerisation could be carried out without the need for a chain stopper. On analysis the reason for this was that the added flexibility in the chain resulted in the formation of cyclic oligomers which obviously prevented further polymerisation. This formation of cyclic oligomers was not unexpected. The possibility of forming a cyclic oligomer had already been considered in the discussion on calixarenes in Section 5.2.1.

Cyclic oligomers with a propylene bridge **(59)** showed 3-7 repeat units with a molecular weight range from 500-1100. These showed better solubility and were soluble enough in dichloromethane for the Friedel-Crafts acylation to be carried out. This reaction produced a cyclic oligomeric photoinitiator **(62)** which also had 3-7 repeat units and a molecular weight range of 800-1800 of which 71% were photoinitiator groups. This indicated that the resorcinol polymer was readily acylated as every aromatic group on the cyclic oligomer had been converted to the photoinitiating group forming the cyclic oligomer **(62)**, cyclo-oligo[oxy(1,3-{4-benzoyl}phenylene)oxypropylene]. Whether the exact structure of this oligomer is basket like, as with the calixarenes, or another conformation is yet to be determined.

The oligomeric photoinitiator showed UV absorption maxima at 243 nm and 282 nm with extinction coefficients of 13 820 L mol^{-1} cm^{-1} and 7 280 L mol^{-1} cm^{-1} respectively. This shows good agreement with the 2,4-diethoxybenzophenone **(53)** from the pilot study as illustrated in Table 5.3.

Sample	λ_{max} / nm	ε / L mol^{-1} cm^{-1}
2,4-diethoxybenzophenone **(53)**	244, 284	16 540, 9 250
Oligomer **62**	243, 282	13 820, 7 280

Table 5.3: Comparison of UV absorbance data for 2,4-diethoxybenzophenone and oligomer 62

It would appear likely that the oligomeric photoinitiators show similar UV spectra to their simulated single molecule equivalents. Hence if a desired UV absorbance maxima is required then it would be possible to tailor this using the appropriate substituent groups.

Oligomer **62** was now taken forward to the performance testing stage. It proved to have some solubility in the resin mixture up to about 3%. Therefore resins were prepared at 2% and 3% initial photoinitiator concentration rather than the usual 2% and 4% The results for the testing of the speed of cure are summarised and compared with benzophenone in Table 5.4.

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone @ 2%	7	10
Oligomer **62** @ 2%	20	29
Benzophenone @ 3%	6	9
Oligomer **62** @ 3%	11	14

Table 5.4: Testing of speed of cure for oligomer 62

This table shows that oligomer **62** shows much slower speeds of cure than benzophenone, particularly at the lower concentration. Again it seems that the oligomeric photoinitiator is much less mobile in the resin, hence the slower cure. However, as the initial concentration of photoinitiator increases the number of passes to cure quickly begins to fall. This is likely due to better distribution of the photoinitiator throughout the resin. Unfortunately, due to

solubility issues, it is not possible to increase the concentration further but the 3% cure speed is quite satisfactory particularly when compared with the cure speeds shown by the acryloyloxybenzophenones earlier. A summary comparing all the successful photoinitiators can be found in section 6.1.

The resins cured with oligomer **62** were also subjected to the migration test. Since it had not been possible to cure a resin with 4% initial photoinitiator concentration a comparison could only be made between the migration at 2% and 3% initial photoinitiator concentration. As it was there were no peaks seen in the UV spectra at either of the UV maxima shown by oligomer **62**. This was true for all three of the migration solvents. It appears that oligomer **62** is successful as a low-migrating oligomeric photoinitiator albeit with compromises on solubility and cure speeds. The full summary of oligomer **62** is shown in Table 5.5.

Sample		Oligomer **62**
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	12 230
	λ_{max}	13 820, 7 280
	395 nm	0
Rate of Cure @ 2% Concentration	Tack Free	20
	Thumb Twist	29
Solubility in Resin		<3%
Odour and Yellowing		Slight Yellowing
Stability		> 6 Months
Toxicity		To be determined
Migration		<4%

Table 5.5: Performance data for c-o-OBPhOP

With this success it is now possible to try to apply the same processes to the substituted benzoyl chlorides however these oligomers have yet to be successfully synthesised and characterised so will form a work beyond the work done for this thesis.

Oligomers were also successfully synthesised using bisphenol A in place of resorcinol with dichloromethane as the linking group. This polymerisation also occurred less readily then the resorcinol/dichloromethane polymerisation giving repeat units of 4-8 with a molecular weight range of 1000-2000 **(41)**. These were also cyclic oligomers, the formation of which was probably aided by the extra flexibility in the chain from the dimethylmethylene group in bisphenol A. The chain stoppered oligomer gave a linear oligomer with 2-10 repeat units and molecular weight range of 900-2800 **(65)**.

The bisphenol A oligomers showed better solubility than their resorcinol counterparts so it was possible to proceed straight to the derivitisation step. This did appear partly successful. The analysis of the product revealed a cyclic oligomer **(44)** with 2-4 repeat units and a molecular weight range of 900-1800. The yield was very low so it seemed that there were some low molecular weight cyclic oligomers in the starting material and that only these has been soluble enough to undergo the derivitisation reaction. However, this reaction had successfully synthesised some oligomeric photoinitiator product and from the analysis data it appeared that both rings of the bisphenol A group had been derivitised to a photoinitiator group. It was not however possible to tell at which point on the ring the substitution had occurred. Still, this did represent a successful synthesis of another oligomeric photoinitiator **(44)**, cyclo-oligo[oxy(1,4-benzoylphenylene)(dimethylmethylene) (1,4-benzoylphenylene)oxymethylene]. Testing against the criteria for a good photoinitiator is shown in Table 5.6.

Sample		Oligomer **44**
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	1 790
	λ_{max}	12 770, 4480
	395 nm	0
Rate of Cure		N/A
Solubility in Resin		Insoluble
Odour and Yellowing		N/A
Stability		> 6 Months
Toxicity		To be determined
Migration		N/A

Table 5.6: Performance data for oligomer 44

Unfortunately again despite the successful synthesis there was again the problem of solubility in the resin. Oligomer **44** was not soluble in the resin mixture and so further performance testing could not be carried out.

Derivitisation of the linear oligomer **(65)** was not possible despite it seeming to have good solubility in the dichloromethane required for the derivitisation step. Since this oligomer is chain stoppered with photoinitiator groups it is an oligomeric photoinitiator, however, as with its resorcinol equivalent, it did not have solubility in the resin so performance testing could not be carried out.

It would now be useful to move on to looking at longer bridging groups for the bisphenol oligomers as was done for those with resorcinol. As stated in the introduction, some work has begun on this by colleagues at Lambson but this has gone beyond the work covered by this thesis.

Only a small amount of work has been carried out with the polymerisation of 2,4-dihydroxybenzophenone shown in Scheme 5.15 and so far this has been unsuccessful. It may, however, provide a viable synthetic route for future development.

5.3.3 Conclusion

Oligomers based on resorcinol and bisphenol A have been successfully synthesised using dichloromethane to form the bridging group. Similar oligomers based on hydroquinone have been less successful.

The resorcinol oligomers are formed very readily so that a chain stopper is necessary to control the polymerisation. However, even with this chain stopper their solubility is poor and so derivitisation to a photoinitiator is not possible.

The introduction of a longer bridging group to the resorcinol polymers leads to the formation of cyclic oligomers which have better solubility. These have been reacted with benzoyl chloride to form a cyclic oligomeric photoinitiator, oligomer **62**, which has some degree of solubility in the resin system and is capable of initiating cure. Cure speeds for oligomer **62** are not so good as those for benzophenone but it does show low migration characteristics and is therefore suitable for use as a low-migrating oligomeric photoinitiator.

Bisphenol A/dichloromethane oligomers are also cyclic and show better solubility that their resorcinol equivalents. The lower molecular weight oligomers have been derivitised to a cyclic oligomeric photoinitiator, oligomer **44**. This oligomer, however, is not soluble in the resin system and so is not capable of initiating cure.

The use of 4-hydroxybenzophenone as a chain stopper with both resorcinol and bisphenol A has resulted in oligomers with a terminal photoinitiating group. However, these are also insoluble in the resin system and therefore unsuitable for use as a photoinitiator.

It has also been seen that there is considerable scope for using this synthetic route to produce a variety of oligomeric photoinitiators with different characteristics, suitable for a variety of applications.

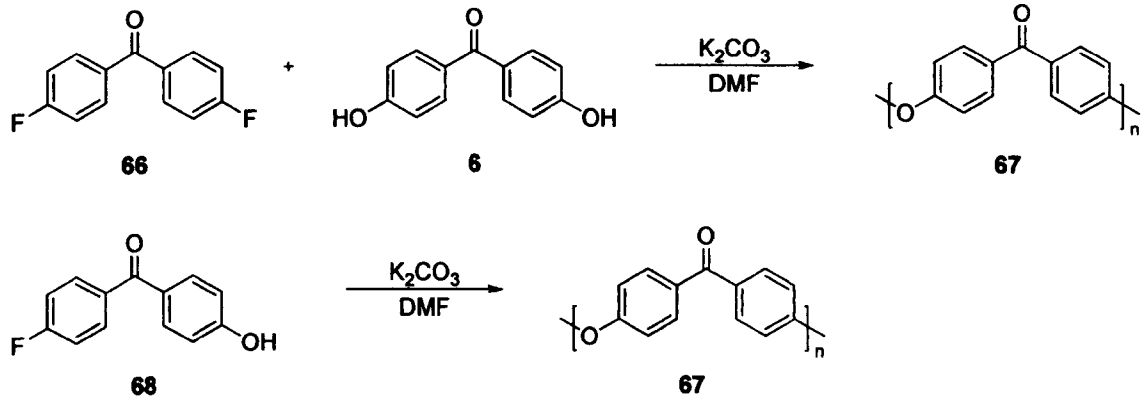
Overall this work has seen some success in the development of low-migrating oligomeric photoinitiators and has provided a useful basis for further development work. Further work has already begun in developing this work for use in an industrial setting.

5.4 Poly-ether-ketones (PEKs) and Poly-ether-ether-ketones (PEEKs)

5.4.1 Introduction

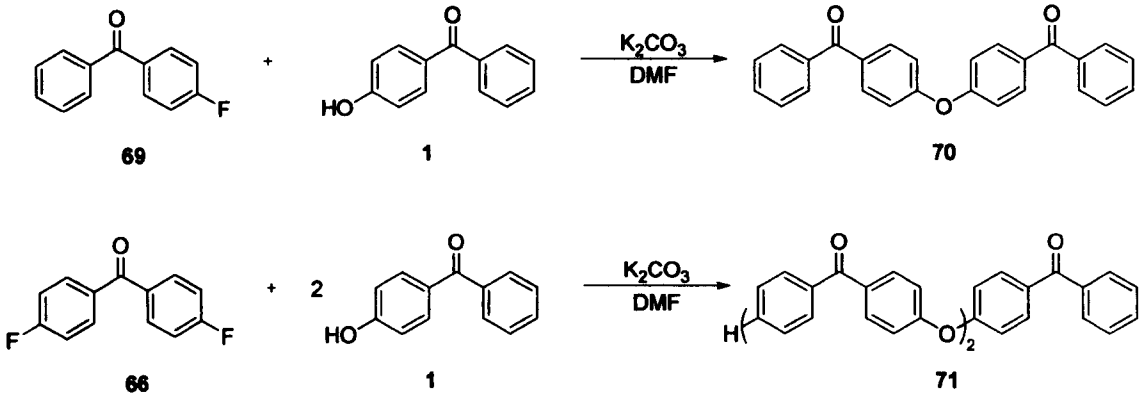
The work on the resorcinol and bisphenol A oligomers looked at the type of synthesis where an oligomer is produced and then converted to the photoinitiator. An alternative idea would be to use the same type of synthesis to produce oligomers which already contained the repeat photoinitiating unit.

As with the other oligomers the aim was to synthesise an oligomeric photoinitiator with repeat photoinitiating units and with the greatest possible percentage of the oligomer to be the photoinitiator group. With regard to this it was thought to react halobenzophenones and hydroxybenzophenones to directly link the photoinitiating groups with only an oxygen atom. This could be achieved either by reacting 4,4'-difluorobenzophenone (**66**) with 4,4'-dihydroxybenzophenone (**6**) or by simply polymerising 4-fluoro-4'-hydroxybenzophenone (**68**) to form a poly-ether-ketone (PEK) (**67**) as shown in Scheme 5.16.



Scheme 5.16: Synthesis of polyetherketones (PEK)

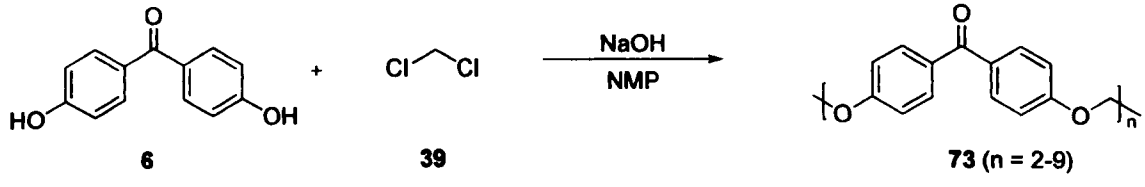
A preliminary to this work was carried out by reacting 4-fluorobenzophenone (**69**) and 4-hydroxybenzophenone (**1**) to form the dimer (**70**) of this type of oligomer and reacting 4,4'-difluorobenzophenone (**66**) with 4-dihydroxybenzophenone (**1**) to form the trimer (**71**) as shown in Scheme 5.17.



Scheme 5.17: Synthesis of ether linked benzophenone dimer and trimer

The dimer **70** and trimer **71** were also tested as photoinitiators to see whether short oligomers would have an effect of reducing migration.

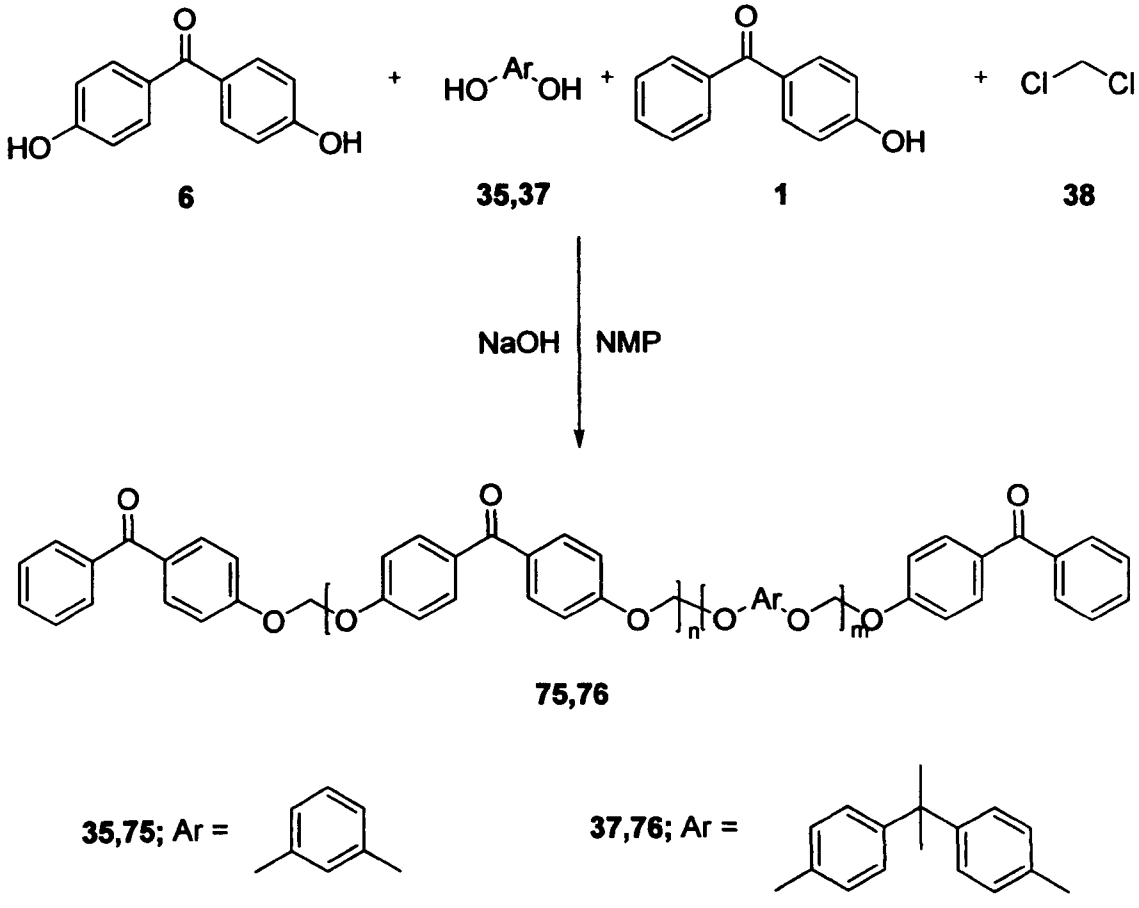
Rather than the direct ether linkages it was also attempted to synthesise oligomers using the resorcinol/bisphenol A route using 4,4'-dihydroxybenzophenone (**6**) as the aromatic diol to synthesise a poly-ether-ether-ketone (PEEK) is shown in Scheme 5.18. This reaction was carried out to synthesise both a non chain stoppered oligomer (**72**) and using octyl bromide (**45**) or 4-dihdroxybenzophenone (**1**) to synthesise chain stoppered oligomers (**73,74**).



Scheme 5.18: Synthesis of poly-ether-ether-ketone (PEEK)

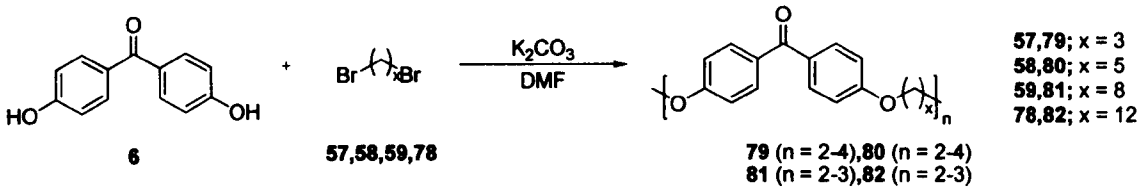
Also explored was the possibility of carrying out this synthesis as a copolymerisation. The idea was to copolymerise 4,4'-dihydroxybenzophenone (**6**) with either resorcinol (**35**) or Bisphenol A (**37**). Although this would increase the amount of non-photoinitiator in the polymer, it would also add further aromatic groups which could potentially be derivitised to form photoinitiators with different properties. It could even be possible to convert them

into a synergist such that photoinitiator and synergist were incorporated onto the same oligomer. The copolymerisation was carried out in a 1:1 monomer ratio with 4-hydroxybenzophenone (**1**) as a chain stopper, shown in Scheme 5.19.



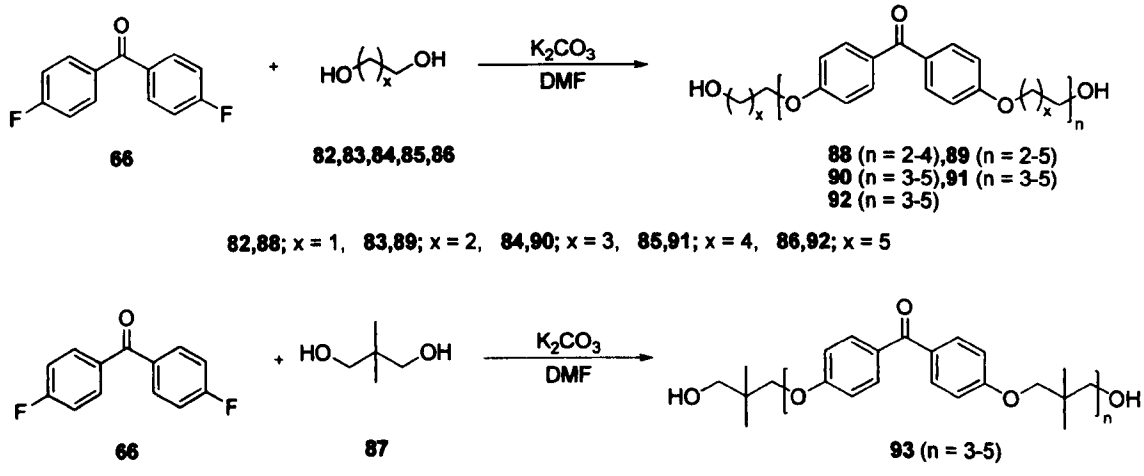
Scheme 5.19: Copolymerisation of 4-hydroxybenzophenone with resorcinol or bisphenol A

As with previous syntheses it was also thought beneficial to increase the length of the bridging group in the PEEK oligomers in order to increase flexibility and hopefully increase solubility. Oligomers were synthesised by the same method as the resorcinol oligomers using 1,3-dibromopropane (**56**), 1,5-dibromopentane (**57**), 1,8-dibromooctane (**58**) and 1,12-dibromododecane (**77**) to synthesise the PEEKs (**78-81**) as shown in Scheme 5.20.



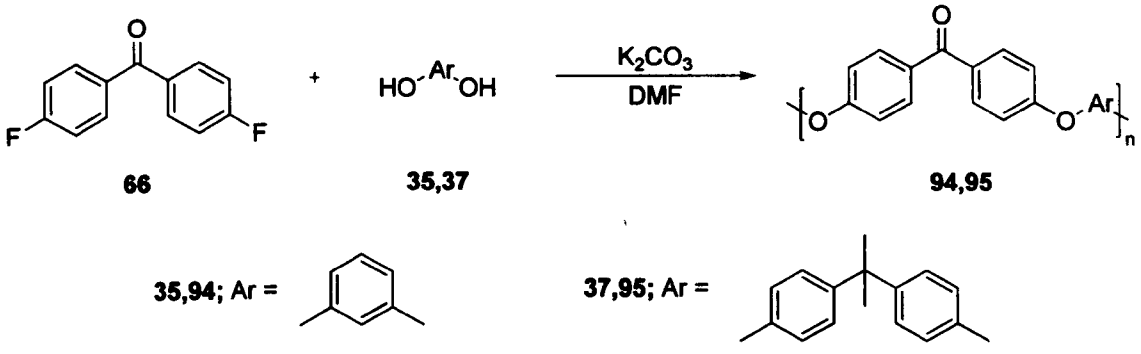
Scheme 5.20: Synthesis of PEEKs with longer bridging groups

An alternative synthetic route to the same type of oligomer was to use 4,4'-difluorobenzophenone (**66**) and an alkyl diol. This was carried out with 1,2-ethanediol (**82**), 1,3-propanediol (**83**), 1,4-butanediol (**84**), 1,5-pentanediol (**85**), 1,6-hexanediol (**86**) and 2,2-dimethyl-1,3-propanediol (**87**) to give the PEEKs (**88-93**) shown in Scheme 5.21.



Scheme 5.21: Alternative synthesis of PEEKs with longer bridging groups

Finally this synthesis was also carried out using the aromatic diols resorcinol (**35**) and bisphenol A (**37**) as shown in Scheme 5.22.



Scheme 5.22: Synthesis of PEEKs with aromatic diols

5.4.2 Results and Discussion

The directly ether linked dimer, 4-(4-benzoylphenoxy)benzophenone **(70)**, and trimer, 4,4'-bis(4-benzoylphenoxy)benzophenone **(71)**, were successfully synthesised and characterised. They were then tested for their performance as photoinitiators. The trimer showed the recurring problem of being insoluble in the resin. The dimer however was soluble and was able to initiate photoinitiation. The speed of cure for the dimer is shown in Table 5.7. Again benzophenone is included as a comparison.

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone @ 2%	7	10
4-(4-benzoylphenoxy)benzophenone **(70)** @ 2%	6	10
Benzophenone @ 4%	4	8
4-(4-benzoylphenoxy)benzophenone **(70)** @ 4%	4	6

Table 5.7: Testing of speed of cure for 4-(4-benzoylphenoxy)benzophenone

As can be seen, the dimer showed cure rates comparable with benzophenone. This is perhaps not surprising since it is still a relatively small molecule and therefore will have a similar distribution in the resin to benzophenone. Its UV extinction coefficient in ethanol of 15 340 L mol^{-1} cm^{-1} was also comparable with benzophenone, at a slightly longer wavelength of 259 nm. The migration test was carried out on the resins for the dimer and the results of this are shown in Table 5.8:

Sample	Solvent	Absorbance		Tendency to migrate / %
		2%	4%	
4-(4-benzoylphenoxy) benzophenone (70)	85% Ethanol	0.188	0.504	33
	Acetic acid	0.190	0.474	35
	Diethyl ether	0.177	0.508	34

Table 5.8: Migration data for 4-(4-benzoylphenoxy)benzophenone

The benzophenone dimer does migrate although there is a reduction in the tendency to migrate compared with the results seen for benzophenone in the validation work. This supports the theory that larger molecules are less likely to migrate but bulkier molecules than a simple dimer are necessary to result in low migration. The dimer is a new photoinitiator so its performance against the "good photoinitiator" criteria are summarised in Table 5.9. However it is not a low-migrating photoinitiator.

Sample		4-(4-benzoylphenoxy)benzophenone (70)
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	14 650
	λ_{max}	15 340
	395 nm	0
Rate of Cure @ 2% Concentration	Tack Free	7
	Thumb Twist	10
Solubility in Resin		>4%
Odour and Yellowing		Slight Yellowing
Stability		> 6 Months
Toxicity		To be determined
Migration		34%

Table 5.9: Performance data for 4-(4-benzoylphenoxy)benzophenone

Since the trimer **71** is neither oligomeric nor soluble in the resin its performance has not been reported. Also the lack of solubility meant it was not worth pursuing the oligomeric version of this synthetic route and work moved on to the dichloromethane oligomers.

4,4'-dihydroxybenzophenone was successfully polymerised with dichloromethane to give a linear oligomer **(72)**, oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxymethylene]. This oligomer had 3-10 repeat units and a molecular weight range of 700-2300 of which 81% were photoinitiator groups. It also showed a good UV absorbance with an extinction coefficient of 10 280 L mol^{-1} cm^{-1} at 284 nm based on the molecular weight of the repeat unit. However, solubility was again an issue. A lack of solubility in the resin system meant it was not suitable for use as an oligomeric photoinitiator.

The same synthesis with a chain stopper gave similar results. The oligomers chain stoppered with octyl bromide **(73)** had 2-9 repeat units and a molecular weight range of 700-2300, ~67% photoinitiator, while those chain stoppered with 4-hydroxybenzophenone **(74)** had 1-8 repeat units and also had a molecular weight range of 700-2300, ~58% photoinitiator. Of course this oligomer also had terminal photoinitiating groups. However as with the non chain stoppered oligomer they were also insoluble in the resin. Although these are all oligomers with repeat photoinitiating groups they are not suitable for use as photoinitiators. Their performance data is summarised in Table 5.10.

Sample		Oligomer 72	Oligomer 73	Oligomer 74
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	5 380	3 040	3 160
	λ_{max}	10 280	5 980	6 670
	395 nm	0	0	0
Rate of Cure @ 2% Concentration	Tack Free	N/A	N/A	N/A
	Thumb Twist	N/A	N/A	N/A
Solubility in Resin		Insoluble	Insoluble	Insoluble
Odour and Yellowing		N/A	N/A	N/A
Stability/Months		> 6 Months	> 6 Months	> 6 Months
Toxicity		To be determined	To be determined	To be determined
Migration (Tendency to Migrate)		N/A	N/A	N/A

Table 5.10: Performance data for oligomers 72-74

The copolymers with resorcinol and bisphenol A **(76,77)** were also successfully synthesised as shown in Scheme 5.19. Those with resorcinol showed a preference for polymerisation of the resorcinol over the 4,4'-dihydroxybenzophenone. The molecular weight range of this oligomer was 800-1400 but only showed one benzophenone group in the polymer chain. The bisphenol A polymer showed more photoinitiating groups with the polymers being roughly 50:50 between bisphenol A and benzophenone groups. The molecular weight range for this oligomer was 900-2300. These, however, were also insoluble in the resin system. Since they also do not fit the intention to limit the amount of non-photoinitiating groups their performance data has not been reported.

Oligomers were also successfully synthesised using the longer bridging groups. Synthesis with the dibromoalkanes produced linear oligomers **(78-81)** with a repeating benzophenone group as shown in Scheme 5.20. Polymerisation appeared to reach a limit at molecular weights of around 1400 for all syntheses. As such the shorter linking groups gave more repeat units. The propylene oligomer **(78)**, oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypropane-1,3-diyl, had 2-4 repeat units and a molecular weight range of 750-1250, for oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypentane-1,5-diyl] **(79)** there was 2-4 repeat units and molecular weight range 800-1400, for oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyoctane-1,8-diyl] **(80)** there was 2-3 repeat unit and molecular weight 900-1200 and for oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxydodecane-1,12-diyl] **(81)** 2-3 repeat units and molecular weight range 1000-1400. These oligomers had photoinitiator unit percentages of 72%, 65%, 56% and 48% respectively. Unfortunately none of these oligomeric photoinitiators were soluble in the resin, however their performance data are summarised in Table 5.11.

Sample		Oligomer 78	Oligomer 79	Oligomer 80	Oligomer 81
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	1 370	760	0	0
	λ_{max}	5 130	3 410	1 940	2 360
	395 nm	0	0	0	0
Rate of Cure @ 2% Concentration	Tack Free	N/A	N/A	N/A	N/A
	Thumb Twist	N/A	N/A	N/A	N/A
Solubility in Resin		Insoluble	Insoluble	Insoluble	Insoluble
Odour and Yellowing		N/A	N/A	N/A	N/A
Stability/Months		> 6	> 6	> 6	> 6
Toxicity		To be determined	To be determined	To be determined	To be determined
Migration (Tendency to Migrate)		N/A	N/A	N/A	N/A

Table 5.11: Performance data for 4,4'-dihydroxybenzophenone synthesised PEEKs, oligomers 78-81

Better results were obtained with the alternative synthetic route using 4,4'-difluorobenzophenone and alkyl diols shown in Scheme 5.21. These reacted less readily than the dibromoalkane route and this seemed to give a tendency to produce cyclic oligomers. 1,2-ethanediol gave a linear oligomer **(88)** and 1,3-propanediol showed some linear oligomer **(89)** but the rest showed predominantly cyclic oligomers **(90-93)**. Again there seemed to be a limit to the molecular weight that could be synthesised, this time at about 1500. 1,2-ethanediol gave linear oligomers **(88)**, oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyethylene], of 2-4 repeat units with molecular weight range 700-1200, 1,3-propanediol gave mainly cyclic oligomers **(89)**, cyclo-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxypropane-1,3-diyl] with 2-5 repeat units and molecular weight range 750-1300. The rest gave cyclic oligomers with cyclo-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxybutane-1,4-diyl] **(90)** having 3-5 repeat units and molecular weight range 800-1350, cyclo-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypentane-1,5-diyl] **(91)** having 3-5 repeat units and molecular weight range 850-1400, cyclo-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyhexane-1,6-diyl] **(92)** having 3-5 repeat units and molecular weight range 900-1500 and finally the dimethylpropanediol based cyclo-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxy(2,2-dimethyl)propane-1,3-diyl] **(93)** having 3-5 repeat units and molecular weight range 850-1400. The percentage of photoinitiator units in these oligomers were 76%, 72%, 68%, 65%, 62% and 65% respectively.

These oligomers showed some interesting results with regard to their UV spectra, each showed two maxima and these results are summarised in Table 5.12. The extinction coefficients are all given with respect to the molecular weight of the repeat unit.

Sample	UV Maxima 1		UV Maxima 2	
	λ / nm	ε / L mol^{-1} cm^{-1}	λ / nm	ε / L mol^{-1} cm^{-1}
Oligomer **88**	254	4 440	356	2 420
Oligomer **89**	250	9 080	359	12 580
Oligomer **90**	256	10 160	293	10 150
Oligomer **91**	256	19 020	293	5 360
Oligomer **92**	256	20 720	294	3 700
Oligomer **93**	245	11 370	369	23 200

Table 5.12: UV absorbance data for 4,4'-difluorobenzohenone synthesised PEEKs

From this data it can be seen that at the lower wavelength, similar to that seen in benzophenone, the extinction coefficient increases with increasing chain length. At the higher wavelength maxima however, the extinction coefficient decreases as the chain length increases. The possibility here is that adjacent photoinitiator groups have an effect on one another and hence affect the absorbance. As the bridging chain increases these effects are lessoned and the absorbance spectra approaches closer to that of benzophenone. The data from the ethylene oligomer are affected by the fact that it is a linear oligomer while the others are cyclic. It is also interesting to note that looking at the propane-1,3-diyl and the 2,2-dimethylpropane-1,3-diyl the added methyl groups seem to have a significant effect on the way adjacent groups interact causing a much higher extinction coefficient.

The positive fact about all these oligomers is that they showed good solubility and were mostly soluble in the resin system. The linear oligomer **88** was only barely soluble to about 1% while the oligomer with the longest bridging groups, oligomer **92**, was only soluble up to about 3%. This allowed performance testing to be carried out and the results of the cure speed test are summarised in Tables 5.13 and 5.14.

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone	7	10
Oligomer **88** (@ 1%)	14	29
Oligomer **89**	7	10
Oligomer **90**	9	14
Oligomer **91**	6	10
Oligomer **92**	6	11
Oligomer **93**	3	9

Table 5.13: Testing for speed of cure of 4,4'-difluorobenzophenone synthesised PEEK photoinitiators, 2% initial photoinitiator concentration

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone	4	8
Oligomer **88**	-	-
Oligomer **89**	5	7
Oligomer **90**	5	8
Oligomer **91**	3	7
Oligomer **92** (@ 3%)	5	9
Oligomer **93**	2	4

Table 5.14: Testing for speed of cure of 4,4'-difluorobenzophenone synthesised PEEK photoinitiators, 4% initial photoinitiator concentration

These results show that the new oligomeric photoinitiators have cure speeds comparable with, and in some cases surpassing, that of benzophenone. In particular oligomer **93** with its high UV absorbance shows very rapid cure rates. The resins cured here were now able to be subjected to the migration test. Since oligomer **88** had such poor solubility a tendency

to migrate could not be calculated. Tendency to migrate for oligomer **92** had to be calculated from initial photoinitiator concentrations of 2% and 3% as opposed to the usual 2% and 4%. The migration test results are summarised in Table 5.15. In each case the absorbance has been reported at the UV maximum with the highest extinction coefficient.

Sample	Solvent	Absorbance @ λ_{max}		Tendency to migrate / %
		2%	4%	
Oligomer **89**	85% Ethanol	0.214	0.442	20
	Acetic acid	0.247	0.563	29
	Diethyl ether	0.288	0.614	25
Oligomer **90**	85% Ethanol	<0.01	<0.01	<4
	Acetic acid	<0.01	<0.01	<4
	Diethyl ether	<0.01	<0.01	<4
Oligomer **91**	85% Ethanol	<0.01	<0.01	<4
	Acetic acid	<0.01	<0.01	<4
	Diethyl ether	<0.01	<0.01	<4
Oligomer **92** (Absorbance @ 2% and 3%)	85% Ethanol	<0.01	<0.01	<4
	Acetic acid	<0.01	<0.01	<4
	Diethyl ether	<0.01	<0.01	<4
Oligomer **93**	85% Ethanol	0.167	0.236	4
	Acetic acid	0.120	0.226	6
	Diethyl ether	0.106	0.253	7

Table 5.15: Migration data for PEEKs

Mostly the PEEK type oligomers show low migration characteristics. The propane-1,3-diyl oligomer **93** showed a significant amount of migration. This is likely due to the migration of some lower molecular weight material as well as the possibility that the linear oligomers are able to migrate more easily than the cyclic oligomers. Also, looking back at the cure speed testing, while in general cure speed was better for longer bridging groups the propane-1,3-diyl oligomer **89** had better cure speed than the butane-1,4-diyl oligomer **90**

particularly at the lower concentration. This would suggests that the propane-1,3-diyl oligomer was more mobile in the resin hence also accounting for its greater migration.

Oligomer **93** also showed some tendency to migrate albeit at a very low percentage. This, however, does not rule this oligomer out as being suitable as a low-migrating oligomeric photoinitiator. Its excellent cure speeds mean that industrial use could involve the use of a lower initial concentration thereby limiting the amount of photoinitiator potentially able to migrate. With this in mind this oligomer was also tested at an initial photoinitiator concentration of 1%. This gave the number of passes to "tack free" as 4 and the total cure "thumb twist" test as 9. This is comparable with the results of 4 and 8 respectively observed with benzophenone with an initial photoinitiator concentration of 4%.

Carrying out the migration test on this resin showed and absorbance of <0.01 for λ_{max} so that even if there is a low tendency to migrate the actual migration at low photoinitiator concentrations is likely to meet with legislative requirements. This oligomer, therefore, is well worth consideration for further development as a low-migrating oligomeric photoinitiator.

Overall the production of cyclic oligomers via this synthetic route has produced a number of suitable low-migrating oligomeric photoinitiators for further development for use in an industrial setting. The summary of their performance against the "good photoinitiator" characteristics is shown in Table 5.16.

Sample		Oligomer 88	Oligomer 89	Oligomer 90	Oligomer 91	Oligomer 92	Oligomer 93
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	4 440	8 880	10 020	18 910	20 530	9 970
	λ_{max}	4 440	12 580	10 160	19 020	20 720	23 200
	395 nm	0	0	0	0	0	1 020
Rate of Cure @ 2% Concentration	Tack Free	14 @ 1%	7	9	6	6	3
	Thumb Twist	29 @ 1 %	10	14	10	11	9
Solubility in Resin		<2%	>4%	>4%	>4%	<4%	>4%
Odour and Yellowing		Slight Yellowing	Slight Yellowing	Slight Yellowing	Slight Yellowing	Slight Yellowing	Slight Yellowing
Stability/Months		> 6	> 6	> 6	> 6	> 6	> 6
Toxicity		To be determined	To be determined	To be determined	To be determined	To be determined	To be determined
Migration (Tendency to Migrate)		N/A	25%	<4%	<4%	<4%	6%
Cost		N/A	N/A	N/A	N/A	N/A	N/A

Table 5.16: Performance testing of PEEK photoinitiators

Finally, the oligomers using the aromatic diols **(94,95)** were also successfully synthesised as shown in Scheme 5.22. Analysis of these oligomers showed a mixture of linear and cyclic molecules. With resorcinol used as the linking group the oligomer **(94)** showed 3-7 repeat units with molecular weight range of 1100-2300. Cyclic tetramer and pentamer were seen. With bisphenol A **(95)** there were 2-6 repeat units and molecular weight range 1050-2900. Cyclic oligomers were seen between trimer and hexamer.

Again these oligomers had poor solubility and were not soluble in the resin system. Even the cyclic material which had been successful in other similar oligomers would not dissolve in sufficient quantities to be able to initiate cure. These molecules may have uses with the aromatic linkers available for further derivitisation to improve solubility but this will form work for the future.

5.4.3 Conclusion

The possibility of synthesising an oligomer with photoinitiator groups linked only by a single oxygen atom, PEKs seemed to be a possibility when the dimer **70** and trimer **71** were successfully synthesised. However, as only the dimer showed solubility in the resin it was deemed unlikely that the oligomer, if synthesised, would be soluble.

The dimer was tested as a photoinitiator and successfully cured the resin, however, as expected it also migrated. This migration was less than benzophenone suggesting that the increased size of the photoinitiator had caused a reduction in migration.

Using dichloromethane to introduce a short bridging group yielded oligomeric photoinitiators **(72-74)**. However, solubility was an issue and so the were not suitable for use as photoinitiators. This was also the case when copolymerising with resorcinol **(75)** or bisphenol A **(76)**.

Oligomers with longer bridging groups were also synthesised by two routes. Those synthesised with 4,4'-dihydroxybenzophenone tended to give linear oligomers **(78-81)** which were insoluble in the resin system. Again they are another example of an oligomer

with repeat photoinitiating units which is unfortunately not able to be used as a photoinitiator.

However, a synthesis with 4,4'-difluorobenzophenone gave cyclic oligomers **(88-93)** which were soluble in the resin system. These cyclic oligomers were capable of initiating cure and hence were suitable for use as a photoinitiator. Most of these had good solubility with the exception of the ethylene oligomer **(88)** which was barely soluble. The hexane-1,6-diyl oligomer **(92)** was only soluble up to about 3% photoinitiator concentration.

Cure speeds were good for these oligomeric photoinitiators being comparable and even exceeding that of benzophenone. The oligomer synthesised with 2,2-dimethyl-1,3-propanediol **(93)** showed particularly good cure speed.

Migration was low for most of these oligomers. The ethylene oligomer **(88)** was not soluble enough to calculate migration and the propane-1,3-diyl oligomer **(89)** showed a significant tendency to migrate. This was suspected to be due to the oligomer being partially linear. The only other migration seen was a slight migration for the 2,2-dimethylpropane-1,3-diyl oligomer **(93)**. However, since it shows good cure speeds at low photoinitiator concentration then it could still be viable for use as a low migrating oligomeric photoinitiator.

Using aromatic diols also gave successful oligomers with repeat photoinitiating units **(94,95)**. However these were not soluble in the resin system and so again they were not suitable for use as an oligomeric photoinitiator.

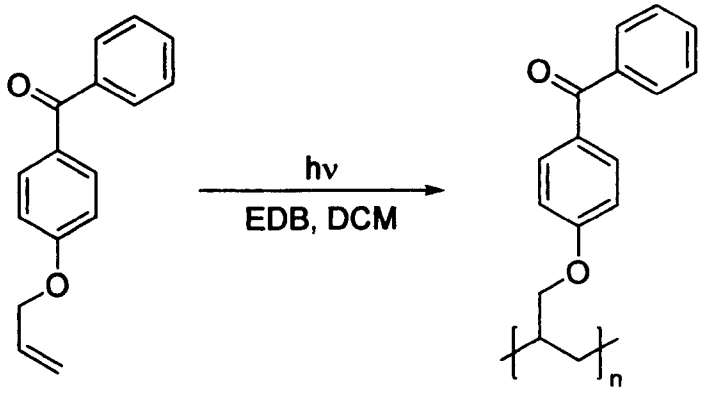
Overall six new functional oligomeric photoinitiators have been synthesised, Oligomers **88-93**. Of these the last 4 are low migrating oligomeric photoinitiators with a repeat photoinitiating unit.

5.5 Acrylate Polymers

5.5.1 Introduction

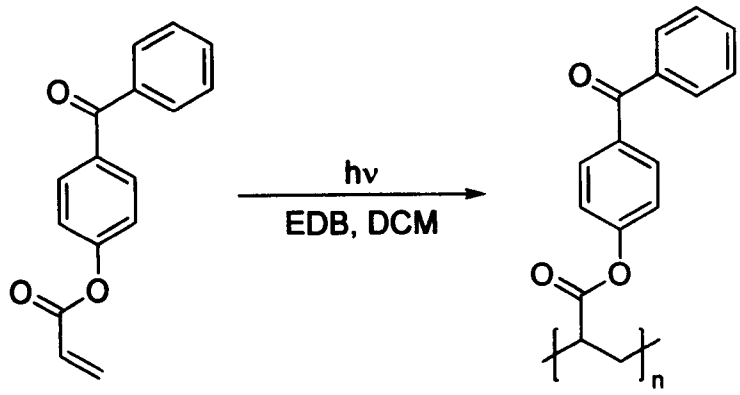
Section 4.3 looked at the possibility of synthesising a polymerisable photoinitiator such that on cure the molecule would either self polymerise or bind to the resin and hence prevent migration. This worked well with the acryloyloxybenzophenones but not so well with the allyloxybenzophenones. Further to this it was thought to see what the effect would be of polymerising these molecules first and then using them to cure the resin. This was looked at using 4-allyloxybenzophenone (**3**) and 4-acyloyloxybenzophenone (**5**) to synthesise an oligomer with pendant benzophenone groups (**96,97**).

Since the monomers themselves already contain a photoinitiator then polymerisation can be achieved simply by use of a suitable solvent, in this case dichloromethane, an amine synergist, ethyl 4-dimethylaminobenzoate (EDB), and exposure to UV light as shown in Schemes 5.23 and 5.24.



3 **96**

Scheme 5.23: Polymerisation of 4-allyloxybenzopheone



5 97

Scheme 5.24: Polymerisation of 4-acryloyloxybenzophenone

A similar polymerisation reaction was also carried out with 4,4'-acryloyloxybenzophenone **(10)** to produce a cross linked oligomer **(98)**.

5.5.2 Results and Discussion

As was seen when looking at the polymerisable photoinitiators the allyloxy group did not polymerise using this method. The double bond in the allyl group may still be possible to polymerise to create an oligomeric photoinitiator but does not polymerise by UV polymerisation so a suitable alternative method would need to be found. This was also the case for the diallyloxybenzophenones.

However, the acryloyloxy group did polymerise. This was in accordance with what had been seen in the section on polymerisable photoinitiators. The oligomer **(97)**, oligo[1-({4-benzoylphenoxy}carbonyl)ethylene], synthesised from the monomer 4-acyloyloxybenzophenone had 3-8 repeat units and a molecular weight range of 750-2000 of which 73% was due to the photoinitiator unit. Synthesis from 4,4'-diacryloyloxybenzophenone also appeared to have been successful although, since this oligomer **(98)** would contain cross linking groups, analysis to characterise the oligomer and obtain an idea of the molecular weight has been unsuccessful, however it has been approximated that 57% of the material would be due to the photoinitiator unit. Systematic

naming of this oligomer has also been difficult. Nevertheless, synthesis of the oligomer was assumed and both of these oligomers were carried forward for performance testing.

Both oligomers were soluble in the resin system and both were capable of initiating cure. The results of the cure speed tests are summarised in Tables 5.16 and 5.17 along with a comparison with benzophenone and their monomeric equivalents.

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone	7	10
4-acryloyloxybenzophenone **(5)**	16	29
4,4'-diacryloyloxybenzophenone **(10)**	19	33
Oligomer **97**	15	24
Oligomer **98**	23	38

Table 5.17: Testing for speed of cure for acrylate oligomer photoinitiators, 2% initial photoinitiator concentration

Sample	Number of Lamp Passes	
	Tack Free	Thumb Twist
Benzophenone	4	8
4-acryloyloxybenzophenone **(5)**	9	13
4,4'-diacryloyloxybenzophenone **(10)**	12	25
Oligomer **97**	10	17
Oligomer **98**	12	25

Table 5.18: Testing for speed of cure for acrylate oligomer photoinitiators, 4% initial photoinitiator concentration

From these results it can be seen that the oligomeric photoinitiators **(97,98)** show similar cure speeds to their monomeric equivalents **(5,10)** but are not as good as benzophenone.

The size of the oligomers limits their movement in the resin affecting the cure speed. This agrees with the result found with the monomers suggesting that these molecules polymerise very quickly on cure to form oligomers and then behave in the same way. It was expected then that they would also not migrate.

The cured resins were tested for migration and as expected no migration was seen into any of the three test solvents. Therefore this represents the synthesis of a further two new low-migrating oligomeric photoinitiators. However, since they behave in much the same way as their monomeric equivalents there does not seem to be any benefit to polymerising the acryloyloxybenzophenones before curing.

The only remaining questions to be answered are long-term stability and toxicity which would be carried out in further development work. It may be that the oligomer has advantages over the monomer for these categories and in which case it is useful to know that synthesis of the oligomer has been successful.

The performance data for the oligomeric photoinitiators assessed against the "good photoinitiator" criteria are shown in Table 5.18.

Sample		Oligomer 97	Oligomer 98
UV Absorptivity $dm^3\ cm^{-1}\ mol^{-1}$	254 nm	12 750	N/A
	λ_{max}	13 200	N/A
	395 nm	0	N/A
Rate of Cure @ 2% Concentration	Tack Free	15	23
	Thumb Twist	24	38
Solubility in Resin		>4%	>4%
Odour and Yellowing		N/A	N/A
Stability/Months		> 6	> 6
Toxicity		To be determined	To be determined
Migration (Tendency to Migrate)		<4%	<4%

Table 5.19: Performance data for acrylate oligomer photoinitiators

5.5.3 Conclusion

Acryloyloxy and diacryloyloxy monomers **(5,10)** are easily polymerised by UV polymerisation to give oligomeric photoinitiators **(97,98)** with a repeat photoinitiating unit. Allyloxy and diallyloxy monomers **(3,8,9)** do not polymerise so readily and an alternative form of polymerisation needs to be found.

The two oligomers synthesised from this polymerisation, oligomer **97** and oligomer **98**, both were able to initiate curing albeit with poor cure speeds. Migration testing on the cured resins showed no migration of the photoinitiator so these can be considered low-migrating oligomeric photoinitiators.

Cure speeds and migration tests for the oligomers are comparable with their monomeric equivalents so it is not clear if there is any benefit to be obtained from polymerising the acyloyloxy groups prior to curing. Whether there is any benefit with stability or toxicity will need to be determined during any detailed development work that the initiators may undergo prior to being used for an industrial application.

The work here is supportive of the fact that the initiators with an acryloyloxy group polymerise on curing while those with an allyloxy group do not. This is supportive of the results found when using the monomeric polymerisable photoinitiators reported on earlier.

6.0 Overall Discussion and Conclusion

6.1 Summary of this thesis

Overall the aim of this project was to create a low-migrating oligomeric photoinitiator with repeat photoinitiating units and with the photoinitiator making up the bulk of the oligomer. In order to test the migration a simple method needed to be developed which would indicate a tendency to migrate for a variety of photoinitiators. With this in mind a UV method was successfully developed and validated to enable easy determination of a tendency to migrate of a particular photoinitiator without the need for lengthy method development every time a new photoinitiator was synthesised.

With all testing methods now in place work turned to the development of the new initiators using a variety of ideas for different synthetic routes.

As is usual with this type of venture there has been a variety of success and failure. Predominantly failure has been due to solubility issues which are often the problem when working with higher molecular weight material. Solubility has been a problem not only with applying the desired synthetic routes but also analysing the synthesised oligomers and finally with their solubility in the resin system which is essential to be able to initiate cure.

However, pleasingly there have also been a number of successes. Eighteen new oligomers **(24,44,62,72-74,78-81,88-93,97,98)** with repeat photoinitiating units have been synthesised and characterised. Of these eighteen, nine **(62,88-93,97,98)** had enough solubility in the resin to be able to initiate cure and of these six **(62,90-92,97,98)** showed no migration and one **(93)** showed low migration. Also one of the synthetic routes, although unsuccessful in producing a soluble oligomer, did produce a dimer **(70)** which was able to function as a photoinitiator. This dimer did show migration but to a lesser degree than benzophenone supporting the theory that increasing the size of the photoinitiator lowers migration.

Also this thesis has been able to look more closely into the possibility of using a polymerisable monomer as a non-migrating photoinitiator. This investigation has considered three allyloxybenzophenones **(3,8,9)**, which do not UV polymerise and hence do

migrate, and two acryloyloxybenzophenones **(5,10)**, which polymerise on cure and hence do not migrate.

The main properties of a photoinitiator considered in this thesis were the cure speed and the tendency to migrate. A summary of the results for all the successful oligomeric photoinitiators is shown in Tables 6.1 and 6.2.

Sample	2% Initial Concentration		4% Initial Concentration	
	Tack Free	Thumb Twist	Tack Free	Thumb Twist
Benzophenone	7	10	4	8
Oligomer **62**	20	29	11 @ 3%	14 @ 3%
Oligomer **88**	14 @ 1%	29 @ 1%	-	-
Oligomer **89**	7	10	5	7
Oligomer **90**	9	14	5	8
Oligomer **91**	6	10	3	7
Oligomer **92**	6	11	5 @ 3%	9 @ 3%
Oligomer **93**	3	9	2	4
Oligomer **97**	15	24	10	17
Oligomer **98**	23	38	12	25

Table 6.1: Comparison of cure speeds of new oligomeric photoinitiators

Sample	Tendency to Migrate / %		
	85% Ethanol	Acetic Acid	Diethyl Ether
Benzophenone	36	43	47
Oligomer **62**	<4	<4	<4
Oligomer **88**	N/A	N/A	N/A
Oligomer **89**	20	29	25
Oligomer **90**	<4	<4	<4
Oligomer **91**	<4	<4	<4
Oligomer **92**	<4	<4	<4
Oligomer **93**	4	6	7
Oligomer **97**	<4	<4	<4
Oligomer **98**	<4	<4	<4

Table 6.2: Comparison of tendency to migrate for new oligomeric photoinitiators

From these tables it is clear that the best photoinitiators with regard to cure speed are the cyclic PEEK oligomers **(89-93)** synthesised from 4,4'-difluorobenzophenone and alkyl diols. Of these the best performance was oligomer **93**, the oligomer synthesised from 2,2-dimethyl-1,3-propanediol. The other oligomeric photoinitiators showed relatively poor cure speeds. If these were to be used for an industrial purpose it would be specifically due to their low-migration characteristics rather than their ability to cure efficiently. If migration is not an issue then benzophenone would still be the preferable choice.

The cyclic PEEK oligomers, however, are comparable with benzophenone for cure speeds. Thus they may also be useful for applications where migration is not an issue but where some other desirable property of the oligomeric photoinitiator may be preferred such as absorbance at a different UV maximum. Of course where migration is an issue these photoinitiators are not only a viable alternative to benzophenone but they provide the low-migration without a loss of performance with regard to cure speeds. In some cases there is even an increase in cure speed.

The cyclic PEEK oligomers **89-92** would seem to be the preferable choices where low migration is required. Each of these showed a tendency to migrate of <4%, the requirement set out at the beginning for a photoinitiator to be considered low-migrating. Of these oligomer **91** showed the best cure speeds so would appear to be the best choice for further development. Oligomer **92** had comparable cure speeds but its solubility was not as good as oligomer **91** giving less scope for use of the photoinitiator.

The other oligomeric PEEK photoinitiator to mention is oligomer **93**. Although this initiator showed a tendency to migrate >4% this tendency to migrate was only slight. The benefits of this photoinitiator were its exceptional cure speed. Cure speeds at 2% photoinitiator concentration were comparable with those of benzophenone at 4% concentration. The advantage of this is that this photoinitiator can be added at lower concentrations while still maintaining an efficient cure speed. This is true for concentrations as low as 1%. By adding less photoinitiator to a resin the amount of initiator available to migrate is less hence with only a very slight tendency to migrate it may be possible for this photoinitiator to be used in concentrations which allow it to meet legislative requirements for migration.

An overall recommendation would be for all of the cyclic PEEK oligomers to be further investigated for use commercially. In the first instance attention should be given to the two best performing photoinitiators oligomer **91** and oligomer **93**.

Formaldehyde polymers, aryl/alkyl polyethers and acrylate polymers have all shown that it is possible to create a variety of oligomers with a repeat photoinitiating group. While they have not seen the success of other synthetic routes, due to solubility issues, they are nonetheless interesting molecules. The evidence seen has suggested that an oligomeric photoinitiator is not likely to migrate. Therefore the issue with these photoinitiators is not a failure to be low-migrating, since this is undetermined, but a failure to be soluble enough to initiate cure. If this could be overcome then it may well be that these oligomers could show

good cure speeds and provide viable alternatives to those which have proved successful so far. It is not that they are failures more that they could be considered a limited success.

An overall summary of the characteristics of all eighteen of the oligomers with repeat photoinitiating units as well as the five potentially polymerisable photoinitiators and the benzophenone dimer synthesised in the PEK section is shown in Tables 6.3 and 6.4.

Sample		4-allyloxy benzophenone (3)	4,4'-diallyloxy benzophenone (8)	2,4-diallyloxy benzophenone (9)	4-acryloyloxy benzophenone (5)	4,4'-diacryloyloxy benzophenone (10)	4-(4-benzoylphenoxy) benzophenone (70)	Oligomer 24	Oligomer 62	Oligomer 44	Oligomer 72	Oligomer 73	Oligomer 74
Type*		SM	SM	SM	SM	SM	SM	LO	CO	CO	LO	LO	LO
Photoinitiator units per molecule		1	1	1	1	1	1	2-8	3-7	2-4	3-10	2-9	1-8
Molecular weight range		238	294	294	252	322	378	400-1800	800-1800	900-1800	700-2300	700-2300	700-2300
% Photoinitiator		N/A	N/A	N/A	N/A	N/A	N/A	87	71	81	81	~67	~58
UV absorbance / nm (L mol^{-1} cm^{-1}	**@ λ_{max} 1**	224 (9840)	225 (10930)	246 (12720)	258 (18510)	264 (16660)	259 (15340)	298 (14520)	243 (13820)	230 (12770)	284 (10280)	275 (5980)	283 (6670)
	@ λ_{max} 2	292 (16640)	296 (18320)	281 (6630)	-	-	-	-	282 (7280)	284 (4480)	-	-	-
Solubility in resin system / %		>4	>4	>4	>4	>4	>4	<1	<4	<1	<1	<1	<1
Rate of Cure (Tack free/Thumb twist)	**@2%**	8/14	10/16	6/12	16/29	19/33	6/10	-	20/29	-	-	-	-
	@4%	5/11	6/12	4/8	9/13	12/25	4/6	-	-	-	-	-	-
Tendency to migrate / %		30	22	23	<4	<4	34	-	<4	-	-	-	-
Low migrating oligomeric photoinitiator / Y/N		N	N	N	N	N	N	N	Y	N	N	N	N

* SM – Single Molecule, LO – Linear Oligomer, CO – Cyclic Oligomer, MO – Mixed Oligomer, CLO – Cross Linked Oligomer

Table 6.3: Overall summary of photoinitiators (Part 1)

Sample		Oligomer 78	Oligomer 79	Oligomer 80	Oligomer 81	Oligomer 88	Oligomer 89	Oligomer 90	Oligomer 91	Oligomer 92	Oligomer 93	Oligomer 97	Oligomer 98
Type*		LO	LO	LO	LO	LO	MO	CO	CO	CO	CO	LO	CLO
Photoinitiator units per molecule		2-4	2-4	2-3	2-3	2-4	2-5	3-5	3-5	3-5	3-5	3-8	N/A
Molecular weight range		750-1250	800-1400	900-1200	1000-1400	700-1200	750-1300	800-1350	850-1400	900-1500	850-1400	750-2000	N/A
% Photoinitiator		72	65	56	48	76	72	68	65	62	65	73	~57
UV absorbance / nm (L mol^{-1} cm^{-1}	**@ λ_{max} 1**	226 (2290)	228 (1470)	295 (1940)	295 (2360)	254 (4440)	250 (9080)	256 (10160)	256 (19020)	256 (20720)	245 (11370)	257 (13200)	265 (N/A)
	@ λ_{max} 2	294 (5130)	295 (3410)	-	-	356 (2420)	359 (12580)	293 (10150)	293 (5360)	294 (3700)	369 (23200)	-	-
Solubility in resin system / %		<1	<1	<1	<1	<2	>4	>4	>4	<3	>4	>4	>4
Rate of Cure (Tack free/Thumb twist)	**@2%**	-	-	-	-	14/29	7/10	9/14	6/10	6/11	3/9	15/24	23/38
	@4%	-	-	-	-	-	5/7	5/8	3/7	-	2/4	10/17	12/25
Tendency to migrate / %		-	-	-	-	-	25	<4	<4	<4	6	<4	<4
Low migrating oligomeric photoinitiator / Y/N		N	N	N	N	N	N	Y	Y	Y	Y/N	Y	Y

* SM – Single Molecule, LO – Linear Oligomer, CO – Cyclic Oligomer, MO – Mixed Oligomer, CLO – Cross Linked Oligomer

Table 6.4: Overall summary of photoinitiators (Part 2)

6.2 Future Work

This thesis has opened up new possibilities for the synthesis of low-migrating oligomeric photoinitiators, looking at creating a functional photoinitiator with as much active material as possible. Each synthetic route that has been explored has seen some degree of success and given options for work to progress further.

The formaldehyde polymers were perhaps the least successful. Since the option of using the synthesis to create a variety of different types of photoinitiator was not successful and the only photoinitiator created by this route was insoluble in the resin, this would not be a route which would be recommended to be pursued in any great depth. Future work would first need to address the issue of solubility with the photoinitiator that has been synthesised before looking at any more developments of the derivitisation step. The recommendation here is that preferable synthetic routes have been seen and should take priority.

The aryl/alkyl polyethers have been more successful and hence this provides considerable scope for further study. Although only two oligomeric photoinitiators have been created and only one of these is soluble in the resin system, this photoinitiator did show low-migration. This is encouragement that both the polymerisation and derivitisation steps can be successful and that low-migrating oligomeric photoinitiators can be synthesised. Continuing on from this would involve altering the length of the alkyl chain and the synthesis of different photoinitiator with different properties. Work has already looked at synthesising a type I photoinitiator. Alternatives could involve the synthesis of substituted benzophenone photoinitiators, some work on which has been started during this thesis, synthesis of thioxanthones or possibly using the oligomeric backbone to create an oligomeric amine synergist. Following on from the success in this thesis then the best place for future work to continue would be from the cyclic resorcinol oligomers with a short alkyl bridging group.

PEK oligomers would seem likely to have too little solubility to be viable as an oligomeric photoinitiator. This route may be one for the future when all other possibilities have been

exhausted but for now should not continue to be explored ahead of other, more promising, synthetic routes.

However, PEEK oligomers are definitely an area for future work. A variety of this type of oligomer have been synthesised and in particular a range of cyclic oligomers with varying alkyl bridges have been created and shown to function effectively as low-migrating oligomeric photoinitiators. These are now able to be taken forward to detailed development for use in an industrial setting. The best of these, and hence the oligomer to be developed first would be the pentane-1,5-diyl oligomer, c-o-OPhCPhOPe. At the same time the 2,2-dimethylpropane-1,3-diyl oligomer, c-o-OPhCPhODMP, should also be further looked at as, despite a small tendency to migrate, it provides excellent speed of cure even at low concentrations so could well be viable as a particularly economic oligomeric photoinitiator.

The limitation of this synthetic route is that it is specific for benzophenone photoinitiator although future work could look at alternatives, possibly the synthesis could be applied to a thioxanthone type photoinitiator.

The acrylate polymers are low-migrating oligomeric photoinitiators, however, since their performance is not as good as their monomeric analogues there would seem little point in using the oligomeric derivative. It would be better to concentrate on the synthesis of improved versions of the monomeric photoinitiator. A possibility for future work would be to look at polymerising the allyloxybenzophenones to see if this provided an alternative low-migrating oligomeric photoinitiator.

Finally a note should be made on the UV method for the determination of migration created for this thesis. While this method has been validated to a satisfactory standard to estimate migration for the photoinitiators synthesised here, and to provide recommendations for those viable for development, there are still possibilities for further development of this method. Adaptations of the method could look at the use of the method with different resins, using different solvents and looking at photoinitiators other than those based on benzophenone. It was also decided for this thesis only to look at photoinitiator systems

where migration of the photoinitiator or synergist may be an issue. Further development of the method could look at systems using a sensitiser and investigate how this affects the UV spectra of the migration solvent.

Also this method was developed to a level where it was possible to confidently recommend an oligomeric photoinitiator for more detailed investigation. Further development of the method could look at more accurate quantification of the amount of migration as well as improving the limit of detection so that the exact level within the legislative requirement could be determined.

This thesis has represented a successful opening of new areas for development in oligomeric photoinitiator technology and now the link between the research laboratory and the industrial production line can be put in to place to bring this technology to the commercial market.

7.0 Experimental

The following section outlines the details of the syntheses carried out in this thesis. It also includes any starting materials used, referenced by an identification number. All chemicals were used as bought with no further purification.

^{1}H-NMR and ^{13}C-NMR data were obtained using a JEOL Eclipse 400 FT NMR Spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane and coupling constants are given in Hz. Where signal overlapping has occurred the splitting pattern has been interpreted as expected for the molecule and the coupling constants have been approximated. For complex polymeric spectra a chemical shift range has been given identifying the key characteristics of the molecule. As discussed in section 5.3.2, for a couple of the polymers NMR data was impossible to obtain or interpret accurately and this has been noted accordingly.

Mass Spectrometry data for single molecules were obtained using a Perkin Elmer Turbomass Spectrometer with a Perkin Elmer Autosystem XL Gas Chromatograph.

Mass Spectrometry data for oligomers were obtained using Matrix Assisted Laser Desorption Ionisation Time Of Flight (MALDI-TOF) spectrometry. The samples were prepared by dissolving in DMF and then adding 5μL of this solution to 20 μL of a saturated solution of 2,5-dihydroxybenzoic acid in DMF with a drop of acetone. The plate was spotted with 1 μL of this solution and the excess solvent was removed with a tissue prior to loading the plate. The instrument used was a Bruker Reflex IV Mass Spectrometer.

It was discussed in section 5.3.2 that it would have been preferable to obtain mass spectrometry data by GPC but that, due to solubility issues, it was decided to rely on the MALDI-TOF data and leave GPC analysis to be carried out as future work for any oligomers that were to be developed commercially.

Since no specific system exists for the reporting of Mass Spectrometry data of polymers it was necessary to create one. Section 7.1 on page 144 lists the major polymer fragments

used in this thesis identified by a letter. Alkyl bridging groups are identified by a number according to the length of the chain, 1 = methylene, 2 = ethylene, i5 = isopentylene, etc. Mass specification labelling is then given in chemical formula notation using these number/letter combinations. End groups where identified would either be represented in standard chemical notation or by α and ω as identified in the name of the oligomer. I.e. A sodium ionised tetramer consisting of resorcinol and methylene groups terminated with an ethyl group, an example of which is shown in Figure 7.1, would be represented as $[(F1)_4EtMeNa]^+$.

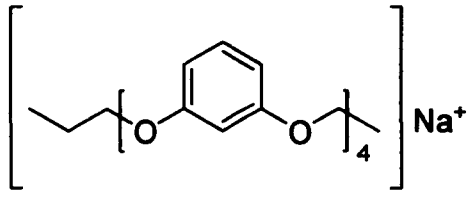


Figure 7.1: Molecular ion to illustrate polymer labelling system

All of the mass spectra showed a Boltzman type distribution. The major peak in each case has been highlighted in bold in the experimental data.

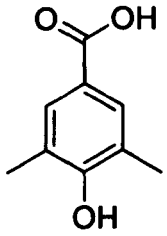
UV data was obtained using a Perkin Elmer Lambda 25 UV/Vis Spectrometer. The substance was dissolved in ethanol at a concentration of 2mg/100ml with THF used as a blank reference.

Elemental Analysis and T_g values were kindly provided by the Chemistry Department at the University of Hull.

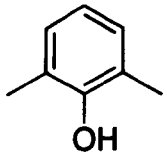
All chemicals were used as bought with no further purification.

7.1 List of oligomer fragments for mass spectrometry labelling

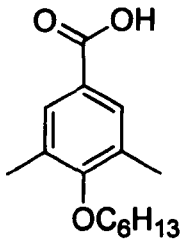
A



B



C



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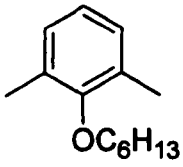

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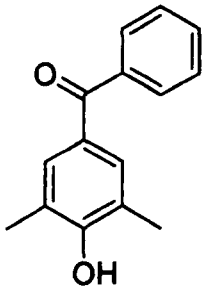

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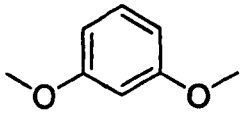

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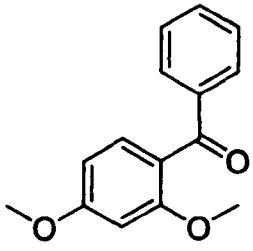

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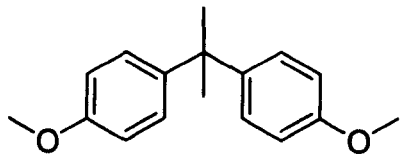

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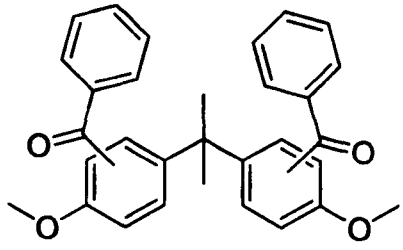

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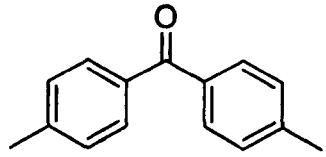

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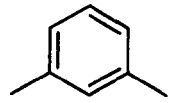

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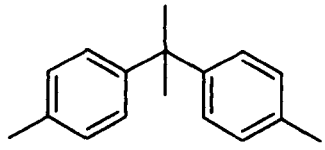
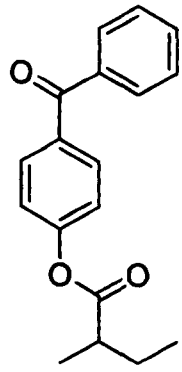


M



7.2 Experimental Details

4-hydroxybenzopheone (1): Supplied by Acros, Purity 99%

Allyl bromide (2): Supplied by Aldrich, Purity 97%

4-allyloxybenzophenone (3): 4-hydroxybenzophenone (19.97g, 0.10mol) and allyl bromide (13.41g, 0.11mol) were dissolved in acetone (60ml). Potassium carbonate (14g, 0.10mol) was added and the solution was heated under reflux for 18 hours. The resultant solution was cooled and water (40ml) was added. The product was extracted into ether (2 x 60ml) and washed with 1M NaOH (2 x 60ml) before being dried over magnesium sulphate and filtered. The ether was removed by rotary evaporation and the product was recrystallised from methanol to give needle-like white crystals of 4-allyloxybenzophenone (yield 16.17g, 67%, mp 74-76°C, lit. 77-78°C). Expected C% 80.67, H% 5.88, O% 13.45, Found C% 80.31, H% 6.20, UV: λ_{max}(EtOH)/nm 224 (ε/dm^3 cm^{-1} mol^{-1} 9 840), 292 (16 640), ^{1}H-NMR: (400Mhz, $CDCl_3$, δ in ppm): 4.63 (ddd, 2H, *J* 5.3, ~1.4, ~1.4, -O-CH_2-), 5.33 (ddt, 1H, *J* 10.6, ~1.5, ~1.4, =CH_A), 5.54 (ddt, 1H, *J* 17.2, ~1.5, ~1.4, =CH_B), 6.07 (ddt, 1H, *J* 17.2, 10.6, 5.3, -CH=), 6.98 (dd, 2H, *J* 9.0, 2.8, 2 x CH; Ph_A), 7.48 (ddd, 2H, *J* 7.4, 7.1, 1.3, 2 x CH_{meta}; Ph_B), 7.57 (tt, 1H, *J* 7.4, 1.4, CH_{para}; Ph_B), 7.76 (dt, 2H, *J* 7.1, 1.4, 1.3, 2 x CH_{ortho}; Ph_B), 7.82 (dt, 2H, *J* 9.0, 2.8, 2 x CH; Ph_A), ^{13}C-NMR:(100Mhz, $CDCl_3$, δ in ppm): 68.9 (-O-CH_2-), 114.2 (=CH_2), 118.2 (-CH=), 128.2 (2 x CH_{meta}; Ph_B), 129.7 (2 x CH; Ph_A), 130.2 (C-CO; Ph_B), 131.9 (CH_{para}; Ph_B), 132.48 (2 x CH_{ortho}; Ph_B), 132.50 (2 x CH; Ph_A), 138.2 (C-CO; Ph_A), 162.2 (C-O; Ph_A), 195.5 (C=O), M.S.: m/z 238 (M^+), 197, 161, 105, 77, 41

Acryloyl chloride (4): Supplied by Fluka, Purity 96%+

4-acryloyloxybenzophenone (5): 4-hydroxybenzophenone (7.52g, 0.038mol), sodium hydroxide (1.69g, 0.042) and tetrabutylammonium bromide (0.6g, 0.002mol) were dissolved in water (150ml). To this was added a solution of acryloyl chloride (7.2g, 0.079mol) in dichloromethane (100ml). The resulting solution was stirred in an ice bath for 3 hours. The organic layer was separated and the solvent was removed by rotary evaporation to give a product of white crystals of 4-acryloylbenzophenone (yield 7.76g, 81%). Expected C% 76.2, H% 4.7, O% 19.1, UV: λ_{max}(EtOH)/nm 258 (ε/dm^3 cm^{-1} mol^{-1} 18510), ^{1}H-NMR (400MHz, $CDCl_3$, δ in ppm): 6.06 (dd, 1H, J 10.4, 1.2, =CH_A), 6.34 (dd, 1H, J 17.4, 10.4, -CH=), 6.64 (dd, 1H, J 17.4, 1.2, =CH_B), 7.26 (dd, 2H, J 8.9, 2.5, 2 x CH;

Ph_A), 7.48 (ddd, 2H, J 7.4, 7.1, 1.4, 2 x CH_{meta}; Ph_B), 7.59 (tt, 1H, J 7.4, 1.6, CH_{para}; Ph_B), 7.79 (ddd, 2H, J 7.1, 1.6, 0.7, 2 x CH_{ortho}; Ph_B), 7.92 (dd, 2H, J 8.9, 2.3, 2 x CH; Ph_A), ^{13}C-NMR (100MHz, $CDCl_3$, δ in ppm): 121.5 (=CH_2), 127.5 (-CH=), 128.3 (2 x CH_{meta}; Ph_B), 129.9 (2 x CH; Ph_A), 131.7 (2 x CH; Ph_A), 132.5 (CH_{para}; Ph_B), 133.3 (2 x CH_{ortho}; PH_B), 135.0 (C-CO; Ph_B), 137.4 (C-CO; Ph_A), 153.7 (C-O; Ph_A), 164.0 (O-C=O), 195.6 (C=O).

4,4'-dihydroxybenzopheone (6): Supplied by Acros, Purity 97%

2,4-dihydroxybenzophenone (7): Supplied by Acros, Purity 99%

4,4'-diallyloxybenzophenone (8): 4,4'-dihydroxybenzophenone (2.14g, 0.010mol) and allyl bromide (2.69g, 0.022mol) were dissolved in acetone (30ml). Potassium carbonate (2.8g, 0.020mol) was added and the solution was heated under reflux for 18 hours. The resultant solution was cooled and water (20ml) was added. The product was extracted into ether (2 x 30ml) and washed with 1M NaOH (2 x 30ml) before being dried over magnesium sulphate and filtered. The ether was removed by rotary evaporation and the product was recrystallised from methanol to give needle-like white crystals of 4,4'-allyloxybenzophenone (yield 0.57g, 19%). Expected C% 77.6, H% 6.1, O% 16.3, Found C% 77.8, H% 6.3, UV: λ_{max}(EtOH)/nm 225 (ε/dm^3 cm^{-1} mol^{-1} 10 930), 296 (18 320), ^{1}H-NMR: (400Mhz, $CDCl_3$, δ in ppm): 4.67 (d, 4H, *J* 5.2, 2 x -O-CH_2-), 5.29 (dd, 2H, *J* 10.4, 1.2, 2 x =CH_A), 5.42 (dd, 2H, *J* 17.2, 1.2, 2 x =CH_B), 6.05 (ddt, 2H, *J* 17.2, 10.4, 5.2, 2 x –CH=), 7.08 (dd, 4H, *J* 8.8, 2.7, 2 x CH; Ph), 7.68 (dd, 4H, *J* 8.8, 2.7, 2 x CH; Ph), ^{13}C-NMR: (100Mhz, $CDCl_3$, δ in ppm): 68.5 (2 x -O-CH_2-), 114.4 (2 x =CH_2), 117.9 (2 x -CH=), 130.1 (2 x C-CO; Ph), 131.8 (4 x CH; Ph), 133.2 (4 x CH; Ph), 161.5 (2 x C-O; Ph), 194.8 (C=O), M.S.: 294 (M^+), 253, 225, 161, 121, 41

2,4-diallyloxybenzophenone (9): 2,4-dihydroxybenzophenone (2.14g, 0.010mol) and allyl bromide (2.69g, 0.022mol) were dissolved in acetone (30ml). Potassium carbonate (2.8g, 0.020mol) was added and the solution was heated under reflux for 18 hours. The resultant solution was cooled and water (20ml) was added. The product was extracted into ether (2 x 30ml) and washed with 1M NaOH (2 x 30ml) before being dried over magnesium sulphate and filtered. The ether was removed by rotary evaporation to give a yellow oil of 2,4-allyloxybenzophenone (yield 1.60g, 54%). Expected C% 77.6, H% 6.1, O% 16.3, Found C% 76.8, H% 6.4, UV: λ_{max}(EtOH)/nm 246 (ε/dm^3 cm^{-1} mol^{-1} 12 720), 281 (6 630), ^{1}H-NMR: (400Mhz, $CDCl_3$, δ in ppm): 4.46 (d, 2H, *J* 5.0, -O-CH_2-), 4.65 (d, 2H, *J* 5.0, -O-CH_2-), 4.83 (dd, 1H, *J* 17.2, 1.8, =CH), 4.94 (dd, 1H, *J* 10.8, 1.6, =CH), 5.28 (dd, 1H, *J*

10.6, 1.8, =CH), 5.43 (dd, 1H, *J* 17.2, 1.6, =CH), 5.64 (tdd, 1H, *J* 5.0, 17.2, 10.8, -CH=), 6.06 (tdd, 1H, *J* 5.0, 17.2, 10.6, -CH=), 6.67 (dd, 1H, *J* 8.4, 2.2, CH; Ph_A), 6.70 (d, 1H, *J* 2.2, CH; Ph_A), 7.40 (d, 1H, *J* 8.4, CH; Ph_A), 7.46 (ddd, 1H, *J* 7.9, 6.6, 1.5, CH_{meta}; Ph_B), 7.58 (tt, 1H, *J* 6.6, 1.3, CH_{para}; Ph_B), 7.65 (ddd, 1H, *J* 7.9, 1.3, 1.1, CH_{ortho}; Ph_B), ^{13}C-NMR: (100Mhz, $CDCl_3$, δ in ppm): 68.3 (-O-CH_2-), 68.6 (-O-CH_2-), 100.3 (=CH_2), 106.5 (=CH_2), 116.3 (-CH=), 117.9 (-CH=), 120.7 (C-CO; Ph_B), 128.3 (2 x CH_{meta}; Ph_B), 128.9 (2 x CH_{ortho}; Ph_B), 131.3 (CH_{para}; Ph_B), 132.5 (CH; Ph_A), 132.6 (CH; Ph_A), 133.3 (CH; Ph_A), 138.5 (C-CO; Ph_A), 157.8 (C-O; Ph_A), 161.9 (C-O; Ph_A), 194.9 (C=O), M.S.: m/z 294 (M^+), 105, 77, 41

4,4'-diacryloyloxybenzophenone (10): 4,4'-dihydroxybenzophenone (2.14g, 10 mmol), sodium hydroxide (0.9g, 22 mmol) and tetrabutylammonium bromide (0.3g, 1 mmol) were dissolved in water (75ml). To this was added a solution of acryloyl chloride (3.6g, 40 mmol) in dichloromethane (50ml). The resulting solution was stirred in an ice bath for 3 hours. The organic layer was separated and the solvent was removed by rotary evaporation to give a product of white crystals of 4,4'-diacryloylbenzophenone (yield 2.07g, 64%). Expected C% 70.8, H% 4.3, O% 24.9, Found C% 70.5, H% 4.5, UV: λ_{max}(EtOH)/nm 264 (ε/dm^3 cm^{-1} mol^{-1} 16 660), ^{1}H-NMR (400MHz, $CDCl_3$, δ in ppm): 6.06 (dd, 1H, J 10.4, 1.2, =CH_A), 6.34 (dd, 1H, J 17.4, 10.4, -CH=), 6.64 (dd, 1H, J 17.4, 1.2, =CH_B), 7.26 (dd, 2H, J 8.9, 2.5, 2 x CH; Ph_A), 7.48 (ddd, 2H, J 7.4, 7.1, 1.4, 2 x CH_{meta}; Ph_B), 7.59 (tt, 1H, J 7.4, 1.6, CH_{para}; Ph_B), 7.79 (ddd, 2H, J 7.1, 1.6, 0.7, 2 x CH_{ortho}; Ph_B), 7.92 (dd, 2H, J 8.9, 2.3, 2 x CH; Ph_A), ^{13}C-NMR (100MHz, $CDCl_3$, δ in ppm): 121.5 (=CH_2), 127.5 (-CH=), 128.3 (2 x CH_{meta}; Ph_B), 129.9 (2 x CH; Ph_A), 131.7 (2 x CH; Ph_A), 132.5 (CH_{para}; Ph_B), 133.3 (2 x CH_{ortho}; PH_B), 135.0 (C-CO; Ph_B), 137.4 (C-CO; Ph_A), 153.7 (C-O; Ph_A), 164.0 (O-C=O), 195.6 (C=O), M.S.: 322 (M^+), 185, 121, 55

Polystyrene (11): Not used for synthesis, included for illustration only

Benzoyl chloride (12): Supplied by Lancaster, Purity 99%+

Benzoylated polystyrene (13): Not synthesised, included for illustration only

Polyvinylchloride (PVC) (14): Not used for synthesis, included for illustration only

Photoinitiator based on PVC (15): Not synthesised, included for illustration only

Polyvinylalcohol (PVA) (16): Not used for synthesis, included for illustration only

Photoinitiator based on PVA (17): Not synthesised, included for illustration only

Phenol (18): Supplied by BDH, Purity 99.5%

Formaldehyde (19): Supplied by Fisher, Purity 37%

Phenol/formaldehyde polymer (20): Not synthesised, included for illustration only

4-hydroxybenzoic acid (21): Supplied by Aldrich, Purity 99%

oligo[(5-carboxy-2-hydroxy-1,3-phenylene)methylene] (22): 4-hydroxybenzoic acid (34.48g, 0.25mol) was stirred in water (250ml). Concentrated sulphuric acid (3ml) was added and the temperature of the solution was raised to 80°C. Formaldehyde solution (20.30g, 37%w/v, 0.25mol) was added dropwise over 40 minutes after which the temperature was raised to 95°C. The solution was heated for 72 hours by which time an off-white solid had precipitated. The precipitate was isolated by filtration and ground to an off-white powder of the desired oligomer. (yield = 24.3g, ~65%), ^{1}H-NMR (400MHz, Acetone-D6, δ in ppm): 4.1 (m, ~2H, Ph-CH_2-Ph), 7.0-7.8 (m, ~4H, CH; Ph), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 115.6-115.9 (CH_2), 122.3-122.8 (C-CH_2; Ph), 127.7-127.9 (CH; Ph), 130.5-131.4 (C-O; Ph), 132.7-133.5 (C-CO; Ph), 167.7-167.9 (C=O), M.S.: 461 $[(A1)_2ANa]^+$, 567 $[(A1)_2(B1)ANa]^+$, **611 $[(A1)_3ANa]^+$**, 717 $[(A1)_3(B1)ANa]^+$, 761 $[(A1)_4ANa]^+$, 823 $[(A1)_3(B1)_2ANa]^+$, 867 $[(A1)_4(B1)ANa]^+$, 973 $[(A1)_4(B1)_2ANa]^+$, 1017 $[(A1)_5(B1)ANa]^+$, 1123 $[(A1)_5(B1)_2ANa]^+$, 1273 $[(A1)_6(B1)_2ANa]^+$

oligo[(5-chlorocarboxy-2-hydroxy-1,3-phenylene)methylene] (23): oligo[(5-carboxy-2-hydroxy-1,3-phenylene)methylene] (1.0g) was stirred in thionyl chloride (30 ml) under nitrogen for 24 hours. The thionyl chloride was removed by evaporation and left a dark brown residue which proved impossible to isolate and characterise.

oligo[(5-benzoyl-2-hydroxy-1,3-phenylene)methylene] (24): 4-hydroxybenzophenone (10.0g, 0.05mol) was stirred in water (150ml). Concentrated sulphuric acid (3ml) was added and the temperature of the solution was raised to 80°C. Formaldehyde solution (10.12g, 37%w/v, 0.12mol) was added dropwise over 60 minutes. The temperature of the solution was raised to 95°C for 45 hours after which a solid precipitate had been produced along with some residual crystalline material. The solid oligomer was isolated by filtration (yield = 8.61g, 82%) and the crystalline material (shown to be unreacted 4-hydroxybenzophenone) was removed by washing with ethanol. UV: λ_{max}(EtOH)/nm 298 (ε/dm^3 cm^{-1} mol^{-1} 14 520), ^{1}H-NMR (400MHz, Acetone-D6, δ in ppm): 4.1 (m, 2H, Ph-CH_2-Ph), 7.0-7.8 (m, ~7.2H, CH; Ph), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 115.6-115.9 (CH_2), 127.4-127.8 (C-CH_2; Ph_A), 128.9-129.0 (CH_{meta}; Ph_B), 130.1-130.3 (CH; Ph_A and CH_{ortho}; Ph_B), 131.2-131.4 (C-CO; Ph_B), 132.1-132.5 (C-O; Ph_A), 133.3 (CH_{para}; Ph_B), 134.1-134.2 (C-CO; Ph_A), 206.3 (C=O), M.S.: 410 $[E1E]^+$, 620 $[(E1)_2E]^+$, 830 $[(E1)_3E]^+$, 1030 $[(E1)_4E]^+$, 1241 $[(E1)_5E]^+$, 1470 $[(E1)_6E]^+$, 1681 $[(E1)_7E]^+$, 1891 $[(E1)_8E]^+$

4-ethoxybenzoic acid (25): 4-hydroxybenzoic acid (20.03g, 0.145mol), 1-bromoethane (15.80g, 0.145mol), potassium hydroxide (20g, 0.357mol) and potassium iodide (0.1g, 0.0006mol) were dissolved in 85% ethanol (150ml). The resultant solution was heated under reflux for 21 hours. On cooling the solution was filtered and the resultant crystals were washed with water (250ml) and concentrated hydrochloric acid (25ml). The crystals were dried overnight at 55°C and then recrystallised from chloroform to yield a product of fine white crystals of 4-ethyloxybenzoic acid (yield = 17.39g, 72%). Expected C% 65.06, H% 6.02, O% 28.92, Found C% 65.21, H% 6.09, ^{1}H-NMR (400MHz, DMSO-D6, δ in ppm): 1.32 (t, 3H, J 7.0, CH_3-), 4.04 (t, 2H, J 7.0 -O-CH_2-), 6.96 (dd, 2H, J 6.9,2.0, 2 x CH; Ph), 7.85 (dd, J 6.9, 2.0, 2 x CH, Ph), ^{13}C-NMR (100MHz, DMSO-D6, δ in ppm): 28.9

(CH_3), 67.6 (-CH_2-O-), 114.3 (2 x CH; Ph), 122.8 (C-O-; Ph), 131.3 (2 x CH; Ph), 162.3 (-C-COOH; Ph), 167.5 (-COOH).

4-isopropyloxybenzoic acid (26): Synthesis as for 4-ethoxybenzoic acid (25) with 2-bromopropane (17.80g, 0.145mol) in place of the 1-bromoethane. Gave a product of fine white crystals of 4-isopropyloxybenzoic acid (yield = 3.51g, 13%). Expected C% 66.67, H% 6.67, O% 26.67, Found C% 66.23, H% 6.80, ^{1}H-NMR (400MHz, DMSO-D6, δ in ppm): 1.26 (d, 6H, J 6.0, 2 x CH_3-), 4.68 (sept, 1H, J 6.0 -O-CH<), 6.95 (dd, 2H, J 9.0, 2.8, 2 x CH; Ph), 7.83 (dd, J 9.0, 2.8, 2 x CH, Ph), ^{13}C-NMR (100MHz, DMSO-D6, δ in ppm): 23.9 (2 x CH_3), 68.4 (-CH_2-O<), 114.2 (2 x CH; Ph), 122.8 (C-O-; Ph), 131.4 (2 x CH; Ph), 162.3 (-C-COOH; Ph), 167.2 (-COOH).

4-hexyloxybenzoic acid (27): Synthesis as for 4-ethoxybenzoic acid (25) with 1-bromohexane (23.98g, 0.145mol) in place of the 1-bromoethane. Gave a product of fine white crystals of 4-hexyloxybenzoic acid (yield = 18.04g, 56%). Expected C% 70.27, H% 8.11, O% 21.62, Found C% 69.70, H% 8.18, ^{1}H-NMR (400MHz, DMSO-D6, δ in ppm): 0.83 (t, 3H, J 7.1, CH_3-), 1.26 (m, 4H, 2 x -CH_2-), 1.37 (quin, 2H, J 7.0, -CH_2-), 1.68 (quin, 2H, J 7.0, -CH_2-), 3.98 (t, 2H, J 6.5 -O-CH_2-), 6.95 (dd, 2H, J 6.9,2.1, 2 x CH; Ph), 7.84 (dd, J 6.9, 2.1, 2 x CH, Ph), ^{13}C-NMR (100MHz, DMSO-D6, δ in ppm): 13.9 (CH_3), 22.1 (-CH_2-), 25.2 (-CH_2-), 28.5 (-CH_2-), 31.0 (-CH_2-), 67.8 (-CH_2-O-), 114.1 (2 x CH; Ph), 122.9 (C-O-; Ph), 131.3 (2 x CH; Ph), 162.3 (-C-COOH; Ph), 167.2 (-COOH).

4-octyloxybenzoic acid (28): Synthesis as for 4-ethoxybenzoic acid (25) with 1-bromooctane (27.96g, 0.145mol) in place of the 1-bromoethane. Gave a product of fine white crystals of 4-octyloxybenzoic acid (yield = 18.74g, 49%). Expected C% 72.00, H% 8.80, O% 19.20, Found C% 71.73, H% 8.68, ^{1}H-NMR (400 MHz, DMSO-D6, δ in ppm): 0.80 (t, 3H, J 6.9, CH_3-), 1.22 (m, 8H, 4 x -CH_2-), 1.34 (quin, 2H, J 7.1, -CH_2-), 1.66 (quin, 2H, J 6.9, -CH_2-), 3.95 (t, 2H, J 6.5, -O-CH_2-), 6.94 (dd, 2H, J 6.8, 2.0, 2 x CH; Ph), 7.80 (dd, 2H, J 6.8, 2.0, 2 x CH; Ph). ^{13}C-NMR (100 MHz, DMSO-D6, δ in ppm): 13.9 (-CH_3), 22.1 (-CH_2-), 25.5 (-CH_2-), 28.6 (-CH_2-), 28.7 (-CH_2-), 28.8 (-CH_2-), 31.3 (-CH_2-), 67.8 (-CH_2-O-), 114.1 (2 x CH; Ph), 122.8 (C-O-; Ph), 131.5 (2 x CH; Ph), 162.3 (-C-COOH; Ph), 167.0 (-COOH).

oligo[(5-carboxy-2-ethoxy-1,3-phenylene)methylene] (29): 4-ethoxybenzoic acid (16.60g, 0.10mol) was stirred in water (100ml). Concentrated sulphuric acid (2ml) was added and the temperature of the solution was raised to 80°C. Formaldehyde solution (8.12g, 37%w/v, 0.25mol) was added dropwise over 40 minutes after which the temperature was raised to 95°C. The solution was heated for 72 hours. On cooling a white crystalline solid precipitated which was shown to be the starting material.

oligo[(5-carboxy-2-isopropyloxy-1,3-phenylene)methylene] (30): Synthesis as for oligo[(5-carboxy-2-ethoxy-1,3-phenylene)methylene] (29) with 4-isopropyloxybenzoic acid (18.00g, 0.10mol) in place of the 4-ethoxybenzoic acid. Produced a white crystalline solid shown to be the starting material.

oligo[(5-carboxy-2-hexyloxy-1,3-phenylene)methylene] (31): Synthesis as for oligo[(5-carboxy-2-ethoxy-1,3-phenylene)methylene] (29) with 4-hexyloxybenzoic acid (22.20g, 0.10mol) in place of the 4-ethoxybenzoic acid. Produced a white crystalline solid shown to be the starting material.

Alternative synthesis: oligo-[(5-carboxy-2-hydroxy-1,3-phenylene)methylene] (2.20g, ~15mmol), 1-bromohexane (2.80g, 17mmol), potassium hydroxide (2.0g, 35.7mmol) and potassium iodide (0.1g, 0.6mmol) were dissolved in 85% ethanol (50ml). The resultant solution was heated under reflux for 21 hours. On cooling the solution was filtered and the resultant powder was washed with water (250ml) and concentrated hydrochloric acid (25ml). The powder was dried overnight at 55°C and ground to a fine olive-brown powder of the desired oligomer (yield = 3.20g, ~91%). ^{1}H-NMR (400MHz, Acetone-D6, δ in ppm): 1.2-4.0 (m, Alkyl), 4.1 (m, Ph-CH_2-Ph), 7.0-7.8 (m, CH; Ph), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): ~15-~80 (Alkyl), 115.7-116.1 (CH_2), 122.4-122.8 (C-CH_2; Ph), 127.7-128.1 (CH; Ph), 130.4-131.2 (C-O; Ph), 132.4-133.3 (C-CO; Ph), 167.8-168.2 (C=O), M.S. 714 $[(C1)_2CNa]^+$, 904 $[(C1)_2(D1)CNa]^+$, 948 $[(C1)_3CNa]^+$, 1138 $[(C1)_3(D1)CNa]^+$

oligo[(5-carboxy-2-octyloxy-1,3-phenylene)methylene] (32): Synthesis as for oligo[(5-carboxy-2-ethoxy-1,3-phenylene)methylene] (29) with 4-octyloxybenzoic acid (25.00g, 0.10mol) in place of the 4-ethoxybenzoic acid. Produced a white crystalline solid shown to be the starting material.

oligo[(5-chlorocarboxy-2-hexyloxy-1,3-phenylene)methylene] (33): oligo[(5-carboxy-2-hexyloxy-1,3-phenylene)methylene] (1.0g) was stirred in thionyl chloride (30 ml) under nitrogen for 24 hours. The thionyl chloride was removed by evaporation and left a dark greenish brown residue which proved impossible to isolate and characterise.

oligo[(5-benzoyl-2-hexyloxy-1,3-phenylene)methylene] (34): Product not synthesised due to unsuccessful synthesis of oligo[(5-chlorocarboxy-2-hexyloxy-1,3-phenylene)methylene].

Resorcinol (35): Supplied by Acros, Purity 98%

Hydroquinone (36): Supplied by Acros, Purity 99%

Bisphenol A (37): Supplied by Acros, Purity 97%

Dichloromethane (38): Supplied by Fisher, Purity 99%+

Generic resorcinol/dichloromethane polymer (39): Sodium hydroxide (4.2g, 0.1mol) was added to a stirred solution of resorcinol (5.5g, 50mmol) in dichloromethane (20ml, 0.3mol) and *N*-methyl pyrrolidone (25ml). The solution was heated to 75°C for 20 hours and allowed to cool. The polymer was precipitated with water (400ml) and hydrochloric acid (50ml). The precipitate was isolated by filtration, washed with acetone to remove any low molecular weight organic material, dried overnight and ground to a white powder (Yield 6.08g, ~100%). This was assumed to be the desired oligomer but analysis was unsuccessful.

Generic hydroquinone/dichloromethane polymer (40): Synthesis as for generic resorcinol/dichloromethane polymer with hydroquinone (5.5g, 50mmol) in place of the resorcinol. Gave a precipitate of a grey material which could not be identified.

Generic bisphenol A/dichloromethane polymer (41): Synthesis as for generic resorcinol/dichloromethane polymer with bisphenol A (9.1g, 40mmol) in place of the resorcinol. Gave a white powder determined as the oligomer by mass spectrometry only. (Yield 9.51g, ~100%), M.S. 983 $[(H1)_4Na]^+$, **1223 $[(H1)_5Na]^+$**, 1463 $[(H1)_6Na]^+$, 1703 $[(H1)_7Na]^+$, 1943 $[(H1)_8Na]^+$

Benzoylated generic resorcinol/dichloromethane polymer (42): Not synthesised due to failure to characterise generic resorcinol/dichloromethane polymer (39).

Benzoylated generic hydroquinone/dichloromethane polymer (43): Not synthesised due to failure to characterise generic hydroquinone/dichloromethane polymer (40).

Benzoylated generic bisphenol A/dichloromethane polymer (44): Benzoyl chloride (1.4g, 10mmol) in dichloromethane (25ml) was added dropwise to a stirred suspension of oligo[oxy(1,4-phenylene)(dimethylmethylene)(1,4-phenylene) oxymethylene] (2.4g, ~10mmol) and aluminium chloride (1.5g, 12mmol) in dichloromethane (25ml). Stirring was continued for 2 hours then the mixture was heated under reflux for 2 hours. The cooled mixture was poured into ice (~50g) and HCl (25ml). The white precipitate was isolated by filtration, dried overnight and ground to a yellow powder identified as the desired oligomer by mass spectrometry only (Yield 1.1g, ~25%), M.S. 907, 919 $[(I1)_2Na]^+$, 1117, 1355, **1368 $[(I1)_3Na]^+$**, 1566, 1803, 1816 $[(I1)_4Na]^+$

Octyl bromide (45): Supplied by Aldrich, Purity 99%

α-octyl-ω-heptyl-oligo[oxy(1,3-phenylene)oxymethylene] (46): Synthesis as for generic resorcinol/dichloromethane polymer with octyl bromide (1.93g, 10mmol) added as a chain stopper. Gave light brown powder identified as the desired oligomer by mass spectrometry

only (Yield 5.98g, ~100%), M.S. 724 $[(F1)_4OcHpNa]^+$, 846 $[(F1)_5OcHpNa]^+$, 968 **$[(F1)_6OcHpNa]^+$**, 1090 $[(F1)_7OcHpNa]^+$, 1212 $[(F1)_8OcHpNa]^+$, 1334 $[(F1)_9OcHpNa]^+$, 1456 $[(F1)_{10}OcHpNa]^+$, 1578 $[(F1)_{11}OcHpNa]^+$, 1700 $[(F1)_{12}OcHpNa]^+$, 1822 $[(F1)_{13}OcHpNa]^+$

α-phenoxymethyl-ω-phenoxy-oligo[oxy(1,3-phenylene)oxymethylene] (47): Synthesis as for generic resorcinol/dichloromethane polymer with phenol (0.94g, 10mmol) added as a chain stopper. Gave orange powder identified as the desired oligomer by mass spectrometry only (Yield 5.88g, ~100%), M.S. 1322 $[(F1)_9(PhOMe)(PhO)Na]^+$, 1444 $[(F1)_{10}(PhOMe)(PhO)Na]^+$, 1566 $[(F1)_{11}(PhOMe)(PhO)Na]^+$, 1688 **$[(F1)_{12}(PhOMe)(PhO)Na]^+$**, 1810 $[(F1)_{13}(PhOMe)(PhO)Na]^+$, 1932 $[(F1)_{14}(PhOMe)(PhO)Na]^+$, 2054 $[(F1)_{15}(PhOMe)(PhO)Na]^+$

α-(4-benzoylphenoxy)methyl-ω-(4-benzoylphenoxy)-oligo[oxy(1,3-phenylene) oxymethylene] (48): Synthesis as for generic resorcinol/dichloromethane polymer with 4-hydroxybenzophenone (1.98g, 10mmol) added as a chain stopper. Gave cream powder identified as the desired oligomer by mass spectrometry only (Yield 6.81g, ~100%), M.S. 553 $[(F1)(HbzOMe)(HbzO)Na]^+$, 675 $[(F1)_2(HbzOMe)(HbzO)Na]^+$, 797 **$[(F1)_3(HbzOMe)(HbzO)Na]^+$**, 919 $[(F1)_4(HbzOMe)(HbzO)Na]^+$, 1041 $[(F1)_5(HbzOMe)(HbzO)Na]^+$, 1164 $[(F1)_6(HbzOMe)(HbzO)Na]^+$, 1286 $[(F1)_7(HbzOMe)(HbzO)Na]^+$ 1408 $[(F1)_8(HbzOMe)(HbzO)Na]^+$, 1530 $[(F1)_9(HbzOMe)(HbzO)Na]^+$, 1652 $[(F1)_{10}(HbzOMe)(HbzO)Na]^+$

Ethyl iodide (49): Supplied by Acros, Purity 98%

1,3-diethoxybenzene (50): Potassium carbonate (26.0g, 0.15mol) and ethyl iodide (15ml, 0.19mol) were added to a stirred solution of resorcinol (9.0g, 80 mmol) in acetone (100ml). The mixture was heated under reflux for 15 hours, diluted to 250ml with water and extracted into ether (3 x 50 ml). The ether was separated, dried ($MgSO_4$) filtered and the solvent was removed. 1,3-diethoxybenzene was purified by distillation *in vacuo* (78-80°C) as a clear orange oil (Yield 4.45g, 34%). Expected C% 72.3, H% 8.5, O% 19.2, Found C%

72.1, H% 8.8, ^{1}H-NMR (400MHz, $CDCl_3$, δ in ppm): 1.40 (t, 6H, *J* 7.0, 2 x CH_3), 4.0 (q, 4H, *J* 7.0, 2 x -O-CH_2-), 6.47 (ddd, 2H, *J* 8.2, 2.5, 2.0, 2 x $CH_{ortho,para}$; Ph), 6.49 (d, 1H, *J* 2.5, $CH_{ortho,ortho}$; Ph), 7.15 (t, 1H, *J* 8.2, $CH_{para,para}$; Ph), ^{13}C-NMR (100MHz, $CDCl_3$, δ in ppm): 14.8 (2 x CH_3), 63.3 (2 x -CH_2-O-), 101.4 ($CH_{meta,meta}$; Ph), 106.8 (2 x $CH_{ortho,para}$; Ph), 129.7 (2 x CH-O; Ph), 160.0 ($CH_{ortho,ortho}$: Ph), M.S. *m/z* 166 (M^+), 138, 110, 94, 81

4-chlorobenzoyl chloride (51): Supplied by Lancaster, Purity 98%

4-dimethylaminobenzoyl chloride (52): Supplied by Lancaster, Purity 97%

2,4-diethoxybenzophenone (53): Benzoyl chloride (2.8g, 20 mmol) in dichloromethane (30ml) was added dropwise to a stirred suspension of aluminium chloride (3.0g, 23mmol) and 1,3-diethoxybenzene (3.15g, 19 mmol) in dichloromethane (40ml) and stirred for 1 hour. The resulting solution was poured into ice (~50g) and HCl (20ml). The organic layer was separated and washed with water (25ml), 10% NaOH (25ml) and water (3 x 25ml), dried ($MgSO_4$) and the solvent was removed. The crude product recrystallised from water as white crystals of 2,4-diethoxybenzophenone (Yield , %), Expected C% 75.55, H% 6.67, O% 17.78, Found C% 75.25, H% 6.24, UV λ_{max}(EtOH)/nm 244 (ε/dm^3 cm^{-1} mol^{-1} 16 540), 284 (9 250), ^{1}H-NMR (400MHz, $CDCl_3$, δ in ppm): 0.85 (t, 3H, *J* 7.0, CH_3), 1.33 (t, 3H, *J* 7.0, CH_3), 3.88 (q, 2H, *J* 7.0, O-CH_2), 4.09 (q, 2H, *J* 7.0, O-CH_2), 6.6-7.6 (m, 8H, CH; Ph), ^{13}C-NMR (100MHz, $CDCl_3$, δ in ppm): 13.8 (CH_3), 14.5 (CH_3), 63.5 (O-CH_2), 63.8 (O-CH_2), 120.0-164.0 (CH; Ph), 195.0 (C=O), M.S. *m/z* 270 (M^+), 253, 241, 225, 213, 193, 165, 137, 105, 77

4-chloro-2',4'-diethoxybenzophenone (54): 4-chlorobenzoyl chloride (3.5g, 20 mmol) in dichloromethane (30ml) was added dropwise to a stirred suspension of aluminium chloride (3.0g, 23mmol) and 1,3-diethoxybenzene (3.15g, 19 mmol) in dichloromethane (40ml) and stirred for 1 hour. The resulting solution was poured into ice (~50g) and HCl (20ml). The organic layer was separated and washed with water (25ml), 10% NaOH (25ml) and water (3 x 25ml), dried ($MgSO_4$) and the solvent was removed. The crude product recrystallised from water as fine yellow crystals of 4-chloro-2',4'-diethoxybenzophenone (Yield 2.75,

45%), Expected C% 67.00, H% 5.58, O% 15.76 Cl% 11.66 Found C% 66.20 H% 5.29, UV λ_{max}(EtOH)/nm 254 (ε/dm^3 cm^{-1} mol^{-1} 4960), ^{1}H-NMR (400MHz, $CDCl_3$, δ in ppm): 0.88 (t, 3H, *J* 6.9, CH_3), 1.34 (t, 3H, *J* 7.0, CH_3), 3.93 (q, 2H, *J* 6.9, O-CH_2), 4.09 (q, 2H, *J* 7.0, O-CH_2), 6.64 (dd, 2H, *J* 7.3, 2.2, 2 x CH; Ph_A), 7.37 (d, 1H, *J* 7.3, CH; Ph_A), 7.52 (dd, 2H, *J* 8.4, 1.8, CH; Ph_B), 7.61 (dd, 2H, *J* 8.4, 1.8, CH; Ph_B), ^{13}C-NMR (100MHz, $CDCl_3$, δ in ppm): 13.9 (CH_3), 14.5 (CH_3), 63.5 (O-CH_2), 63.8 (O-CH_2), 100.6-164.6 (CH; Ph), 193.7 (C=O), M.S. *m/z* 306 (M^+), 304 (M^+), 289, 287, 193, 165, 139, 137, 111

4-dimethylamino-2',4'-diethoxybenzophenone (55): 4-dimethylaminobenzoyl chloride (3.7g, 20 mmol) in dichloromethane (30ml) was added dropwise to a stirred suspension of aluminium chloride (3.0g, 23mmol) and 1,3-diethoxybenzene (3.15g, 19 mmol) in dichloromethane (40ml) and stirred for 1 hour. The resulting solution was poured into ice (~50g) and HCl (20ml). The organic layer was separated and washed with water (25ml), 10% NaOH (25ml) and water (3 x 25ml), dried ($MgSO_4$) and the solvent was removed to leave a purple liquid of 4-dimethylamino-2',4'-diethoxybenzophenone (Yield 2.65, 42%), Expected C% 72.84, H% 7.35, O% 15.34 N% 4.47 Found C% 72.87 H% 8.22 N% 2.52, UV λ_{max}(EtOH)/nm 228 (ε/dm^3 cm^{-1} mol^{-1} 26 490), 345 (19 690), ^{1}H-NMR (400MHz, $CDCl_3$, δ in ppm): 1.19 (t, 3H, *J* 6.9, CH_3), 1.34 (t, 3H, *J* 7.0, CH_3), 2.17 (s, 6H, N-CH_3) 3.96 (q, 2H, *J* 6.9, O-CH_2), 4.03 (q, 2H, *J* 7.0, O-CH_2), 6.64 (dd, 2H, *J* 7.3, 2.2, 2 x CH; Ph_A), 7.37 (d, 1H, *J* 7.3, CH; Ph_A), 7.52 (dd, 2H, *J* 8.4, 1.8, CH; Ph_B), 7.61 (dd, 2H, *J* 8.4, 1.8, CH; Ph_B), ^{13}C-NMR (100MHz, $CDCl_3$, δ in ppm): 14.4 (CH_3), 14.8 (CH_3), 30.9 (N-CH_3) 63.3 (O-CH_2), 63.6 (O-CH_2), 100.2-160.1 (CH; Ph), 196.9 (C=O), M.S. *m/z* 313 (M^+), 296, 268, 148, 137, 120, 114

1,3-dibromopropane (56): Supplied by Lancaster, Purity 98%

1,5-dibromopentane (57): Supplied by Fluka, Purity 98%

1,8-dibromooctane (58): Supplied by Lancaster, Purity 98%

oligo[oxy(1,3-phenylene)oxypropane-1,3-diyl] (59): Resorcinol (2.2g, 20mmol), dichloropropane (2.3g, 20mmol) and potassium carbonate (5g, 30mmol) in dimethylformamide (50ml) were heated under reflux for 48 hours. After cooling the solid material was isolated by filtration and washed with acetone to remove any low molecular weight material. The solid was dried overnight and ground to a fine off-white powder characterised as the desired oligomer by ^{13}C-NMR and mass spectrometry (Yield 2.95g, ~100%), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 64.2-68.3 (CH_2), 101.4-160.0 (CH and C-O; Ph), M.S. 473 $[(F3)_3Na]^+$, **623 $[(F3)_4Na]^+$**, 773 $[(F3)_5Na]^+$, 923 $[(F3)_6Na]^+$, 1113 $[(F3)_7Na]^+$

oligo[oxy(1,3-phenylene)oxypentane-1,5-diyl] (60): Synthesised as oligo[oxy(1,3-phenylene)oxypropane-1,3-diyl] (59) with dibromopentane (4.6g, 20 mmol) in place of the dichloropropane. Gave off-white powder assumed to be the desired oligomer but not characterised.

oligo[oxy(1,3-phenylene)oxyoctane-1,8-diyl] (61): Synthesised as oligo[oxy(1,3-phenylene)oxypropane-1,3-diyl] (59) with dibromoocttane (5.4g, 20 mmol) in place of the dichloropropane. Gave off-white powder assumed to be the desired oligomer but not characterised.

cyclo-oligo[oxy(1,3-{4-benzoyl}phenylene)oxypropane-1,3-diyl] (62): Benzoyl chloride (1.4g, 10mmol) in dichloromethane (25ml) was added dropwise to a stirred suspension of oligo[oxy(1,3-phenylene)oxypropane-1,3-diyl] (59) (1.5g, ~10mmol) and aluminium chloride (1.5g, 12mmol) in dichloromethane (25ml). Stirring was continued for 2 hours then the mixture was heated under reflux for 2 hours. The cooled mixture was poured into ice (~50g) and HCl (25ml). The white precipitate was isolated by filtration, dried overnight and ground to a cream powder characterised as the desired oligomer by ^{13}C-NMR and mass spectrometry (Yield 0.79g, ~31%), UV: λ_{max}(EtOH)/nm 243 (ε/dm^3 cm^{-1} mol^{-1} 13 820), 282 (7 380), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 64.4-68.4 (CH_2), 101.8-160.1 (CH and C-O; Ph), 198.6 (C=O), M.S.: 785 $[(G3)_3Na]^+$, **1039 $[(G3)_4Na]^+$**, 1293 $[(G3)_5Na]^+$, 1547 $[(G3)_6Na]^+$, 1801 $[(G3)_7Na]^+$

cyclo-oligo[oxy(1,3-{4-benzoyl}phenylene)oxypentane-1,5-diyl] (63): Not synthesised, included for illustration only

cyclo-oligo[oxy(1,3-{4-benzoyl}phenylene)oxyoctane-1,8-diyl] (64): Not synthesised, included for illustration only

α-(4-benzoylphenoxy)methyl-ω-(4-benzoylphenoxy)-oligo[oxy(1,4-phenylene) (dimethylmethylene)(1,4-phenylene)oxymethylene] (65): Synthesis as for generic resorcinol/dichloromethane polymer with bisphenol A (9.1g, 40mmol) in place of resorcinol and 4-hydroxybenzophenone (2.0g, 10mmol) added as a chain stopper. Gave a white powder characterised as the desired oligomer by mass spectrometry only (Yield 11.63g, ~100%), M.S. 912 $[(H1)_2(HbzOMe)(HbzO)Na]^+$, 1152 $[(H1)_3(HbzOMe)(HbzO)Na]^+$, 1392 $[(H1)_4(HbzOMe)(HbzO)Na]^+$, 1632 $[(H1)_5(HbzOMe)(HbzO)Na]^+$, 1872 $[(H1)_6(HbzOMe)(HbzO)Na]^+$, 2112 $[(H1)_7(HbzOMe)(HbzO)Na]^+$ 2352 $[(H1)_8(HbzOMe)(HbzO)Na]^+$, 2592 $[(H1)_9(HbzOMe)(HbzO)Na]^+$, 2832 $[(H1)_{10}(HbzOMe)(HbzO)Na]^+$

4,4'-diflurobenzophenone (66): Supplied by Acros, Purity 99%

oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)] (67): Not synthesised, included for illustration only

4-fluoro-4'-hydroxybenzophenone (68): Supplied by Aldrich, Purity 97%

4-fluorobenzophenone (69): Supplied by Acros, Purity 98%

4-(4-benzoylphenoxy)benzophenone (70): 4-fluorobenzophenone (2.0g, 10mmol) and potassium carbonate (3.0g, 17mmol) in dimethylformamide (20ml) were heated to 140°C. 4-hydroxybenzophenone (1.98g, 10mmol) in dimethylformamide (20ml) was added slowly and heating was continued for 2 hours. The product was precipitated with water (100ml),

isolated by filtration, recrystallised (MeOH) and dried to a fine white powder of 4-(4-benzoylphenoxy)benzophenone (Yield 2.03g, 54%), UV: λ_{max}(EtOH)/nm 259 (ε/dm^3 cm^{-1} mol^{-1} 15 340), ^{1}H-NMR (400MHz, Acetone-D6, δ in ppm): 7.46 (dd, 4H, *J* 6.8, 2.0, 2 x CH; Ph_B, 2 x CH; Ph_C), 7.50 (ddd, 4H, *J* 7.5, 7.2, 1.4, 2 x CH_{meta}; Ph_A, 2 x CH_{meta}; Ph_D), 7.60 (tt, 2H, *J* 7.5, 1.4, CH_{para}; Ph_A, CH_{para}; Ph_D), 7.76 (dd, 4H, *J* 6.8, 2.0, 2 x CH; Ph_B, 2 x CH; Ph_C), 7.78 (dt, 4H, *J* 7.2, 1.4, 1.3, 2 x CH_{ortho}; Ph_A, 2 x CH_{ortho}; Ph_D), ^{13}C-NMR: (100Mhz, $CDCl_3$, δ in ppm): 128.3 (2 x CH_{meta}; Ph_A, 2 x CH_{meta}; Ph_D), 129.7 (2 x CH; Ph_B, 2 x CH; Ph_C), 129.9 (C-CO; Ph_A, C-CO; Ph_D), 130.0 (CH_{para}; Ph_A, CH_{para}; Ph_D), 132.5 (2 x CH_{ortho}; Ph_A, 2 x CH_{ortho}; Ph_D), 132.6 (2 x CH; Ph_B, 2 x CH; Ph_C), 138.2 (C-CO; Ph_B, C-CO; Ph_C), 160.2 (C-O; Ph_B, C-O; Ph_C), 195.8 (2 x C=O)

4,4'-bis(4-benzoylphenoxy)benzophenone (71): 4,4'-difluorobenzophenone (2.18g, 10mmol) and potassium carbonate (6.0g, 34mmol) in dimethylformamide (20ml) were heated to 140°C. 4-hydroxybenzophenone (4.0g, 20mmol) in dimethylformamide (20ml) was added slowly and heating was continued for 2 hours. The product was precipitated with water (100ml), filtered, recrystallised (MeOH) and dried to a fine white powder shown to be 4,4'-bis(4-benzoylphenoxy)benzophenone by mass spectrometry only (Yield 5.18g, 90%), UV: λ_{max}(EtOH)/nm 264 (ε/dm^3 cm^{-1} mol^{-1} 13 310), M.S.: 574 (M^+), 412, 335, 301, 139, 105, 77

α-hydro-ω-(4-(4-hydroxybenzoyl))phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypropane-1,3-diyl] (72): Synthesis as for generic resorcinol/dichloromethane polymer with 4,4'-dihydroxybenzophenone (10g, 45mmol) in place of resorcinol. Gave a yellowish powder shown to be the desired oligomer by ^{13}C-NMR and mass spectrometry (Yield 4.77g, ~47%), UV: λ_{max}(EtOH)/nm 284 (ε/dm^3 cm^{-1} mol^{-1} 10280), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 64.0-68.7 (CH_2), 101.3-161.5 (CH and C-O; Ph), 196.6 (C=O), M.S. 689 $[(J1)_2(H)(HbzOH)Na]^+$, **915 $[(J1)_3(H)(HbzOH)Na]^+$**, 1141 $[(J1)_4(H)(HbzOH)Na]^+$, 1367 $[(J1)_5(H)(HbzOH)Na]^+$, 1593 $[(J1)_6(H)(HbzOH)Na]^+$, 1819 $[(J1)_7(H)(HbzOH)Na]^+$ 2045 $[(J1)_8(H)(HbzOH)Na]^+$, 2271 $[(J1)_9(H)(HbzOH)Na]^+$

α-octyl-ω-heptyl-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxymethylene] (73): Synthesis as for generic resorcinol/dichloromethane polymer with 4,4′-dihydroxybenzophenone (10g, 45mmol) in place of resorcinol and 1-bromooctane (1.93g, 10mmol) as a chain stopper. Gave a white powder shown to be the desired oligomer by mass spectrometry only (Yield 6.72g, ~66%), UV: λ_{max}(EtOH)/nm 275 (ε/dm^3 cm^{-1} mol^{-1} 5 980), M.S.: 687 $[(J1)_2OcHpNa]^+$, **913 $[(J1)_3OcHpNa]^+$**, 1139 $[(J1)_4OcHpNa]^+$, 1365 $[(J1)_5OcHpNa]^+$, 1591 $[(J1)_6OcHpNa]^+$, 1817 $[(J1)_7OcHpNa]^+$ 2044 $[(J1)_8OcHpNa]^+$, 2271 $[(J1)_9OcHpNa]^+$

α-(4-benzoylphenoxy)methyl-ω-(4-benzoylphenoxy)-oligo[oxy(1,4-phenylene)carbonyl (1,4-phenylene)oxymethylene] (74): Synthesis as for generic resorcinol/dichloromethane polymer with 4,4′-dihydroxybenzophenone (10g, 45mmol) in place of resorcinol and 4-hydroxybenzophenone (1.98g, 10mmol) as a chain stopper. Gave a white powder shown to be the desired oligomer by mass spectrometry only (Yield 11.09g, ~100%), UV: λ_{max}(EtOH)/nm 285 (ε/dm^3 cm^{-1} mol^{-1} 6 670), M.S. 657 $[(J1)(HbzCH_2)(Hbz)Na]^+$, 883 $[(J1)_2(HbzCH_2)(Hbz)Na]^+$, **1109 $[(J1)_3(HbzCH_2)(Hbz)Na]^+$**, 1336 $[(J1)_4(HbzCH_2)(Hbz)Na]^+$, 1561 $[(J1)_5(HbzCH_2)(Hbz)Na]^+$, 1787 $[(J1)_6(HbzCH_2)(Hbz)Na]^+$, 2013 $[(J1)_7(HbzCH_2)(Hbz)Na]^+$, 2238 $[(J1)_8(HbzCH_2)(Hbz)Na]^+$

α-(4-benzoylphenoxy)methyl-ω-(4-benzoylphenoxy)-oligo[oxy(1,3-phenylene)oxy methylene/oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxymethylene] (75): Synthesis as for generic resorcinol/dichloromethane polymer with resorcinol (2.2g, 20mmol) and 4,4′-dihydroxybenzophenone (4.28g, 20mmol). Gave off white powder shown to be the desired oligomer by mass spectrometry only (Yield 5.69g, ~64%), M.S.: 798 $[(F1)_3(HbzCH_2)(Hbz)Na]^+$, **902 $[(F1)_3(J1)(HbzCH_2)(Hbz)Na]^+$**, 920 $[(F1)_4(HbzCH_2)(Hbz)Na]^+$, 1024 $[(F1)_4(J1)(HbzCH_2)(Hbz)Na]^+$, 1042 $[(F1)_5(HbzCH_2)(Hbz)Na]^+$, 1145 $[(F1)_5(J1)(HbzCH_2)(Hbz)Na]^+$, 1164 $[(F1)_6(HbzCH_2)(Hbz)Na]^+$, 1268 $[(F1)_6(J1)(HbzCH_2)(Hbz)Na]^+$, 1390 $[(F1)_7(HbzCH_2)(Hbz)Na]^+$, 1408 $[(F1)_7(J1)(HbzCH_2)(Hbz)Na]^+$

α-(4-benzoylphenoxy)methyl-ω-(4-benzoylphenoxy)-oligo[oxy(1,4-phenylene) (dimethylmethylene)(1,4-phenylene)oxymethylene/oxy(1,4-phenylene)carbonyl (1,4-phenylene)oxymethylene] (76): Synthesis as for α-(4-benzoylphenoxy)methyl-ω-(4-benzoylphenoxy)-oligo[oxy(1,3-phenylene)oxymethylene/oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxymethylene] with biphenol A (4.56g, 20mmol) in place of resorcinol. Gave white powder shown to be the desired oligomer by mass spectrometry only (Yield 9.08g, ~80%), M.S.: 898 $[(H1)(J1)(HbzCH_2)(Hbz)Na]^+$, 1124 $[(H1)(J1)_2(HbzCH_2)(Hbz)Na]^+$, 1364 **$[(H1)_2(J1)_2(HbzCH_2)(Hbz)Na]^+$**, 1590 $[(H1)_2(J1)_3(HbzCH_2)(Hbz)Na]^+$, 1830 $[(H1)_3(J1)_3(HbzCH_2)(Hbz)Na]^+$, 2057 $[(H1)_3(J1)_4(HbzCH_2)(Hbz)Na]^+$, 2296 $[(H1)_4(J1)_4(HbzCH_2)(Hbz)Na]^+$

1,12-dibromododecane (77): Supplied by Lancaster, Purity 98%

α-hydro-ω-(4-(4-hydroxybenzoyl))phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypropane-1,3-diyl] (78): 4,4'-dihydroxybenzophenone (4.28g, 20mmol), 1,3-dibromopropane (4.04g, 20mmol) and potassium carbonate (5g, 30mmol) in dimethylformamide (50ml) were heated under reflux for 48 hours. After cooling the solid material was isolated by filtration and washed with acetone to remove any low molecular weight material. The solid was dried overnight and ground to a fine off-white powder identified as the desired oligomer by ^{13}C-NMR and mass spectrometry (Yield 5.12g, ~100%), UV: λ_{max}(EtOH)/nm 226 (ε/dm^3 cm^{-1} mol^{-1} 2 290), 294 (5 130), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 64.3-68.7 (CH_2), 101.8-160.5 (CH and C-O; Ph), 196.9 (C=O), M.S.: 745 $[(J3)_2(H)(OHbz)Na]^+$, 761 $[(J3)_2(BrC_5H_{10})(Br)Na]^+$, 999 **$[(J3)_3(H)(OHbz)Na]^+$**, 1015 $[(J3)_3(BrC_5H_{10})(Br)Na]^+$, 1253 $[(J3)_4(H)(OHbz)Na]^+$, 1269 $[(J3)_4(BrC_5H_{10})(Br)Na]^+$

α-hydro-ω-(4-(4-hydroxybenzoyl))phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypentane-1,5-diyl] (79): Method as for α-hydro-ω-(4-(4-hydroxybenzoyl)) phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypropylene] with 1,5-dibromopentane (4.64g, 20mmol) in place of 1,3-dibromopropane. Gave cream powder identified as the desired oligomer by ^{13}C-NMR and mass spectrometry (Yield 5.99g,

~100%), UV: λ_{max}(EtOH)/nm 228 (ε/dm^3 cm^{-1} mol^{-1} 1 470), 295 (3 410), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 53.6-68.8 (CH_2), 101.6-160.3 (CH and C-O; Ph), 195.7 (C=O), M.S.: 801 $[(J5)_2(H)(OHbz)Na]^+$, 817 $[(J5)_2(BrC_5H_{10})(Br)Na]^+$, **1083 $[(J5)_3(H)(OHbz)Na]^+$**, 1099 $[(J5)_3(BrC_5H_{10})(Br)Na]^+$, 1365 $[(J5)_4(H)(OHbz)Na]^+$, 1381 $[(J5)_4(BrC_5H_{10})(Br)Na]^+$

α-hydro-ω-(4-(4-hydroxybenzoyl))phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyoctane-1,8-diyl] (80): Method as for α-hydro-ω-(4-(4-hydroxybenzoyl)) phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypropylene] with 1,8-dibromooctane (5.48g, 20mmol) in place of 1,3-dibromopropane. Gave off-white powder identified as the desired oligomer by ^{13}C-NMR and mass spectrometry (Yield 7.16g, ~100%), UV: λ_{max}(EtOH)/nm 295 (ε/dm^3 cm^{-1} mol^{-1} 1 940), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 42.6-68.9 (CH_2), 101.8-161.3 (CH and C-O; Ph), 196.2 (C=O), M.S.: **885 $[(J8)_2(H)(OHbz)Na]^+$**, 1209 $[(J8)_3(H)(OHbz)Na]^+$

α-hydro-ω-(4-(4-hydroxybenzoyl))phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxydodecane-1,12-diyl] (81): Method as for α-hydro-ω-(4-(4-hydroxybenzoyl) phenoxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxypropylene] with 1,12-dibromododecane (6.60g, 20mmol) in place of 1,3-dibromopropane. Gave off-white powder identified as the desired oligomer by ^{13}C-NMR and mass spectrometry (Yield 6.90g, ~91%), UV: λ_{max}(EtOH)/nm 295 (ε/dm^3 cm^{-1} mol^{-1} 2 360), ^{13}C-NMR (100MHz, Acetone-D6, δ in ppm): 41.6-68.4 (CH_2), 100.8-161.1 (CH and C-O; Ph), 196.5 (C=O), M.S.: **998 $[(J12)_2(H)(OHbz)Na]^+$**, 1378 $[(J12)_3(H)(OHbz)Na]^+$

1,2-ethanediol (82): Supplied by Aldrich, Purity 99%+

1,3-propanediol (83): Supplied by Aldrich, Purity 98%

1,4-butanediol (84): Supplied by Lancaster, Purity 99%

1,5-pentanediol (85): Supplied by Aldrich, Purity 99%

1,6-hexanediol (86): Supplied by Lancaster, Purity 97%

2,2-dimethyl-1,3-propanediol (87): Supplied by Acros, Purity 99%

oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyethylene] (88): 4,4'-difluorobenzophenone (4.32g, 20mmol), 1,2-ethanediol (1.34g, 20mmol) and potassium carbonate (5g, 30mmol) in dimethylformamide (50ml) were heated under reflux for 48 hours. After cooling the solid material was isolated by filtration and washed with acetone to remove any low molecular weight material. The solid was dried overnight and ground to a fine off-white powder shown to be the desired oligomer by mass spectrometry only (Yield 4.03g, ~84%), UV: λ_{max}(EtOH)/nm 254 (ε/dm^3 cm^{-1} mol^{-1} 4 440), 356 (2 420), M.S.: 722 $[(J2)_2\alpha\omega Na]^+$, **962 $[(J2)_3\alpha\omega Na]^+$**, 1202 $[(J2)_4\alpha\omega Na]^+$

oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxypropane-1,3-diyl] (89): Method as for α-hydroxyethyl-ω-hydroxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxyethylene] with 1,3-propanediol (1.52g, 20mmol) in place of 1,2-ethanediol. Gave a fine beige powder shown to be the desired oligomer by mass spectrometry only (Yield 5.04g, 100%), UV: λ_{max}(EtOH)/nm 250 (ε/dm^3 cm^{-1} mol^{-1} 9 080), 359 (12580), M.S.: 750 $[(J3)_2\alpha\omega Na]^+$, 786 $[(J3)_3Na]^+$, 1004 $[(J3)_3\alpha\omega Na]^+$, **1040 $[(J3)_4Na]^+$**, 1258 $[(J3)_4\alpha\omega Na]^+$, 1294 $[(J3)_5Na]^+$

oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxybutane-1,3-diyl] (90): Method as for α-hydroxyethyl-ω-hydroxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxyethylene] with 1,4-butanediol (1.80g, 20mmol) in place of 1,2-ethanediol. Gave a fine beige powder shown to be the desired oligomer by mass spectrometry only (Yield 4.52g, ~84%), UV: λ_{max}(EtOH)/nm 256 (ε/dm^3 cm^{-1} mol^{-1} 10 160), 293 (10 150), M.S.: 828 $[(J4)_3Na]^+$, **1096 $[(J4)_4Na]^+$**, 1364 $[(J4)_5Na]^+$

oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxypentane-1,3-diyl] (91): Method as for α-hydroxyethyl-ω-hydroxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxyethylene] with 1,5-pentanediol (2.08g, 20mmol) in place of 1,2-ethanediol. Gave a fine

beige powder shown to be the desired oligomer by mass spectrometry only (Yield 4.05g, ~72%), UV: λ_{max}(EtOH)/nm 256 (ε/dm^3 cm^{-1} mol^{-1} 19 020), 293 (5 360), M.S.: 870 $[(J5)_3Na]^+$, **1152 $[(J5)_4Na]^+$**, 1434 $[(J5)_5Na]^+$

oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxyhexane-1,3-diyl] (92): Method as for α-hydroxyethyl-ω-hydroxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene) oxyethylene] with 1,6-hexanediol (2.36g, 20mmol) in place of 1,2-ethanediol. Gave a fine beige powder shown to be the desired oligomer by mass spectrometry only (Yield 4.58g, ~77%), UV: λ_{max}(EtOH)/nm 256 (ε/dm^3 cm^{-1} mol^{-1} 20 720), 294 (3 700), M.S.: 912 $[(J6)_3Na]^+$, **1208 $[(J6)_4Na]^+$**, 1504 $[(J6)_5Na]^+$

oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxy(2,2-dimethyl)propane-1,3-diyl] (93): Method as for α-hydroxyethyl-ω-hydroxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyethylene] with 2,2-dimethylpropane-1,3-diol (2.08g, 20mmol) in place of 1,2-ethanediol. Gave a fine beige powder shown to be the desired oligomer by mass spectrometry only (Yield 6.75g, ~100%), UV: λ_{max}(EtOH)/nm 245 (ε/dm^3 cm^{-1} mol^{-1} 11 370), 369 (23 200), M.S.: 870 $[(Ji5)_3Na]^+$, **1152 $[(Ji5)_4Na]^+$**, 1434 $[(Ji5)_5Na]^+$

α-(3-(4-(4-fluorobenzoyl)phenoxy)phenyl)-ω-(4-(4-fluorobenzoyl)phenoxy)-oligo[oxy (1,4-phenylene)carbonyl(1,4-phenylene)oxy(1,3-phenylene)] (94): Method as for α-hydroxyethyl-ω-hydroxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyethylene] with resorcinol (2.2g, 20mmol) in place of 1,2-ethanediol. Gave a brown powder shown to be the desired oligomer by mass spectrometry only (Yield 3.88g, ~67%), M.S.: 1106 $[(JK)_2(\alpha)(\omega)Na]^+$, **1176 $[(JK)_4Na]^+$**, 1394 $[(JK)_3(\alpha)(\omega)Na]^+$, 1464 $[(JK)_5Na]^+$, 1682 $[(JK)_4(\alpha)(\omega)Na]^+$, 1971 $[(JK)_5(\alpha)(\omega)Na]^+$, 2259 $[(JK)_6(\alpha)(\omega)Na]^+$

α-(4-(4-(4-(4-fluorobenzoyl)phenoxy)phenylenedimethylmethylene)phenyl)-ω-(4-(4-fluorobenzoyl)phenoxy)-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxy(1,4-phenylene)(dimethylmethylene)(1,4-phenylene)] (95): Method as for α-hydroxyethyl-ω-hydroxy-oligo[oxy(1,4-phenylene)carbonyl(1,4-phenylene)oxyethylene] with bisphenol A (4.56g, 20mmol) in place of 1,2-ethanediol. Gave a brown powder shown to be the desired

oligomer by mass spectrometry only (Yield 8.47g, ~100%), M.S.: 1054 $[(JL)_1(\alpha)(\omega)Na]^+$, 1242 $[(JL)_3Na]^+$, 1460 $[(JL)_2(\alpha)(\omega)Na]^+$, **1668 $[(JL)_4Na]^+$**, 1866 $[(JL)_3(\alpha)(\omega)Na]^+$, 2074 $[(JL)_5Na]^+$, 2271 $[(JL)_4(\alpha)(\omega)Na]^+$, 2479 $[(JL)_6Na]^+$, 2678 $[(JL)_5(\alpha)(\omega)Na]^+$, 2885 $[(JL)_7Na]^+$

oligo[1-({4-benzoylphenoxy}methyl)ethylene] (96): 4-allyloxybenzophenone (1.0g, 4mmol) and ethyl 4-dimethylamiobenzoate (0.02g, 0.1mmol) in dichloromethane (20ml) were exposed to UV light. The solvent was evaporated and the resultant product was dried and ground to a fine off white powder shown to be the starting material.

oligo[1-({4-benzoylphenoxy}carbonyl)ethylene] (97): 4-acryloyloxybenzophenone (1.0g, 4mmol) and ethyl 4-dimethylamiobenzoate (0.02g, 0.1mmol) in dichloromethane (20ml) were exposed to UV light. The solvent was evaporated and the resultant product was dried and ground to a fine off white powder shown to be the desired oligomer by mass spectrometry only (Yield 0.99g, ~100%), M.S.: 747 $[\sim M_3]^+$, 999 $[\sim M_4]^+$, 1251 $[\sim M_5]^+$, **1503 $[\sim M_6]^+$**, 1755 $[\sim M_7]^+$, 2008 $[\sim M_8]^+$

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