Fundamental studies of high-aspect ratio UV embossing of poly(ethylene glycol)

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FUNDAMENTAL STUDIES OF HIGH-ASPECT RATIO UV EMBOSSING OF POLY(ETHYLENE GLYCOL)

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SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING
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2005

Fundamental Studies of High-Aspect Ratio UV Embossing of Poly(ethylene glycol)

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School of Mechanical & Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
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Summary

In UV embossing, a resin is contacted with a micro-patterned mold, cured with UV light, and then demolded, thereby embossing the mold's microstructure onto it. Micropatterning of poly(ethylene glycol) (PEG) has important biomedical applications. Two critical aspects determining if the embossed polymer could be demolded cleanly are the mold-resin chemical interaction, and the conversion and shrinkage upon curing. This thesis examines the fundamentals of these physical processes using PEG as the base material. For the former, it was found that the chemical interaction could be made favorable for demolding by adding a little silicone (<5%), which forms micelles that migrate to the mold-resin interface. For the latter, the current model for coupled conversion and shrinkage during curing was reviewed, improved upon, and verified experimentally. With it, we could predict conversion and shrinkage for different UV intensities with a fair amount of accuracy. This is helpful in evaluating the potential performance of the resin at different UV intensities.

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List of Publications

Chan-Park, M. B.; Neo, W. K. *Microsystem Technologies* **2003**, 9, 501-506.

Chan-Park, M. B.; Yan, Y.; Neo, W. K.; Zhou, W.; Zhang, J.; Yue, C. Y. *Langmuir* **2003**; *19(10)*, 4371-4380.

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The Sciences do not try to explain,
they hardly even try to interpret,
they mainly make models.

By a model is meant a mathematical construct which,
with the addition of some verbal interpretations,
describes observed phenomena.

The justification of such a construct
is solely and precisely
that it is expected to work.

John von Neumann

Chapter 1

Introduction

Polymeric *micro-electromechanical* systems (MEMS) are important as low-cost alternatives to silicon-based MEMS technologies for a range of present and future commercially viable products. These include applications in life sciences such as DNA microarrays or disposable devices on biocompatible substrate^{1,2}, micro-optics like diffractive optical elements or waveguide elements³, and display technology like optical backplane⁴. Making polymeric MEMS typically involves using a microstructured mold to shape the polymeric material with features in the micrometer range.

Microstructures with high aspect ratio are needed in many applications since they offer a higher active area per unit substrate surface area, the possibility of higher packing density of microstructural elements and higher throughput in continuous flow systems due to higher cross-sections per unit substrate area.² Larger surface area and multilevel microstructures are particularly important for chemical or biochemical applications like microreactors, micromixers, chromatographic columns or DNA concentrators to allow long microchannel length for good analysis performance and multitasking within a small area. Similar considerations are important in micro-optics, for example in waveguide applications, which typically involve comparatively large devices with dimensions of several centimeters. Higher packing densities and planar multifunctionality are observed in trends of massive parallelization of MEMS functions⁵ e.g. in DNA separations, protein microarrays, biosensors or nanowell-plates.

UV embossing is a promising technique by which to mass-produce these microstructures.⁶⁻¹⁰ In this technique, a substrate, such as a polyethylene terephthalate film, is coated with liquid UV curable resin, and then pressed against a micro-patterned

embossing mold. The resin in the mold is subsequently irradiated with UV light, causing the resin to cure (hardened by chemical reactions) and attain the pattern on the mold. The process also causes the resin to adhere strongly to the substrate. Finally, the substrate, with the cured, micro-patterned resin, is peeled off the mold.

Typically, the resin is a formulation containing several carefully chosen types of acrylates (or methacrylates). The reason for this practice is to optimize the characteristics of the resin, both before and after curing. Some of these characteristics are listed below.⁹

- ❑ Ease of applying the resin. The viscosity of the acrylate largely determines this.
- ❑ Ability to wet substrates. The surface tension of the acrylates is a gauge to this.
- ❑ Volatility.
- ❑ Speed of curing.
- ❑ Adhesion to substrates upon curing.
- ❑ Shrinkage upon curing.
- ❑ Solvent resistance of cured films.
- ❑ Mechanical properties of cured films such as flexibility, Young's modulus, ultimate tensile stress (UTS) and elongation at UTS.
- ❑ Glass transition temperature.
- ❑ Toxicity.
- ❑ Colour.

UV embossing offers many advantages. Firstly, UV curing is rapid and can involve curing on the order of tenth second time scales. Secondly, unlike thermal embossing, UV embossing is usually done at room temperature and low pressure. This is critical to the patterning of delicate substrates such as protein-encapsulated polymers or water-containing hydrogels for biomedical applications.⁷ Further, the requirements of the mold for such a process are less stringent and such molds can be duplicated economically from a master mold by electroforming¹¹ or machining on plastics. Thirdly, in contrast to photolithography, which is a batch process involving exposure and wet development in a clean room environment, UV embossing can be a roll-to-roll process outside the clean room environment (Figure 1.1). Large areas of the patterns (up to a few meters long by a meter wide) can be generated easily.^{4,8} Fourthly, the properties of the embossed polymer can be easily fine-tuned by the mix ratio of the components and made superior to those of the thermoplastic equivalents made by thermal embossing. Fifthly, UV embossing has

been shown to produce parts with good dimensional replication due mainly to the fact that UV embossing may be done at low temperature.³ UV embossing can be done at room temperature and low pressure and is suitable for applications where the patterning condition or material is restrictive. Patterning of biologically active molecules and on highly brittle indium tin oxide (ITO) patterned plastic substrate for biomedical and flexible display applications respectively are two such examples.

Figure 1.1. Continuous fabrication process using a roller-mold.

However, demolding of UV embossed high aspect ratio microstructures from a metallic mold is typically difficult since there is no differential thermal contraction between the mold and the embossing as in the case of thermal embossing. Release agents are usually employed to ease this demolding process so that, firstly, the microstructures are not damaged during this process, and secondly, the cured resin does not become permanently stuck onto the mold, and hence damaging it. Several factors have been identified to influence demolding of UV embossed microstructures: (1) roughness of the mold; (2) taper angle of microstructures of the mold; (3) chemical interaction between the mold and the resin; (4) extent of conversion of resin as well as its the depth-wise uniformity; and (5) shrinkage during photopolymerization.¹² These factors could be conveniently placed into two categories: (1) and (2) are mold-related; and (3) to (5) are material-related.

1.1 Objectives

High aspect ratio polymeric MEMS are gaining importance in numerous applications such as DNA microarrays, bio/bio-chemical microreactors and flat panel

display technology. For bio-related applications, the polymer must be bio-compatible and poly(ethylene glycol) (PEG) is one of the most well-known in this respect.

UV embossing is a promising technique that can mass-produce these polymeric MEMS economically. In this process, a formulation of acrylates (or methacrylates) is photopolymerized while in contact with a microstructured mold, and formed microstructures are then demolded. A major issue with this technique is that the demolding process may critically damage the microstructures. To overcome this problem, fundamental studies into the physical processes that may affect this demolding process are required. Three such factors are investigated in this thesis, *viz.* the chemical interaction between the mold and the resin; extent of conversion of resin achieved; and shrinkage of resin during photopolymerization. Specifically, this work attempts to:

1. demonstrate the viability of fabricating PEG-based microstructures having an aspect ratio of four using the UV embossing technique.
2. study the effects of adding a reactive silicone release agent to PEG-based formulations on the chemical compositions of the embossed polymer surface in contact with the mold as well as the photopolymerization kinetics.
3. study and model the simultaneous conversion and shrinkage during the photopolymerization of PEG diacrylate.

Previously, microfabrication of PEG-based polymer has only been done using photolithography. This work thus presents an alternative, more economical and rapid method of fabricating microstructures using this material.

Release agents are important for increasing the ease of the demolding process so that the microstructures and the mold would not be damaged during the process. Silicone-based release agents are the most ubiquitous and effective. By studying their impacts on our PEG-based formulations, we could then deduce the fundamental processes taking place.

Conversion and shrinkage are coupled events during photopolymerization, and they critically affect the mechanical and dimensional properties of the embossed polymer. For a particular material, conversion and shrinkage are determined mainly by the UV intensity used for photopolymerization. A model that could predict the dependence of these two parameters on UV intensity would thus be helpful. While the model at hand could work for only single-component formulations and not the complex multi-component formulations that are usually used for the actual embossing, it is nonetheless moving a step ahead in this direction.

1.2 Overview of Thesis

This thesis presents our investigation into the material-related factors. The goal of this work is to gain fundamental insights into the physical processes underlying these factors. Thematically, this thesis can be divided into five chapters. The first (this chapter) introduces this thesis and states its objectives. This is followed by a literature review on the main material used, *viz.* poly(ethylene glycol), as well as the free radical polymerization that takes place during UV irradiation in Chapter 2. In Chapter 3, the results of our embossing trials are presented and discussed. Chapter 4 dwells on the chemical compositions of the surfaces of films cured in contact with a simulated mold, and from these, we deduce the chemical interaction that occurs between the mold and the resin. Chapter 5 presents a mechanistic model of conversion and shrinkage of photopolymerization, which could be used to predict these two important factors for a wide range of UV intensity. Lastly, the conclusions (Chapter 6) as well as recommendations for future works are given.

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Chapter 2

Literature Review

In this work, the main material investigated was poly(ethylene glycol) diacrylate with M_n 700 (PEG700). PEG is a well-known biocompatible polymer and the micropatterning of PEG has important biomedical applications such as tissue engineering, bio-analytic sensing and protein patterning.¹ The following section gives an introduction to this material as well as the previous microfabrication works done using it. In the second part of this chapter, the process of free radical polymerization, which underlies the UV embossing technique, will be reviewed in details.

2.1 Introduction to Poly(ethylene glycol)

Poly(ethylene glycol) (PEG) is a polymer with the molecular structure shown in Figure 2.1.

Figure 2.1. Molecular structure of the PEG.

More specifically, the name PEG is used when the molecular weight involved is less than 20,000 g/mol, poly(ethylene oxide) (PEO) when it is more than 20,000 g/mol, and poly(oxyethylene) (POE) and poly(oxirane) when no molecular weight is to be implied.²

Low molecular weight PEG (< 1000 g/mol) is a viscous liquid at room temperature, and higher molecular weight ones are solids with melting points that are proportional to their molecular weights, reaching to a plateau at about $67\text{ }^{\circ}\text{C}$.²

PEG is soluble in many common organic solvents as well as water. The solubility parameter of PEG is $20.2\text{ (MPa)}^{1/2}$ and is thus soluble in organic solvents such as acetone [$20.3\text{ (MPa)}^{1/2}$] and toluene [$18.2\text{ (MPa)}^{1/2}$].³ In water, the polar ether groups (C—O—C) in PEG readily form hydrogen bonds with the water molecules, leading to the solvation of the PEG molecule.² PEG is hence highly hydrophilic.

There is a strong interest in using PEG as a biomaterial because it is one of the most universally biocompatible polymers⁴ and it has strong protein rejection capability. The latter is a result of its high solubility in an aqueous medium and its very large size in the solution. The solvated PEG molecules sterically exclude other molecules such as protein from the solution, and hence forcing them to precipitate out of the solution⁴. An application of this property of PEG is in the modification of other biomaterials' surfaces. By incorporating PEG onto these surfaces, they would be protected from adhesion by proteins because the PEG molecules would exclude the proteins and keep them away from the biomaterials' surfaces. As such, PEG is able to render a surface non-thrombogenic.⁵

Besides the use as a surface modification agent, PEG can also be made into hydrogels for biomedical applications. Hydrogels are water-swollen, cross-linked polymeric structures, and there are applications in contact lenses, artificial tendon materials, wound-healing adhesives, artificial kidney membranes, articular cartilage, artificial skin, maxillofacial and sexual organ reconstruction materials, and vocal cord replacement materials.⁶

Free-radical polymerization (to be discussed in details in the next section, Section 2.2) can be used to create a cross-linked network of PEG. For UV photopolymerization, the PEG molecule is first modified to incorporate acrylate or methacrylate groups. For example, the one shown in Figure 2.2 has two acrylate groups (and hence difunctional), one at each end. Higher functional PEG acrylates are also

possible. The cross-linked PEG network is readily swollen by water (because of its strong hydrophilicity) to form hydrogel.

Figure 2.2. An acrylate-terminated PEG molecule.

Micropatterning of PEG hydrogels have hitherto been achieved with photolithography technique.^{1,7} In Revzin *et al.*'s work⁷, PEG diacrylate (PEGDA, M_n 575), PEG dimethylacrylate (PEGDMA, M_n 1000) and PEG tetraacrylate (PEGTeA, M_n 18500) were used to make a series of cylinders of diameters ranging from 7 μm to 600 μm , and depth, from 3 to 12 μm , on a silicon substrate that had been treated with a self-assembled monolayer (SAM) of 3-(trichlorosilyl)propyl methacrylate. This SAM serves to immobilise the created microstructure and prevent their delamination upon swelling in water. Ward *et al.*¹ used a 50/50 (wt%) of PEG methacrylate (PEGMA, M_n 200) and PEGDMA (M_n 200) mixtures to make crosses of various width, from 5 μm to 20 μm , and depth, from 60 μm to 100 μm , on a pre-cross-linked PEGDMA substrate. In addition, by photopolymerising another layer of 50/50 (wt%) PEGMA/PEGMA mixture on top of a previously patterned layer, lines of an aspect ratio of ten (width 10 μm and height 100 μm) were created.

2.2 Free Radical Polymerization

In our UV embossing technique, the acrylate is cured via free radical polymerization. This is a type of chain polymerization reaction, otherwise known as addition reaction. The monomer in chain polymerization reaction inevitably has at least one C=C unsaturation, the simplest of which is ethene ($\text{CH}_2=\text{CH}_2$). In the case of UV polymerization, the acrylate and methacrylate unsaturations, as shown in Figure 2.3, are the most commonly used. The free radical polymerization is triggered by the decomposition of a special chemical called an initiator I to form a free radical $R\bullet$ that then attack the π -bond of the monomer's unsaturation to produce a new radical. As this process repeats, the monomers are added successively to the growing polymer chain and

the reactive centre is propagated. This propagation is stopped when the reactive centre is terminated by some other reactions and a 'dead' polymer chain is thus formed.⁸

Figure 2.3. (a) Acrylate unsaturation, and (b) methacrylate unsaturation.

There are a few basic steps in free radical polymerization reaction, namely, initiation, propagation, termination and chain transfer.

2.2.1 Initiation

Initiation is usually achieved by adding a small amount of a chemical, termed an initiator, that decomposes easily to form radicals. In the case of UV curing, this chemical is called a photoinitiator. The initiation step generally consists of two sequential reactions – the dissociation of the initiator molecule I into free radicals $R\bullet$ followed by the attack of the radical on the monomer molecule M to produce the chain initiating species $M_1\bullet$. These are shown in eqs 2.1 and 2.2 respectively.⁹ An example showing the initial attack on the acrylate unsaturation is shown in eq 2.3.

In photoinitiation, there are a few possibilities to the fate of the photoinitiator molecule after it has become electronically excited by photon absorption. It may, as shown in eq 2.4, dissociate into radicals, decay by fluorescence or be quenched by oxygen. The first reaction is desired as it produces the free radicals required for the initial attack, and the latter two are side reactions that have to be avoided.

The dissociation of the excited molecule into radicals can proceed via two reaction pathways, namely the Type I and Type II reactions.⁸⁻¹⁰

Type I reaction involves the homolytic decomposition of the excited molecule into a radical pair by a highly efficient α -cleavage process. Should there be solvent in the reacting mixture, the radicals will be trapped momentarily by a solvent cage and the radicals may decompose within it into neutral molecules that do not attack the monomers, and hence reducing the efficiency of the initiation. Besides decomposing, they may also recombine, and this does not affect the initiation efficiency. The radicals that survived would then diffuse away from the solvent cage and become the true ‘free radicals’ that launch the initial attack on the monomer molecules. Some examples of photoinitiators that undergo Type I reaction are acetophenones, bezoin ethers and acylphosphines, and their molecular structures are shown in Table 2.1.⁹ The reaction of 2, 2-dimethoxy-2-phenylacetophenone (commercially available as Irgacure 651 from Ciba Specialty Chemicals, Basel, Switzerland) is illustrated in eq 2.5 as an example of Type I reaction.¹¹

Type II reaction involves the reaction of the excited initiator molecule with a suitable hydrogen donating molecule RH by hydrogen abstraction. The radical pair is formed either by the homolytic cleavage of the $R-H$ bond or via an intermediate charge transfer complex followed by proton (H^+) transfer^{9,10}. Some examples of Type II photoinitiators are benzophenone, thioxanthenes and anthracinones, and their molecular structures are shown in Table 2.2.⁹ Benzophenone is used as an example to illustrate Type II reaction in eq 2.6.¹⁰ This example and that of the Type I in eq 2.5 shows the most visible difference between these two types of initiation; in Type I reaction, the initiator

molecule is cleaved into two smaller molecules whereas in the Type II one, the initiator molecules remains intact.

Benzophenone

Acetophenones

R1 = H, C₃H₇, OCH₃, OCH₂CH₂OH

R2 = CH₃, OCH₃, OC₂H₅

R3 = H, Ph, OH

Benzoin ethers

R1 = H, alkyl

R2 = H, alkyl, substituted alkyl

Acylphosphines

R = C₆H₅, OCH₃

Table 2.1. Examples of Type I photoinitiators.

Thioxanthones

Anthraquinones

Table 2.2. Examples of Type II photoinitiators.

2.2.1.1 Propagation

Following the initial attack of the free radical on the monomer molecule shown in eq 2.2, the propagation stage proceeds by the successive addition of a large number (up to thousands) of monomer molecules according to eq 2.7.⁸

2.2.1.2 Termination

There are two mechanisms by which termination could occur, leading to dead polymer chains.^{8,10} The first is by the combination (or coupling) of two live polymer chains, and the second, by their disproportionation in which a hydrogen radical that is *beta* to one of the radical centre is transferred to the other radical centre, resulting in one saturated polymer chain and another unsaturated one. The combination and disproportionation mechanisms as well as an example of each are shown in eqs 2.8 and 2.9 respectively.

For example:

For example:

2.2.1.3 Chain Transfer

Chain transfer refers to the transfer of an atom (usually hydrogen) to the growing polymer chain from some other species, such as the monomer or the photoinitiator, present in the system. The extension of the polymer chain is thus terminated prematurely, and this process effectively creates shorter chains, or equivalently, lower molecular weight polymer than if chain transfer has not occurred. The chain transfer mechanism is depicted in eq 2.10, in which the atom *X* in the species *XA* is being transferred to the growing polymer $M_n \bullet$. The new radical formed, $A \bullet$, reinitiates the polymerization reaction by attacking a new monomer, as depicted in eq 2.11.⁸

The effect of chain transfer on the polymer molecular weight presents the opportunity to synthesise polymer with a specifically desired molecular weight by adding special compounds known as chain transfer agents to control the chain transfer kinetics.⁸

A most interesting situation occurs when XA is also a polymer molecule, in which A is then a hydrogen atom. Such a chain transfer to polymer becomes more prevalent towards the end of the polymerization reaction when the polymer concentration is high. This reaction forms branched polymer as shown in eq 2.12, and thus, produces polymer of even higher molecular weight.

2.2.1.4 Influence of Oxygen

In photopolymerization reaction, where the polymerization is initiated by a photoinitiator, atmospheric oxygen exerts detrimental effects on the reaction on two fronts, namely, photoinitiator quenching and radical quenching. The former has previously been described in Section 2.2.1. In the latter, the oxygen reacts with the growing polymer chain to form peroxy radicals that are much less reactive towards double bonds as shown in eq 2.13.

These unwanted reactions lead to significant retardation and even inhibition of the polymerization. As evident, polymerization at air interface experiences the worst impediment because oxygen concentration is the highest there, about 10^{-2} M, as compared with 10^{-3} to 10^{-4} M in the bulk phase.¹⁰ Along the same line, thin coatings exposed to the atmosphere could be difficult to be UV cured as they have unfavourable surface-to-volume ratios, which create optimal conditions for oxygen diffusion into the coatings.

Fortunately, the peroxy radicals readily abstract hydrogen atoms from monomers, polymer chains, or additive molecules, and this reaction, called peroxidation and shown in eq 2.14, produces radicals.

Hence, in thin coating UV curing, if the consumption of oxygen and peroxidation are faster than the ingress of oxygen from the atmosphere, oxygen inhibition would be less prominent.¹⁰

2.2.2 Network Formation in Photopolymerization

When the monomer M contains only one site of unsaturation, i.e. has a structural formula like those in Figure 2.3, propagation leads to the lengthening of the polymer chains, and this is known as a linear system (eq 2.15).

In the case where there is more than one site of unsaturation, cross-linking of the polymer chains will also occur, leading to network formation, and this is known as a cross-linking system. The functionality of an acrylate refers to the number of unsaturation sites it possesses, and values ranging from two to six are common. Figure 2.4 shows an example of a difunctional monomer, 1, 6-hexanediol diacrylate (HDDA). Eq 2.16 depicts the possible reactions for a difunctional monomer.

Figure 2.4. Molecular structure of 1, 6-hexanediol diacrylate (functionality = 2).

The pendant bonds in the polymer chain are the results of the additional unsaturation sites, and they give rise to reactions unseen in linear systems. Reaction (a) depicts the simple chain elongation as per linear systems. Reactions (b) and (c) involve the pendant bonds and are hence peculiar to cross-linking systems. In Reaction (b), the radical attacks another polymer chain's pendant bond, leading to network formation, and in Reaction (c), the attack is on its own chain's, leading to cyclization. The overall effect is the formation of a complex and extensive network that traps the monomer molecules as well as the growing polymer chains, immobilizing them, and preventing them from diffusing and reacting further.

Cyclization is prevalent during the initial period of polymerization as the pendant bonds involved are closer to the radical sites, and compact structures, called microgels, are formed. Microgels can trap pendant bonds, rendering them incapable of further reactions because of steric hindrance. After the initial period, the microgels would combine to form a vast cross-linked network. Such is the scenario for the homopolymerization of a multi-unsaturated acrylates. The most undesirable consequence of this microgel formation is the inhomogeneity of the formed network, as this can lead to a significant reduction of its bulk mechanical strength as compared with a homogenous network.

In both types of system, the termination stage plays an important role in the photopolymerization kinetics. The termination stage consists of two main events in

sequence: the diffusion of two macro-radicals towards each other, and the chemical reaction between them when they finally meet. The chemical reaction is an extremely fast event compared with the macro-radicals' diffusion, and the observed termination rate is thus controlled by the diffusion step.

2.2.2.1 Propagation and Termination in a Linear System

In a linear system, there are generally three modes of radical diffusion, namely, translational diffusion, segmental diffusion, and reaction diffusion. The first refers to the diffusion of the centre-of-mass of the macro-radicals; the second, to the segmental re-orientation of two macro-radicals so that their ends with the radicals encounter each other; and the third, to the diffusion of radicals through the propagation reaction. This third mode may be the only way for a radical to diffuse when the evolving network starts to severely restrict all motions of the radicals, and the termination rate will then be closely pegged to the propagation rate.

Where translational and segmental diffusion are involved, the termination is said to be diffusion-controlled, as compared with reaction diffusion-controlled termination when the reaction diffusion mode is involved. These two termination modes are competitive events, and thus the observed termination rate will follow the faster mode. In the initial stage of photopolymerization, diffusion-controlled termination is much faster because the nascent network allows for relatively unimpeded diffusion. After some time, the evolving network will slow it down (as explained in the previous paragraph), and be overtaken by reaction diffusion termination.

Translational and segmental diffusion are co-operative actions that lead to termination, and hence the termination rate will depend on the slower diffusion mode. Enlargement of macro-radicals (another name for the growing polymer chains) as the polymerization proceeds is expected to have opposite effects on them. It slows down the translational diffusion, and speeds up the segmental one, and at some point during polymerization, the former would become the rate-determining step. In fact, it could be the rate-controlling step from the very beginning of photopolymerization, until when the reaction diffusion mode comes to the forth.

Whereas termination involves two large macro-radicals, propagation entails only one large macro-radical, plus another small monomer molecule. As such, propagation is much less hindered by diffusion. Its rate remains relatively unaffected while the termination rate suffers a steep decline, and this greatly boosts the photopolymerization rate. This is known as the gel or auto-acceleration effect. Auto-acceleration continues until a fairly high conversion is reached. When the propagation stage becomes diffusion-controlled due to the evolved network, and the propagation rate plummets. At this point, the termination rate would have been reaction diffusion-controlled, which causes it to follow the dive of the propagation rate. This step is known as auto-deceleration.

2.2.2.2 Propagation and Termination in a Cross-linking System

The above discussion on termination and propagation stages in a linear system could also be applied to a cross-linking system, but there are a few important differences.

The formation of microgels in the early stage of photopolymerization of a cross-linking system seriously suppresses diffusion-controlled termination, and reaction diffusion termination is the dominant mode from a lower degree of conversion. This means that the auto-acceleration process is very much shortened. The microgels formation would also impede the diffusion of the monomer molecules sooner than in the linear system, and thus causing auto-deceleration to set in earlier.

As shown in eq 2.16, radicals are trapped in the network. These radicals are no longer accessible for further reaction. Hence, radical trapping may be considered to be another termination mechanism, besides the usual combination and disproportionation mechanisms. A special feature of this monomolecular termination mechanism is that it is reversible because the trapped radicals could be reactivated by an increase in network mobility caused, most likely, by a temperature rise.

2.3 References

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Chapter 3

UV Embossing

UV embossing trials were firstly done for polyurethane acrylate-based as well as polyester-based formulations as these materials are known from experience to be highly embossable. These are followed by the PEG-based formulations. A nickel mold was used for these embossing trials. Aspect ratio achieved was about four. The dimensions of the embossed polymers and mold were measured using an optical profilometer, compared, and found to be in good agreement, proving this technique could give good replication. However, for some formulations, it was observed from SEM that there was prevalent peeling off of the top surface layer. The possible cause is discussed.

This chapter begins with a summary of the chemicals used, followed by the various sample preparation steps for embossing and characterization.

3.1 Chemicals

The oligomeric acrylates studied were poly(ethylene glycol) diacrylate with average molecular weight (M_n) of 700 purchased from Sigma-Aldrich (designated as PEG700) and poly(urethane) diacrylate supplied as EB210 from UCB Chemicals. The monomers studied were dipentaerythritol pentaacrylate, supplied as SR399, and trimethylolpropane triacrylate (TMPTA) from Sartomer Chemicals. The release agents investigated were a reactive silicone hexaacrylate and isodecyl acrylate, supplied as EB1360 from UCB Chemicals and SR395 from Sartomer respectively. Some of their physical properties are shown in Table 3.1; these data are all available in the respectively

companies' catalogue except unless it is specified otherwise in the table. All chemicals were used as received. Figure 3.1 illustrates the structures of the monomers and oligomers used except EB1360 and EB210, the structures of both have not been disclosed by their supplier (only the number of acrylate groups in them are reported, which are six and two respectively). However for EB1360, we had determined its molecular weight, M_n , to be about 3281 (with a polydispersity index of 1.34) using multi-angle light scattering (MiniDawn from Wyatt Technology Corp., Santa Barbara, CA). All of the photopolymerizations were initiated with the photoinitiator 2,2-dimethoxy-2-phenylacetophenone supplied as Irgacure 651 (Ciba Specialty Chemicals, Basel, Switzerland). Sodium hydroxide was purchased from Fisher Scientific, and Triton X-100 (t-Octylphenoxypolyethoxyethanol) and acetone (99+% purity) from Aldrich Chemical Co.

3.1.1 Acrylate Formulations and Their Preparations

Preparation of the acrylate formulations began with dissolving Irgacure 651 in HDDA to make a 15:85 (by weight) mixture in a bottle. This was to ensure the dissolution and homogenous distribution of Irgacure 651 in the formulations. In all the formulations used in this work, the amount of Irgacure 651 used was 0.2wt% of the acrylate mixtures i.e. if an acrylate mixture was 100 g, 0.2 g of Irgacure 651 would be required, and to obtain this amount, $0.2 / 0.15 = 1.333$ g of the 15wt% Irgacure 651 in HDDA mixture would be added to the acrylate mixture. As this amount was small compared with the overall weight, the additional HDDA added was insignificant. The components were pipetted into a bottle on a high precision weighing balance until their desired amounts were added. The bottle was manually shaken and then placed in an ultrasonic bath for several hours to ensure complete mixing. For highly viscous formulations, the bottle was first placed on a roller-stirrer for several hours since manual shaking was ineffective. All the bottles used were fully covered with aluminium foils to keep out the light and all preparations were done under dim lighting.

(a)

(b)

(c)

(d)

Figure 3.1. Chemical structures of (a) PEG700 (n=13, 32 C, 16 O), (b) SR399 (25 C, 12 O), (c) TMPTA (15 C, 6 O), and (d) SR395 (13 C, 2 O).

Name	Full Name	Supplier ^a	n ^b	MW	Density [g/cm ³]	Viscosity [mPa.s] at 25 °C	Surface tension [dyne/cm] at 20 °C	T _g [°C]
PEG700	Poly(ethylene glycol) diacrylate	Aldrich	2	700	1.12	~ 120 ^c	42.6	~ -42 ^d
SR399	Dipentaerythritol pentaacrylate	Sartomer	5	525	1.192	13,600	39.9	90
SR395	Isodecyl acrylate	Sartomer	1	212	0.881	5	28.6	-60
TMPTA	Trimethylpropane triacrylate	UCB	3	296	1.11	115	36	~ 36 ^e
HDDA	1, 6 hexanediol diacrylate	UCB	2	226	1.03	10	35	~ 43 ^f
EB830	Polyester hexaacrylate	UCB	6	1500	1.18	50,000	38	60
EB210	Polyurethane diacrylate	UCB	2	1500	1.11	1,300,000 ^g	N.A.	-19
EB1360	Silicone hexaacrylate	UCB	6	N.A.	1.11	2100	N.A.	N.A.

Table 3.1. Some properties of the acrylates used in this work

^a Aldrich refers to Aldrich Chemical Co., Milwaukee, WI; Sartomer refers to Sartomer Chemicals, Exton, PA; UCB refers to UCB Chemicals, Drogenbos, Belgium

^b n refers to the functionality of the chemical i.e. number of acrylate groups in the molecule.

^c PEG700's viscosity is not available in Aldrich's catalogue, and is actually that of Ebercyl 11, a PEGDA with MW of 740, from UCB Chemicals Co.

^d PEG700's T_g is not available in Aldrich's catalogue, and is actually that of SR 610, a PEGDA with MW of 742, from Sartomer Chemicals Co.

^e TMPTA's T_g is not available in UCB's catalogue, and is actually that of an equivalent product (SR 351) from Sartomer Chemicals Co.

^f HDDA's T_g is not available in UCB's catalogue, and is actually that of an equivalent product (SR 238) from Sartomer Chemicals Co.

^g EB210's viscosity is given as 3900 mPa.s at 60 °C in UCB's catalogue. The value at 25 °C is estimated using the Williams-Landel-Ferry (WLF) equation as follow.²

$$\log\left(\frac{\eta}{\eta_g}\right) = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

The 'universal values' of C₁ and C₂ are 17.44 and 51.6 respectively.²
At T = 60 °C, η = 3900 mPa.s. The value of η_g at T_g = -19 °C is then

$$\log\left(\frac{3900}{\eta_g}\right) = -\frac{17.44[60 - (-19)]}{51.6 + [60 - (-19)]}$$

$$\eta_g = 1.38 \times 10^{14} \text{ mPa.s}$$

The value of η at T = 25 °C is thus calculated.

$$\log\left(\frac{\eta}{1.38 \times 10^{14}}\right) = -\frac{17.44[25 - (-19)]}{51.6 + [25 - (-19)]}$$

$$\eta = 1.30 \times 10^6 \text{ mPa.s}$$

Prior to embossing PEG-based formulations, EB210 (polyurethane)-based and EB830 (polyester)-based formulations were tested. Polyurethane has high flexibility and low shrinkage whereas polyester has high strength and high shrinkage; these polymers were chosen as preliminary trial materials to illustrate that UV embossing is a very versatile technique that could be applied for materials with a diverse range of properties. Their compositions are shown in Table 3.2.

	Proportions [%]	
	EB210-based	EB830-based
EB210	65	-
EB830	-	65
SR399	20	20
HDDA	10	10
EB1360	5	5
Total	100	100
Irgacure 651	0.2	0.2

Table 3.2. Compositions of the EB210-based and EB830-based formulations.

Trials were then done with four PEG700-based formulations whose compositions are shown in Table 3.3. The additives in Formulations 1 and 2 were different release agents. The former had EB1360 (a silicone hexaacrylate) and the latter, SR 395 (isodecyl acrylate). For SR395, the long alkyl chain causes weak intermolecular interaction and this is evident from its low surface tension (28.6 dyne/cm; from Table 3.1). In Formulations 3 and 4, the proportions of EB1360 were different, the former having 1%, and the latter, 5%.

	Proportions [%]			
	Formulation 1	Formulation 2	Formulation 3	Formulation 4
PEG700	69	69	69	65
SR399	-	-	30	30
TMPTA	29	29	-	-
EB1360	2	-	1	5
SR395	-	2	-	-
Total	100	100	100	100
Irgacure 651	0.2	0.2	0.2	0.2

Table 3.3. Compositions of PEG-based formulations used in this work.

3.2 Features of the Embossing Mold

A round nickel mold, approximately 12 cm in diameter, with an orthogonal micro-array of raised squares separated by trenches was used in this project. In addition, its surface had been treated with an anti-adhesion silicone layer. SEM images of the mold are shown in Figure 3.2.

Figure 3.2. SEM images of the mold.

3.2.1 Dimensioning Scheme

It is noticeable, from Figures 3.2 to 3.4, that the corners of the mold's micro-cuboids are not absolutely sharp as the mold was made by photolithography using SU-8. In addition, the micro-cuboids are not perfectly uniform; each one differs slightly in shape and size from another. Naturally, the micro-cavities of the embossed polymer would not have sharp corners or be perfectly uniform. Due to the micro-scale of replication, it is impossible to make 'corresponding comparison', that is, to compare a particular micro-cuboid on the mold with the corresponding micro-cavity it produced on the embossed polymer. We could only obtain an average difference between the mold and embossed polymer by measuring a large number of random points (eight to be specific). In addition, we would have to eliminate the complications arising from the slight difference in the shape by devising a simple dimensioning scheme. In it, we define only four critical dimensions, that is, a , b , c and d , as shown in Figure 3.4, and measure them as straight lines. This scheme is actually adequate for our application because the feature size of the corners is generally in the region of $10^{-1} \mu\text{m}$ whereas the width and height dimensions we are interested in are in the range of $1 \mu\text{m}$, that is, one magnitude of order larger.

The dimensions of the mold were accurately determined with the optical profilometer. Figure 3.3 shows a top view image taken with the profilometer; Table 3.4, the critical dimensions at eight random locations on the mold; and Figure 3.4, the cross-sectional profile of the mold with the average critical dimensions inserted. The aspect ratio of the mold was calculated as follow.

$$\begin{aligned}\text{Aspect ratio} &= \frac{\text{height of trench}}{\text{average width of trench}} \\ &= \frac{52}{0.5(7.5 + 16)} \\ &= 4.4\end{aligned}$$

As some cured formulations were unable to peel off cleanly from the mold, the parts of the mold they had covered were irreparably damaged and were not used for subsequent embossing.

Figure 3.3. Top view image of the mold.

Critical dimensions [μm]					
No.	a	B	c	d	height
1	7.3	15.4	67.1	57.4	52.1
2	8.1	16.2	66.7	57.8	52.1
3	8.1	16.2	66.3	59.8	51.5
4	7.3	14.6	67.5	59.4	52.1
5	7.3	15.4	67.1	58.2	51.7
6	7.7	16.2	66.7	57.8	51.6
7	7.7	15.8	67.1	59.0	51.3
8	7.3	15.0	67.5	59.4	51.4
average	7.5	15.6	67.0	58.4	51.7
s.d.	0.4	0.6	0.4	0.9	0.3

Table 3.4. Critical dimensions at different locations on the mold (s.d. means standard deviation; a, b, c and d refer to dimensions shown in Figure 3.4).

Figure 3.4. Cross-sectional profile of the mold (values are obtained from Table 3.4).

3.3 Determination of UV Irradiation Times

In UV embossing, UV exposure must be controlled to achieve a degree of crosslinking such that two competing imperatives are simultaneously satisfied. Firstly, the cohesive strength of the embossing must be great enough to support demolding; this increases as exposure time and crosslink density increases. Secondly, the shrinkage and brittleness of the embossing must be limited to achieve faithful replication and avoid

cracking during demolding; this too increases with exposure time and crosslink density. A simple procedure was devised to determine the optimal UV exposure time for each formulation.

In this procedure, a nickel plate (0.040" $\times$ 5.0" $\times$ 5.0"; Nickel 200 ASTM B-162; from Priority Metals Inc., Anaheim, CA) was used as the substrate to simulate a microstructured nickel mold. The resin under test was coated onto a narrow strip (about 1cm) of Melinex[®] film (Type 454, Gage 300; from DuPont Teijin Films, Wilmington, DE) with a #28 wire-wound rod (from Paul N. Gardner Co., Pompano Beach, FL), and the strip was gently placed with resin-side facing down on the nickel plate. A wider strip (about 1.5 cm) of a step wedge (Type T4105C from Stouffer Graphics Art Equipment Co., South Bend, IN) was placed over the Melinex[®] film. This step wedge is a piece of plastic film with a graduated gray scale with optical density varying in 41 equal steps from 0.05 at one end to 1.00 at the other; its purpose here was to discretely grade the amount of UV radiation reaching the resin. This setup is illustrated in Figure 3.5. The curing reaction was performed with a UV flood exposure system (PK102 from I & J Fishnar Inc., Fair Lawn, NJ.). The area-averaged UV intensity at 365 nm was adjusted to be about 16 mW/cm². On areas of the step wedge where the transmitted UV intensity was high, the resin became solid; in other regions where the transmission was low, it remained liquid-like. By adjusting the UV exposure time energy dose in successive test cures for each formulation, the solid-to-liquid transition visually-evident on the nickel plate was controlled to coincide with the 13th step, which has an optical density of 0.65 (or equivalently a transmittance of $10^{-0.65} \times 100\% = 22\%$). This UV energy dose E_{gel} was the energy required to just cause the resin to gel; the exposure time was noted as the step-13 time of the resin. To prepare the XPS samples, the resin was exposed, without the overlay of the step-wedge, for its step-13 time and was thus given a UV energy dose of $1/22\% \times 100\% = 4.5 E_{gel}$. Assuming that the E_{gel} is independent of the UV intensity, this would translate to $t_{13} = 4.5 t_{gel}$, where t_{13} and t_{gel} are the step-13 time and gelation time respectively. This value, $4.5 t_{gel}$, is only an empirical estimate, obtained through our experience in embossing. A high multiple of t_{gel} is needed to ensure that the resin is sufficiently cured to attain good mechanical properties. However, excessively high multiple would generally cause micro-cracking of the walls of the embossed polymer due to severe shrinkage of the polymer. On the other hand, lower multiple would lead to

under-curing and the embossed polymer would be torn apart during the demolding step. This method provided each formulation with a controlled and specific UV energy dose, resulting in a defined and appropriate degree of crosslinking for the different formulations. Nevertheless, t_{13} is only a rule-of-thumb guide and has to be fine tuned for some formulations. For these formulations, we found that using slightly shorter irradiation time would reduce the extent of micro-cracking without compromising the mechanical integrity of the embossed film during demolding.

Figure 3.5. Schematic of the step wedge experiment setup for finding the step-13 time.

3.4 UV Embossing Procedure

The formulation was coated onto a narrow strip (~ 1 cm) of Melinex film (Gage 300) using the #60 wire-wound rod (from Paul N. Gardner Company), which gives the coating an approximate thickness of $150\ \mu\text{m}$, and the strip was placed gently onto a clean area on the mold. (The mold was beforehand cleaned by rinsing it with acetone and air-dried.) After this, it was laminated between rubber-coated rollers of a laminator (GBC ‘Eagle 35’ laminator from JSI Corp., Atlanta, GA) as shown in Figure 3.6a. It was subsequently irradiated with the flood UV exposure system (Figure 3.6b). After the exposure, the back of the Melinex film was glued to a rigid acrylic disc with an aluminium holder using a double-sided tape (VHB Type 4950 double-sided tape from 3M, St Paul, MN). The disc, with the attached embossed film, was then pulled out from the mold perpendicularly (Figure 3.6c).

Figure 3.6. Schematic of the embossing procedure.

Some variations of this procedure were also used.

- For the highly viscous EB210-based formulation, it was diluted with acetone to 67wt% before being coated onto the Melinex film using the #60 wire-wound rod. The coating was left in a fume cupboard for 15 minutes to allow the acetone to evaporate away. As the densities of EB210 and acetone are about the same ($\sim 1.1 \text{ g/cm}^3$), the coating thickness after the acetone had evaporated away would be $229 \times 0.67 = 153 \text{ } \mu\text{m}$, which was about the same as that produced by the #60 wire-wound rod.

- For the PEG-based formulations, they were too fluid to allow coating on the Melinex film because they would spread out rapidly. In addition, the fluidity of the formulations made the #60 wire-wound rod too large for use with them. Hence, they were coated onto the nickel mold directly using the #28 wire-wound rod (resulting coating thickness is about 60 μm) and the Melinex films were laminated over them.

3.5 SEM and Optical Profilometer Characterization

SEM images were taken using Jeol JSM 5600 scanning electron microscope from Jeol USA, Inc, Peabody, MA. The embossed polymers were coated with a layer of gold using a gold coater at 12 μA for 1.5 minutes to make their surfaces electrically conductive before being examined with the SEM. A tilt of 30 ° was used to capture the three-dimensional view of the mold and the embossed polymers.

The optical profilometer used for measuring the dimensions of the embossed polymer and mold was Wkyo NT 2000 optical profilometer from Veeco Instruments Inc, Woodbury, NY.

3.6 Results and Discussion

The results of the step-13 times are first presented, and are followed by the SEM and optical profilometer characterisation of the embossed formulations, and a comparison of the critical dimensions of the embossed formulations and the mold.

3.6.1 Step-13 Times

The step-13 times of the acrylates and formulations are shown in Table 3.5. Further analysis of the step-13 times will be covered in the next chapter in Section 4.4.5.

Acrylate/Formulation	Step-13 time [s]
PEG700	13
SR399	15
TMPTA	45
EB1360	$2 \times 31^{\dagger}$
SR395	45
EB210-based formulation	11
EB830-based formulation	13
PEG-based Formulation 1	14
PEG-based Formulation 2	10
PEG-based Formulation 3	15
PEG-based Formulation 4	16

Table 3.5. Step-13 times of the acrylates and formulations († due to the limitation of the UV flood system, a single exposure could not exceed 45 s, and hence, two exposures, with an intermission of about 30 s, were used).

3.6.2 Characterization of Embossed Polymers

The SEM images of the embossed polymer from various formulations are discussed first. This is followed by a comparison of the dimensions of the embossed PEG-based formulations with those of the mold. Dimensioning was not done for EB210- and EB830-based formulations because these were only trial materials used to show that they could be conveniently UV embossed as well, and hence, exact dimensioning was not warranted.

3.6.2.1 Polyurethane (EB210)-based Formulation

There was much success in embossing polyurethane-based formulation. Using its step-13 time (11 s) as the irradiation duration, regions (approximately 1 cm by 1 cm) of defect-free microstructures were produced and a part of it was shown in the SEM images in Figure 3.7.

Figure 3.7. SEM images of EB210-based formulation.

3.6.2.2 Polyester (EB830)-based Formulation

The polyester-based formulation also yielded good result. The SEM images were for an irradiation time of 10 s, three seconds shorter than the formulation's step-13 time.

Figure 3.8. SEM images of EB830-based formulation.

3.6.2.3 PEG-based Formulations

Table 3.6 presents the embossing results of the PEG-based formulations.

Formulation No.	Step-13 time [s]	Irradiation time [s]	Figure No.	Description
1	14	11	Figure 3.9	Defect-free microstructures.
2	10	8	Figure 3.10	Defect-free microstructures.
3	15	12	Figure 3.11	Surface peeling.
4	16	14	Figure 3.12	Worse surface peeling.
4	16	16	Figure 3.13	Worst surface peeling.

Table 3.6. Embossing results of PEG-based formulations.

Formulations 1 and 2 both gave good embossing results, as evident from Figure 3.9 and Figure 3.10 respectively, although the release agents used were different. Formulations 3 and 4 had used SR399 as the diluent instead of the TMPTA used in Formulations 1 and 2. Apparently, as shown in Figure 3.11 to Figure 3.13, this caused the

surface that was in contact with the mold during embossing to peel. The peeling exacerbated when the proportion of EB1360 was increased from 1% in Formulation 3 to 5% in Formulation 4.

Figure 3.9. SEM images of embossed PEG-based Formulation 1 (irradiation time 11 s).

Figure 3.10. SEM images of embossed PEG-based Formulation 2 (irradiation time 8 s).

Figure 3.11. SEM images of embossed PEG-based Formulation 3 (irradiation time 12 s).

Figure 3.12. SEM images of embossed PEG-based Formulation 4 (irradiation time 14 s).

Figure 3.13. SEM images of embossed PEG-based Formulation 4 (irradiation time 16 s).

3.6.2.4 Comparison of Dimensions

The top view image taken with the optical profilometer of the embossed PEG-based Formulation 1 is shown in Figure 3.14. The embossed polymer dimensions (a' to d') are shown in Table 3.7 and Figure 3.15. The wall of the embossed polymer is $7.3 \pm 0.7 \mu\text{m}$ at the top (a'), $13.8 \pm 0.9 \mu\text{m}$ at the bottom (b'), and, and $52.2 \pm 1.5 \mu\text{m}$ high. These values are in close agreement with those corresponding ones of the trench of the mold, which are $7.6 \pm 0.4 \mu\text{m}$ (a), $15.6 \pm 0.6 \mu\text{m}$ (b) and $51.7 \pm 0.3 \mu\text{m}$ respectively, taking into account the standard deviations of the measurements involved. Similarly, the trench of the embossed polymer is about $67.1 \pm 0.9 \mu\text{m}$ at the top (c') and $59.4 \pm 0.8 \mu\text{m}$ at the bottom (d') and these compares well to those corresponding ones of the wall of the mold, which are $67.0 \pm 0.4 \mu\text{m}$ (c) and $58.6 \pm 0.9 \mu\text{m}$ (d) respectively. In terms of the height of the microstructures, the embossed polymer and the mold compare favorably, the former being $52.2 \pm 1.5 \mu\text{m}$, and the latter $51.7 \pm 0.3 \mu\text{m}$.

Figure 3.14. Top view image of the embossed PEG-based Formulation 1.

No.	Mold's Dimensions [μm]					PEG Formulation 1's Dimensions [μm]				
	A	b	c	d	height	a'	b'	c'	d'	height
1	7.3	15.4	67.1	57.4	52.1	8.1	12.9	66.3	60.2	52.5
2	8.1	16.2	66.7	57.8	52.1	6.1	12.5	66.7	57.8	52.0
3	8.1	16.2	66.3	59.8	51.5	7.3	14.1	66.7	59.0	53.1
4	7.3	14.6	67.5	59.4	52.1	7.7	14.1	66.7	59.4	52.8
5	7.3	15.4	67.1	58.2	51.7	6.5	14.1	68.7	59.8	49.6
6	7.7	16.2	66.7	57.8	51.6	7.3	15.0	67.1	59.0	53.3
7	7.7	15.8	67.1	59.0	51.3	7.7	14.6	66.3	59.4	50.4
8	7.3	15.0	67.5	59.4	51.4	7.7	12.9	68.3	60.2	53.7
mean	7.6	15.6	67.0	58.6	51.7	7.3	13.8	67.1	59.4	52.2
s.d.	0.4	0.6	0.4	0.9	0.3	0.7	0.9	0.9	0.8	1.5

Table 3.7. Critical dimensions of embossed PEG-based Formulation 1 (mold's dimensions are reproduced from Table 3.4 for easy comparison; s.d means standard deviation)

Figure 3.15. Cross-sectional profile of embossed PEG-based Formulation 1.

3.7 Conclusions

UV embossing of acrylates were successfully demonstrated. Polyurethane-based and polyester-based formulations are easily embossed, giving almost defect-free microstructures, as seen from the SEM images. PEG-based formulations could also yield similar results, but when the amount of silicone acrylate was increased to 5%, serious

surface peeling occurred. The cause of this surface peeling could be the segregation of a particular component of the formulation at this surface; this could adversely affect the mechanical integrity of the surface, making it prone to be peeled off when the embossed polymer is demolded. This is the subject of investigation of the next chapter. The dimensions of a defect-free embossed polymer from a PEG-based formulation were measured using an optical profilometer and compared with the corresponding ones of the mold, and they were found to be in good agreement, proving that the UV embossing technique could replicate microstructure faithfully.

3.8 References

- ¹ Sperling, L. H. *Introduction to Physical Polymer Science*, 2nd Ed., Wiley: New York.

Chapter 4

Effects of Silicone Acrylate on Morphology, Kinetics and Surface Composition of Photopolymerized Acrylate Mixtures

Films (*ca.* 150 μm thick) of twelve acrylate mixtures which contained various proportions of hydrocarbon acrylates [mainly poly(ethylene glycol) diacrylate; (PEGDA)] and small amounts of a silicone hexaacrylate (in proportion of 5% or less), were cured on a nickel substrate. XPS analysis of the nickel-side surface compositions showed that for formulations with and without the silicone hexaacrylate, this surface was enriched with PEGDA and saturated (up to 50%) with the silicone hexaacrylate respectively. The silicone hexaacrylate phase separated and formed micelles which migrated to the resin-nickel interface. Silicone hexaacrylate, inherently less reactive, also significantly slowed the photopolymerization of the mixtures. The sequential homopolymerization of PEGDA and silicone hexaacrylate in a formulation was elicited using real-time FTIR. The Design of Experiment approach was used to quantify the influence of the components on gelation time and the nickel-side surface composition as well as provide the statistical models to predict these two properties for new compositions.

4.1 Introduction

In UV embossing, the resin is typically a mixture of acrylates carefully selected to control characteristics such as viscosity, adhesion to mold and shrinkage in order to optimize the resin processability and performance. These acrylates may differ in their functionalities, molecular weights and chemical characteristics. Oligomers such as urethane acrylate and epoxy acrylate impart flexibility, strength and hardness to the cured resin; monomers such as 1,6-hexanediol diacrylate (HDDA) and trimethylopropane triacrylate (TMPTA) reduce the viscosity of the liquid resin so as to improve mold filling; high functionality monomers like dipentaerythritol pentaacrylate increase the extent of crosslinking in the cured resin and thereby enhance its solvent and thermal resistance; reactive mold release agents such as silicone-based acrylates prevent adhesion of the cured resin to the mold and thus facilitate the demolding process.¹ Regarding the last point, the use of silicone acrylates is usually an additional measure to pre-treatment of the mold with an anti-stick coating, which by itself, may not be adequate to effectively prevent mold-polymer adhesion. The resin is hence a complex polymer blend and the macromolecular structure attained upon curing is expected to be inhomogenous.²

Preferential segregation at surfaces and interfaces is a general phenomenon known to occur in almost all polymer blends, and is caused by the difference in the solubility parameters and surface energies of the components³. In particular, when silicones or their copolymers, with their low surface tensions (20-22 mN/m) and solubility parameters ($14-16 \text{ (J/cm}^3)^{1/2}$), are blended with hydrocarbon polymers (whose values are 30-50 mN/m and $16-28 \text{ (J/cm}^3)^{1/2}$ respectively), readily phase-separate in bulk and migrate to the polymer blend-air interface to lower the surface energy as favored by thermodynamics.³ In addition, their micellization would occur when present in excess of their critical micelle concentrations (cmc).^{4,5} It has also been reported that the type of substrates may cause anomalous segregations at the polymer blend/substrate interfaces.^{5,6}

It is our experience that silicone acrylates, when added in the recommended amounts of 3-5 wt%⁷ to hydrocarbon acrylates, caused the blends to become macro-emulsions, the former being the dispersed phase (*ca.* 10 μm in diameter). The resulting haziness is of concern because it would increase the optical attenuation due to light scattering, adding to that caused by the absorption of the photoinitiator. Optical

attenuation is responsible for the non-uniformity in photoinitiation rate,^{8,9} and consequently decreased monomer conversion rate,¹⁰ in the direction where the UV light penetrates the system. Thus far, we have not found any literature addressing this issue of haziness on polymerization kinetics. The formation of macro-emulsions also affects the morphology of the interpenetrating network formed because phase separation before crosslinking would enlarge the phase domains.^{4,11}

One of our aims is to study systematically how each component in a formulation affects the performance of the formulation in UV embossing (and eventually to design the optimum formulations). In most cases, the characteristics of a formulation e.g. viscosity depend on the relative amounts of the components. Clearly, it is not possible to adjust the proportion of one component without affecting the proportions of the remaining ones (since their sum must be unity), and hence, changes to the characteristics of the formulation could not be unambiguously attributed to the effect of just one component. However, by careful and systematic adjustments to the proportions and analysis of the results, it is possible to elicit unequivocally the individual effect of each component, and this method of approach is known as the mixture experiment method, which is a kind of design-of-experiment (DOE) technique. Mixture experiment method has been widely used for such analysis-and-design of mixtures,^{12,13} for example, in the optimization of paint formulations¹⁴ and pharmaceutical drugs^{15,16}. The main difference between mixture experiment and other DOE techniques such as factorial experiment is that in the latter, a factor could be changed while holding the others constant, and as explained above, such adjustments are not possible in the former.¹³ If a mixture has a large number of components (≥ 6), then it is likely that some of them would be significantly more important than the others in determining certain characteristics of the formulations. Hence, it is useful to screen out the unimportant components, so that future mixtures would be simpler and more economical to formulate. Details of the exact mathematical treatment are presented in the Experiment section.

In this study, correlation of the composition of thin films (about 150 μm) of mixtures of hydrocarbon acrylates (principally poly(ethylene glycol) diacrylate) and a silicone hexaacrylate to the gelation time and surface composition measured by X-ray photoelectron spectroscopy (XPS) was carried out. The critical component here was the silicone acrylate as its presence in a formulation significantly altered these two properties.

The effects of the silicone acrylate on the morphology, optical properties and polymerization kinetics of the formulation were investigated to determine if they could account for the silicone hexaacrylate's influence on the gelation time and surface composition. In addition, real-time FTIR would be used to track the sequential polymerization kinetics of the silicone hexaacrylate and hydrocarbon acrylate domains. While it is recognized that the silicone hexaacrylate may also affect the mechanical properties of the cured formulation, it is not in the scope of this investigation.

4.2 Experiment Section

4.2.1 Chemicals

The chemicals used are described in Table 3.1.

Twelve formulations were mixed and their compositions are shown in Table 4.1 (the design of the formulations is dealt with in Section 4.3). The amount of Irgacure 651 used was 0.2% of the total weight of the acrylates.

Formulation	Proportions [%]						Total
	PEG700	EB210	SR399	TMPTA	EB1360	SR395	
1	0.7	0	0	0.3	0	0	1
2	0.7	0.15	0	0	0.05	0.1	1
3	0.5	0.3	0	0.1	0	0.1	1
4	0.5	0	0.05	0.3	0.05	0.1	1
5	0.5	0.15	0.3	0	0.05	0	1
6	0.5	0	0.3	0.1	0	0.1	1
7	0.7	0	0.25	0	0.05	0	1
8	0.5	0.2	0	0.3	0	0	1
9	0.573	0.116	0.116	0.116	0.027	0.053	1
10	0.5	0	0.05	0.3	0.05	0.1	1
11	0.5	0	0.3	0.1	0	0.1	1
12	0.7	0	0	0.3	0	0	1

Table 4.1. Compositions of formulations.

4.2.2 UV Irradiation Time

The UV irradiation times for each of the formulations were determined as described in Section 3.3.

4.2.3 X-ray Photoelectron Spectroscopy (XPS)¹⁷

A #90 wire-wound rod (Paul N. Gardner Company, Inc. Pompano Beach, FL) was used to coat the resin onto a Melinex[®] film (Type 454, Gage 300; DuPont Teijin Films, Wilmington, DE). The coated film was then gently placed on a nickel plate (0.040" × 5.0" × 5.0" Nickel 200 ASTM B-162) from Priority Metals Inc., Anaheim, CA) so that the resin became sandwiched between the nickel plate and the Melinex[®] film. This nickel plate had been pre-cleaned by immersing it in ultrasonic baths of acetone, hexane, 5wt% sodium hydroxide in double distilled water and 1 wt% Triton X in double distilled water each for thirty minutes. Finally, it was rinsed four times with double distilled water, each time with a fresh bath and a thirty-minute ultrasonic immersion. The plate was then dried in an oven at 120°C for 1 hour and left to cool in a desiccator at 40% humidity and 25°C.

After UV curing the formulation for its step-13 time, the film, about 150 μm thick, was lifted carefully from the nickel plate and its nickel-side surface was then characterized by XPS. The measurements were made on an AXIS Ultra spectrometer (Kratos Analytical Ltd., Surface Analysis Product Group, England) with a monochromated Al Kα X-ray source (1486.6 eV). It comes with a concentric hemispherical electron energy analyzer and a hybrid electrostatic-magnetic lens. Working in the fixed analyzer transmission mode, the energy resolution is 25 meV and the pass energy used was 40 eV. The sampling area on the specimen was typically about 700 μm by 400 μm. A step-scan interval of 1 eV was used for wide scans and 0.1 eV for high-resolution scans, and for both, the acquisition times were the same at 60 s. The UV cured film on the Melinex[®] substrate was mounted on the standard sample stud using a double-sided adhesive tape. The X-ray source was operated at a reduced power of 150 W (15 kV and 10mA). The operating pressure in the analysis chamber was maintained at 3.0x10⁻⁹ Torr or lower during the measurements. The core-level spectra were obtained at a photoelectron take-off angle (measured with respect to the sample surface) of 90°. Two

spots were analyzed per sample, and for Formulations 1, 4 and 6, their replicates (Formulations 12, 10 and 11 respectively) served as further checks.

The Vision software package (pre-release version 2.1.3; May 28, 2002) was used for data processing and analysis. Background subtraction was performed using the linear method. The peak synthesis procedure closely followed that used by Beamson and Briggs¹⁸ and is briefly described here. The molecular structures of the chemicals were used to decide the number and positions of the component peaks in the core-line envelope curve. The peaks were synthesized using the Gaussian (70%)-Lorentzian (30%) functions. After inputting a set of initial guesses for the values of peak position, height and full-width-at-half-maximum (FWHM), the fitting was iterated until the chi-square converged. The FWHM values for all the synthesized peaks were checked to be approximately equal ($\sim 1.5 \pm 0.2$), and if otherwise, the fitting procedure was repeated using a different set of initial guesses. The reference binding energy used is 284.5 eV for saturated hydrocarbon C(1s).¹⁹ For quantification, the relative sensitivity factors used are from the library in the software package and the value for carbon is 0.278; oxygen, 0.780; silicon, 0.328; and nitrogen, 0.477. Atomic concentrations of the components were quantified using the areas under the peaks. When necessary, the detection limit, defined as the concentration that would give rise to a signal peak (after background subtraction) that is three times the standard deviation of the background noise peaks (after background subtraction), is also calculated.²⁰

4.2.4 UV-Vis Spectrophotometry

A Shimadzu UV3101PC UV-Vis spectrophotometer was used to measure the absorbance of the acrylates used in this study and measurements were made on dilute solutions (0.1 to 0.3 wt%) of the acrylates in toluene in quartz cuvettes with 1 cm pathlength; the reference used was a similar quartz cuvette filled with toluene.

The transmittance of the actual formulations, in various film thickness approximate to those used in UV embossing, was also measured. The formulations were sandwiched between two quartz plates with a spacer made from Melinex[®] film and by using different thickness of the Melinex[®] film (from 75 μm to 175 μm), the thickness of

the films of formulations was varied. A quartz plate was used as the reference to take into account the reflection loss.

4.2.5 Real-time Infrared Spectroscopy

The real-time conversions of the acrylates were tracked using a Nicolet Magna IR 560 ESP spectrophotometer (Thermo Nicolet Corp., Madison, WI) incorporated with a 'Golden Gate' ATR module (Graseby Specac Inc., Smyrna, GA). A bead of the sample was dropped gently on the ATR diamond crystal and within a ring of Melinex[®] film (Type 454, Gage 300). The sample was then covered with a thin (2 mm) glass plate. The Melinex[®] film helped to control the thickness of the sample within the range of 140 μm to 160 μm . Data collection was started and continued for 10 seconds for the uncured sample before the UV light was switched on. The UV source used was a Superlite SUV-DC-P UV spot cure unit with a Series 300 liquid light-guide (diameter 8mm) (Lumatec GmbH, Deisenhofen, Germany). The end tip of the light guide was placed at a distance from the ATR crystal such that the UV intensity reaching the formulation was 16 mW/cm^2 . After a curing period of 90 seconds, data collection was stopped and the UV light switched off. The cured sample was then carefully removed and its thickness measured with a micrometer. The spectral resolution used was 4 cm^{-1} and spectra were collected at approximately one-second interval.

4.2.6 Optical Microscopy

The optical microscope used was a Olympus IX51 fitted with a IX2-SLD phase contrast and a DP70 camera. All images were taken with 40X magnification.

4.2.7 SEM/EDX

The cured films were fractured and mounted on SEM sample stubs with the cross-sections of the films exposed. The films are coated with platinum prior to SEM/EDX analysis. The samples were examined using a Hitachi 4100 field emission SEM equipped with a Quantum energy dispersive X-ray detector (Kevex Instruments). The accelerating voltage is 15 keV and the working distance is 15mm. X-ray dot maps of C, O, N and Si were collected from each sample. Two areas were investigated for each sample.

4.3 Mixture Experiment

This was primarily a screening experiment to help us quantify the relative importance of the six components in influencing the step-13 time of a formulation as well as the nickel-side surface silicon content of its cured film. Clearly, the two responses, step-13 time and surface silicon content, depend only on the proportions of the components in the formulation and not the amount of the formulation, and thus, the mixture experiment method is employed. For a screening experiment, the first-degree Scheffé model is typically used:¹³

$$y = \sum_{\text{all } i} b_i x_i \quad (4.1)$$

where y is the response, and x_i and b_i are the proportion and the parameter estimate of component i . The ranges of proportions of the components were determined from preliminary trials as well as information supplied by the chemical suppliers and they were $0.5 \leq x_{PEG700} \leq 0.7$, $0 \leq x_{EB210} \leq 0.3$, $0 \leq x_{SR399} \leq 0.3$, $0 \leq x_{TMPTA} \leq 0.3$, $0 \leq x_{EB1360} \leq 0.05$ and $0 \leq x_{SR395} \leq 0.1$. For a first-degree model with six components, six design points were needed. To test for the lack-of-fit of the model, three replicates and three augmenting points were added, leading to a total of twelve design points. Design Expert software (version 5.0.7; Stat-Ease Corporation, Minneapolis, MN) was used to generate these design points based on the D-optimality criterion, which minimizes the variances of the parameter estimates,¹³ and they are listed in Table 4.1.

Typically, when the proportions do not span from zero to one, the actual values of the proportions are not used for analysis, but are transformed into L -pseudo-components' proportions (eq 4.2) because this would improve the accuracy of the coefficient estimates (see Appendix for details).

$$x'_i = \frac{x_i - L_i}{1 - \sum_{\text{all } j} L_j} \quad (4.2)$$

where L_i is the actual lower bound of component i . As follows from the eq 4.2, $0 \leq x'_i \leq 1$ and $\sum x'_i = \sum x_i = 1$. When the accuracy of the coefficient estimates is assured, we could then meaningfully interpret the values of the coefficient estimates. For a more rigorous treatment, suitable for cases in which the components' proportions are highly constrained, another technique known as response tracing¹³ was used to analyze the effects of the

components on the responses; briefly, in this technique, a reference formulation is chosen as the starting formulation and the change to the response was traced as the proportion of a specified component was varied and the relative proportions of the remaining components kept constant.

4.4 Results and Discussion

4.4.1 Optical Properties of the Acrylates and Their Formulations

All the acrylates used, except EB1360, were found to be non-absorbing at 365 nm, which is the wavelength of one of the main emission peaks of the mercury lamp. EB1360, which is orange-red in color, shows increasing absorbance from the blue end of the visible spectrum to the UV region (Figure 4.1).

Figure 4.1. Absorbance of solutions of EB1360 in toluene with a pathlength of 1 cm (insert shows the absorbance at 365 nm as a function of concentrations and the slope gives the absorption coefficient of EB1360 at 365 nm as 9.823 ml/g-cm).

Figures 4.2(a) and 4.2(b) present the optical microscope images of Formulations 1 (without EB1360) and 4 (with 5% EB1360), which typify the cases of a formulation without and with EB1360 respectively, and they show that the former is optically clear whereas the latter have globules of EB1360 with diameters ranging from a few microns to 10 μm dispersed throughout the formulation, causing it to be hazy. As explained in the introduction, the phase separation is due to the large disparity in the surface tensions and solubility parameters of silicone and hydrocarbon polymers. Thus, for formulations not containing EB1360, the only cause of light attenuation would be the adsorption of the photoinitiator, whereas for formulations containing EB1360, there are two additional

sources of light attenuation, namely, the absorption of EB1360 and the scattering caused by the EB1360 globules.

Figure 4.2. Optical microscope images of (a) Formulations 1 and (b) 4.

This increase in attenuation was illustrated by difference in the transmittance, at 365 nm, of Formulations 1 and 4 in Figure 4.3. For film thickness of less than 100 μm, the difference in transmittance was merely 1 to 2 %. As the thickness increased, the disparity widened; at above 200 μm, the gap was greater than 8%. Nevertheless, a difference in transmittance of this magnitude would not significantly affect the double bond conversion rate, which was tracked using real-time ATR-FTIR spectroscopy on the vinyl C-H scissoring vibration²¹ at around 1407 cm⁻¹ (the methyl C-H stretching²² at around 2862 cm⁻¹ was used as the internal reference). For Formulation 4, its transmittance was reduced by 10%, from 96% to 86%, by increasing its thickness from 50 μm to 220 μm, but its maximum rate of conversion, $R_{p, max}$, remained constant at about

0.15 s^{-1} ; and for the case of Formulation 1, the reduction was only about 5%, from 98% to 93% and the maximum rate of conversion was constant at about 0.32 s^{-1} . The reason for the apparent independence of $R_{p, \max}$ on film thickness is that the transmittance for both cases was still very high, corresponding to an absorbance of less than 0.1, and for such low absorbance, the spatial variation in the photoinitiation rate^{8,9} and conversion rate is negligible.¹⁰

Figure 4.3. Transmittance at 365 nm of Formulations 1 ($\square$) and 4 ($\circ$); maximum rate of polymerization for Formulations 1 ($\blacksquare$) and 4 ($\bullet$).

4.4.2 SEM/EDX Analysis of Cured Films of Formulations

The cross-sectional elemental compositions of the cured formulations were of interest as they would reveal if there was any change to the phase separation in formulations containing EB1360 during the photopolymerization process. Figure 4.4 shows the SEM and EDX mapping images of the cross-section of a film of Formulation 4, which contained EB1360. Carbon and oxygen are largely homogenous throughout the entire cross-section whereas silicon is concentrated in a few globules between a few microns and $10 \mu\text{m}$ in diameter, and these globules clearly came from those in the uncured formulation Figure 4.2(b)). Hence, the cured film retained the kind of phase separation that already existed in the uncured state. Besides the large globules, there are also many small specks of silicon (*ca.* $1 \mu\text{m}$) dispersed throughout the entire thickness almost homogeneously, and we interpret them to be the cured silicone acrylate micelles.

Figure 4.4. SEM/EDX images of the cross-section of a cured film of Formulation 4: (a) SEM image, (b) EDX mapping of carbon, (c) of oxygen, and (d) of silicon.

4.4.3 Sequential Homopolymerization of PEG700 and EB1360

Using ATR-FTIR, it was elicited that in the two-phase PEG700-EB1360 mixture, each phase homopolymerize within itself, and in a sequential order as explained below. The double bond conversion of pure PEG700, pure EB1360 and a 90/10 (w/w) PEG700/EB1360 mixture (all with an additional 0.2% Irgacure 651) were tracked at two wavenumbers, approximately 810 cm^{-1} and 1407 cm^{-1} , which represent the olefinic C=C twisting vibration and vinyl C-H scissoring vibration respectively.²¹ For the internal reference, the methyl C-H stretching vibration at approximately 2862 cm^{-1} was used.²² Unlike PEG700 which had a diminishing peak at approximately 810 cm^{-1} (Figure 4.5(a)), the silicone acrylate did not have a 810 cm^{-1} peak corresponding to the olefinic C=C twisting.²³ The peak at approximately 800 cm^{-1} was due to the rocking vibration of CH_3 in the Si- CH_3 bond and thus it did not diminish during polymerization (Figure 4.5(b)). Thus, for the mixture, the diminishing 810 cm^{-1} peak (Figure 4.5(c)) represented the double bonds of PEG700 only and not of EB1360, and the 1407 cm^{-1} peak represented the double bonds of both of them. In Figure 4.5(d), conversion profiles of PEG700 tracked using both 810 cm^{-1} and 1407 cm^{-1} peaks were found to coincide, showing that the conversion profiles followed using the two different peaks were consistent. For the 90/10 PEG700/EB1360 mixture, the conversion profile tracked using the 1407 cm^{-1} peak (representing the entire mixture) coincided with that using the 810 cm^{-1} peak (representing the PEG700 fraction of the mixture) in the first 11 seconds, suggesting that only the PEG700 fraction was homopolymerizing during this period. After the 11th second, the 1407 cm^{-1} profile continued to increase while the 810 cm^{-1} one had nearly reached a plateau. This timing closely coincided with the start of the polymerization of the pure EB1360 as well as the end of polymerization of the pure PEG700. Hence, we infer that during the period after the 11th second, only the EB1360 was polymerizing. Thus, a mixture of PEG700 and EB1360 would phase-separate due to the difference in their surface tensions and solubility parameters and each phase would homopolymerize within itself.

Figure 4.5. (a) IR spectrum of PEG700 in the 810 cm^{-1} region; (b) IR spectrum of EB1360 at the 800 cm^{-1} region; (c) IR spectrum of 90/10 (w/w) PEG700/EB1360 mixture in the 810 cm^{-1} region; (d) Conversion profiles of EB1360 and PEG700 systems tracked using two different peaks (the numbers in brackets are the wavenumbers, in cm^{-1} , of the peaks tracked).

4.4.4 XPS Analyses of Nickel-side Surfaces of Cured Films

The results of the XPS analyses on the nickel-side surfaces of the cured films of the six individual components are tabulated in Table 4.2 and a set of representative XPS spectra are shown in Figure 4.6. In this and the subsequent tables, the measured values are averages of two readings with standard deviations of less than 10% of the average value. The XPS wide-scan spectrum of the PEG700 (Figure 4.6(a)) has strong C(1s) and O(1s) peaks and this coincides with its chemical structure (Figure 1a of Chapter 1). This was also found for TMPTA, SR399 and SR395. The wide-scan spectrum of cured EB210 (Figure 4.6(b)) shows also the N(1s) peak attributed to the urethane linkage in the polymer, and that of silicon-containing EB1360 (Figure 4.6(c)) shows the presence of Si(2p) peak. In Table 4.2, the relative percentages of carbon, oxygen, nitrogen and silicon measured on the nickel-side surfaces of films made with PEG700, SR399, TMPTA and SR395 are compared with those calculated from their known chemical structures. It is noted that the high-resolution scans for Si(2p) of the non-silicon containing components turned up small Si(2p) peaks and they were quantified to be less than 1 atomic%, and for some, are very close to its detection limit (0.1 atomic%). We believe this to be the result of minor contamination caused by the repeated use of the nickel mold despite the rigorous cleaning regime used (see Section 4.2.3). It is likely that there would be some silicone, which is known to be extremely difficult to remove from surfaces, left on the mold. From the small values of the silicon concentration measured, it is reassuring that this contamination was only a very minor one and has no bearing on our results. For nitrogen, except in EB210, the measured values are less than its detection limit (0.2 atomic%). Measured values of the C and O contents for PEG700, SR399 and TMPTA are relatively close to the calculated values. Those for SR395 deviate from the calculated values; the measured oxygen content appears relatively high. This could be attributed to the oxidation of SR395, which has a relatively long pendant alkyl side chain. Clark and Thomas,²⁴ in their detailed ESCA analyses of C and O peaks for a series of polyacrylates, also observed such oxidation of poly(n-decyl) acrylate. As the chemical structures of EB210 and EB1360 were unknown, only the measured compositions are given (Table 4.2). Neat EB1360 films were found to consist of approximately 12 atomic% of silicon and neat EB210 films approximately 2.6 atomic% of nitrogen. The measured silicon and nitrogen contents for neat EB1360 and EB210 were used for subsequent analyses of mixtures containing these components.

Peak [eV]	Atomic composition [%]						Atomic composition [%] by types of C(1s) bonds					
	Calculated			Measured			Calculated			Measured		
	O	C	Si	N	O	C	Si	N	C-I	C-II	C-III	C-III
					~532	~285	~102	~400				288.5
PEG700	33.3	66.7	0	0	31.9	67.3	0.8	0	12.5	81.3	3.2	15.0
EB210	-	-	-	-	25.6	71.5	0.3	2.6	-	-	-	29.7
SR399	32.4	67.6	0	0	31.7	68.0	0.3	0	48.0	32.0	20.0	57.5
TMPTA	28.6	71.4	0	0	29.0	70.0	0.9	0	60.0	20.0	20.0	65.1
EB1360	-	-	-	0	28.6	59.4	12.0	0	-	-	-	60.6
SR395	13.3	86.7	0	0	23.4	76.6	0	0	84.6	7.7	7.7	69.8

Table 4.2. Calculated and measured compositions of neat films of individual components. Standard deviations of measured values are typically less than 10% of the average value. Where a value is below the detection limit (0.1 atomic% for silicon and 0.2 atomic% for nitrogen), it is denoted with zero. For EB210 and EB1360, the ‘calculated’ columns are blank because their chemical structures are unknown.

Figure 4.6. Representative XPS spectra of some components: (a) wide-scan of PEG700, (b) wide-scan of EB210, (c) wide-scan of EB1360, (d) peak synthesis of C(1s) peak of PEG700.

Each of the high-resolution C(1s) spectra for the cured films of the six individual components was fitted with three synthesized peaks centered at 284.5, 285.9 and 285.5 eV, and they represent, respectively, the hydrocarbon bond ($\underline{\text{C}}-\text{C}$ and $\underline{\text{C}}=\text{C}$; for the case of EB1360, it would also include the $\underline{\text{C}}-\text{Si}$ bond), ether bond ($\underline{\text{C}}-\text{O}-\text{C}$) and ester bond [$\text{C}-\underline{\text{C}}(=\text{O})-\text{O}$; for the case of EB210, it would also include the urethane bond $\text{N}-\underline{\text{C}}(=\text{O})-\text{O}$]. For convenience, we shall denote these peaks as C-I, C-II and C-III respectively. Again the measured and calculated values for the 3 C(1s) peaks for PEG700, SR399 and TMPTA matched closely. The measured contents of C-II and C-III of SR395 seem relatively high by comparison with the calculated values and this is again attributed to oxidation as explained above.

The nickel-side surface compositions of the films from the twelve formulations were analyzed next (Table 4.3). Comparisons of the replicate formulations (i.e. 1 with 12, 4 with 10, and 6 with 11) shows that the data obtained were repeatable within experimental errors; the standard deviations of the repeated readings were about only 10% of their mean values. Although Formulations 2, 3, 5, 8 and 9 contained the urethane diacrylate (EB210), the measured concentrations of nitrogen were all lower than the detection limit, indicating the absence or very low proportion of EB210 on the nickel-side surfaces.

Of the six components, only PEG700 and EB210 have relatively high percentages (79% and 65% respectively) of C-II (Table 4.2). The C-II contents in other non-silicon containing components (TMPTA, SR399, and SR395) were less than 20%. Assuming post-cure compositional homogeneity, a cured formulation's C-II content can be approximated from the measured C-II contents of the individual components using the following equation:

$$E_j = \sum_{\text{all } i} w_i E_i \quad (4.3)$$

where E_j and E_i are the percentages of C-II in Formulation j and component i respectively; and w_i is the weight proportion of component i in the formulation (see Appendix A.2 for derivation). The measured percentages of C-II of the various formulations were compared with the calculated values in Figure 4.7, and it is apparent that the surfaces of formulations not containing EB1360, namely Formulation 1, 3, 6 and 8 (as well as the replicates, Formulations 11 and 12), had higher C-II contents than the

calculated values based on the homogeneous composition approximation of eq 3. High C-II content could be attributed to only PEG700 or EB210, but nickel-side surface EB210 is ruled out by the absence of the N(1s) peak in XPS spectra of these formulations. It follows that the nickel-side surfaces of films not containing EB1360 were enriched in PEG700 with respect to the bulk mixture. It has been reported that if the substrate is polar, the likewise polar component in a UV curable resin aggregates at the surface.⁶ In our case, we have a polar substrate i.e. nickel, which would thus cause the likewise polar molecule PEG700 to aggregate at the nickel side, leading to the higher C-II content there.

Formulation	%O	%C	%Si	%N
1	29.4	70.6	0.2	0
2	28.0	64.6	7.4	0
3	23.0	77.0	0.2	0
4	28.6	63.7	7.7	0
5	30.4	64.0	5.6	0
6	25.6	74.4	0.2	0
7	30.8	63.2	6.0	0
8	29.0	71.0	0	0
9	28.5	65.8	5.7	0
10	29.8	63.7	6.4	0
11	28.3	71.7	0.2	0
12	26.8	73.2	0.2	0

Table 4.3. Measured O, C, Si and N content of Formulations 1 to 12. The value zero carries the same meaning as in Table 4.2. Standard deviations of measured values are typically less than 10% of the average value.

Figure 4.7. Percentage of total C-II: measured values versus calculated values. Solid line is $y=x$.

On the other hand, for the formulations that contained EB1360, namely Formulations 2, 4, 5, 7 and 9, the nickel sides had lower PEG700 contents than expected. For these formulations, the percentage of Si(2p) measured (5.6 to 7.7% in Table 4.3) were extremely high in comparison with the value obtained for neat EB1360 films (12% in Table 4.2) because, if the film had been homogenous, then the amount of Si on the surface of a formulation containing 5% EB1360 would have been only $0.05 \times 12\% = 0.6\%$. This implies that the nickel-side surfaces of formulations containing 5% or less of EB1360 were highly enriched with the silicone. Evidently, this release agent aggregated at the nickel side. As this layer was not revealed in the EDX mapping of silicon in Figure 4.4d, it must be a very thin layer, perhaps in the region of a few nanometers, and was picked up strongly by XPS. This aggregation is a very desirable phenomenon because addition of a small amount of this release agent could highly saturate the nickel-side surface of the embossing, concentrating the release agent precisely where it is needed to facilitate demolding.

In a most interesting paper by Petijean et al.,⁵ it was found that there was an anomalously high amount of poly(dimethylsiloxane) (PDMS) on the polymer/aluminum and polymer/glass interfaces when a diblock copolymer, poly(styrene-*b*-dimethylsiloxane), in a polystyrene matrix was solvent-cast or spin-cast onto aluminum and glass substrates respectively. The thickness of this segregation was about 40 nm. They explained that the diblock copolymer first migrates to the polymer/air interface, and then above a critical concentration, it forms micelles, which migrate to and accumulate at

not only the air side of the polymer (which was exposed), but also the interface with these substrates. The tendency of diblock copolymer micelles to aggregate at pre-existing interfaces was partly attributed to the thermodynamic driving force for the system to reduce the number of sharp interfaces that are present, and consequently, increase the entropy of the system.²⁵ We believe that similar mechanism is at work here. In the uncured state, the silicone acrylate forms micelles in the formulation, and when the formulation is contacted with the nickel, the micelles migrate and aggregate at the interface with the nickel. The subsequent crosslinking then anchors the silicone acrylate micelles to the nickel-side of the cured film.

4.4.5 Analysis of Mixture Experiment Data

The measured step-13 times of the twelve formulations are presented in Table 4.4 and the first degree Scheffé model correlating the step-13 times to the pseudocomponents' proportions is

$$t_{13} = 17.65x'_{OEGDA700} + 9.22x'_{EB210} + 9.55x'_{SR399} + 9.47x'_{TMPTA} + 99.95x'_{EB1360} + 31.08x'_{SR395} \quad (4.4)$$

(2.30) (2.03) (1.60) (1.43) (9.38) (4.60)

where the numbers in parentheses are the standard error of the coefficient estimates. This model is an adequate one based on the favourable regression summary statistics (see Appendix A.3) and the close agreement between the measured and predicted values (Table 4.4).

As we have used pseudo-components in our model, the standard errors of the coefficient estimates were relatively small in magnitude and this allows us to meaningfully interpret the values of the coefficient estimates. The coefficient estimates as well as the associated standard errors of the EB210, SR399 and TMPTA terms are very close to one another. This strongly indicates that these three components affected the step-13 times (and hence the polymerization kinetics) in the same way. The response traces shown in Figure 4.8 confirmed this, as the traces for the three components are indistinguishable from one another, with the step-13 time decreasing from about 20 s at zero proportion to about 14 s at the upper bound proportion of 0.30. Whereas it is clear the high functionalities of SR399 and TMPTA increase the polymerization rate and hence hasten the attainment of gel point, the reason for EB210 to have similar effect is less clear. The most likely reason is that its high viscosity causes auto-acceleration to step in

earlier, or even immediately, during the polymerization reaction,²⁶ and thus causing the formulation to gel faster. Next, the response trace using PEG700 is almost constant at about 18 s, indicating that PEG700 is an inert component in the proportion range of 0.5 to 0.7. The reason could be that at the lower bound proportion of 0.5, its proportion is already very high, and increment to it has little effect on the response. The component that has the largest effect on the step-13 time is expectedly EB1360 (it has the largest coefficient estimate in eq 4), with an increase from about 13 s to 22 s when its proportion increases from 0 to 0.05, indicating a significant decrease in the polymerization rate.

Formulation	t_{13} [s]		m_{Si} [%]	
	measured	eq 4	measured	eqs 5 and 6
1	12	12.7	0.2	0.2
2	26	26.0	7.4	7.5
3	14	13.6	0.2	0.6
4	23	22.9	7.7	7.2
5	17	18.5	5.6	6.0
6	14	13.8	0.2	0.1
7	24	21.8	6.0	6.3
8	11	9.4	0	-0.1
9	16	17.8	5.7	3.7
10	23	22.9	6.4	7.2
11	14	13.8	0.2	0.1
12	12	12.7	0.2	0.2

Table 4.4. Measured and predicted values of step-13 times (t_{13}) and surface silicone contents. The value zero carries the same meaning as in Table 4.2.

Figure 4.8. Step-13 time response traces. Each line represents the response trace of a component whose proportion is being varied according to its own x-axis. As EB210, SR399 and TMPTA have the same proportion range, they are made to share the same x-axis.

As mentioned, this strong influence is not due to the slight increase in optical attenuation arising from EB1360; rather, as shown by the polymerization profiles in Figure 4.5d, it is because the polymerization rate of EB1360 itself is very slow. Free-radical photopolymerization is known to be prone to inhibition by oxygen because oxygen is a prolific scavenger for primary radicals as well as macro radicals, and silicone acrylates are especially affected because of their high permeability to, and high saturation concentration of, oxygen,^{26,27} and prolonged induction periods have been observed during their photopolymerization.^{23,28-30} This explains the lengthy induction period (11 s) observed for EB1360. (Note that further diffusion of oxygen into the film from the atmosphere during curing was prevented by the Melinex® cover.) Furthermore, it is known that flexible monomers would cause more primary cyclization,³¹ and hence, EB1360, with its flexible siloxane backbone (the siloxane bond is known to have a wide variability of bond angle, ranging from 105° to 180°³²), is expected to primary-cyclize significantly. Primary cyclization forms only small loops and does not contribute significantly to the overall network structure unlike crosslinking, which connects and stiffens the entire network; consequently, gel point conversion is delayed³³ and this is manifested here by the increase in the step-13 time. Other related phenomena due to primary cyclization, namely, subdued autoacceleration³⁴, and reduced final conversion³⁵, are also observed for EB1360 (Figure 4.5d).

The screening experiment result for the surface silicon content (with the pseudo-components) yields

$$m_{Si} = 0.47x'_{OEGDA700} - 0.70x'_{EB210} - 2.51x'_{SR399} - 0.55x'_{TMPTA} + 132.51x'_{EB1360} + 6.21x'_{SR395} \quad (4.5)$$

(1.45) (3.01) (2.55) (2.70) (12.45) (5.68)

The coefficient estimates for all the components, except EB1360, have very large standard errors, which make the coefficient estimates difficult to interpret. Hence, despite using pseudo-components, large standard errors were still incurred in the coefficient estimates. A method to reduce the large standard errors is to modify the L -pseudo-components by substituting the lower bound value in the numerator of eq 4.2 by the average value.¹³

$$x''_{u,k} = \frac{x_{u,k} - L_k}{L'} \text{ and } x''_{u,i} = \frac{x_{u,i} - \bar{x}_i}{L'}, \quad i \neq k$$

where k is the component with the largest range (EB210 was chosen here), L_k the lower bound of k , $\bar{x}_i = \left(\sum_{u=1}^N x_{u,i} \right) / N$ and $L' = \bar{x}_k - L_k$. The resulting Scheffé model is:

$$m_{Si} = 3.32x''_{OEGDA700} + 3.24x''_{EB210} + 3.10x''_{SR399} + 3.25x''_{TMPTA} + 13.40x''_{EB1360} + 3.76x''_{SR395} \quad (4.6)$$

(0.41) (0.28) (0.37) (0.37) (0.98) (0.60)

Thus, after the modification, the standard errors were reduced significantly, and the coefficient estimates are now interpretable. The regression summary statistics (Appendix A.3) and predicted values in Table 4.4 are unchanged by the modification.

The coefficient estimates as well as their associated standard errors of the first four components are approximately the same, and those of SR395 are not far off. In terms of response tracing in Figure 4.9, these five components have response traces that lie very close together, and hence their effects on the response are very similar. If we lumped these five terms together, the resulting model would be

$$m_{Si} = c_1(x''_{OEGDA700} + x''_{EB210} + x''_{SR399} + x''_{TMPTA} + x''_{SR395}) + c_2x''_{EB1360} \quad (4.7)$$

$$\therefore m_{Si} = c_1 + (c_2 - c_1)x''_{EB1360}$$

where c_1 and c_2 are the new coefficient estimates. Eq 4.7 implies that the surface silicon content depends only on the proportion of EB1360 in the formulation. In other words, as long as the proportion of EB1360 is kept constant, variations in the proportions of the other components have no effect on the surface silicon content. Of course, this linear

relationship between the surface silicon content and EB1360 proportion is too simplistic (the Langmuir isotherm $y = kx/(1 + kx)$ would more appropriately describe the saturation of silicone at the surface after a critical amount of EB1360 has been added to the formulation), but it is nonetheless useful in that it reveals the almost sole dependence of the surface silicon content on EB1360.

Figure 4.9. Surface silicon content response tracing.

These screening experiments have helped us quantify the relative importance of the components on the step-13 time and the surface silicon content of the formulations. In both cases, it is confirmed that EB1360 has the strongest influence, increasing the step-13 time and surface silicon content significantly. For step-13 time, PEG700 is the inert component and EB210, SR399 and TMPTA have approximately similar negative effects on it. For the surface silicon content, besides the obvious conclusion that EB1360 has the strongest influence, it is also noteworthy that none of the other components has significant retardation effect on EB1360 reaching the surface.

4.5 Conclusions

When the silicone acrylate EB1360 was used as a release agent in formulations containing mainly PEG700, the formulations were found to be hazy because the silicone phase-separated from remaining hydrocarbon acrylate components and formed large dispersed domains of about 10 μm in diameter. Micelles of silicone acrylate were also formed. Although the haziness led to increased attenuation of the UV light, the effect on the polymerization rates was found to be insignificant because the formulations were applied as thin films (*ca.* 150 μm thick), which have apparent absorbance (scattering plus

absorbance) of less than 0.1. Using FTIR, the phases of the silicone acrylate and PEG700 were found to homopolymerize in sequence (the silicone being last) rather than copolymerize. The formulations were cured as thin films (*ca.* 150 μm) on a nickel substrate and XPS analysis of the nickel-side of the films revealed that for formulations with and without the silicone acrylate, this side was enriched with PEG700 and the silicone acrylate respectively. The reasons are that without the silicone acrylate, PEG700, being highly polar, were attracted to the likewise polar nickel surface; and when silicone acrylate was present, it formed micelles, which migrated to and aggregated at the nickel side. The length of UV exposure for curing each formulation was determined with a simple procedure that allowed us to control the extent of crosslinking. This curing time and the amount of the release agent (silicone acrylate) on the surface are important parameters for successful UV embossing. To quantify the effects of the components in the formulations on these two properties, Design of Experiment was used, and the results were that the silicone acrylate was the critical component that strongly influenced these two properties. The statistical models would be useful in predicting these two properties for new compositions.

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Chapter 5

Modeling of Coupled Conversion and Shrinkage during Photopolymerization

The Bowman and Peppas'¹ model that couples shrinkage and kinetics of polymerization is critically reviewed. This model was applied to predict the change in conversion when different UV intensities are used. In this work, this model is applied to predict shrinkage as well. Although the framework of the model is largely sound, a number of critical shortcomings with it are identified, the most significant being the treatment of free volume, which was found to produce the unrealistic trend of increasing free volume during polymerization. After extensive review of the free volume concept, a new treatment of free volume is proposed. For the first time (to our knowledge), experiments were designed and performed to determine the relaxation parameters. Two monomers were investigated, namely PEG diacrylate (average M_n 700) and TMPTA. These experiments involved precisely synchronized simultaneous collection of conversion and shrinkage data using an FTIR spectrometer and a laser displacement meter respectively. The improved model was found to be satisfactory in predicting conversion profiles for three different UV intensities, 3, 16 and 130 mW/cm², which span a large range. For shrinkage, the model significantly overestimates at the highest intensity of 130 mW/cm², and this is believed to be due to its inability to factor in early vitrification due to the fast collapse of free volume at such high intensity. Overall, the improved model now has a stronger theoretical foundation than before, and has been shown experimentally to be valid for predicting conversion over a wide range of UV intensity; however further improvement is needed for similar success in shrinkage prediction.

5.1 Introduction

In their much-quoted paper, Bowman and Peppas¹ presented a model that couples the kinetics of cross-linking polymerization of multi-acrylates and multi-methacrylates to the shrinkage observed during polymerization of these systems. With this model, they could simulate three important characteristic features of these polymerization systems that previous models could not. They are: (1) a maximum conversion that is less than 100%; (2) a maximum conversion that increases when a higher UV intensity is used; and (3) an upward shift in the conversion at which the maximum rate of conversion occurs when a higher UV intensity is used. Previously, these three phenomena have been rationalized using the free volume concept by Kloosterboer *et al.*^{2,3} Shrinkage of the polymerizing system decreases the amount of free volume available for diffusion of the reacting species, and when this free volume hits a critical value, diffusion becomes almost impossible, so that even if there are still unreacted double bonds, no reaction could take place, and thus the maximum conversion reached is less than 100%. When a high UV intensity is used, the polymerization rate would significantly exceed the shrinkage rate so that a higher conversion would be obtained by the time the free volume hits the critical amount. This is equivalent to saying that at any value of conversion, there is an excess of free volume in the high UV intensity case over the low UV intensity case. For similar reasons, the maximum rate of conversion would also occur at a higher conversion in the high UV intensity case. It should also be added here that the maximum rate of shrinkage would likewise occur at a higher conversion. With their approach of coupling shrinkage to kinetics, these important aspects would thus be factored into their model.

As described by Kloosterboer *et al.*,^{2,3} the polymerization rate exceeding the shrinkage rate causes shrinkage to be delayed with respect to conversion. Unfortunately, that shrinkage is delayed in this sense has sometimes been misconstrued to mean that the *onset* of shrinkage is delayed. This is definitely not the case. They clearly stated that the delay happens only after the system has become a gel, so that the process of converting the free volume generated into observable shrinkage would involve the motion of the entire gel in a cooperative way, a process that is necessarily slower than the diffusion of the reacting species. Hence, before gelation i.e. in the liquid state, shrinkage is expected to be in tandem with conversion, and definitely, the onset of shrinkage must necessarily

coincide with the onset of conversion. Their experiment data back this up unequivocally; the shrinkage rate and conversion rate overlap in the initial period, and only fork after about 10 s, which presumably is the time gelation sets in. It is noted that Kloosterboer *et al.*^{2,3} had worked with tetraethylene glycol diacrylate (TEGDA), a low molecular weight and low viscosity monomer. With a much higher molecular weight and viscous monomer or oligomer, it is likely that shrinkage and conversion may not be in tandem even before gelation; this is because the high viscosity and pronounced chain entanglement could significantly retard the molecular motion required for shrinkage to occur.

Although this is undoubtedly an insightful paper, there are a few critical shortcomings. Most importantly, their analogy of shrinkage during polymerization reaction to volume relaxation during physical aging requires careful interpretation. Physical aging, by definition, does not involve permanent modifications to the material's chemical structure, and changes to the material are reversible.⁴ The example they quoted of the volume relaxation during thermal cycling of polymers illustrates this; the polymer shrinks when quenched, and expands to its original state when heated. However, during polymerization, the material's chemical structure is surely altered; C=C bonds are converted to C-C bonds and the material becomes chemically cross-linked. Hence, *shrinkage during polymerization* is induced by chemical reactions and is irreversible, and these two aspects are antithesis of *volume relaxation during physical aging*. Such a distinction is critical in designing experiments to determine the volume relaxation parameters. They had proposed to determine these parameters by obtaining polymers at various stages of conversion and then analyzing their relaxation times, presumably using an isothermal volume recovery experiment as per Kovacs^{5,6}. Certainly, such experiments would give us the parameters appropriate for the volume relaxation during physical aging, and not for shrinkage during polymerization (a method of determining the latter would be presented in this work). How then are these two phenomena analogous to each other? The answer is that, apparently, they could be rationalized in the same way using the free volume concept, and be modeled by the same equations albeit with very different parameter values since the time scales for them are many orders of magnitude apart (seconds for polymerization and hours to days for physical aging). Note that from here on, the terms shrinkage and volume relaxation would be used interchangeably.

In their model simulation, the kinetic parameters, specific volumes and coefficients of thermal expansion used were chosen in order to give agreement between the simulated results and observed polymerization behavior of a particular material (EGDMA). Such a procedure is rather dubious since these parameters should rightly be obtained by experiments or by independent methods such as group contribution schemes. Indeed, in the course of this work, we found that by using independently-obtained estimates of these parameters, we could end up getting a physically unreasonable result *viz.* an increasing fractional free volume during polymerization. To overcome this problem, we re-examined their treatment of free volume, which is based on the works by Williams *et al.*⁷ and Kovacs^{5,6,8}, and proposed important changes to it.

In addition, in this work, we have used an improved equation for the termination reaction constant, k_t , which includes the effect of reaction-diffusion.⁹ This equation appeared after the publication of their paper, which used a simplified equation that could model only the chemical reaction- and diffusion-controlled behavior of the termination reaction, and not the reaction-diffusion aspect.

As the free volume concept and volume relaxation phenomenon are vital aspects of this work, we shall give a brief review of these two topics.

5.1.1 Free Volume Concept and Definitions

The free volume concept is an intuitive one: the macroscopic volume could be microscopically partitioned into volume occupied by molecules and free volume, and the relative sizes of free and occupied volumes affect the physical properties of the material. A survey on free volume-related papers reveals that in different applications, the definitions of free and occupied volumes could vary significantly. We will present a brief discussion of these different definitions and then make and justify our choice of definitions of free and occupied volumes. Note that the notations as found in the papers quoted are used in this discussion.

The free volume concept is widely used in molecular lattice theories of liquids and dense gases to formulate their equations of states (EOS)¹⁰. In the cell theory e.g. of Eyring¹¹ and of Lennard-Jones and Devonshire¹², the total volume is partitioned into cells, with one cell to one molecule, which is taken to be a hard sphere, and the space that

is thus available for the molecule to move within the cell is described as the free volume. In the hole theory (e.g. of Rowlinson and Curtiss¹³ and of Ono¹³), a number of the cells are allowed to be empty and these empty lattice sites called holes are, in addition to the free space in the occupied cells, counted as part of the free volume. Such a description free volume clearly implies that the occupied volume is the van der Waals' (VDW's) volume, which depends on only the chemical structure. This free volume is, in Hildebrand's terminology, the empty volume.¹⁴ However, in Simha and Somcynsky's EOS, only the empty cells (holes) are considered as the free volume.¹⁵ In an application of S-S theory, the free space inside an occupied site is considered as part of the occupied volume and is termed the interstitial volume. This occupied volume is then temperature and pressure-dependent as the interstitial volume could expand/contract and be compressed/uncompressed like the hole free volume.¹⁶

Another major application of the free volume concept is in the studies of viscosity of liquids and polymers. Doolittle¹⁷ defined free volume as $v_f = v - v_0$, where v_0 is the volume of the liquid extrapolated to 0 K (neglecting phase change), and hence, the occupied volume also depends on only the chemical structure. Hildebrand had termed this free volume the expanded volume.¹⁴ The two most popular methods of estimating this occupied volume are by Doolittle¹⁷ ($v_0 = e^{10/M}$, where M is the molecular weight) and by Bondi¹⁸ ($v_0 = 1.3v_w$ where v_w is the VDW's volume). Williams *et al.*⁷ related the temperature shift factor a_T they have derived to the free volume concept of Doolittle. Based on the works of Fox and Flory¹⁹ (see next paragraph) and Bueche²⁰, they wrote the temperature dependence of fractional free volume as $f = f_g + \alpha_2(T - T_g)$ where f_g is f at T_g and α_2 is the difference between the coefficients of thermal expansion above and below T_g . With these, the universal value of 0.025 for f_g was arrived at, and they tentatively compared this to the value of 0.022 observed for the relative excess volume $[(v_g - v_c) / v_g]$ where the subscripts g and c stand for glass and crystal respectively] of glycerol at its T_g . This comparison is rather dubious since the f in Doolittle's sense is defined with respect to expanded volume, and not excess volume as in Williams *et al.*'s treatment. They indirectly admitted to this inconsistency by disclaiming that their fractional free volume is yet an ill-defined quantity. Nevertheless, based on the glycerol example, it is apparent that the occupied volume in Williams *et al.*'s sense is the crystal volume (at the temperature of interest), which comprises the VDW's and interstitial

volumes, and thus, when the temperature is raised, the total volume expansion is due to the expansion of both free and occupied volumes. Despite the vagueness of their definition of free volume, the Williams *et al.*'s expression for fractional free volume is perhaps the most ubiquitous free volume expression because of its simplicity and availability of convenient universal values.

Besides EOS formulation, the lattice theory has also been applied to describe molecular transport. In the cell theory of Cohen and Turnbull (the 'improved' version)^{21,22}, there is a critical cell volume above which the cell is considered liquid-like and below, solid-like. In the former, the volume in excess of the critical amount is taken to be the free volume, which could be redistributed without energy change, and diffusion would occur when this redistribution creates a volume at least the size of the diffusing entities. (We interpret here that the critical volume is the occupied volume.) In one of their papers²¹, it was proposed that, macroscopically, this occupied volume could be taken to be that of a random assembly of hard spheres as investigated by Bernal and associates²³⁻²⁶. The densest of such an amorphous structure has a volume roughly 1.16 times²⁷ of that of the close-packed crystal (faced-centered cubic or hexagonal close-packed), and is believed to be the structure of the 'ideal glass', a non-crystalline solid that has the closest packing possible of any amorphous structure, is in internal equilibrium (because reconfiguration of the internal structure is impossible due to the absence of free space), and is attained only if the glass transition state is reached in an infinitesimally slow manner (akin to Adam and Gibbs'²⁸ entropy theory of glass transition which predicts an equilibrium glass transition). The occupied volume in this sense thus definitely includes some interstitial volume, and in amount greater than that of the crystalline form as proposed by Williams *et al.*⁷ In contrast to the free volume, this interstitial volume could not be redistributed freely as it would entail energy changes. A 'normal glass' would have, in addition to some free volume, an occupied volume greater than Bernal's dense random packing form as a result of greater interstitial volume being trapped; it was, however, not elaborated on how such an occupied volume could be computed. We interpret the Bernal's volume to be an 'equilibrium occupied volume'; a 'normal glass' will then, due to a greater amount of trapped interstitial volume, have a non-equilibrium occupied volume, which if annealed infinitesimally slowly, will attain the equilibrium state. The idea of a non-equilibrium occupied volume will be significantly utilized in this

work. To reiterate, for the ‘ideal glass’, the occupied volume equals the total volume as there is no free volume.

The glass transition phenomenon has also been explained using the free volume concept by Fox and Flory,¹⁹ and by Cohen and Turnbull.^{21,22,29} In the former, the glass transition was shown to be an iso-free volume state i.e. the amount of free volume at the glass transition is the same regardless of the molecular weight and T_g , and remains the same below T_g . The occupied volume is defined as $v_o = A_0 + (dv/dT)_3 T$, where A_0 is the hypothetical volume of the solid (glass) at 0 °C; $(dv/dT)_3$ the volume-temperature coefficient in the glassy regime; and T the temperature; the free volume is subsequently derived as $v_f = A_f + [(dv/dT)_2 - (dv/dT)_3]T + 53/M$ where A_f is a constant; $(dv/dT)_2$ the volume-temperature coefficient in the rubbery regime (up to 160 °C); and M the molecular weight. Clearly then, this occupied volume is temperature-dependent. Significantly, they are the first to propose that glass transition sets in when the free volume collapses to a critical value. The idea that glass transition is an iso-free volume state has been refuted before as fractional free volume has been shown to increase with increasing T_g .^{30,31} In Cohen and Turnbull’s version, a glass is formed from a liquid when the fraction of liquid-like cells drops below a critical value so that the liquid-like cell cluster no longer extends infinitely. As only liquid-like cells have free volume, this translates to a reduction in free volume as well.

In Vrendas and Duda’s diffusion theory,³²⁻³⁴ the occupied volume (V_o) is defined as per Doolittle,¹⁷ and the free volume is separated into interstitial and hole free volumes (V_{FI} and V_{FH} respectively). Invoking the Cohen and Turnbull’s theory,^{21,22,29} the former requires some energy for redistribution, and the latter, none, and hence for diffusion, only the hole free volume is involved. Significantly, they eschewed calculating V_{FH} based on the defining equation $V_{FH} = V - (V_o + V_{FI})$, thus circumventing any quantitative definition of V_{FI} , and derived a new equation $V_{FH} = K_{11}(K_{12} + T - T_g)$, where K_{11} and K_{12} are some functions of the material properties, for evaluating V_{FH} .³⁵ Another prominent diffusion theory is by Fujita³⁶, who adopted the Williams *et al.*’s⁷ version of free volume with some modifications.

In addition to diffusion and glass transition, the Cohen and Turnbull's theory could also be used to derive the Doolittle's viscosity-free volume equation, and hence giving this previously empirical relationship a theoretical foundation.²²

Volume relaxation during physical aging of polymer is another phenomenon that utilizes the free volume concept for modeling.^{4,37}. As it is an important component of this work, it would be covered as a single topic in the next section.

A useful way of summarizing the discussion will be to recap, as presented in Table 5.1, what constitutes occupied volume. For convenience and clarity, the following generic notations will be used in lieu of those in the original publications; with reference to Vrendas and Duda's³²⁻³⁴ works, 'specific hole free volume' and 'specific interstitial free volume' will be shortened to 'specific hole volume' and 'specific interstitial volume'.

v_w	VDW's volume
v_o	specific occupied volume
v_f	specific free volume
v_h	specific hole volume
v_i	specific interstitial volume

	Occupied volume definition	Examples	Remarks
1.	$v_o = v_w$	Eyring ¹¹ ; Lennard-Jones and Devonshire ¹² ; Curtiss and Rowlinson ¹³ .	
2.	$v_o = v_{liquid}(0\text{ K})$	Doolittle ¹⁷ .	$v_{liquid}(0\text{ K}) = e^{10/M}$
3.	$v_o = v_{liquid}(0\text{ K})$	Vrendas and Duda ³²⁻³⁴ .	The total free volume is partitioned into hole and interstitial volumes ($v_f = v_h + v_i$); only the hole volume is responsible for molecular transport.
4.	$v_o = v_{crystalline}$	Williams <i>et al.</i> ⁷	Only a tentative definition.
5.	$v_o = v_w + v_i$	Cohen and Turnbull ^{21,22,29} ; Fox and Flory ¹⁹ ; Simha and Somcynsky ¹⁵ (Dlubek's ¹⁶ interpretation)	Occupied volume is temperature (and pressure) dependent.

Table 5.1. Recap of different definitions of occupied volumes.

5.1.2 Volume Relaxation Phenomenon

As mentioned, volume relaxation during polymerization could be rationalized and modeled in the same way as that during physical aging using the free volume concept. The latter has been previously investigated, most notably by Kovacs and associates.^{5,6,8} We shall briefly review their works.

Physical aging is described as the phenomenon of ‘observed change in a property of the polymer as a function of storage time, at constant temperature, at zero stress, and under no influence from any other external conditions’; some of these properties observed are specific volume, enthalpy, and mechanical and dielectric responses.⁴ The physical aging of specific volume is commonly called ‘volume relaxation’, although as Hutchinson⁴ points out, the term ‘retardation’ is technically more correct than ‘relaxation’ (the former applies to the response of the *strain* to a constant stress; and the latter, of the *stress* to a constant strain³⁸).

When an amorphous polymer is brought to below its T_g and the temperature held there, the molecular structure is ‘frozen in’, and over time as the structure ‘thaws’, the excess free volume trapped will be ‘released’, causing the polymer to shrink. Importantly, the kinetics of physical aging depends not only on temperature, but also on the instantaneous state or structure, and this is clearly manifested in its self-retardation nature.^{4,8,37,39} As Kloosterboer³⁹ puts it, there is a ‘close-loop dependence between free volume V_f , segment mobility μ and rate of shrinkage dV_f/dt ’; this is illustrated in Figure 5.1. The free volume concept is by no mean the only approach to modeling physical aging. Other notable approaches are by using the fictive temperature concept of Tool⁴⁰ and configuration entropy concept of Gibbs and DiMarzio⁴¹. However, for volume relaxation, the free volume approach is the most intuitive and popular.⁴

Figure 5.1. Close-loop dependence in volume relaxation kinetics.

Models on the kinetics of physical aging center on the use of a characteristic relaxation time τ . Simple relaxation theories assume that τ depends on temperature alone in the form of Arrhenius's equation⁴²⁻⁴⁷ or of WLF equation⁴⁸ but they are found to be inadequate in modeling the nonlinear and highly asymmetric characteristics of isothermal volume relaxation (since τ in an isothermal situation is a mere constant). More elaborate and successful theories link τ to, besides temperature and pressure, the actual state of the material by means of free volume⁶ or other parameters such as fictive temperature⁴⁹ and configurational entropy²⁸ as mentioned above.

The most important phenomenological model of volume relaxation based on the free volume concept is by Kovacs^{6,8}, which is known as the single-parameter theory. This would be covered in details when this model is presented in the next section.

5.2 Model Development

5.2.1 Kinetics model: Free Radical Reaction Mechanism

Following Terrones and Pearlstein⁵⁰, the elementary reactions taking place are:

In the initiation step (eq 5.1), the photoinitiator A decomposes upon irradiation to give j primary radicals $R^\bullet$. They subsequently react with the monomer M to initiate the propagation reactions (eqs 5.2 and 5.3), forming the macro-radicals $RM_m^\bullet$, $m > 1$. It is assumed that the rate constant k_p is independent of m i.e. the chain length of the macro-radicals. This is a reasonable assumption because propagation is controlled by the diffusion of the more mobile monomer molecules rather than the bulky macro-radicals. The termination step is assumed to be only bimolecular in nature (eq 5.4) and the rate constant k_t is also assumed to be chain length independent.

The mathematical treatment of the kinetic mechanisms, from the rate laws describing these elementary reactions and the material balances on the species involved, gives

$$\frac{dC_A}{dt} = -\Phi\kappa_A C_A I \quad (5.5)$$

$$\frac{dC_{R^\bullet}}{dt} = j\Phi\kappa_A C_A I - k_p C_M C_{R^\bullet} - 2k_t C_{R^\bullet}^2 - 2k_t \sum_{n=1}^{\infty} C_{R^\bullet} C_{RM_n^\bullet} \quad (5.6)$$

$$\frac{dC_{RM_m^\bullet}}{dt} = k_p C_M [C_{RM_{m-1}^\bullet} - C_{RM_m^\bullet}] - 2k_t C_{RM_m^\bullet} \sum_{\substack{n=0 \\ m \neq n}}^{\infty} C_{RM_n^\bullet} - 2k_t C_{RM_m^\bullet}^2, m \geq 1 \quad (5.7)$$

$$\frac{dC_M}{dt} = -k_p C_M \sum_{n=0}^{\infty} C_{RM_n^\bullet} \quad (5.8)$$

$$\frac{dC_{RM_m R}}{dt} = 2k_t \sum_{n=0}^{[m/2]} C_{RM_n^\bullet} C_{RM_{m-n}^\bullet}, m \geq 0 \quad (5.9)$$

In the above equations, C_i (mol/m³) is the concentration of the species i , Φ is the quantum yield of initiation (dimensionless; $\Phi \leq 1$ i.e. not all photons absorbed will result in the formation of primary radicals), κ_A (m²/mol) is the molar napierian absorption coefficient⁵¹ of the photoinitiator A , I (einsteins/m².s) is the intensity of the radiation in the reaction system, and $[m/2]$ is the largest integer not exceeding $m/2$. From the Beer's Law,

$$I = I_0 e^{-\kappa_A C_A z} \quad (5.10)$$

where I_0 (einsteins/m².s) is the incident intensity at the surface, nearest to the radiation source, of the reaction system, and z is the depth into the system from this surface. Note that, generally, C_A is a function of both time and depth⁵²; however because of our choice of photoinitiator and its concentration, the dependence on depth is negligible, and C_A could be expressed as

$$C_A = \frac{1}{\kappa_A L} \ln[1 + (e^{\kappa_A C_{A0} L} - 1)e^{-\Phi\kappa_A I_0 t}] \quad (5.11)$$

where L is the thickness of the film and C_{A0} is the initial photoinitiator concentration. See Appendix A.4 for justification and derivation of eq 5.11.

We now show an example on how to compute the rate of change of a species. The rate law describing the termination of two identical radicals (primary and macro) (eq 5.12), is shown in eq 5.13.

$$\nu = k_t C_{RM_m^\bullet}^2 \quad (5.13)$$

where ν is the rate of reaction, and, for a constant volume batch reactor, is equal to the rate of change of the chemical species divided by its stoichiometric coefficient⁵¹, i.e. for $RM_m^\bullet$:

$$\nu = -\frac{1}{2} \frac{dC_{RM_m^\bullet}}{dt} \quad (5.14)$$

Combining eqs 5.13 and 5.14, we have

$$\frac{dC_{RM_m^\bullet}}{dt} = -2k_t C_{RM_m^\bullet}^2 \quad (5.15)$$

In the case of termination of two different radicals, a modification is needed in order to obtain the form shown in eq 5.15. The various equations are:

Rate law: $\nu = k'_t C_{RM_m^\bullet} C_{RM_n^\bullet} \quad (5.17)$

Rate of change: $\nu = -\frac{dC_{RM_m^\bullet}}{dt} \quad (5.18)$

The modification is to make the substitution $k'_t = 2k_t$ (as is implicitly done in Odian⁵³), and the final form is

$$\frac{dC_{RM_m^\bullet}}{dt} = -2k_t C_{RM_m^\bullet} C_{RM_n^\bullet} \quad (5.19)$$

Note that this treatment is different from the one by Terrones and Pearlstein⁵⁰, where the termination kinetic constant for identical radicals, $k_{t,m,m}$, is defined as $k_{t,m,m} = k_t/2$, which gives the generic termination kinetic constant k_t a value that is different from the one used in Odian⁵³ by a factor of 2.

Eqs 5.15 and 5.19 are then used in conjunction with the other rate laws involving $RM_m^\bullet$ to derive the total material balance on $RM_m^\bullet$ (eq 5.7).

It is noted that the use of concentrations, rather than the number of moles, in the rate of change equations implicitly assumes that the volume of the reaction system is constant. However, due to shrinkage, this volume is decreasing during reaction. Nevertheless, as the shrinkages in the acrylate systems examined here are typically less than 10%, making the constant-volume reaction system assumption remains appropriate.

The total radical concentration is obtained by summing eq 5.7 for $m \geq 1$ and then adding the result to eq 5.6. We get

$$\frac{d}{dt} \sum_{m=0}^{\infty} C_{RM_m} = j\Phi\kappa_A C_A I - 2k_t \left(\sum_{m=0}^{\infty} C_{RM_m} \right)^2 \quad (5.20)$$

Invoking the pseudo-steady state assumption,

$$\begin{aligned} \frac{d}{dt} \sum_{m=0}^{\infty} C_{RM_m} &= 0 \\ j\Phi\kappa_A C_A I - 2k_t \left(\sum_{m=0}^{\infty} C_{RM_m} \right)^2 &= 0 \\ \sum_{m=0}^{\infty} C_{RM_m} &= \sqrt{\frac{j\Phi\kappa_A C_A I}{2k_t}} \end{aligned} \quad (5.21)$$

Putting eqs 5.10 and 5.21 into eq 5.8, and noting that the conventional definition of rate of polymerization R_p is $-\frac{dC_M}{dt}$, gives

$$R_p = -\frac{dC_M}{dt} = k_p C_M \sqrt{\frac{j\Phi\kappa_A C_A I_0 e^{-\kappa_A C_A z}}{2k_t}} \quad (5.22)$$

Note that R_p is a function of z and the mean rate of polymerization is then

$$\begin{aligned} \overline{R_p} &= \frac{\int_0^L R_p dz}{L} \\ &= \frac{k_p C_M}{L} \sqrt{\frac{j\Phi\kappa_A C_A I_0}{2k_t}} \int_0^L \sqrt{e^{-\kappa_A C_A z}} dz \\ &= \frac{k_p C_M}{\sqrt{k_t}} \sqrt{\frac{2j\Phi I_0}{\kappa_A C_A}} \left(\frac{1 - e^{-\kappa_A C_A L/2}}{L} \right) \end{aligned} \quad (5.23)$$

This expression for the mean rate of polymerization is different from the more commonly found form e.g. in Odian⁵³; refer to Appendix A.5 for details.

5.2.2 Free Volume Model

Apparently, the idea of an interstitial volume is highly relevant in molecular transport (Cohen and Turnbull^{21,22,29}; Vrendas and Duda³²⁻³⁴) and physical aging (Hutchinson and Kovacs⁴); hence, it shall also be utilized in our modeling of diffusion and shrinkage during acrylate crosslinking polymerization. Consequently, we would use convention #5 in Table 5.1 for occupied and free volumes. Two important points are reiterated here. Firstly, the occupied volume in a ‘normal’ glass is not in equilibrium; it is greater than the equilibrium volume (as represented by the Bernal’s dense random structure) because there is a greater amount of interstitial volume being trapped. Secondly, the rate of volume relaxation and the instantaneous structure of the material are inter-dependent as shown in Figure 5.1; incorporating the first point, we could then add the occupied volume into the loop as shown in Figure 5.2.

Figure 5.2. Close-loop dependence in volume relaxation kinetics (incorporating occupied volume). Note that we have used our generic notations in lieu of Kloosterboer’s, and that dV_f/dt has been replaced with dv/dt as both free and occupied volumes are involved now.

We shall now proceed to write equations for and compute the various specific volumes using PEG700 as an example, and with Figure 5.3 illustrating the relationships between these volumes. Appendix A.6 provides a list of the symbols used in this section.

□ Monomer volumes

- Monomer’s VDW’s volume v_{wm} is computed from the group contribution scheme of van Krevelen¹⁸. $v_{wm} = 0.569 \text{ cm}^3/\text{g}$.
- Specific monomer volume v_m could be computed from group contribution scheme, or if available, from the product catalogues. Using the latter⁵⁴, $v_m = 0.893 \text{ cm}^3/\text{g}$ (van Krevelen’s¹⁸ method gives almost the same value; $v_m = 0.910 \text{ cm}^3/\text{g}$). Naturally, this volume, as well the following specific monomer volumes, is understood to be the equilibrium volume since the monomer is in the liquid state.

- Specific monomer occupied volume v_{om} is, following Cohen and Turnbull's argument²¹, the volume of the Bernal's dense random packing structure. Hence, $v_{om} = 1.16 v_{cm}$, where v_{cm} is the specific volume of its close-packed crystalline form. The group contribution scheme of van Krevelen¹⁸ does give an estimate of specific volume of crystalline form ($=1.435 v_w$) but this is the average value of the various crystalline forms, not exclusively of the close-packed one. From the list of polymers examined, the smallest volume (corresponding to the close-packed form) is in the region of $1.2 v_w$; we shall adopt this as the estimate of v_{cm} . Thus, $v_{om} = 1.16 v_{cm} = 1.16 \times (1.21 v_{wm}) = 1.39 v_{wm} = 0.791 \text{ cm}^3/\text{g}$.

- Specific monomer free volume v_{fm} is

$$\begin{aligned} v_{fm} &= v_m - v_{om} \\ &= 0.102 \text{ cm}^3/\text{g} \end{aligned} \quad (5.24)$$

- Monomer fractional free volume f_m is

$$\begin{aligned} f_m &= \frac{v_{fm}}{v_m} \\ &= 0.102/0.893 = 0.114 \end{aligned} \quad (5.25)$$

This figure is somewhat high compared with that using the Williams *et al.*'s fractional free volume equation $f = f_g + \alpha_2(T - T_g) = 0.025 + 3.504 \times 10^{-4} [25 - (-103)] = 0.070$ (the terms here have already been defined in the third paragraph of Section 5.1.1.); value of α_2 is calculated from van Krevelen¹⁸, and T_g from Reference 55. However as revealed by free volume measurements by positron annihilation spectroscopy (PALS), this equation tends to underestimate f and values of f in the region of 0.1 and above are commonly obtained from these experiments⁵⁶⁻⁵⁹.

□ Polymer volumes

- Polymer's VDW's volume v_{wp} is similarly computed as v_{wm} . $v_{wp} = 0.559 \text{ cm}^3/\text{g}$.
- Equilibrium specific polymer volume v_p is the volume of the hypothetical 100%-converted polymer in internal equilibrium (the 'ideal glass'). Hence, $v_p = 1.39 v_{wp} = 0.777 \text{ cm}^3/\text{g}$.

- Equilibrium specific polymer free volume v_{fp} is zero since the ‘ideal glass’ does not have any volume that could be redistributed freely.
- Equilibrium specific polymer occupied volume v_{op} is hence, by virtue of the polymer being an ‘ideal glass’, exactly the same as v_p . $v_{op} = v_p = 0.777 \text{ cm}^3/\text{g}$.
- Volumes during polymerization (refer to Figure 5.3)
 - Equilibrium specific total volume v_∞ is the volume that the polymerizing system would have if it is in internal equilibrium, and is computed by assuming that the initial monomer volume shrinks to the equilibrium polymer volume in a linear fashion i.e.

$$v_\infty = v_m(1 - \varepsilon_\infty x) \quad (5.26)$$

where

$$\begin{aligned} \varepsilon_\infty &= \frac{v_m - v_p}{v_m} \\ &= (0.893 - 0.777)/0.893 = 0.130 \end{aligned} \quad (5.27)$$

is the total volume contraction factor.

- Equilibrium specific occupied volume $v_{o\infty}$ is the defined and computed likewise.

$$v_{o\infty} = v_{om}(1 - \varepsilon_o x) \quad (5.28)$$

where

$$\begin{aligned} \varepsilon_o &= \frac{v_{om} - v_{op}}{v_{om}} \\ &= (0.791 - 0.777)/0.791 = 0.0176 \end{aligned} \quad (5.29)$$

is the occupied volume contraction factor.

- Equilibrium specific free volume $v_{f\infty}$ is the defined and computed likewise.

$$v_{f\infty} = v_{fm}(1 - \varepsilon_f x) \quad (5.30)$$

where

$$\begin{aligned} \varepsilon_f &= \frac{v_{fm} - v_{fp}}{v_{fm}} \\ &= (0.102 - 0)/0.102 = 1 \end{aligned} \quad (5.31)$$

is the free volume contraction factor.

- Equilibrium fractional free volume f_∞ is

$$\begin{aligned} f_\infty &= \frac{v_{f_\infty}}{v_\infty} \\ &= \frac{v_{fm}(1 - \varepsilon_f x)}{v_m(1 - \varepsilon_\infty x)} \\ &= f_m \frac{1 - \varepsilon_f x}{1 - \varepsilon_\infty x} \end{aligned} \quad (5.32)$$

Notably, it could be readily shown that this equation is equivalent to $f_\infty = f_m \phi_m + f_p(1 - \phi_m)$, which is commonly seen in literature^{1,60-62}

($\phi_m = \frac{1-x}{1-x+(v_p/v_m)x}$ is the volume ratio of the monomer).

- Actual specific total volume v is computed from the measured shrinkage, S , which is

$$S = \frac{v_m - v}{v_m} \quad (5.33)$$

Rearranging the terms, we have

$$v = v_m(1 - S) \quad (5.34)$$

- Actual specific free volume v_f is written in the same form as v with a hypothetical free volume shrinkage S_f .

$$v_f = v_{fm}(1 - S_f) \quad (5.35)$$

- Actual specific occupied volume v_o is written in the same form as v with a hypothetical occupied volume shrinkage S_o .

$$v_o = v_{om}(1 - S_o) \quad (5.36)$$

- Actual fractional free volume f is

$$\begin{aligned} f &= \frac{v_f}{v} \\ &= \frac{v_{fm}(1 - S_f)}{v_m(1 - S)} \\ &= f_m \frac{1 - S_f}{1 - S} \end{aligned} \quad (5.37)$$

- Excess volume (v_e , v_{fe} and v_{oe}) is defined as the difference between the equilibrium and actual volumes.

$$v_e = v - v_\infty = v_m(\varepsilon_\infty x - S) \quad (5.38)$$

$$v_{fe} = v_f - v_{f\infty} = v_{fm}(\varepsilon_f x - S_f) \quad (5.39)$$

$$v_{oe} = v_o - v_{o\infty} = v_{om}(\varepsilon_o x - S_o) \quad (5.40)$$

Figure 5.3. Diagrammatic representation of the various volumes.

We will now discuss how the hypothetical occupied and free volume shrinkages (S_o and S_f) could be computed. Naturally, the best method will be to measure the variation in the free volume during polymerization using PALS. In the absence of such experiment data, we could only give some theoretically reasonable estimation. The volume contraction factors, ε_o and ε_f , could be thought of as representing the tendency for shrinkage of occupied and free volumes respectively to occur when the system stays in equilibrium during polymerization; with $\varepsilon_f \gg \varepsilon_o$, this leads to the logical statement that the tendency for the free volume to shrink is much greater than for occupied volume.

Let's assume that such a tendency is not altered when the volume falls out of equilibrium; hence, we could write

$$\frac{S_f}{S_o} = \frac{\varepsilon_f}{\varepsilon_o} \quad (5.41)$$

To express S_f or S_o in terms of the measurable S , we have to derive the relationship between these three terms. This could be easily done as follows.

$$\begin{aligned} v &= v_o + v_f \\ v_m(1-S) &= v_{om}(1-S_o) + v_{fm}(1-S_f) \\ S &= \frac{v_{om}}{v_m} S_o + \frac{v_{fm}}{v_m} S_f \\ S &= (1-f_m)S_o + f_m S_f \end{aligned} \quad (5.42)$$

Similarly, by considering the equilibrium volumes, we could also derive

$$\varepsilon_\infty = (1-f_m)\varepsilon_o + f_m \varepsilon_f \quad (5.43)$$

Combining these equations, we then obtain

$$\frac{S_f}{S} = \frac{\varepsilon_f}{\varepsilon_\infty} \quad (5.44)$$

Hence, we have obtained S_f in terms of the measurable quantities. Putting this last equation into the actual fractional free volume equation, eq 5.37, we have the following equation that allows us to compute f with only the shrinkage data.

$$\begin{aligned} f &= f_m \frac{1-S_f}{1-S} \\ f &= f_m \frac{1-(\varepsilon_f/\varepsilon_\infty)S}{1-S} \end{aligned} \quad (5.45)$$

The various specific volumes and contraction factors of TMPTA are listed in Table 5.2.

Monomer's specific volumes [g/cm ³]	PEG700	TMPTA
v_{wm}	0.569	0.556
v_m	0.893	0.901
v_{om}	0.791	0.773
v_{fm}	0.102	0.128
f_m	0.114	0.142
Polymer's specific volumes [g/cm ³]		
v_{wp}	0.559	0.522
v_p	0.777	0.726
v_{fp}	0	0
v_{op}	0.777	0.726
Contraction factors		
ε_∞	0.130	0.195
ε_o	0.0176	0.0610
ε_f	1	1

Table 5.2. Specific volumes and contraction factors of TMPTA.

We have thus made and justified our choice of definitions of free and occupied volumes, which are computed based on the established van Krevelen's group contribution scheme¹⁸. The next section examines the free volume treatment by Bowman and Peppas¹ and compares it with the treatment that is just presented.

5.2.2.1 Comparison with Bowman and Peppas' Treatment

Bowman and Peppas started with the typical fractional free volume equation of Williams *et al.*⁷, which is reproduced here:

$$f = f_0 + \alpha(T - T_g)^\ddagger \quad (5.46)$$

where $\alpha = \alpha_R - \alpha_G$ is the expansion coefficient of the free volume (α_R and α_G are the expansion coefficients of the material in its rubbery and glassy state respectively), and $f_0 = 0.025$ is the fractional free volume at T_g , the glass transition temperature.

[‡] (1). In their paper, the fractional free volume is denoted by v_f instead.

In an acrylate system undergoing polymerization, it is assumed that the fractional free volumes of the monomer, f_m , and polymer, f_p , add up in a thermodynamically ideal way to give the total equilibrium free volume, f_∞ , of the system:

$$f_\infty = f_m \phi_m + f_p (1 - \phi_m) \quad (5.47)$$

where ϕ_m is the volume fraction of the monomer in the system, given as a function of the conversion x , by

$$\phi_m = \frac{1 - x}{1 - x + (v_p / v_m) x} \quad (5.48)$$

The actual total free volume, f , is given by the equilibrium free volume plus an excess free volume, f_e :

$$f = f_\infty + f_e \quad (5.49)$$

Following Kovacs^{4-6,63}, they expressed the excess free volume, f_e , as

$$f_e = \frac{v - v_\infty}{v_\infty} \quad (5.50)$$

where v is the actual specific volume and v_∞ is the equilibrium specific volume, a function of conversion, determined from

$$v_\infty = v_m (1 - \varepsilon_v x) \quad (5.51)$$

The term ε_v is the contraction factor i.e.

$$\varepsilon_v = \frac{v_m - v_p}{v_m} \quad (5.52)$$

The subscripts m and p represent monomer and polymer respectively.

Comparing their treatment to the one in this work, there are two important differences. The most obvious is their use of eq 5.46, which we avoided here due to the uncertainties of the definitions of free and occupied volumes. A more practical reason for eschewing eq 5.46 is that it is valid only for $T > T_g$; this rule is somehow overlooked in their paper and several other similar works⁶⁰⁻⁶²; the result is that $f_p < 0$ for polymers having $T_g \gg 25^\circ\text{C}$, which is a totally unacceptable situation. There are also works that do address this issue upfront; Kurdikar and Peppas⁶⁴ used $f(T \leq T_g) = 0.025$, which is really the original intention of Williams *et al.*⁷, and Fox and Flory¹⁹; in Soh and

Sundberg's work⁶⁵, they noted that Vrendas and Duda^{32-34,66-70} had used the form $f = f_g + \lambda \alpha_f (T - T_g)$ for $T < T_g$ where λ is a constant related to the ratio of the coefficients of thermal expansion above and below T_g (e.g. $0.2 \leq \lambda \leq 0.4$ for poly(vinyl acetate)). As already presented, we circumvent this awkward situation by defining free and occupied volumes unambiguously and computed them using well-established group contribution schemes. The more critical difference is that in their treatment, the excess volume generated during polymerization is entirely 'assigned' to the free volume whereas in this work, it is apportioned to both free and occupied volumes. To be presented in the Results and Discussion section, our experiment data show that the former approach leads to an *increasing* amount free volume during polymerization, a notion that is entirely out of sort with conventional theories; no such abnormal trend is obtained using the latter approach.

5.2.3 Model of Kinetic Constants Based on Free Volume Theory

Free volume theory provides a simple mean of modeling kinetic constants because such models have few parameters, and importantly, these parameters could be determined readily from experiments; in comparison, more complicated models based on molecular diffusion involved parameters, such as entanglement distances and diffusion coefficients, that are extremely difficult to estimate for complex crosslinking systems like those of acrylates.⁷¹

The definitive free volume theory based kinetic constants model proposed by Anseth and Bowman⁹ is

$$k_p = k_{p0} \left(\frac{1}{1 + e^{A_p (1/f - 1/f_{cp})}} \right) \quad (5.53)$$

$$k_t = k_{t0} \left(1 + \frac{1}{R \frac{k_p}{k_{p0}} + e^{-A_t (1/f - 1/f_{ct})}} \right)^{-1} \quad (5.54)$$

In this model, the kinetics are controlled by either chemical reaction or by diffusion; and for the termination kinetics, there is also a third regime known as reaction-diffusion-controlled, in which the termination kinetics is dictated by the propagation one. A description of the kinetic parameters in these equations will provide a clearer picture.

- f_{cp} and f_{ct} are the critical fractional free volumes for propagation and termination respectively; at fractional free volumes less than the critical values, the amount of free space available for movement of the reacting species is severely limited and hence, the propagation or termination step becomes diffusion-controlled.
- A_p and A_t are dimensionless parameters that control the rate of auto-deceleration and auto-acceleration respectively.
- k_{p0} is the chemical reaction-controlled propagation kinetic constant. This could be readily understood: the exponential term represents the effect of diffusion on propagation via the fractional free volume; when $f \gg f_{cp}$, diffusion effect is negligible (i.e. in chemical reaction-controlled regime), the exponential term goes to zero, and thus, $k_p = k_{p0}$.
- k_{t0} is the chemical reaction-controlled termination kinetic constant by the same reasoning.
- R is the reaction diffusion parameter, which is a dimensionless proportionality constant relating the mass transfer coefficient for reaction diffusion to the chemical reaction-controlled kinetic rate (eq 5.55). Reaction diffusion occurs at high conversion, when segmental and translational diffusions of the macro-radicals are severely limited by the crosslinked network, and reaction diffusion is the only route to termination. The proportionality equation is

$$\left(\frac{k_t}{k_p} \right)_{rd} = R \frac{k_{p0}}{k_{t0}} \quad (5.55)$$

where the subscript rd denotes reaction diffusion.

5.2.4 Volume Relaxation Model

Following Bowman and Peppas¹, we shall use the single-parameter theory of volume relaxation as presented in Hutchinson and Kovacs⁸. We shall briefly review this model and then propose some modifications to it.

In this theory, it is assumed that the relaxing system could be completely determined in its non-equilibrium state by its temperature T , pressure P and a *single ordering parameter* Z . As such, an infinitesimal change in specific volume could be broken down into three components, viz.

$$\frac{dv}{dt} = \left(\frac{\partial v}{\partial T} \right)_{P,Z} \frac{dT}{dt} + \left(\frac{\partial v}{\partial P} \right)_{T,Z} \frac{dP}{dt} + \left(\frac{\partial v}{\partial Z} \right)_{P,T} \frac{dZ}{dt} \quad (5.56)$$

In this work, T and P are constant, and hence, this equation is reduced to

$$\frac{dv}{dt} = \left(\frac{\partial v}{\partial Z} \right)_{P,T} \frac{dZ}{dt} \quad (5.57)$$

In addition, it is assumed that the rate of change of $\delta_v \equiv (v - v_\infty)/v_\infty$, the relative departure of the specific volume from equilibrium, effected by a change in Z , is proportional to the actual departure from equilibrium (linear approximation) via a retardation time τ i.e.

$$\left(\frac{\partial \delta_v}{\partial Z} \right)_{P,T} \frac{dZ}{dt} = -\frac{\delta_v}{\tau} \quad (5.58)$$

Differentiation of the defining expression of δ_v gives

$$\delta_v = \frac{v - v_\infty}{v_\infty}$$

$$\left(\frac{\partial \delta_v}{\partial Z} \right)_{P,T} = \frac{1}{v_\infty} \left(\frac{\partial v}{\partial Z} \right)_{P,T} \quad (5.59)$$

Combining eqs 5.57, 5.58 and 5.59, we then obtain

$$\frac{dv}{dt} = -\frac{v_\infty \delta_v}{\tau}$$

$$\frac{dv}{dt} = -\frac{v - v_\infty}{\tau} \quad (5.60)$$

The form of dependence of τ on free volume is in the form of Doolittle's¹⁷ equation

$$\tau = \tau_0 \exp\left(\frac{b}{f}\right) \quad (5.61)$$

where τ_0 and b are constants and b is found to be in the order of unity. Letting τ_g and f_g to be the relaxation time and fractional free volume at T_g , eq 5.61 is thus rewritten as

$$\tau = \tau_g \exp \left[b \left(\frac{1}{f} - \frac{1}{f_g} \right) \right] \quad (5.62)$$

and τ_g is estimated to be about 100 s. Notably, Hutchinson and Kovacs chose to define f to be

$$f = \frac{v - v_o}{v_\infty} \quad (5.63)$$

so that, with some manipulations,

$$\begin{aligned} f &= \frac{v - v_o}{v_\infty} \\ &= \frac{v_\infty - v_o}{v_\infty} + \frac{v - v_\infty}{v_\infty} \\ &= f_\infty + \delta_v \end{aligned} \quad (5.64)$$

they could conveniently express f in terms of the equilibrium f (i.e. f_∞) and δ_v . In Bowman and Peppas' paper¹, the expression of f_∞ is given by eq 5.47.

Three modifications will be implemented here. Firstly, we will be using the new expression for f (eq 5.45) rather than eqs 5.49 or 5.64. Secondly, it is impractical here to use τ_g and f_g as the reference point in eq 5.62 because the T_g of our reacting system changes with conversion, and thus, τ_g and f_g are not constant values. Instead, we will use the monomer's relaxation time, τ_m , and its fractional free volume, f_m , i.e.

$$\tau = \tau_m \exp \left[b \left(\frac{1}{f} - \frac{1}{f_m} \right) \right] \quad (5.65)$$

Lastly, as had already been implemented in the Bowman and Peppas' paper¹, it is regarding the relaxation parameter, b , in eq 5.61.⁷² Generally, b is taken to be unity^{7,8} due to the work of Doolittle¹⁷ on the viscosity of n -paraffin hydrocarbons. However, in applying to acrylate polymerization, which happens on a time scale of a few seconds as compared to hours⁸ or days⁴ for isothermal volume relaxation, b may not necessarily be unity; like in their paper, it will be treated here as an unknown constant whose value is to be determined from experiments. The working expression for evaluating τ is obtained by substituting eqs 5.26 and 5.34 into eq 5.60, and rearranging it.

$$\tau = \frac{\varepsilon_{\infty} x - S}{dS/dt} \quad (5.66)$$

which is a function of the measured shrinkage, S , and conversion, x . Subsequently, the volume relaxation parameters τ_m and b could be determined from a least-square regression of $\ln(\tau)$ on $1/f$.

5.2.5 Simulation Model

The set of equations for simulating shrinkage and conversion simultaneously is compiled below. Note that we are not using the pseudo-steady state rate of polymerization reaction, eq 5.23; instead we use the set of equations, eqs 5.11, 5.67 and 5.68, that describes the unsteady state polymerization; eqs 5.67 and 5.68 are obtained directly from eqs 5.20 and 5.8 respectively, by replacing the symbol $\sum_{m=0}^{\infty} C_{RM_m}^{\bullet}$ with a more convenient one, $C_{p^{\bullet}}$. As for eq 5.69, it is obtained by substituting eq 5.65 into eq 5.66 and then rearranging it. Eq 5.70 is simply the definition of conversion, x . The remaining equations have already been introduced earlier.

$$C_A = \frac{1}{\kappa_A L} \ln \left[1 + \left(e^{\kappa_A C_{A0} L} - 1 \right) e^{-\Phi \kappa_A I_0 t} \right] \quad (5.11)$$

$$\frac{dC_{p^{\bullet}}}{dt} = \frac{j \Phi_A I_0}{L} \left(1 - e^{-\kappa_A C_A L} \right) - 2k_t C_{p^{\bullet}}^2 \quad (5.67)$$

$$\frac{dC_M}{dt} = -k_p C_M C_{p^{\bullet}} \quad (5.68)$$

$$\frac{dS}{dt} = \frac{\varepsilon_{\infty} x - S}{\tau_m \exp \left[b \left(\frac{1}{f} - \frac{1}{f_m} \right) \right]} \quad (5.69)$$

$$k_p = k_{p0} \left(\frac{1}{1 + e^{A_p (1/f - 1/f_{cp})}} \right) \quad (5.53)$$

$$k_t = k_{t0} \left(1 + \frac{1}{R \frac{k_p}{k_{t0}} + e^{-A_t (1/f - 1/f_{ct})}} \right)^{-1} \quad (5.54)$$

$$f = f_m \frac{1 - (\varepsilon_f / \varepsilon_\infty) S}{1 - S} \quad (5.45)$$

$$x = 1 - \frac{C_M}{C_{M0}} \quad (5.70)$$

5.3 Methods of Determining Kinetic Parameters

An accurate and convenient procedure for determining the kinetic parameters has been proposed by Goodner *et al.*⁶², and would be used here with some alterations. In their work, the treatment of free volume follows that by Bowman and Peppas¹, as described in the previous section. We will of course use our treatment of free volume instead.

In this method, the complicated k_p and k_t expressions of eqs 5.53 and 5.54 are simplified based on assumptions on the relative sizes of f , f_{cp} and f_{ct} , and then applying them in eq 5.23. For this purpose, eq 5.23 needs to be rewritten in a more convenient form; noting that $C_M = C_{M0}(1 - x)$ and $\overline{R_p} = C_{M0} \left(\frac{dx}{dt} \right)$, where x is the conversion, eq 5.23 is then rearranged as

$$\overline{R_p} = \frac{k_p C_M}{\sqrt{k_t}} \sqrt{\frac{2j\Phi I_0}{\kappa_A C_A} \left(\frac{1 - e^{-\kappa_A C_A L/2}}{L} \right)} \quad (5.23)$$

$$\frac{k_p}{\sqrt{k_t}} = \frac{1}{1 - x} \left(\frac{dx}{dt} \right) \sqrt{\frac{2j\Phi I_0}{\kappa_A C_A} \left(\frac{1 - e^{-\kappa_A C_A L/2}}{L} \right)}$$

Let $h(t) \equiv \frac{1}{1 - x} \left(\frac{dx}{dt} \right) \sqrt{\frac{2j\Phi I_0}{\kappa_A C_A} \left(\frac{1 - e^{-\kappa_A C_A L/2}}{L} \right)}$, therefore,

$$\frac{k_p}{\sqrt{k_t}} = h(t) \quad (5.71)$$

and $h(t)$ is a function of time only and whose values are known from conversion data obtained from experiment.

The progress of polymerization is broken up into four stages and analyzed separately.

stage (i) The initial stage in which there is a lot of free volume and hence no diffusion limitation. The kinetics are all chemical reaction-controlled. In this case, $f \gg f_{cp}, f_{ct}$ and eqs 5.53 and 5.54 reduce to

$$k_p \approx k_{p0} \quad (5.72)$$

$$k_t \approx k_{t0} \quad (5.73)$$

Substituting into eq 5.71, we have

$$h(t) = \frac{k_{p0}}{\sqrt{k_{t0}}} \quad (5.74)$$

As k_{p0} and k_{t0} are constants, $h(t)$ becomes a constant in this stage. Denoting this constant value of $h(t)$ as $h_{(i)}$, eq 5.74 is then rearranged as eq 5.75 below.

$$k_{t0} = \left(\frac{k_{p0}}{h_{(i)}} \right)^2 \quad (5.75)$$

stage (ii) Some free volume has been consumed by the polymerization reaction, and this causes the mobility of the growing macro-radicals to be reduced dramatically in the polymer network; the termination kinetics hence becomes diffusion-controlled. The propagation kinetics are not yet affected as the relatively much smaller monomer molecules can still move freely in the network. This event causes the auto-acceleration behavior. In this case, $f_{ct} > f \gg f_{cp}$ and eqs 5.53 and 5.54 reduce to

$$k_p \approx k_{p0} \quad (5.72)$$

$$k_t \approx k_{t0} \left(\frac{1}{\exp[A_t (1/f - 1/f_{ct})]} \right) \quad (5.76)$$

Substituting into eq 5.71, rearranging and defining a new parameter β ,

$$\beta \equiv \ln \left(\frac{k_{t0} h(t)^2}{k_{p0}} - 1 \right) = A_t \left(\frac{1}{f} \right) - \frac{A_t}{f_{ct}} \quad (5.77)$$

stage (iii) More free volume is being consumed. The macro-radicals are now essentially immobile while the monomer molecules are still unaffected. As in stage (ii), $f_{ct} > f \gg f_{cp}$. Despite the immobility of the macro-radicals, termination could still proceed via the reaction-diffusion route; the propagation reaction increases the length of the macro-radicals, and in the process, transporting the active radical centers to other places where they may meet and terminate. The relationship between k_t and k_p is then given by eq 5.55; rewriting it here with a new constant $B \equiv R(k_{p0}/k_{t0})$ and noting that eq 5.72 still applies:

$$k_p \approx k_{p0} \quad (5.72)$$

$$k_t = B \cdot k_p \quad (5.78)$$

Substituting into eq 5.71, we have

$$h(t) = \sqrt{\frac{k_{p0}}{B}} \quad (5.79)$$

As k_{p0} and B are constants, $h(t)$ becomes a constant in this stage. Denoting this constant value of $h(t)$ as $h_{(iii)}$, eq 5.79 is then rearranged as eq 5.80 below.

$$k_{p0} = B \cdot h_{(iii)}^2 \quad (5.80)$$

stage (iv) The amount of free volume has hit such a low level that even the diffusion of the small monomer molecules is becoming restricted, and this adds to the effect of decreasing monomer concentration in reducing the polymerization rate. This event is known as auto-deceleration. Meanwhile, termination is still reaction-diffusion controlled. In this case, $f < f_{cp}, f_{ct}$ and eq 5.53 could not be simplified, and eq 5.78 still applies:

$$k_p = k_{p0} \left(\frac{1}{1 + \exp[A_p(1/f - 1/f_{cp})]} \right) \quad (5.53)$$

$$k_t = B \cdot k_p \quad (5.78)$$

Substituting into eq 5.71, rearranging, and defining a new parameter δ ,

$$\delta \equiv \ln \left(\frac{k_{p0}}{B \cdot h(t)^2} - 1 \right) = A_p \left(\frac{1}{f} \right) - \frac{A_p}{f_{cp}} \quad (5.81)$$

The parameters would be determined in this sequence: (1) k_{p0} using eq 5.80; (2) A_p and f_{cp} using eq 5.81 by means of regressing δ on $1/f$; (3) k_{t0} using eq 5.75; (4) A_t and f_{ct} using eq 5.77 by means of regressing β on $1/f$.

For this method to work, we would have to first find out the value of B , the proportionality constant linking k_p and k_t in the reaction-diffusion regime. This could be done by means of ‘in the dark’ experiments, in which the UV light is removed from the system during polymerization and measuring the conversion rate of reactions happening in the absence of UV light i.e. in the dark. The set of equations governing these reactions are given next.

5.3.1 Kinetic Equations for ‘in-the-dark’ Reactions

After removing the UV source (for convenience, let’s term this the shutter-off event), the initiation step will cease but the propagation and termination steps will continue to occur in the dark. In this case, eq 5.20 will become

$$\frac{d}{dt} \sum_{m=0}^{\infty} C_{RM_m^\bullet} = -2k_{t,so} \left(\sum_{m=0}^{\infty} C_{RM_m^\bullet} \right)^2 \quad (5.82)$$

where the subscript *so* denotes this shutter-off event. Denoting $\sum_{m=0}^{\infty} C_{RM_m^\bullet}$ by $C_{P^\bullet}$ for simpler representation (as was done previously in Section 5.2.5), eq 5.82 is then integrated.

$$\int_{C_{P^\bullet,so}}^{C_{P^\bullet}} \frac{dC_{P^\bullet}'}{C_{P^\bullet}'^2} = -2k_{t,so} \int_{t_{so}}^t dt' \quad , t \geq t_{so}$$

$$\sum_{m=0}^{\infty} C_{RM_m^\bullet} = C_{P^\bullet} = \frac{C_{P^\bullet,so}}{1 + 2k_{t,so} C_{P^\bullet,so} (t - t_{so})} \quad , t \geq t_{so} \quad (5.83)$$

Substituting eq 5.83 into eq 5.8 and integrating,

$$\frac{C_M}{C_{M0}} = \frac{C_{M,so}}{C_{M0}} \left[1 + 2k_{t,so} C_{P^*,so} (t - t_{so}) \right]^{\frac{k_{p,so}}{2k_{t,so}}}, t \geq t_{so} \quad (5.84)$$

where C_{M0} is the initial concentration of M .

The reaction constants k_p and k_t could be determined from eqs 5.23 and 5.84 using real-time FTIR to monitor the relative double bond concentrations in the reaction system.

Using FTIR, the absorbance (Abs) at an appropriate peak (such as the one corresponding to the alkenyl C=C stretching vibration at 1647 cm^{-1} ⁷³) was used to quantify the concentration of double bonds. Noting that the ratio Abs/Abs_0 is equal to C_M/C_{M0} , eq 5.84 could be rewritten as

$$\frac{C_M}{C_{M0}} = \frac{Abs}{Abs_0} = \frac{Abs_{so}}{Abs_0} \left[1 + 2k_{t,so} C_{P^*,so} (t - t_{so}) \right]^{\frac{k_{p,so}}{2k_{t,so}}}, t \geq t_{so} \quad (5.85)$$

The parameters $2k_{t,so} C_{P^*,so}$ and $k_{p,so}/(2k_{t,so})$ could be then found from a non-linear least-square curve-fitting of Abs/Abs_0 on t .

At the shutter-off time (t_{so}), we assume that the rate of polymerization is at pseudo-steady state⁷⁴ and hence, eq 5.23 could be used to obtain another equation involving $k_{p,so}$ and $k_{t,so}$. Writing for the conditions at t_{so} , eq 5.23 becomes

$$\begin{aligned} \overline{R_{p,so}} &= \frac{k_{p,so} C_{M,so}}{\sqrt{k_{t,so}}} \sqrt{\frac{2j\Phi I_0}{\kappa_A C_A}} \left(\frac{1 - e^{-\kappa_A C_A L/2}}{L} \right) \\ \frac{k_{p,so}}{\sqrt{k_{t,so}}} &= \frac{\overline{R_{p,so}}}{C_{M,so}} \sqrt{\frac{\kappa_A C_A}{2j\Phi I_0}} \left(\frac{L}{1 - e^{-\kappa_A C_A L/2}} \right) \end{aligned} \quad (5.86)$$

The value of $\overline{R_{p,so}}$ could be found using the equation

$$\overline{R_{p,so}} = -\frac{dC_M}{dt} \Big|_{t=t_{so}} = -C_{M0} \cdot \frac{d}{dt} \frac{Abs}{Abs_0} \Big|_{t=t_{so}} \quad (5.87)$$

The value $\left. \frac{d}{dt} \frac{Abs}{Abs_0} \right|_{t=t_{so}}$ could be obtained by graphical differentiation of the Abs/Abs_0 vs t plot at $t = t_{so}$, but as FTIR data are inherently noisy, this method may produce unreliable value. The alternative method is to use eq 5.85 to calculate the value of $\left. \frac{d}{dt} \frac{Abs}{Abs_0} \right|_{t=t_{so}}$, which is then

$$\left. \frac{d}{dt} \frac{Abs}{Abs_0} \right|_{t=t_{so}} = \frac{Abs_{so}}{Abs_0} \left[2k_{t,so} C_{P^*,so} \right] \cdot \left[\frac{k_{p,so}}{2k_{t,so}} \right] \quad (5.88)$$

This way, using eqs 5.85 and 5.86, $k_{p,so}$ and $k_{t,so}$ could be individually solved for.

5.4 Experiment Section

The real-time conversions of the acrylates were tracked using a Nicolet Magna IR 560 ESP spectrophotometer (Thermo Nicolet Corp., Madison, WI) incorporated with a ‘Golden Gate’ ATR module (Graseby Specac Inc., Smyrna, GA). A drop of the acrylate was placed on the ATR crystal and then covered with a 125 μm thick Melinex film (Type 454, Gage 300; from DuPont Teijin Films, Wilmington, DE), as shown in Figure 5.4. The alkenyl C=C stretching vibration peak at 1637 cm^{-1} was monitored to determine the conversion as a function of time⁷³, and the methyl C-C stretching peak at *ca.* 2961 cm^{-1} was used as the internal reference⁷⁵.

The position of the Melinex film was monitored using a high-precision laser displacement meter LC-2401 (sensor head model: LC-2430; from Keyence Co., Kyoto, Japan), which could detect a minimum change of $0.32\text{ }\mu\text{m}$. The meter was linked to a computer that logs the displacement data. The laser beam, initially zeroed on the ATR crystal, would now be reflected off the Melinex film, and hence gave the thickness of the film and the acrylate.

The UV source used is Superlite SUV-DC-P UV spot cure unit with a Series 300 liquid lightguide (diameter 8mm) (Lumatec GmbH, Deisenhofen, Germany).

Figure 5.4. Experiment setup for simultaneously collecting the shrinkage and conversion data (not to scale).

The FTIR and shrinkage data collection would be started, and after a pre-set time lag of two seconds (the IR spectra of the uncured monomer will be collected during this interval), the UV lightguide's shutter, controlled by the FTIR instrument's remote start accessory, would be opened. In this way, the change in the thickness and conversion could be measured in a synchronized manner. The IR spectra, at a resolution of 4 cm^{-1} , were collected at 1.06 s interval (this is the mandatory interval set by the instrument for the resolution selected) for 100 s. The laser displacement meter collected the displacement data at 1 s interval for the same duration. To match the data interval spacing, the conversion data were then linearly interpolated at 1 s interval.

The experiment conditions and material properties are summarized in Table 5.3.

	PEGDA700	TMPTA
ρ_m [g/cm ³] ^(a)	1.12	1.11
MW	698 ^(b)	296
N ^(c)	2	3
C_{M0} [mol/m ³] ^(d)	3209	11250
L [μm]	220 ± 15 (4 samples)	160 ± 22 μm (4 samples)
UV intensity and photoinitiator		
$I_0 = 16 \text{ mW/cm}^2$ at 365 nm = $4.88 \times 10^{-4} \text{ einstein/m}^2 \cdot \text{s}$ ^(e)		
$\Phi = 0.7$ ^(f)		
$j = 2$		
$\kappa_A = 9.25 \text{ m}^2/\text{mol}$ ^(a)		
$C_{A0} = 0.2 \text{ wt\%} = 781.25 \text{ mol/m}^3$		

Table 5.3. Material properties and experiment conditions. ^(a) Taken from products' catalogue⁵⁴. ^(b) Based on 13 ethylene glycol groups. ^(c) N = number of double bonds per molecule. ^(d) $C_{M0} = \rho_m / \text{MW} \times N \times 10^6$. ^(e) 1 einstein = $N_A h \nu$ (J/mol) where N_A (1/mol) is the Avogadro's Number, h (J.s) is the Planck's constant and ν (1/s) is the frequency of the light. ^(f) From Reference 76.

The shrinkage measured in our experiment is actually the linear shrinkage, not the volumetric shrinkage as required by eq 5.33. However, as the x and y dimensions of the reaction system are much greater than the z one (Figure 5.5), the linear shrinkage closely approximates the volumetric shrinkage. Consider the reaction system in Figure 5.5 shrinking in the x direction by dx and so on. Then, we have

$$S = -\frac{\Delta V}{V} = -\frac{(x-dx)(y-dy)(z-dz) - xyz}{xyz} \quad (5.89)$$

As dx , dy and dz are small, higher order terms such as $dx \cdot dy \cdot dz$ and $dx \cdot dy$ are negligible, and hence eq 5.89 becomes

$$S \cong \frac{dx}{x} + \frac{dy}{y} + \frac{dz}{z} \quad (5.90)$$

Typically, $x = y = 1 \text{ cm}$, and dx and dy are in the regions of μm , and hence the first two terms on the right of eq 5.90 are negligible, and thus

$$S \cong \frac{dz}{z} \quad (5.91)$$

The volumetric shrinkage is then approximated by the change in the z direction only, which is the change monitored by the laser displacement meter.

Figure 5.5. Schematic of the reaction system.

5.5 Results and Discussion

We firstly present and discuss the conversion and shrinkage profiles obtained from experiments. With these data, the fractional free volume profiles of the reacting system were then plotted. Next, results of the experiments leading to the determination of the kinetic parameters (k_p , A_p , f_{cp} , k_t , A_t , f_{ct}) followed. In this procedure, the range of f in which reaction-diffusion controls the kinetics was identified; ‘in-the-dark’ experiments were carried out in this range and the reaction-diffusion parameter, R , was found; lastly, stage-by-stage analysis of the conversion profile gave the kinetic parameters. Following this, we present the variation of relaxation time with conversion. Finally, all these experimentally obtained parameters were inputted into our simulation model, and we present and discuss the simulation results.

5.5.1 Conversion and Shrinkage Profiles

The conversion and shrinkage data for PEG700 and TMPTA, obtained from 4 separate runs of experiments each, are plotted in Figures 5.6 and 5.7. The plots have been smoothed by least-square curve-fitting of the data with a non-linear function to remove the noise; details are covered in the Appendix A.7. These plots show that the experiments were repeatable within experimental errors.

From these plots, it is seen that PEG700 can attain higher maximum conversion than TMPTA, but its maximum shrinkage is lower. These two observations could be accounted for by the longer spacer group of PEG700. Long spacer group has been shown

to make the polymer network less stiff, and this helps to delay the onset of diffusion-controlled propagation, and thus allowing conversion to proceed to a higher value.⁷⁷ Shrinkage is principally due to the reaction of the C=C bonds into C-C bonds, and it is conceivable that if the molar ratio of C=C bonds to spacer group is lower, the maximum percentage shrinkage will also be lower, as in the case of PEG700.

Figure 5.6. Conversion-time plots for (a) PEG700 and (b) TMPTA. The dotted lines are one standard deviation away from the solid line representing the mean of 4 runs. The bottom plots are close-ups of the first 20 s.

Figure 5.7. Shrinkage-time plots of (a) PEG700 and (b) TMPTA. Legends are as per Figure 5.6. The bottom plots are close-ups of the first 20 s.

5.5.2 Free Volume Profiles

Using eqs 5.32 and 5.45, the values of f_{∞} and f were calculated for each set of data and a typical plot of them, shown in Figure 5.8, clearly show the departure from equilibrium. Evidently, the PEG700 system shows a greater departure from equilibrium than the TMPTA one. This could be rationalized by the long spacer group of PEG700 as well because they would likely prevent the molecules from rearranging quickly enough (on the time scale of photopolymerization) to attain the equilibrium dense amorphous structure form. As a result, the deviation from equilibrium is larger in PEG700 than in TMPTA, which has a much shorter spacer group.

From these plots, we could also attempt to rationalize the impact of the rate of free volume collapse on the maximum conversion attainable. We estimate from the plots

that, for PEG700, the rate of collapse of free volume (relative to the initial free volume) is $-\frac{d(f/f_m)}{dx} \approx -\frac{(0.114 - 0.07)/0.114}{0 - 1} = 0.386$. Compared this with the TMPTA case, $-\frac{d(f/f_m)}{dx} \approx -\frac{(0.142 - 0.075)/0.142}{0 - 0.6} = 0.786$. Apparently, PEG700 could reach almost 100% conversion because the slow rate of collapse generates a large excess of free volume, whereas for TMPTA, the much higher rate of collapse does not generate sufficient excess free volume to sustain reaction beyond about 60%.

Figure 5.8. Typical plots of f (solid line) and f_∞ (dashed line) against conversion x for (a) PEG700 and (b) TMPTA.

5.5.2.1 Profiles using Bowman and Peppas' Treatment

As mentioned in Section 5.2.2.1, using Bowman and Peppas' treatment could give a fractional free volume that is increasing with conversion, a situation that is against conventional theories. This is illustrated using the TMTPA data here. The material properties needed are tabulated in Table 5.4, and were calculated from independent sources. The results are plotted in Figure 5.9. The cause of this increasing trend is that the large amount of excess volume ($v - v_\infty$) generated has all been 'assigned' to the free volume as it was thought that only free volume could fall out of equilibrium. In our treatment, both free and occupied volumes could go into inequilibrium, and therefore the large excess volume has to be partitioned between them, a procedure that would lead to a reasonable decreasing free volume trend with conversion.

Monomer	Polymer
$v_m = 0.893 \text{ cm}^3/\text{g}$ ^(a)	$v_p = 0.686 \text{ cm}^3/\text{g}$ ^(b)
$T_{gm} = -50 \text{ }^\circ\text{C}$ ^(c)	$T_{gp} = 141 \text{ }^\circ\text{C}$ ^(c)
$\alpha_m = 4.64 \times 10^{-4} \text{ K}^{-1}$ ^(d)	$\alpha_p = 2.78 \times 10^{-4} \text{ K}^{-1}$ ^(d)

Table 5.4. Material properties. ^(a) From product catalogue⁵⁴. ^(b) From the group contribution scheme of Reference . Calculated from the group contribution scheme of Reference 55. ^(d) From the Simha-Boyer's empirical relationship, $\alpha = 0.115 / T_g$, where α is the difference between the coefficients of thermal expansion above and below T_g .¹⁸

Figure 5.9. Fractional free volume profiles obtained using Bowman and Peppas' treatment. Dashed line: equilibrium case, f_∞ ; solid line: calculated from experiment data, f .

5.5.3 Kinetic Parameters

The normalized rate of polymerization, as represented by dx / dt , is plotted against $1/f$ with the four stages of polymerization marked out in Figure 5.10. It is noted that the four stages do not span the entire $1/f$ axis; the gap between the stages are considered to be the transition zones in which more than one mechanism is in operation, and hence, in which the simplified kinetic constants' relationships, eqs 5.75, 5.77, 5.80 and 5.81, are inapplicable (the exception is stage (i), which will be elaborated in the next paragraph). The general rules for demarcating the stages in the dx / dt vs $1/f$ plots are described below.

Figure 5.10. Typical plot of dx/dt against $1/f$ for (a) PEG700, and (b) TMPTA. The four stages of polymerization are indicated.

In stage (i), the kinetic constants are not functions of $1/f$ since the kinetics are not diffusion-controlled; hence, the normalized rate of polymerization is approximately constant in this stage, and a plateau region should be seen in the initial part of the dx/dt vs $1/f$ plot.⁶² However, for multi-functional acrylates, stage (i) is usually not obvious because microgels are formed almost immediately once the polymerization starts, thereby imposing limitations to diffusion of macro-radicals.^{62,77} Therefore, stage (i) actually becomes one with a mixed termination mode (both chemical-reaction-controlled and diffusion-controlled). Such is the case we observed in our PEG700 and TMPTA system; the expected plateau region is not seen in both plots in Figure 5.10. What we do observe in the initial part is a change in the slope, which is due to the transition of the termination mode, from a mixed one to a solely diffusion-controlled one. We shall use this initial part to approximate stage (i).

Stage (ii), where the termination mode is one of diffusion-controlled, follows stage (i) immediately, as described in the previous paragraph. We could readily identify stage (ii) as the part of the plot with an increasing the rate of polymerization with $1/f$. It has this increasing behavior in spite of a decreasing monomer concentration because termination is suppressed by being diffusion-limited (the termination kinetic constant falls drastically in this stage); this is the well-known auto-acceleration effect.

Stage (iii) marks the end of the fall of the termination kinetic constant from stage (ii). Thus, we could identify stage (iii) as one in which the rate of polymerization stops increasing and begins to take a downturn. In some cases e.g. di(ethylene glycol) dimethacrylate (DEGDMA), a plateau may be seen.⁶² We do not, however, observed this plateau for both PEG700 and TMPTA.

Finally and naturally, stage (iv) is at the tail end of the plot, where the rate of polymerization is decreasing with $1/f$ as the propagation kinetic becomes hindered by the stiffening network.

To find the exact ranges of $1/f$ in which the stages span, we have to make the plots as shown in Figure 5.13. For example, for stage (ii) of PEG700, the general rules above will give a range of about $9 \leq 1/f \leq 10.5$. Plotting the parameter β vs $1/f$ for this range, a straight line could then be approximated for the reduced range of $9.1 \leq 1/f \leq 9.5$, which is the span shown in Figure 5.13(a).

Using Figure 5.10(a), for PEG700, we could estimate that the reaction-diffusion occurs when $1/f > 10$, which translates to a conversion of about 0.3 [from Figure 5.8(a)], which in turn translates to about 3 s after initiation [from Figure 5.6(a)]. For TMPTA, following the same procedure, the shutter-off time thus obtained is also about 3 s. Hence, to determine the value of the proportionality constant B , two ‘in the dark’ experiments were done, one using a shutter-off time of 3 s, and the other 4 s.

5.5.3.1 ‘In the Dark’ Experiment Results

In the least-square curve-fitting of Abs/Abs_0 on t using eq 5.85, the time span that is utilized for the fitting affects the values of the kinetic constants’ estimates, as shown in Figure 5.11. For too short a time span, too few data points are used in the regression, leading to unstable estimates since FTIR data are rather noisy. Generally, it was found that time spans of greater than 20 s are suitable. For this work, the average values of the estimates obtained from using time spans from 20 s to 90 s would be used. The regression model using these estimates, as shown in Figure 5.12, is found fit the experiment data closely.

Figure 5.11. Changes to the estimates of k_p (top plot; dotted line) and k_t (top plot; solid line), and the k_t / k_p ratio (bottom plot) in the reaction-diffusion regime when different time spans are used for regression for (a) PEG700 and (b) TMPTA for $t_{so} = 3$ s.

Figure 5.12. Fit of regression model (solid line) on experiment data (circles) for (a) PEG700 and (b) TMPTA for the case of $t_{so} = 3$ s.

The ratio k_t / k_p thus obtained is the value of proportionality constant B in eq 5.78. We can then proceed to estimate the kinetic parameters.

5.5.3.2 Stage-by-stage Analysis

The four stages are analyzed separately as shown in Figure 5.13. The values of k_{p0} and k_{t0} are not constant over the range of $1/f$ as assumed in eqs 5.80 and 5.75 respectively, and are estimated by averaging over the range. The coefficients of determination, R^2 , of the linear regression fit are typically in the region of 0.90 and above.

5.5.4 Volume Relaxation Parameters

Figure 5.14(a) shows, for PEG700, the plot of τ , calculated using eq 5.66, against $1/f$ and it reveals that the two kinds of volume relaxation on different time scales were operating in the PEG700 system. The primary relaxation, with the shorter time scale of *ca.* 10^{-1} s to 10^2 s, occurred for approximately $1/f \leq 13.5$ (corresponding to approximately $x \leq 0.95$, the maximum conversion reached), and was certainly due to the polymerization reaction, and is the one we are solely concerned with in this work. The secondary relaxation, with time scale of 10^3 s to 10^6 s, was the relaxation of the formed polymer towards its equilibrium state (the actual physical aging process). To find the relaxation parameters applicable to only the polymerization reaction, the regression was done for $1/f \leq 13.5$. In the TMPTA system, as shown in Figure 5.14(b), it seems that the secondary relaxation is not present, or rather, has not become dominant yet in the duration we used to collect the data (100 s). Looking at the conversion and shrinkage profiles of TMPTA in Figures 5.6(b) and 5.7(b), it is seen that at 100 s, the system is still reacting (albeit slowly) and hence, the volume relaxation due to the reaction is still the dominant one. Compare this with the PEG700 case in Figures 5.6(a) and 5.7(a) in which the system is no longer reacting after about 20 s and thus paving the way for secondary relaxation to become dominant.

Figure 5.13. Plots for determining the kinetic parameters of (a) PEG700 and (b) TMPTA. Dashed line: experiment data; solid line: regression line.

Figure 5.14. Plot of τ against $1/f$. Dashed line: experiment data; solid line: regression line. The coefficients of determination R^2 are typically greater than 0.90.

5.5.4.1 Summary of Numerical Results

The numerical results are summarized in Table 5.5. Unfortunately, the standard deviations for most of the parameters are fairly high; this could be attributed to the high level of noise inherent in the FTIR data. Nevertheless, the simulation results using these values are still respectable, as will be presented in the next section.

	PEG700		TMPTA	
	mean	sd	mean	sd
k_{p0} [m ³ /mol.s]	25.6	3.6	1910	370
A_p	3.32	0.9	2.85	1.29
f_{cp}	0.085	0.001	0.14	0.007
k_{t0} [m ³ /mol.s]	7560	1500	1.21×10^7	0.39×10^7
A_t	5.35	1.1	7.05	1.5
f_{ct}	0.113	0.001	0.142	0.0006
R	0.00535	0.002	0.00200	0.0005
b	2.10	0.2	2.17	0.7
τ_m [ms]	19.6	1.7	12.4	4.0

Table 5.5. Summary of experiment results for PEG700 and TMPTA.

5.5.5 Simulated Results

The simulated results for the important variables, namely conversion, shrinkage and the kinetic constants, are plotted with the experiment data in Figures 5.15 to 5.17. For conversion, the simulated results generally fall within one standard deviation from the mean. For shrinkage, the simulated results are not as good. In Figure 5.16(a), the simulated shrinkage trend for PEG700 after about 15 s is an increasing one whereas experiments show that the shrinkage has already reached a plateau. The reason for this could be seen from Figure 5.14(a); in our model, we could only consider the primary relaxation, and thus ignore the secondary relaxation that sets in after about $1/f = 13.5$ (this translate to a time of about 15 s), and hence, the plateau region, which is caused by this secondary relaxation, could not be simulated by our model. For TMPTA, which has negligible secondary relaxation during the first 100 s, the simulated result has expectedly the correct trend, although their values are somewhat too high. Moving on to Figure 5.17, which shows the profiles of the kinetic constants, k_p and k_t , with conversion, we find that the simulated results agree well with the two experiment points we have obtained. Some common features of multifunctional acrylate polymerization could be seen from these plots. Firstly, k_t decreases, i.e. auto-acceleration sets in, almost immediately after the reaction starts; this is because multifunctional acrylates could form the polymer network, which reduces the mobility of the macro-radicals, very quickly. Secondly, termination becomes reaction-diffusion controlled fairly early on in the reaction due to the stiffening

network, which essentially prevents all translational and segmental motions of the macro-radicals. Interestingly for TMPTA, we see that propagation enters the diffusion-controlled regime almost immediately after the reaction started; this is actually expected because TMPTA is a high functionality monomer and thus the polymer network would stiffen very quickly, and the mobility of the monomer molecules would be curbed early in the reaction.

Figure 5.15. Actual and simulated conversion profiles of (a) PEG700 and (b) TMPTA. (Bottom plots are close-ups of the first 20 s.) Solid line and dotted line as per Figure 5.6; dashed line: simulated results.

Figure 5.16. Actual and simulated shrinkage profiles of (a) PEG700 and (b) TMPTA. (Bottom plots are close-ups of the first 20 s.) Solid line and dotted line as per Figure 5.6; dashed line: simulated results.

Figure 5.17. Simulated profiles of k_p (dotted line) and k_t (solid line) as well as k_p values (circles) and k_t values (stars) from 'in the dark' experiments for (a) PEG700 and (b) TMPTA.

5.5.5.1 Simulated Results for Different UV Intensities

The most important application of this model is to predict the shrinkage and conversion profiles when different UV intensities are used. To check if this model has this capability, experiment results were obtained at two UV intensities, 3 mW/cm² and 130 mW/cm², which were chosen to be on either side of the original intensity of 16 mW/cm², and compared with the simulated ones. Figures 5.18 and 5.19 show the conversion and shrinkage profiles for the 3 mW/cm² case; and Figures 5.20 and 5.21 show likewise for the 130 mW/cm² case.

Consider the lower intensity (3 mW/cm²) case. Based on the model, lower intensity decreases the photoinitiation rate and thus the conversion rate. Furthermore, less excess free volume will be generated and thus the shrinkage rate will also decrease. Consequently, the maximum conversion and shrinkage attained within 100 s of irradiation are reduced. All these predicted trends were observed in the experiments. The numerical results are generally in good agreement except for PEG700's conversion, in which the simulated profile becomes lower than the experiment one after about 5 s. This is apparently due to the model predicting an earlier onset of auto-deceleration, i.e. the propagation becoming diffusion-controlled, than what the experiment shows. This under-prediction is also seen in TMPTA albeit to a lesser extent.

For the higher intensity case (130 mW/cm²), the model predicts higher conversion and shrinkage rates as well as higher maximum conversion and shrinkage attained within 100 s of irradiation. The predictions for conversion are essentially correct as shown by the close agreement between the simulated and experiment results in Figure 5.20. However, those for shrinkage were partially wrong. In Figure 5.21, the experiments show that although the initial shrinkage rates increase as correctly predicted by the model, the maximum values of shrinkage attained actually decrease, and not increase as the model predicts. Apparently, at high intensity, vitrification sets in much earlier and thus the shrinkage becomes inhibited at a lower value. The model could not simulate such a behavior because this 'vitrification' event was not built into it, and this is a major shortcoming of this model.

Figure 5.18. UV intensity = 3 mW/cm^2 . Conversion profiles for (a) PEG700 and (b) TMPTA. Dashed line: model; solid and dotted lines: as per Figure 5.6.

Figure 5.19. UV intensity = 3 mW/cm^2 . Shrinkage profiles for (a) PEG700 and (b) TMPTA. Dashed line: model; solid and dotted lines: as per Figure 5.6.

Figure 5.20. UV intensity = 130 mW/cm^2 . Conversion profiles for (a) PEG700 and (b) TMPTA. Dashed line: model; solid and dotted lines: as per Figure 5.6.

Figure 5.21. UV intensity = 130 mW/cm². Shrinkage profiles for (a) PEG700 and (b) TMPTA. Dashed line: model; solid and dotted lines: as per Figure 5.6.

5.5.6 Mixtures

While a considerable amount of studies on the conversion of mixtures of monomers has been done⁷⁹⁻⁸², there is apparently no mechanistic model yet that can predict the conversion behavior of mixtures given the properties of the constituent monomers. Nevertheless, a simple rule-of-mixture model (based on mol C=C) has been shown by Wen *et al.*⁸⁰ to work for a few mixture systems, *viz.* MMA/DEGDMA, MMA/PETrA, EGDMA/PETrA[#]. They concluded that for rule-of-mixture to work for a A/B mixture, the reactivity ratios, r_A and r_B , defined as $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$, where k_{AA} is a characteristic kinetic constant for the reaction between A and A (and

[#] MMA = methyl methacrylates; DEGDMA = di(ethylene glycol) dimethacrylate; PETrA = pentaerythritol triacrylate; DEGDMA = di(ethylene glycol) diacrylate.

likewise for k_{AB} and k_{BB}), should be equal (or roughly so). Jager *et al.*⁷⁹ had previously observed that the conversion profile of a 50/50 (by wt) TMPTA/DEGDA[#] mixture lies almost exactly in between those of pure TMPTA and pure DEGDA. A simple calculation reveals that 50/50 (by wt) composition corresponds to 52/48 (by mol% C=C), and hence the rule-of-mixture model of Wen *et al.* applies to their case too. To examine if such a simple rule could apply to our PEG700/TMPTA system, three mixtures were prepared. By weight proportion of PEG700/TMPTA, they are 75/25, 50/50 and 25/75 (all with an additional 0.2wt% of Irgacure 651); they correspond to, by mol% C=C, 46/54, 22/78 and 9/91 respectively. Figure 5.22 shows the results for the case of UV intensity of 16 mW/cm². Clearly, the rule-of-mixture does not apply for our mixture systems at all. PEG700 seems to have much a stronger influence on the mixture than TMPTA. At only 9% (mol% C=C) of PEG700, the mixture conversion profile in the initial 5 s has shifted up to almost in between those of PEG700 and TMPTA; and by 46% (mol% C=C) of PEG700, the mixture profile is almost coincident with the pure PEG700. This could be because PEG700 has a strong plasticizing effect on the mixture; as mentioned in Section 5.5.1, PEG700 has a very long spacer group, which helps to delay the onset of diffusion-controlled propagation, and thus allowing conversion to proceed to a higher value⁷⁷

Figure 5.22. Conversion profiles from experiments. PEG700 (gray solid line), TMPTA (black solid line), 46/54 (by mol% C=C) PEG700/TMPTA mixture (dotted line), 22/78 (by mol% C=C) PEG700/TMPTA mixture (dashed line), and 9/91 (by mol% C=C) PEG700/TMPTA mixture (dot-dashed line). RHS plot is a close-up of the first 20 s. UV intensity = 16 mW/cm².

Whereas there is a monotonous trend in the conversion profiles of mixtures (i.e. in a A/B mixture, increasing the concentration of A will push the profile towards A), such regularity is apparently missing in the shrinkage profiles. This is illustrated in Figure

5.23. By adding 9% (mol% C=C) of PEG700 to TMPTA, the shrinkage increases the most to about 10%; increasing this amount to 22% reduces the shrinkage increase to about 9%; and at 46% proportion, the shrinkage reaches about 8% only, and is almost coincident with the pure TMPTA's profile. Perhaps we could rationalize such behavior by the plasticizing effect of PEG700 since the increase in shrinkage must partly be due to the increase in conversion. Adding only a small amount of PEG700 makes the network more pliable while still keeping the molar ratio of C=C bonds to spacer group high; this way, the increase in conversion would lead to significant increase in shrinkage. When more PEG700 is added, the molar ratio of C=C bonds to spacer group will decrease, so that although there is now a higher conversion, this does not translate into higher percentage shrinkage. From the trend, it could be readily extrapolated that at even higher PEG700 proportion, the mixture shrinkage profile will eventually coincides with that of pure PEG700.

Figure 5.23. Shrinkage profiles from experiments. Legends as per Figure 5.22. RHS plot is a close-up of the first 20 s.

As it stands now, there is still some way to go before conversion and shrinkage of mixtures could be successfully modeled. It requires understanding on how the kinetic parameters vary as functions of the proportions of the constituent monomers. In addition, the monotonous dependence of shrinkage on conversion does not hold for mixtures; a new functional form that may include the molar ratio of C=C bonds to spacer group is necessary.

5.6 Conclusions

The Bowman and Peppas' model for coupling the kinetics and shrinkage of cross-linking polymerization reaction of multi-acrylates and multi-methacrylates is reviewed and modified. The most critical modification is to the treatment of free volume as it is found that their treatment could lead to physically unrealistic increasing fractional free volume trend during polymerization. The free volume concept of Cohen and Turnbull was used, in which the occupied volume of a 'normal glass' could be in excess of the equilibrium occupied volume as represented by the Bernal's dense random packing structure. This way, the excess volume generated during polymerization is apportioned to both free and occupied volumes, rather than to the former only, as is done in Bowman and Peppas' paper, and the physically reasonable trend of a decreasing fractional free volume during polymerization is obtained. Two materials that showed very different maximum conversion are investigated, viz. PEG700 and TMPTA. It is found that the rate of free volume collapse $[-d(f/f_m)/dx]$ in PEG700 is only half of that of TMPTA; hence, the larger relative amount of free volume in PEG700 could drive the conversion to near 100%, whereas the corresponding smaller amount could only drive TMPTA to about 60%. Using the model, we simulated their conversion profiles and found the results to be in good agreement. As for shrinkage, the model over-predicts the profiles an initial period (*ca.* 5 s). Lower shrinkage was observed probably because the high rate of free volume collapse triggers an early onset of vitrification, and hence preventing shrinkage from occurring. The model needs to be further improved to take into account this event.

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Chapter 6

Conclusions

UV embossing has been shown to be a viable technique for fabricating high aspect ratio PEG-based microstructures. These polymeric MEMS are potentially biocompatible and could be used in a myriad of bio/biochemical applications such as DNA separations, protein microarrays and biosensors.

The demolding process of the embossed polymer from the mold is a critical step in UV embossing. Release agents in UV embossing formulations are important in easing this demolding process, so that, firstly, the microstructures are not damaged during this process, and secondly, the cured resin does not become permanently stuck onto the mold, and hence damaging it. We investigated the effect of a silicone acrylate on PEG-based formulations photopolymerized in contact with a simulated nickel mold. It was found that the silicone acrylate phase separated and formed micelles that migrated to the formulation-nickel interface. It is also inherently less reactive, and thus significantly slowed the photopolymerization of the mixtures. Using real-time FTIR, the sequential homopolymerization of PEG acrylate and silicone acrylate in a formulation was elicited. The Design of Experiment approach was used to quantify the influence of the components on gelation time and the nickel-side surface composition as well as provide the statistical models to predict these two properties for new compositions.

The mechanical and dimensional properties of the embossed polymer depend critically on the extent of conversion and shrinkage during photopolymerization. The Bowman and Peppas' model that could describe the coupled behavior of conversion and shrinkage was improved upon in this work. To verify this model, experiment data for conversion and shrinkage must be collected simultaneously and be synchronized, and this

was achieved by coupling an FTIR spectrophotometer, a high-resolution laser displacement meter and a UV spot cure unit. The simulated results for three widely differing UV intensities, 3, 16 and 130 mW/cm², were compared with the experiment results. The conversion profiles were found to be in good agreement at all intensities, but the shrinkage profiles were significantly over-predicted after the initial period (*ca.* 5 s) in the high UV intensity case. This is believed to be due to early onset of vitrification at high UV intensity, and which is not captured by the model. This points to a shortcoming of this model where more development is needed. This model, however, applies only to single-component formulations, not the multi-component formulations that are usually used in UV embossing; the latter exhibits complex behavior such as plasticizing effect that are absent in the former.

In this regard, this model here is but a small step towards a model that could apply to multi-component formulations. To arrive at that, detailed investigations into the dependence of kinetic parameters on the proportions of the constituent monomers are required. In addition, we need to reexamine the relationship between conversion and shrinkage, which we have shown experimentally that to be not necessarily a monotonous dependence. Early onset of vitrification and plasticizing effect are two causes that could affect conversion and shrinkage in opposite directions.

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Appendix A

Section-specific Appendices

A.1 Section 4.3: L-pseudo-components

A measure of the stability of a coefficient estimate b_i is its variance inflation factor (VIF), defined as $VIF(b_i) = (1 - R_i^2)^{-1}$ where R_i^2 is the coefficient of determination of the regression of x_i on all the other terms in the model, and if any of the coefficient estimates has a VIF exceeding 10, it would indicate that there is significant collinearity in the values of the proportions, and this would adversely affect the accuracy of the coefficient estimates.¹ When the actual values of the proportions are used, the VIFs of the coefficient estimates b_1 to b_6 are 9.16, 1.83, 2.46, 3.87, 2.20 and 2.17, and thus, there is a problem with the the large value of the VIF of b_1 . Using pseudo-component proportions would reduce this collinearity as could be seen from the smaller values of the VIFs (1.50, 1.33, 1.54, 1.72, 1.99, 2.28). Hence, the regression was done with the pseudo-components.

A.2 Section 4.4.4: Derivation of eq 4.3

Assuming a homogenous formulation, its C-II content could be calculated from corresponding measured values of the individual components using the following equation:

$$E_j = \frac{\sum_{\text{all } i} \frac{w_i}{MW_i} C_i E_i}{\sum_{\text{all } i} \frac{w_i}{MW_i} C_i} \quad (\text{A.1})$$

where E_j and E_i are the percentages of C-II in Formulation j and component i respectively; w_i is the weight proportion, MW_i is the molecular weight, and C_i is the number of carbon atoms in a molecule of component i . As the molecular weight of a component is almost entirely accounted for by carbon and oxygen, it could be approximated by $MW_i \approx C_i \times 12.0 + O_i \times 16.0$, where O_i is the number of oxygen in a molecule of component i ; furthermore, the ratio C_i/O_i was approximately the same for all the components (from Table 4.2, it is about 2.5), and thus, the ratio C_i/MW_i was essentially constant for all the components. The equation could then be simplified to one of rule-of-mixture by weight proportions as shown by eq 4.3.

A.3 Section 4.4.5: Regression Statistics

For step-13 time, the regression F -value was calculated to be 25.8, with the corresponding p -value of 0.0005, which means that the probability that the step-13 times depended on the compositions of the formulations is $(1-0.0005) \times 100\% = 99.95\%$. In addition, the model fit has a high R_A^2 (adjusted coefficient of determination) value of 0.919, which implies that the model accounts for more than 91% of the variation observed in the values of the step-13 time. The R_{PRESS}^2 (PREdiction-Sum-of-Squares R^2) value is 0.7952, meaning that the model is expected to explain about 80% of the variability in predicting new observations. Regarding the lack-of-fit (LOF) test, the F -value is infinity because the step-13 times for the replicate runs were exactly the same, and hence all the residuals from the regression were from the lack-of-fit (LOF) of the model. Clearly, the main cause of this severe LOF is that the step-13 times could only be accurately measured as integer values, and the small differences between the values for replicate runs could not be captured. Hence, this is not entirely a problem with the inadequacy of the model.

For the model on surface silicon content, the regression F -value is 26.57 (associated p -value is 0.0005), LOF F -value is 6.09 (associated p -value is 0.0860, hence, there is no lack of fit at 5% significant level), R_A^2 is 0.9208 and R_{PRESS}^2 is 0.8991.

A.4 Section 5.2.1: Derivation & Justification of Eq 5.11

A.4.1 Model

Consider an acrylate film of thickness L , containing an initial concentration C_{A0} of a photoinitiator A with a molar napierian absorption coefficient of κ_A . The photoinitiator quantum yield of Φ is assumed to be constant throughout the reaction. A UV intensity of I_0 reaches the top surface of the film. The photoinitiator concentration and UV intensity at time t after the start of irradiation and at a distance z from the top surface of the film are C_A and I respectively. The acrylate itself is assumed to be optically transparent at the wavelength of interest and the photoinitiator is assumed to be of the photobleachable type. Reflection loss at the air-liquid boundary is ignored (it does not matter anyway because we are only interested in the variation within the acrylate).

The rate of change of the concentration of the photoinitiator during reaction is then given by

$$\frac{\partial C_A}{\partial t} = -\Phi \kappa_A C_A I \quad (\text{A.2})$$

where I is given by

$$\frac{\partial I}{\partial z} = -\kappa_A C_A I \quad (\text{A.3})$$

Eq A.3 is formed from the differential form of the Beer's Law:

$$\frac{\partial A_e}{\partial z} = \kappa_A C_A \quad (\text{A.4})$$

where A_e is the napierian absorbance, which is related to I by

$$A_e = -\ln\left(\frac{I}{I_0}\right) \quad (\text{A.5})$$

It is clear that C_A and I have spatial and temporal variations. Eqs A.2 and A.3 form a system of PDEs, which could be solved by first discretizing eq A.3 in the spatial direction using forward difference method, and then substituting the discretized form of I into eq A.2, turning eq A.2 into a system of ODEs, which is an initial value problem (IVP). The IVP can then be solved numerically.

The non-dimensionalized and discretized form of I at the k^{th} spatial step at time t is given by

$$y_2(k, t) = \prod_{i=1}^{k-1} [1 - h\beta_2 y_1(i, t)] \quad , k \geq 2 \quad (\text{A.6})$$

where $y_1 = C_A/C_{A0}$, $y_2 = I/I_0$, $\beta_2 = \kappa_A C_{A0} L$ (this is the initial absorbance of the film), and h is the spatial step size in the w direction ($w = z/L$ is the non-dimensionalized thickness). For $k = 1$ (i.e. at the top surface of the film), $y_2(1, t) = 1$ for all t .

The non-dimensionalized and discretized form of the IVP is

$$\frac{dy_1(k, t)}{d\eta} = -y_1(k, t)y_2(k, t) \quad , k \geq 1 \quad (\text{A.7})$$

where $\eta = \frac{t}{\Phi \kappa_A I_0}$ is the non-dimensionalized time. The initial condition is $y_1(k, 0) = 1$ for all $k \geq 1$.

A.4.2 Results and Discussion

Consider a typical system of PEGDA700 containing 0.2 wt% of Irgacure 651. PEGDA700 itself is optically transparent at 365 nm as shown by its UV-Vis spectrum in Figure A.1. Irgacure 651 is a photobleachable photoinitiator as shown by its spectra in Figure A.2; after irradiation with UV light, its absorbance decreases.

Figure A.1. UV-Vis spectrum of PEGDA700 prepared as a 3 wt% solution in toluene.

Figure A.2. UV-Vis spectrum of Irgacure 651 prepared as a 0.2 wt% solution in methanol. Solid line: before irradiation; dashed line: after 640 s of irradiation with 16 mW/cm² of UV light.

The values for the various parameters in the model are given in Table 5.3; the thickness of film was set to be 200 μm.

A spatial step size of $h = 10^{-3}$ was used, and convergence was confirmed by changing h from 10^{-2} to 10^{-4} and checking that the solutions overlapped.

Variation of C_A

Figures A.3 and A.4 and shows the temporal variations of C_A at the top and bottom surfaces of the film and its spatial variations at different time points.

Figure A.3. Temporal variations of C_A / C_{A0} . Solid line: top surface of film; dashed line: bottom surface of film.

Figure A.4. Spatial variations of C_A / C_{A0} . Solid line: $t = 0$; dashed-dot line: $t = 50$ s; dashed line: $t = 100$ s.

From Figure A.3, during the time period when most of the reaction takes place (up to $t = 20$ s), only about 5% of the photoinitiator is consumed. Furthermore, the photoinitiator concentration could be readily assumed homogeneous throughout the film since the temporal profiles at the top and bottom surfaces are almost overlapping each other. This is also illustrated in Figure A.4, which shows that the concentration increases only slightly down the film (*ca.* 0.5% higher at the bottom than at the top). Hence, for all practical purposes, the spatial variation could be considered negligible throughout the entire reaction period.

Variation of Intensity

Figures A.5 and A.6 shows the temporal variation of I at the middle section and bottom surface of the film and its spatial variations at different time points. (Note that the intensity at the top surface is always equal to the incident intensity).

Figure A.5. Temporal variations of I / I_0 . Solid line: in the middle of the film; dashed line: bottom surface of film.

Figure A.6. Spatial variations of I / I_0 . Solid line: $t = 50$ s; dashed line: $t = 100$ s; dot-dashed line: $t = 500$ s.

Evidently, Figure A.5 shows that the film is nearly perfectly transparent to UV light as the intensity at the bottom of the film is always at least 98% of the incident intensity. The transparency increases over time as the photoinitiator was consumed and photobleached. This is further ascertained in Figure A.6, which shows the flattening UV intensity profiles across the thickness of the film as time progresses.

A.4.3 Simplification of Model for Negligible Spatial Variation

Given that the spatial variation is insignificant, we could simplify the exact model described by the PDEs of eqs A.2 and A.3. From eq A.3, we get the more familiar form of Beer's Law, which is

$$I = I_0 e^{-\kappa_A C_A z} \quad (\text{A.8})$$

where C_A is now independent of z . Putting this equation into eq A.2, we have

$$\frac{dC_A}{dt} = -\Phi \kappa_A C_A I_0 e^{-\kappa_A C_A z} \quad (\text{A.9})$$

The spatial-averaged form is then

$$\frac{\overline{dC_A}}{dt} = \frac{\int_0^L \frac{dC_A}{dt} dz}{L} = -\frac{\Phi I_0}{L} (1 - e^{-\kappa_A C_A L}) \quad (\text{A.10})$$

Integration of the above equation gives

$$C_A = \frac{1}{\kappa_A L} \ln \left[1 + (e^{\kappa_A C_{A0} L} - 1) e^{-\Phi \kappa_A I_0 t} \right] \quad (\text{5.11})$$

The agreement between the results obtained from this simplified model and from the exact model is shown in Figure A.7.

Figure A.7. Temporal variations of C_A / C_{A0} at the bottom of the film. Solid line: exact model; dashed line: simplified model.

Figure A.8. Temporal variation of I / I_0 at the mid-depth of the film. Legends as per Figure A.7.

Figure A.9. Spatial variation of I / I_0 at $t = 50$ s. The two lines are indistinguishable.

For the purpose of reducing computation time for simulation of the entire reaction kinetics, the simplified model will be used.

A.5 Section 5.2.1: Rate of Polymerization Expression by Odian²

The rate of initiation, defined as the rate of appearance of the primary radicals due to photoinitiation (eq 5.1), is

$$\begin{aligned} R_i &= j\phi\alpha_A C_A I \\ &= j\phi\alpha_A C_A I_0 (1 - e^{-\alpha_A C_A z}) \end{aligned} \quad (\text{A.11})$$

The spatial-average rate of initiation is then

$$\begin{aligned} \overline{R_i} &= \frac{\int_0^L R_i dz}{L} \\ &= j\phi\alpha_A C_A I_0 \int_0^L e^{-\alpha_A C_A z} dz \\ &= j\phi \frac{I_0}{L} (1 - e^{-\alpha_A C_A L}) \end{aligned} \quad (\text{A.12})$$

Let I_{av} (einstein/m³.s) be the volumetric intensity absorbed by the reaction system i.e.

$$I_{av} = \frac{I_0(1 - e^{-\alpha_A C_A L})}{L} \quad (\text{A.13})$$

Hence,

$$\overline{R_i} = j\phi I_{av} \quad (\text{A.14})$$

This is the form of R_i found in Odian² ($R_i = 2\phi I_a$), which is commonly quoted in literature; it is actually the spatial-average rate of initiation when $j=2$. Furthermore, in Odian², the rate of polymerization

$$R_p = \frac{k_p C_M}{\sqrt{k_t}} \sqrt{\phi I_{av}} \quad (\text{A.15})$$

is expressed using this spatial-average rate of initiation. Compared this with eq 5.23, which is the spatial-average of the local rates of polymerization; from a theoretical stand, the latter is the more correct approach.

A.6 Section 5.5.2: List of Symbols

v_{wm}	van der Waal's volume of monomer	[cm ³ /g]
v_m	specific volume of monomer	[cm ³ /g]
v_{om}	specific occupied volume of monomer	[cm ³ /g]
v_{fm}	specific free volume of monomer	[cm ³ /g]
f_m	fractional free volume of monomer	[1]
v_{wp}	van der Waal's volume of polymer ('ideal glass')	[cm ³ /g]
v_p	specific volume of polymer ('ideal glass')	[cm ³ /g]
v_{op}	specific occupied volume of polymer ('ideal glass')	[cm ³ /g]
v_{fp}	specific free volume of polymer ('ideal glass')	[cm ³ /g]
f_p	fractional free volume of polymer ('ideal glass')	[1]
v_∞	equilibrium specific total volume of reacting system	[cm ³ /g]
$v_{o\infty}$	equilibrium specific occupied volume of reacting system	[cm ³ /g]
$v_{f\infty}$	equilibrium specific free volume of reacting system	[cm ³ /g]
f_∞	equilibrium fractional free volume of reacting system	[1]
v	actual specific total volume of reacting system	[cm ³ /g]
v_o	actual specific occupied volume of reacting system	[cm ³ /g]
v_f	actual specific free volume of reacting system	[cm ³ /g]

f	actual fractional free volume of reacting system	[1]
v_e	excess specific total volume of reacting system [†]	[cm ³ /g]
v_{oe}	excess specific occupied volume of reacting system [†]	[cm ³ /g]
v_{fe}	excess specific free volume of reacting system [†]	[cm ³ /g]
ε_∞	total volume contraction factor	[1]
ε_o	occupied volume contraction factor	[1]
ε_f	free volume contraction factor	[1]
S	total volume shrinkage	[1]
S_f	free volume shrinkage	[1]
S_o	occupied volume shrinkage	[1]

[†] ‘Excess volume’ is defined as the difference between the equilibrium and actual volumes of the reacting system.

A.7 Section 5.5.1: Smoothing of Conversion and Shrinkage Data

Figure A.10 shows, for PEG700, the typical plot of the actual conversion and shrinkage data superimposed on the smoothed data.

The smoothing was done by least-square curve-fitting the experiment data, denoted by the generic y (the smoothed data are denoted by $\hat{y}$), with a non-linear equation, eq A.16, which is the addition of two Hill functions; this is an iterative procedure to find the values of the parameters, A ’s, k ’s and n ’s, that give the minimum sum of squares, $\sum (y - \hat{y})^2$. The termination condition for the iteration procedure is either the change in $\sum (y - \hat{y})^2$ is less than 10^{-6} , or the changes in the all the parameters are less than 10^{-6} , whichever that occurs first.

$$\hat{y} = A_1 \frac{t^{n_1}}{k_1^{n_1} + t^{n_1}} + A_2 \frac{t^{n_2}}{k_2^{n_2} + t^{n_2}} \quad (\text{A.16})$$

Figure A.10. Actual (dotted line) and smoothed (solid line) conversion and shrinkage data for PEG700 (bottom plots are close-ups of the first 20 s).

A.8 References

¹ Cornell J. A. *Experiments With Mixtures*, 2nd ed.; Wiley: New York, 1990.

² Odian, G. C. *Principles of Polymerization*, 2nd ed.; Wiley: New York, 1981.

Appendix B

MATLAB Codes

B.1 Materials' Properties and UV Intensity

```
run_peg700_properties.m (properties of PEGDA700)
%-----properties of PEGDA700
%---vdw's volumes
vwm=0.569; %g/cm3
vwp=0.559; %g/cm3

rho_m=1.12; %g/cm3 %catalogue
vm=1/rho_m;

vp=1.39*vwp; %eqm <=> Bernal

Tgm=-102.5+273; %K
Tgp=-48.68+273; %K
alphafm=3.504e-4; %K-1
alphafp=3.792e-4; %K-1
T=25+273; %K

%-----occupied volumes
vom=1.39*vwm; %Bernal
vop=1.39*vwp; %Bernal

%-----free volumes
vfm=vm-vom; %hole
vfp=vp-vop; %hole

%-----calc e's
einf=(vm-vp)/vm;
eo=(vom-vop)/vom;
ef=(vfm-vfp)/vfm;

%-----cM0
MW=698; %g/mol
N=2; %no. of fn groups
cM0=rho_m/MW*N; %mol/cm3
cM0=cM0*100^3; %mol/m3
%-----end-----
```

run_tmpta_properties.m (properties of TMPTA)

```
%-----properties of tmpta
%---vdw's volumes
vwm=0.556; %g/cm3
vwp=0.522; %g/cm3

rho_m=1.11; %g/cm3 %catalogue
vm=1/rho_m;
vp=1.39*vwp; %eqm <=> Bernal
Tgm=-49.7+273; %K
Tgp=140.7+273; %K
alphafm=3.393e-4; %K-1
alphafp=4.182e-4; %K-1
T=25+273; %K

%-----occupied volumes
vom=1.39*vwm; %Bernal
vop=1.39*vwp; %Bernal

%-----free volumes
vfm=vm-vom; %hole
vfp=vp-vop; %hole

%-----calc e's
einf=(vm-vp)/vm;
eo=(vom-vop)/vom;
ef=(vfm-vfp)/vfm;

%-----cM0
MW=296; %g/mol
N=3; %no. of fn groups
cM0=rho_m/MW*N; %mol/cm3
cM0=cM0*100^3; %mol/m3
%-----end-----
```

runuvpi.m (UV intensity and photoinitiator properties)

```
%-----UV intensity and photoinitiator properties
I0mW=<<intensity in mW/cm2>>;

%---convert mW/cm2 to einstein/m2.s
I0=I0mW*1e-3*100^2; %W/m2=J/m2.s
avogadro=6.022e23; %dimensionless
planck=6.626e-34; %J.s
wavelength=365e-9; %m
speedoflight=3e8; %m/s
frequency=speedoflight/wavelength; %1/s; %1
einstein=(avogadro*planck*frequency) J
I0=I0*(1/(avogadro*planck*frequency)); %einstein/m2.s
%---

phi=0.7; %quantum yield
j_radicals=2; %number of radicals formed per photoinitiator molecule
KA=9.24928; %m2/mol;
cA0=7.8125; %mol/m3
%-----end-----
```

B.2 'In-the-dark' Experiments

kpkteq.m (function file for least-square curvfitting)

```
%function file for least-square curve-fitting of FTIR data from 'in-the-
%dark'experiments

function yhat=kpkteq(beta, t, tso, cMso_over_cM0)      %for use with
    lsqcurvefit
%function yhat=kpkt(beta, t);global tso cMso_over_cM0 %for use with
    nlinfit

%y=cM/cM0; y(1)=cMso/cM0;
%t(1)=tso;

yhat=cMso_over_cM0*((1+beta(1)*(t-tso)).^(-beta(2)));
%-----end-----
```

runkpkteq.m (process FTIR data file)

```
% process FTIR data file
clear all;clc;close

%-----contents
%1-----set filenames
%2-----calc monomer thickness
%3-----open material's properties file and UV intensity
%4-----open and process FTIR data file
%5-----set conditions at tso
%6-----solve for kp kt cPStar for different time spans
%7-----calc mean kp kt for time spans 20 to 90 s
%8-----save file

%1-----set filenames
fname_ftir=<<name of FTIR data file>>;
fname_shk=<<name of shrinkage data file>>;
fname_save=<<name of MATLAB data file to be saved later>>;

%2-----calc monomer thickness
[traw, sraw, shutter]=textread(fname_shk, '%f %f %*s %5c');
index_open=strmatch('O',shutter);
L=-sraw(index_open(1));
melinex_thickness=125; %um
L=L-melinex_thickness; %um
L=L*1e-6;%m

%3----- open material's properties file and UV intensity
<<material's properties file>>

runuvpi

%4-----open and process FTIR data file
fid=fopen(fname_ftir, 'r');
A=fscanf(fid, '%e, %e');
status=fclose(fid);
if status===-1; disp('cannot close file'); pause; end
traw=A(1:2:length(A)-1);
Araw=A(2:2:length(A)); %Araw=absorbance

%---interpolate FTIR data
spacing_t=1;
```



```

tinterp=[2:spacing_t:fix(traw(end))]; %start interp. at t=2s becos
%extrapolating not allowed
Ainterp=interp1q(traw, Araw, tinterp);

%---remove 2 sec lag
tdelay=2;
tfull=tinterp-tdelay;
yfull=Ainterp/Ainterp(1);

%5-----set conditions at tso
tso=<<shutter-off time>>;
tso_index=(1/spacing_t)*tso+1; %becos first value is zero
cMso_over_cM0=yfull(tso_index); %cMso/cM0 at tso
cMso=cM0*cMso_over_cM0; %cMso i.e. cM at tso
xso=1-cMso_over_cM0; %conversion at tso
cAso=(1/(KA*L))*log((1-exp(-KA*L*cA0))/exp(-KA*L*cA0)*...
exp(-KA*phi*I0*tso) + 1);

%6-----solve for kp kt cPStar for different time spans
lsqfail_ts=[];
tpt=[];
bhat=[]; %for tspan=1:1:tfull(end)-tso
for tspan=1:1:100
    disp(['tso=' num2str(tso) ' ' '#=' run_num_kpkt ' ' 'tspan='
int2str(tspan)])
    tq=tfull(tso_index:(1/spacing_t)*tspan+tso_index); %tq(1)=tso
    yq=yfull(tso_index:(1/spacing_t)*tspan+tso_index);
    %yq(1)=cMso_over_cM0

    %betahat(1)=2*cPstar*kt %[1/s]
    %betahat(2)=kp/(2kt) %[1]
    if tspan==1; beta0=[1 1]; else; beta0=betahat; end

    options=optimset('LargeScale', 'on', 'MaxIter', 1e10, ...
'MaxFunEvals', 1e10, 'LevenbergMarquardt', 'on',...
'TolFun', 1e-6, 'TolX', 1e-6);
[betahat, resnorm, residual, exitflag, output, lambda, jacobian]=...
lsqcurvefit('kpkteq', beta0, tq, yq, [0 0], [], options, tso,
cMso_over_cM0);

    if exitflag==0;
        lsqfail_ts=[lsqfail_ts; tspan];
    else
        betaci = nlparci(betahat,residual,jacobian);

        Rpso=cMso*betahat(1)*betahat(2); %mol/m3.s

        kp_over_ktroot=Rpso/(cMso*[(1-exp(-KA*cAso*L/2))/L]*...
[(2*j_radicals*phi*I0)/(KA*cAso)].^(1/2));

        kt=(kp_over_ktroot/(2*betahat(2)))^2; %m3/mol.s
        kp=2*kt*betahat(2); %m3/mol.s
        cPstar=betahat(1)/(2*kt);

        tpt=[tpt;tspan kp kt cPstar];
        bhat=[bhat;tspan betahat(1) betahat(2) betaci(1,:) betaci(2,:)];
    end
end

%7-----calc mean kp kt for time spans 20 to 90 s
AA=20;

```

```

BB=90;
[kp,kt]=deal(mean(tpt(AA:BB,2),1),mean(tpt(AA:BB,3),1));

%---plot cM/cM0 for mean kp and kt
tq=tfull(tso_index:end); %tq(1)=tso
betahat=mean(bhat(AA:BB,2:3),1);
yqhat=kpkteq(betahat, tq, tso, cMso_over_cM0); %for use with
    lsqcurvefit
plot(tfull(1:2:end), yfull(1:2:end), 'o', tq, yqhat);axis([0 20 0
    1]);shg
title([base_name ' ; xso=' num2str(xso,'%1.2f') ' ; ' int2str(AA) '-'
    int2str(BB)])
text(.5,.5,[[['k_p=' num2str(kp,'%1.2e')]]];[['k_t='
    num2str(kt,'%1.2e')]]]);
ylabel('C_M / C_M_0');xlabel('t [s]')
set(get(gca, 'Xlabel'), 'position', [0.5, -.068, 0])
set(get(gca, 'Ylabel'), 'position', [-0.13, 0.5, 0])

%8-----save file
saveqn=input('save file?? [y {n}]\n', 's'); %'no' by default
switch saveqn; case 'y';save(fname_save);disp('file saved'); end
%-----end-----

```

B.3 Synchronized FTIR & Shrinkage Experiments

dblhilleq.m (function file for double-Hill equation)

```

%function file for double-Hill equation
function y=dblhilleq(beta,t)

%beta=[ymax k n]
ymax1=beta(1);
k1=beta(2);
n1=beta(3);

ymax2=beta(4);
k2=beta(5);
n2=beta(6);

y=(ymax1*t.^n1)./(k1^n1 + t.^n1) + (ymax2*t.^n2)./(k2^n2 + t.^n2);
%-----end-----

```

runfv.m (process FTIR and shrinkage data file)

```

%-----process FTIR and shrinkage data to obtain conversion,
    %shrinkage, fractional free volume and relaxation parameters.

clear all;clc;close

%-----contents
%1-----set filenames
%2-----calc monomer thickness
%3-----open material's properties file and UV intensity
%4-----open and process FTIR and shrinkage data file
%5-----calc dsdt
%6-----calc fractional free volumes
%7-----calc tau, then regress (invf, tau) and find tau_m and b.

```

```
%8-----save file

%1---set filenames
fname_ftir=<<name of FTIR data file>>;
fname_shk=<<name of shrinkage data file>>;
fname_save=<<name of MATLAB data file to be saved later>>;

%2-----calc monomer thickness
[traw, sraw, shutter]=textread(fname_shk, '%f %f %*s %5c');
index_open=strmatch('O',shutter);
L=-sraw(index_open(1));
melinex_thickness=125; %um
L=L-melinex_thickness; %um
L=L*1e-6;%m

%3----- open material's properties file and UV intensity
<<material's properties file>>

runuvpi

%4-----open and process FTIR and shrinkage data file
samp_rate=1;

tdelay=2;

%---FTIR file
fid=fopen(fname_ftir, 'r');
A=fscanf(fid, '%e, %e');
status=fclose(fid);
if status==-1;disp('cannot close file');pause;end
traw=A(1:2:length(A)-1);
Araw=A(2:2:length(A)); %Araw=absorbance

%interpolate ftir data
spacing_t=1/samp_rate; %create equal spacing as shrinkage data
tinterp=[2:spacing_t:fix(traw(end))];%start interp. at t=2s becoss
    %extrapolating not allowed
Ainterp=interp1q(traw, Araw, tinterp);

%remove 2 sec lag
tdelay=2;
tfull=tinterp-tdelay;
yfull=Ainterp/Ainterp(1);%Ainterp(1) is Abs at time of opening UV
    shutter
xfull=1-yfull;

%---shrinkage data
traw=traw(index_open(1):index_open(end))-traw(index_open(1));
sraw=sraw(index_open(1):index_open(end))-sraw(index_open(1));

soffset=sraw(samp_rate*tdelay+1:length(sraw))-sraw(samp_rate*tdelay+1);
soffset=soffset/(L*1e6); %soffset in micron; L in m.
sfull=soffset(1:length(tfull)); %create equal number of data as ftir
    data

%---smooth xfull and sfull using double-Hill equation
%-----x first
xmaxguess1=xfull(end);
kguess1=2;
nguess1=5;
```

```

xmaxguess2=0.0*xfull(end);
kguess2=40;
nguess2=10;

beta0=[xmaxguess1 kguess1 nguess1 xmaxguess2 kguess2 nguess2];

options=optimset('LargeScale', 'on', 'MaxIter', 1e4, ...
    'MaxFunEvals', 1e4, 'LevenbergMarquardt', 'on',...
    'TolFun', 1e-6, 'TolX', 1e-6);
[x_betahat, x_resnorm, x_residual, x_exitflag, x_output, x_lambda,
    x_jacobian]=...
    lsqcurvefit('dblhilleq', beta0, tfull, xfull, [], [], options);
xfit=dblhilleq(x_betahat, tfull);
plot(tfull, xfull, ':', tfull, xfit, '-');axis([0 1.5 0 .2]);shg
dummy=input('just press enter');clear dummy

%-----s next
smaxguess1=.9*sfull(end);
kguess1=2;%4;
nguess1=2;%4;

smaxguess2=0*sfull(end);
kguess2=40;
nguess2=1.2;

beta0=[smaxguess1 kguess1 nguess1 smaxguess2 kguess2 nguess2];

options=optimset('LargeScale', 'on', 'MaxIter', 1e3, ...
    'MaxFunEvals', 1e3, 'LevenbergMarquardt', 'on',...
    'TolFun', 1e-6, 'TolX', 1e-6);
[s_betahat, s_resnorm, s_residual, s_exitflag, s_output, s_lambda,
    s_jacobian]=...
    lsqcurvefit('dblhilleq', beta0, tfull, sfull, [0 0 0 0 0 1], [],
    options);
sfit=dblhilleq(s_betahat, tfull);
plot(tfull, sfull, ':', tfull, sfit, '-');axis([0 20 0 0.10]);shg
beta0
dummy=input('just press enter');clear dummy

%5-----calc dsdt
smaxhat1=s_betahat(1);skhat1=s_betahat(2);snhat1=s_betahat(3);
smaxhat2=s_betahat(4);skhat2=s_betahat(5);snhat2=s_betahat(6);
dsdt=(smaxhat1*snhat1*skhat1^snhat1*tfull.^(snhat1-1))./((skhat1^snhat1
    + tfull.^snhat1).^2)+ ...
    (smaxhat2*snhat2*skhat2^snhat2*tfull.^(snhat2-1))./((skhat2^snhat2 +
    tfull.^snhat2).^2);
if isinf(dsdt(1)); dsdt(1)=0;end
plot(tfull(1:end-1), diff(sfull), 'b', tfull, dsdt, 'r');axis([0 10 0
    inf]);shg
dummy=input('just press enter');clear dummy

%6-----calc fractional free volumes
vinf=vm*(1-einf*[0:1]);plot([0:1],vinf);shg
voinf=vom*(1-eo*[0:1]);plot([0:1],voinf);shg
vfinf=vfm*(1-ef*[0:1]);plot([0:1],vfinf);shg

%actual volumes
v=vm*(1-sfit);plot(xfit,v, '-', [0:1],vinf, '--');shg

sfito=(eo/einf)*sfit;
vo=vom*(1-sfito);

```

```

plot(xfit,vo,'-', [0:1],voinf,'--')

sfitf=(ef/einf)*sfit;
vf=vfm*(1-sfitf);plot(xfit,vf,'-', [0:1],vfinf,'--');

%fractional free volumes
finf=vfinf./vinf;
f=vf./v;
plot([0:1],finf,'--', xfit,f,'-');shg
ylabel('\itf and {\itf}_{\infty}');xlabel('conversion')
set(gca,'Position',[0.15 0.11 0.795 0.815 ]); %[0.13 0.11 0.775 0.815 ]
dummy=input('just press enter');clear dummy

%7-----calc tau, then regress (invf, tau) and find tau_m and b.
tau(1,1)=0;
tau(2:length(xfit),1)=(einf*xfit(2:end)-sfit(2:end))./dsdt(2:end);

%---removes negative tau and sort remaining items
fpos=f;
taupos=tau;
xpos=xfit;
neg_index=find(tau<=0);
fpos(neg_index)=[];
taupos(neg_index)=[];
xpos(neg_index)=[];
%---register elements that are removed
ftxrem=[f(neg_index) tau(neg_index) xfit(neg_index)];

[bb hh]=sortrows(-[fpos taupos],1);
fpos=-bb(:,1);
taupos=-bb(:,2);
clear bb

%---removes tau data that are non-monotonic
format short g
disp('index taupos(1 to 30)'); disp([(1:30)' taupos(1:30)])
st_index=max(find(diff(taupos(1:50))<=0))+1;
if isempty(st_index); st_index=1; end
disp(['st_index=' int2str(st_index)]);
st_ok=input('st_index ok? [{y} n]', 's'); %default is yes
switch st_ok
case 'n'; st_index=input('index of first usable taupos=');
end

tautruc=taupos(st_index:end);
invftruc=1./fpos(st_index:end);
semilogy(invftruc, tautruc);shg
dummy=input('just press enter'); clear dummy

%---create 1/f and tau data evenly
invfregr=linspace(invftruc(1), invftruc(end))';
tauregr=interp1(invftruc, tautruc, invfregr);

semilogy(1./fpos, taupos, 'y');shg;hold on;semilogy(invfregr, tauregr,
'k');shg
dummy=input('just press enter'); clear dummy;close

%---use regress
numpts=length(tauregr);
aoinvftau=[];
regress_ok=0;

```

```

alpha=0.05;    %significance level
num_tries=0;

while regress_ok==0
    [c12val, bint, r, rint, stats]=regress(log(tauregr), ...
        [ones(size(invfregr)) invfregr], alpha);
    disp(['ln(c1) c2] = ' num2str(c12val)]);
    disp(['R^2 = ' num2str(stats(1))]);
    outlier_1=rint(:,1)>0;
    outlier_2=rint(:,2)<0;
    outlier=outlier_1+outlier_2;
    %calc and plot tauhat
    c12val(1)=exp(c12val(1));    %rememeber eq is tau=C1*exp(C2/f)
    tauhat=c12val(1)*exp(c12val(2)./fpos);
    semilogy(1./fpos, taupos, 'y');hold on;    %full set of positive data
    semilogy(invfregr, tauregr, 'mo');    %current set of data for
        regression
    semilogy(1./fpos, tauhat, 'b');    %regressed line

    status=input('continue to sieve out outliers? [{y} n]', 's');
    if sum(outlier)==0 | status == 'n'
        regress_ok=1;
    else
        outlier_index=find(outlier);
        num_tries = num_tries + 1;
        %register and display outliers
        outinvf=invfregr(outlier_index);
        outtau=tauregr(outlier_index);
        aoinvftau=[aoinvftau;outinvf outtau];
        semilogy(outinvf, outtau, 'g*');shg %data that are sieved out
        disp(' ')
        disp(['# tries=' int2str(num_tries)]);
        disp(strcat('1/f of outlier removed=', num2str(outinvf)));
        disp(['total # outliers=' int2str(length(aoinvftau)) ' out of '
            ...
                int2str(length(invfregr))]);
        %removes outliers
        tauregr(outlier_index)=[];
        invfregr(outlier_index)=[];
    end
    clear outlier_1 outlier_2 outlier outlier_index
end

%---find conversion of outliers
if length(aoinvftau)~=0
    for pqr=1:length(aoinvftau)
        outlier_x(pqr,1)=interp1(f,xfit,1./aoinvftau(pqr,1));
    end
    disp('corresponding outlying x');disp(sort(outlier_x))
end

%---use tau=tau_m*exp[b*(1/f-1/fm)]
taum=exp(log(c12val(1))+c12val(2)/finf(1))

%8-----save file
saveqn=input('save file?? [y {n}]", 's'); %'no' by default
switch saveqn
case 'y';save(fname_save);disp([fname_save '...saved ok']);
otherwise;disp('file not saved');
end
%-----end-----

```

```

runstage.m (stage-by stage analysis of conversion)

%-----stage-by stage analysis of conversion
clc;clear all;close

%-----content
%1-----load processed conversion and shrinkage data from runfv.m
%2-----calc dx.dt
%3-----plot dx/dt vs 1/f to decide the four stages
%4-----stage iii
%5-----stage iv
%6-----region i
%7-----region ii
%8-----append to file

%1-----load processed conversion and shrinkage data
load <<name of file>>

%2-----calc dx.dt and h(t)
xmaxhat1=x_betahat(1);xkhat1=x_betahat(2);xnhat1=x_betahat(3);
xmaxhat2=x_betahat(4);xkhat2=x_betahat(5);xnhat2=x_betahat(6);
dxdt=(xmaxhat1*xnhat1*xkhat1^xnhat1*tfull.^(xnhat1-1))./((xkhat1^xnhat1
+ tfull.^(xnhat1).^2)+(xmaxhat2*xnhat2*xkhat2^xnhat2*tfull.^(xnhat2-
1))./((xkhat2^xnhat2 + tfull.^(xnhat2).^2);
if isinf(dxdt(1)); dxdt(1)=0;end
dxfulldt=dxdt;

%---calc h(t)
runuvpi
cA=(1/(KA*L))*log((1-exp(-KA*L*cA0))/exp(-KA*L*cA0)*exp(-
KA*phi*I0*tfull) + 1);

gt=[((2*j_radicals*phi*I0)./(KA*cA)).^(1/2)].*(1-exp(-KA*cA*L/2))/L];

htfull=B*(dxfulldt./((1-xfit).*gt));

%3-----plot dx/dt vs 1/f to decide the four stages
plot(1./f, dxfulldt, '--');axis([.9./f(1) inf 0 inf]);shg;grid on
ylabel('dx / dt [s^-^1]');xlabel('1/f');shg
set(gca,'Position',[0.15 0.11 0.795 0.815]); % [0.13 0.11 0.775 0.815]
set(get(gca, 'Xlabel'), 'position', [0.5, -.068, 0])
set(get(gca, 'Ylabel'), 'position', [-0.13, 0.5, 0])

%suppose the following stages
%stage (i): 1/f < 9
%stage (ii): 9 < 1/f < 9.5
%stage (iii): 10.5 < 1/f < 11
%stage (iv): 13 > 1/f > 12

%4-----stage iii
[st_dif st_idx]=min(abs(1./f-10.5));1./f(st_idx)
[ed_dif ed_idx]=min(abs(1./f-11));1./f(ed_idx)
fiii=f(st_idx:ed_idx);
kp0=B*htfull(st_idx:ed_idx).^2;[[1:length(kp0)]' kp0]
plot(1./fiii,kp0, '--');shg
ylabel('k_p_0 [m^3/mol.s]');xlabel('1/f');shg
set(gca,'Position',[0.15 0.11 0.795 0.815]); % [0.13 0.11 0.775 0.815]
set(get(gca, 'Xlabel'), 'position', [0.5, -.068, 0])
set(get(gca, 'Ylabel'), 'position', [-0.13, 0.5, 0])
kp0=mean(kp0)

```

```
%5-----stage iv
[st_dif st_idx]=min(abs(1./f-12))
[ed_dif ed_idx]=min(abs(1./f-13));1./f(ed_idx)
fiv=f(st_idx:ed_idx);
rhs=log(kp0./(B*htfull(st_idx:ed_idx).^2)-1);
plot(1./fiv,rhs,'--');hold on;shg

alpha=0.05; %significance level
[beta, bint, r, rint, stats]=regress(rhs,[1./fiv ones(size(rhs))],
    alpha);
Ap=beta(1)
fcp=-Ap/beta(2)
disp(['R^2 = ' num2str(stats(1))]);
plot(1./fiv, [1./fiv ones(size(rhs))*beta];%axis([12 13 -inf inf])
ylabel('\delta');xlabel('1/f');shg
set(gca,'Position',[0.15 0.11 0.795 0.815]); %[0.13 0.11 0.775 0.815 ]
set(get(gca, 'Xlabel'), 'position', [0.5, -.068, 0])
set(get(gca, 'Ylabel'), 'position', [-0.13, 0.5, 0])

%6-----region i
st_idx=1;1./f(st_idx)
[ed_dif ed_idx]=min(abs(1./f-9));1./f(ed_idx)
fi=f(st_idx:ed_idx);
rone=htfull(st_idx:ed_idx);[1:length(rone)]' rone]
plot(1./fi,rone,'--');
ylabel('\alpha [(m^3/mol.s)^1/^2]');xlabel('1/f');shg
set(gca,'Position',[0.15 0.11 0.795 0.815]); %[0.13 0.11 0.775 0.815 ]
set(get(gca, 'Xlabel'), 'position', [0.5, -.068, 0])
set(get(gca, 'Ylabel'), 'position', [-0.13, 0.5, 0])

plot(1./fi, kt0/10^7);
kt0=mean(kt0)

%7-----region ii
[st_dif st_idx]=min(abs(1./f-9));1./f(st_idx)
[ed_dif ed_idx]=min(abs(1./f-9.5));1./f(ed_idx)
fii=f(st_idx:ed_idx);
rhs=log((kt0*htfull(st_idx:ed_idx).^2)/(kp0^2)-1)
plot(1./fii,rhs,'--');hold on

alpha=0.05; %significance level
[beta, bint, r, rint, stats]=regress(rhs,[1./fii ones(size(rhs))],
    alpha);
At=beta(1)
fct=-At/beta(2)
disp(['R^2 = ' num2str(stats(1))]);
plot(1./fii, [1./fii ones(size(rhs))*beta];%axis([9 9.5 -inf inf])
ylabel('\beta');xlabel('1/f');shg
set(gca,'Position',[0.15 0.11 0.795 0.815]); %[0.13 0.11 0.775 0.815 ]
set(get(gca, 'Xlabel'), 'position', [0.5, -.068, 0])
set(get(gca, 'Ylabel'), 'position', [-0.13, 0.5, 0])
fm=f(1)

rdp=mean_kt0kp/(kt0/kp0);
kpm=kp0/(1+exp(Ap*(1/fm - 1/fcp)));

denom=rdp*kpm/kp0 + exp(-At*(1/fm - 1/fct));
ktm=kt0/(1 + 1/denom);

%8-----append to file
save(fname_save, '-append')
```


B.4 Simulations

```

cvskdae.m (function file for simulation equations)
%---function file for simulation equations (differential algebraic
    equations, DAE)
function varargout = cvskdae(t, y, flag)

switch flag
case ''
    % Return dy/dt = f(t,y).
    varargout{1} = f(t, y);
case 'init'
    % Return default
    [tspan,y0,options] = init;
    [varargout{1:3}] = init;
case 'mass'
    % Return mass matrix M.
    varargout{1} = mass;
otherwise
    error(['Unknown flag '' flag ''.']);
end

%----- DAE representation
function dydt=f(t, y)

%exptpara
global cM0 I0 phi j_radicals KA cA0 L
%kinpara
global kp0 kpm Ap fcp kt0 ktm At fct rdp
%fvpara
global fm ef einf taum b

dydt(1)=-y(1) + (1/(cA0*KA*L))*log(1 + (exp(KA*L*cA0)-1)*exp(-
    KA*phi*I0*t));
dydt(2)=(j_radicals*phi*I0)/(cM0*L)*(1 - exp(-KA*L*[cA0*y(1)])) -
    2*[ktm*y(6)].*[cM0*y(2).^2];
dydt(3)=-[kpm*y(5)].*[cM0*y(2)].*y(3);
dydt(4)=(einf*y(8)-y(4))./(taum*exp(b./[fm*y(7)]-b/fm));

dydt(5)=-y(5) + (kp0/kpm)./(1 + exp(Ap*(1./[fm*y(7)] - 1/fcp)));
dydt(6)=-y(6) + (kt0/ktm)./(1 + 1./(rdp*[kpm*y(5)]/kp0 + exp(-
    At*(1./[fm*y(7)] - 1/fct))));
dydt(7)=-y(7) + (1-ef/einf*y(4))./(1-y(4));
dydt(8)=-y(8) + 1-y(3);

dydt=dydt'; %return argument as row vector

%----- set mass matrix
function M = mass
M=[0 1 1 1 0 0 0 0]';
M=spdiags(M, 0, 8, 8);

%----- set initial conditions
function [tspan, y0, options] = init
tspan = [0:.1:100];
y0 = [1 0 1 0 1 1 1 0]'; %returns row vector
options = odeset('Mass','M','MassSingular','yes','OutPutFcn','odeplot',
    'OutPutSel',[8]);
%-----end-----

```

runcvskdae.m (script file for executing cvskdae.m)
--

```

%---script file for executing cvskdae.m
clc;clear all;close

%-----contents
%1-----declare global variables
%2-----load UV intensity and photoinitiator
%3-----material's properties
%4-----solve equations
%-----

%1-----declare global variables
%exptpara
global cM0 I0 phi j_radicals KA cA0 L
%kinpara
global kp0 kpm Ap fcp kt0 ktm At fct rdp
%fvpara
global c1 c2 fm ef einf taum b

%2-----load UV intensity and photoinitiator
runuvpi

%3-----material's properties
%---calc cM0
rho_m=<<denisty of monomer>>; %g/cm3
MW=<<molecular weight of monomer>>; %g/mol
N=<<no. of acrylate functional groups>>>;

cM0=rho_m/MW*N; %mol db/cm3
cM0=cM0*100^3; %mol db/m3

%thickness
L=200e-6; %m

%---kinetic and volume relaxation parameters
kp0=<<enter value>>;
Ap=<<enter value>>;
fcp=<<enter value>>;
kpm=<<enter value>>;
kt0=<<enter value>>;
At=<<enter value>>;
fct=<<enter value>>;
ktm=<<enter value>>;
rdp=<<enter value>>;
taum=<<enter value>>;
b=<<enter value>>;
einf=<<enter value>>;
ef=<<enter value>>;
fm=<<enter value>>;

%4-----solve equations
[tsolve, ysolve]=ode15s('cvskdae');

```

B.5 Spatial and Temporal Variations of UV Intensity and Photoinitiator Concentration

```

CAeq.m (function file for intensity and concentration equations)
function varargout = CAeq(t, y, flag, delw, beta1, beta2)

switch flag
case '' % Return dy/dt = f(t,y).
    varargout{1} = f(t, y, flag, delw, beta1, beta2);
case 'init' % Return default
    [tspan,y0,options].
    [varargout{1:3}] = init(delw);
otherwise
    error(['Unknown flag '' flag ''.']);
end

%ODEs
function dy=f(t, y, flag, delw, beta1, beta2)
n=1/delw+1;
shehen=1-delw*beta2*y;

dy(1,1)=-beta1*y(1);
for i=2:n
    dy(i, 1)=-beta1*y(i)*prod(shehen(1:i-1));
end

%initial conditions
function [tspan, y0, options] = init(delw)
n=1/delw+1;
tspan = [0:10:200];
y0=ones(n, 1); %returns row vector
options = [];

```

```

runCAeq.m (script file for executing CAeq.m)
clc;clear all

%1-----UV intensity
I0mW=<<UV intensity in mW/cm2>>; %mW/cm2
%---convert mW/cm2 to einstein/m2.s
I0=I0mW*1e-3*100^2; %W/m2=J/m2.s
avogadro=6.022e23; %dimensionless
planck=6.626e-34; %J.s
wavelength=365e-9; %m
speedoflight=3e8; %m/s
frequency=speedoflight/wavelength; %1/s; %1
    einstein=(avogadro*planck*frequency) J
I0=I0*(1/(avogadro*planck*frequency)); %einstein/m2.s

%2-----photoinitiator properties
phi=0.7; %quantum yield
KA=9.24928; %m2/mol;
cA0=7.8125; %mol/m3
L=200e-6; %m
beta1=phi*I0*KA;
beta2=L*KA*cA0;%initial absorbance

%3-----solve equations

```

```
%----spatial step size
delw=.001;
n=1/delw+1; %n points

[tsolve, ysolve]=ode45('CAeq', [], [], [], delw, beta1, beta2);

%find I/I0=I/I0(z, t)
shehen=1-delw*beta2*ysolve(:, 1:n-1);
Izt(:,2:n)=cumprod(shehen, 2);
Izt(:,1)=ones(length(tsolve), 1);

%4-----solution based on spatial-average cA
cAave=(1/(KA*L))*log(1 + (exp(KA*L*cA0)-1)*exp(-KA*phi*I0*tsolve));

zOL=[0:delw:1]';
for zOL_index=1:length(zOL)
    Iave(:,zOL_index)=I0*exp(-KA*cAave*zOL(zOL_index)*L);
end
```