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POLYMERS FROM RENEWABLE RESOURCES: CATIONIC PHOTOPOLYMERIZATION OF EPOXIDIZED NATURAL OILS

By

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ABSTRACT

POLYMERS FROM RENEWABLE RESOURCES: CATIONIC PHOTOPOLYMERIZATION OF EPOXIDIZED NATURAL OILS

By

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The interest in producing polymeric materials from renewable feedstocks is motivated by several factors including environmental concerns, economic development of rural areas, and the diversification of the resource base away from the traditional petroleum feedstocks. Cationic photopolymerization of epoxidized oils has tremendous potential for the development of polymer films as well as composite structures. Cationic polymerizations form highly crosslinked polymers which exhibit excellent mechanical and thermal properties. In spite of these advantages, these chain polymerizations have not been well characterized. In this contribution, differential scanning photocalorimetry has been used to obtain important kinetic information on the photopolymerization of epoxidized soybean oil. Anthracene was used as a photosensitizer with a diaryliodonium hexafluoroantimonate salt to initiate the polymerizations using UV light. The effect of temperature and light intensity on the effective propagation rate constant for polymerization has been characterized. Steady state fluorescence monitoring was employed to study the effect of viscosity on the diffusion controlled kinetics, and correlative model has been developed to describe this effect.

To God and my Parents.

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CHAPTER I.

INTRODUCTION AND MOTIVATION

I.1. Issues for the Development of UV Curable Polymers.

An important issue to consider with many traditional polymer formulations is their contribution to atmospheric pollution. The emission of volatile organic components (VOCs) from the drying of inks, films, and coatings is a leading cause of atmospheric pollution. Volatile organic solvents have traditionally been used to impart desirable viscosity and cure rate properties to coating formulations. In order to ensure complete coverage of a surface, a coating formulation must be sufficiently fluid to be easily applied, be able to penetrate inner recesses, but must cure rapidly to a protective film. However, meeting the coating formulation demands through the use of a rapidly evaporating organic solvent results in the formation of photochemical smog and other air pollutants. In light of increasingly stringent clean air regulations, there is substantial motivation for the inclusion of environmental concerns in the development of new high performance coatings.

An improved, pollution-free formulation for coatings must meet several stringent requirements. The cured ink or coating should exhibit excellent adhesion to the substrate, abrasion resistance, and solvent resistance. For applicability in a coating process, the formulation should have a long shelf life and be stable during the application process, but should cure very rapidly when initiated by the energy source.[1] To satisfy safety and environmental concerns, the formulations should be non-toxic, and should emit no volatile organic substances. The abrasion and chemical resistance is provided by a highly crosslinked network. For this reason, many traditional formulations consist of volatile solvents and diluents dispersed in multifunctional oligomers that form highly crosslinked networks upon curing. Improved formulations could be based upon highly reactive monomers of low enough viscosity so that no organic solvents may be necessary. If the low viscosity monomer also has low vapor pressure, no organic vapors are emitted during cure. Formulations used for specific applications have specific needs. For example, the coating systems developed for wood substrates must not cause swelling which may distort the wood grain.[2] A concern with external coatings is the fact that the coating must be sufficiently elastic to expand or contract with the substrate. Coatings that are too rigid will crack under thermal or mechanical expansion of the building. Architectural roofs are often subjected to extreme temperature and pressure gradients, and these forces result in significant deformation of the structure.

The curing of a polymerizable formulation to form a highly crosslinked network could be initiated by a variety of methods including heat, electromagnetic radiation, and electron beam irradiation. Unfortunately, the elevated temperatures in heat initiated systems lead to high energy costs, in addition to causing significant distortions in the final polymer product.[1] High energy radiation methods lead to very rapid curing, but may cause degradation of the substrate. In contrast, ultraviolet and visible light induced polymerizations have many potential advantages for ink and coating applications in terms of rapid reaction rates at ambient temperatures, low energy requirements, wide range of polymerizable monomers and also excellent control over the reaction. With a proper choice of intensity and wavelength of initiating light, the degradation of the substrate can be avoided.

I.2. UV-Initiated Photopolymerizations.

Photopolymerizations initiated by ultraviolet (UV) light have gained prominence in recent years for rapid, pollution-free curing of polymer films (for reviews, see references 3-5). These solventless polymerizations proceed very rapidly with a fraction of the energy requirements of thermally cured systems, and create films with excellent properties. Ultraviolet light is a convenient energy source for photopolymerization because a variety of readily available compounds will initiate chain polymerizations upon absorption of UV/visible light.[3-15] UV-sensitive photoinitiators are currently available for free-radical or cationic polymerizations. These photoinitiators are typically effective for a variety of incident wavelengths. This is useful for UV-curable coatings because commonly used pigments may be strong absorbers of light in the visible and ultraviolet wavelengths, and an initiator which will be effective at a wavelength outside this window must be chosen.

Light induced polymerizations carried through the free radical mechanism were first reported nearly fifty years ago.[8] The most widely used classes of monomers for UV-initiated free-radical photopolymerizations are multifunctional acrylates and methacrylates. These monomers polymerize very rapidly, and are easily modified on the ester group, allowing materials with a variety of properties to be obtained. However, the acrylates are relatively volatile, and have an unpleasant odor.[4] Moreover, recently there has been a growing concern over potential health hazards associated with the acrylates.[3,5,15] Several researchers have also shown that free radical polymerizations of multifunctional acrylates and methacrylates exhibit unusual kinetic behavior, including autoacceleration, formation of heterogeneous polymers,[4,9,10,11,12,13,14] and final conversion considerably lower than a hundred percent.[4] Finally, the free radical photopolymerizations are inhibited by oxygen and must be carried out under an inert atmosphere such as nitrogen, increasing the application costs.[4,5,8]

UV-initiated cationic photopolymerizations exhibit several advantages when compared to the free-radical photopolymerizations discussed above. First, the cationic photopolymerizations are not inhibited by oxygen.[5,8-16] This feature provides an important practical advantage for the coating of large or complex parts since it is not necessary to blanket the system with nitrogen to achieve the rapid cure rates needed for quick application rates. Secondly, in contrast to free-radical polymerizations which experience a rapid decrease in polymerization rate when the light source is removed (due to radical-radical termination reactions), the cationic polymerizations will proceed long after the irradiation has ceased, consuming nearly all of the monomer.[8,17] This is a key feature for the application of cationically photopolymerized coatings for complex shapes, since light need not penetrate into all corners and crevasses of the substrate to achieve a completely cured coating. Finally, cationic photopolymerizations are a very versatile technique, and may be used to polymerize important classes of monomers, including epoxides and vinyl ethers.[15-19] These classes of monomers exhibit many desirable properties, including low volatility, good rheological properties and negligible toxicity.[5]

Furthermore, the cured polymer films associated with these monomers exhibit excellent chemical resistance, adhesion, abrasion resistance, and clarity.[8,15] Although fully formulated mixtures containing the monomer and initiator can react within seconds of exposure to UV light, they are stable for times on the order of months when they are stored protected from light.

I.3. UV-Sensitive Initiators for Cationic Photopolymerizations.

Applicable photoinitiators for cationic polymerizations were not developed until the late 1970s.[27,30] Crivello and Lam reported two classes of thermally stable photoinitiators for cationic polymerizations: diaryliodonium and triarylsulfonium salts in 1976 and 1979, respectively.[20] Upon photolysis, these compounds undergo irreversible photo-fragmentation in which the carbon-iodine or carbon-sulfur bond is cleaved to produce an aryliodonium or an arylsulfonium cation-radical capable of initiating cationic polymerization.[7,8] While the diaryliodonium and triarylsulfonium salts actively initiate cationic polymerization in the presence of UV light, they are remarkably latent in the absence of light. In fact, fully formulated solutions of these salts in epoxide monomers have shelf lives of several years.[7]

The spectral absorbance peaks of diaryliodonium and triarylsulfonium salts are mostly between 225 nm and 275 nm, depending on the substituents attached to the phenyl rings.[7] Diaryliodonium salts of hexafluoroantimonate produce the fastest rates of reaction of the onium salts due to their size and acidity of the anion. In spite of their strong absorbance in the deep ultraviolet region of the spectrum, the absorbance of these initiators is very low in the near UV region.[7] Most of the medium and high pressure mercury vapor lamps used in the industry have their maximum emission bands in the region above 300 nm and the lack of absorbance in this region limits the efficacy of the onium salts. However, the spectral region over which the initiators are effective may be expanded by the addition of a variety of photosensitizers, including hydrocarbons, ketones, and heterocyclic compounds.[7] These compounds actively sensitize the diaryliodonium and triarylsulfonium salts by electron transfer[21,22] or energy transfer,[23] thus rendering them useful in the near UV and visible regions of the light spectrum.

Despite the promise shown by UV light initiated polymerizations, the reactions have received only limited attention so far. This fact may be attributed to the lack of efficient initiators until recent years. In fact, most of the work reported in the literature focuses on the initiation steps of the reaction.[3,724,25,26] The development of thermally stable photoinitiators for cationic chain polymerizations has led to significant progress in the study of photopolymerizations of epoxides and vinyl ethers in the last decade.[27,28,29,30] However, the field is significantly less developed compared to that of free radical photopolymerization.

I.4. Motivation to Use Agricultural Feedstocks as Starting Materials

The use of renewable agricultural feedstocks for the production of chemicals and materials has been identified as a national priority. The interest in renewable feedstocks is motivated by several factors, including environmental concerns, economic development of rural areas, and diversification of the resource base from the traditional petroleum feedstocks.

Epoxides and vinyl ethers are the most conducive monomers for cationic chain polymerizations. The development of the sensitive onium salt photoinitiators in the last two decades has made it possible to polymerize virtually all types of cationically polymerizable monomers. This development has led us to consider what potential monomers can be obtained from natural resources that could lend themselves to cationic polymerization and provide a usable product. Glycerol triesters are produced by most plants as a means of energy storage. These natural oils such as soybean oil, linseed oil, and corn oil can serve as a potentially diverse and inexpensive class of renewable substrates from which cationically polymerizable monomeric species can be generated. The high amount of unsaturation present in these oils can be exploited to introduce moieties such as epoxides which may be polymerized.

While the use of monomers derived from natural feedstocks clearly meets the objectives of a renewable feedstock, the use of cationic polymerization also offers significant practical processing advantages. Since this process is directly based on an agricultural commodity, traditional materials and methods for growing, harvesting and collecting the raw material can be used. In addition, cationic polymerizations are amenable to continuous processing schemes since they exhibit rapid reaction rates and low energy requirements. These processing advantages are important since many proposed schemes based upon renewable feedstocks are limited or disqualified because they are not easily adaptable to large-scale production. This method could make a tremendous impact on the substitution of synthetic polymers by agri-based polymers.

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CHAPTER II.

BACKGROUND

II.1. Overview of Polymerization Mechanisms

Broadly speaking, there are two different types of polymerization mechanisms- step polymerization and chain polymerization.[1] In step polymerization, a monomer reacts with another monomer to form a dimer which may again react with another monomer to form a trimer and so on. As a result, the reaction rates are pretty slow and high molecular weights are attainable only near the end of the reaction.[1,2]

In contrast, chain polymerizations are much faster since large chains of polymer are formed almost immediately after the initiation. The initiator is essential because it creates the initiating species or reactive center $R^{\bullet}$ which may be a free radical, an anion, or a cation. The monomer species react with this active center on the forming polymer rather than other monomers, as in the case of step polymerization. The polymer chains are terminated when the reactive center is transferred to another monomer, solvent or other foreign material. In the case of free radicals, they may also terminate chain growth by combination with each other.

Free radical chain polymerizations are the most commonly used method in the industry. There are a number of radical initiating systems available, depending on the initiating method - the initiator can be decomposed into radicals by exposure to heat, radiation, or a redox reaction. The free radicals generated can be transferred to a monomer molecule allowing this new reactive center to react with other monomer molecules. Every time this reacts with a monomer, the free radical is transferred to the chain end, thus aiding the propagation. Termination of these chains can occur by two ways: i) combination, where two radicals react to produce a dead site, or by ii) disproportion, where a hydrogen is transferred from one chain to the other to consume the radical and produce a double bond.

II.2. Properties of Cationic Polymerizations.

Cationic polymerizations are chain reactions in which a propagating cationic center successively reacts with many monomer units to form long polymer chains. Classes of monomers which will undergo cationic polymerizations include α-olefins, 1,3-dienes, vinyl ethers, and epoxides. Cationic initiators are typically protonic or Lewis acids, and the resulting reactive cations are sufficiently stable to have a reasonable lifetime for chain growth by propagation. The polymer chain growth may be terminated by chain transfer of the reactive center, or occasionally by counterion combination. Compounds such as water, alcohols, and esters are particularly effective chain transfer agents. Although chain transfer results in a decrease in the average primary polymer chain length, it typically will not affect the polymerization rate because the resulting cation will continue to propagate.[1,3,4]

While cationic polymerizations are not used extensively for the commercial synthesis of long polymer chains, they show considerable promise for polymerizations of highly crosslinked polymer coatings as well as thick parts. Due to the predominance of transfer processes during the course of the reaction, linear cationic polymerizations tend to yield polymers of moderate molecular weight and relatively broad molecular weight distribution. These facts tend to limit the usefulness of the reactions for the synthesis of linear high polymers. However, for polymerizations of multifunctional monomers, a high linear primary chain length is not necessary because the resulting highly crosslinked polymers derive their excellent properties from the network structure, not from long linear chains. For these systems, the insensitivity to oxygen and high reaction rates exhibited by cationic polymerizations represent significant advantages. Several classes of monomers exhibiting desirable properties and rapid polymerization rates have been reported, including epoxides,[5,6] novel silicon-containing epoxy resins[7] and a variety of bisvinyl ethers.[5] The selection of commercially available monomers and initiators is now reasonably broad.

II.3. Curing of Epoxy Resins

II.3.1. Conventional Methods

The epoxide group is the smallest possible cyclic ether moiety. The strain in the three membered carbon-carbon-oxygen ring can be exploited to conduct ring-opening polymerizations. Epoxy resins are monomers which typically contain one or more epoxide moieties in their molecular structure. Curing of epoxy resins is being increasingly carried out using either Lewis acids or Lewis bases. Also, Lewis acids being generated photochemically are becoming more important because of their unique advantages.

Most epoxy formulations contain diluents (reactive or non-reactive), fillers or other reinforcement materials, and toughening agents. The toughening or flexibilizing agents aid the crosslinking process and usually consist of polyesters or aliphatic diepoxides. Polymers made from epoxy resins possess high chemical and corrosion resistance, toughness and flexibility, excellent mechanical and electrical properties and superb adhesion to various substrates. For specific uses, proper selection of additives and curing agents is required.

More than 500 million pounds of epoxy plastics are produced and used every year in the United States alone. End uses include structural, non-structural and coating applications. Epoxy composites are in use in military, automotive, aircraft, and piping industry. Laminates made from epoxies are used in the electric and electronic industry whereas other coating applications include roof coatings, coats for roads and bridges, and also for marine and storage drums. Epoxy coatings are used for beer and beverage cans-for decorative purposes on the outside and to prevent reaction between metal and beverage on the inside.

II.3.2. Ring Opening Polymerizations

The polymerization of epoxides is often classified as "ring opening polymerization" because it involves the cleavage of the oxirane or epoxide ring (also known as the cyclic ether ring) to form crosslinking intermolecular chains. Other examples of cyclic monomeric species that undergo ring opening polymerizations are acetals, esters, amides, and siloxanes.

Epoxides or oxiranes are the smallest form of cyclic ether moieties. While the higher cyclic ethers can undergo ring opening polymerizations only when initiated by cationic initiators, epoxides are polymerizable by both anionic and cationic initiators. This is attributable to the great amount of strain in the 3 membered C-O-C ring. The ionic initiators used for the ring opening polymerizations are the same as the ones used for polymerizing monomers with C=C or C=O bonds, including the photochemical initiators. Most cationic polymerizations proceed through the formation and propagation of oxonium ions. Each propagation step involves the nucleophilic attack of a monomer on the cationic site at the end of the growing polymer chain, thus adding itself to the chain and attaining a positive charge on its own oxygen atom. In contrast, anionic polymerizations proceed through an attack on the monomer molecule by the anionic site on the polymer chain.

Ring opening polymerizations are very similar to chain polymerizations because only the monomeric species adds to the polymer chain and species larger than the monomer do not react among themselves. On the other hand, the molecular weight of polymers formed has been found to increase slowly with conversion, which is typical of step polymerizations. Also, the rate constants have been found to be closer to the values obtained for step polymerizations rather than chain polymerizations. Irrespective of these discrepancies, it is easier to describe the kinetics of polymerization in a manner resembling chain polymerizations because the polymers grow monomer by monomer. Unless the mechanism is complicated by the presence of polymerization-depolymerization equilibria, the kinetics are very well modeled. Because of the high strain involved in the 3-membered oxirane ring, the probability of depolymerization is very less.[8]

II.3.3. Kinetics of Ring Opening Polymerizations

The kinetics of ring opening polymerizations of epoxides can be represented by the same expressions used in describing chain polymerizations of alkenes and vinyl ethers. In polymerizations where there is little or no termination involved, the kinetic expression pertaining to living polymerizations can be utilized:

$$R_p = k_p[M][M^+]$$

where $[M]$ is the instantaneous monomer concentration, and $[M^+]$ is the concentration of the propagating cationic species. Since ring opening polymerizations are relatively uncommon, few reports of kinetic parameters are available. For various oxirane polymerizations, k_p has been reported in the range of 10^{-1} to 10^{-3} liters/mol-sec.[9,10,11] The k_p values are much closer to the polyesterification values than to chain polymerizations.

II.3.4. Effect of temperature on reaction rate and degree of polymerization

The effect of temperature on the reaction rate and the degree of polymerization attained is very system dependent in case of cationic ring-opening polymerizations. As in ionic chain polymerizations of alkenes and vinyl ethers, all system components like the types and concentrations of monomer, solvent, initiator, and sensitizer play an important part in the reaction mechanism and kinetics. The activation energy of the forward propagation reaction is always positive and an increase in temperature almost always results in an increase in polymerization rate. The activation energies of propagation are less than the corresponding energies for vinyl ethers.[12]

The effect on the degree of polymerization or percent conversion is much more complex. For most ring opening polymerizations, increasing the temperature results in lower polymer molecular weight and also less conversion of the cyclic ether moieties. This has been propounded to be due to increase in the rates of chain transfer and termination relative to propagation.[13] This leads to formation of cyclic polymers at higher temperatures due to the intramolecular chain transfer. A more reasonable explanation seems to be that the propagation rate keeps increasing while the termination and transfer rates do not show much increase as the temperature rises. The resulting effect is that the polymer molecular weight increases with increasing temperatures up to a certain value, and then starts decreasing. This could be due to the fact that termination is relatively unaffected at lower temperatures but increases with temperature at higher temperatures.

Another reason for this effect, suggested by Rose[13], who conducted experiments on the oxetane ring in Tetrahydrofuran(THF), is that the initiator is being thermally destroyed or decomposed. Another approach which assumes the propagation reaction to be reversible suggests that the propagation-depropagation equilibria shifts towards the monomer at higher temperatures. This causes a temperature ceiling effect.

II.4. Photopolymerizations

Photopolymerizations initiated by ultraviolet (UV) light have gained prominence in recent years for the rapid, pollution-free curing of polymer films.[14,15,16] These solventless polymerizations proceed very rapidly with a fraction of the energy requirements of thermally cured systems, and create films with excellent properties. Ultraviolet light is a convenient energy source for photopolymerization because a variety of readily available compounds will initiate chain polymerizations upon absorption of UV/visible light.[5,17,18,19,25] UV-sensitive photoinitiators are currently available for free-radical or cationic polymerizations and are typically effective at a variety of incident wavelengths. This feature is useful for UV-curable coatings because commonly used pigments may be strong absorbers of light in the visible and ultraviolet wavelengths, and an initiator which will be effective at a wavelength outside this window must be chosen.

II.4.1. Free Radical Photopolymerizations

Free radicals can be produced by photoinitiation in two ways. Either the initiating species itself absorbs the energy from the ultraviolet light or electron beam and dissociates, or a species known as a photosensitizer may be added which is excited by the radiation and reacts with the initiator to dissociate it into radicals. The most widely used classes of monomers for UV-initiated free-radical photopolymerizations are multifunctional acrylates and methacrylates. These monomers polymerize very rapidly, and are easily modified on the ester group, allowing materials with a variety of properties to be obtained. However, the acrylates are relatively volatile and have an unpleasant odor.[15] Moreover, there has been a growing concern over potential health hazards associated with the acrylates.[5,16,25] Finally, the free radical photopolymerizations are inhibited by oxygen and must be carried out under an inert atmosphere, such as nitrogen, increasing the application costs.[15,16,19]

II.4.2. Cationic Photopolymerizations.

UV-initiated cationic photopolymerizations exhibit several advantages when compared with the free-radical photopolymerization discussed above. First, the cationic photopolymerizations are not inhibited by oxygen.[16,19] This feature provides an important practical advantage for the coating of large or complex parts since it is not necessary to blanket the system with nitrogen to achieve the rapid cure rates needed for quick application rates. Secondly, in contrast to the free-radical polymerizations which experience a rapid decrease in polymerization rate when the light source is removed (due to radical-radical termination reactions), the cationic polymerizations will proceed long after the irradiation has ceased, consuming nearly all of the monomer.[19,21] This is a key feature for the application of cationically photopolymerized coatings for complex shapes, since light need not penetrate into all corners and crevasses of the substrate to achieve a completely cured coating. Finally, cationic photopolymerizations are a very versatile technique, and may be used to polymerize important classes of monomers, including epoxides and vinyl ethers.[5,20] These classes of monomers exhibit many desirable properties, including low volatility, good rheological properties and negligible toxicity.[16] Furthermore, the cured polymer films associated with these monomers exhibit excellent chemical resistance, adhesion, abrasion resistance, and clarity.[5,19]

II.5. UV-Sensitive Initiators for Cationic Photopolymerizations.

Despite the advantages of UV-initiated photopolymerizations discussed above, the technique has received considerably less attention than the analogous free-radical reactions. This fact may be attributed to the lack of suitable UV-sensitive cationic photoinitiators until recent years.[20,21] In fact, applicable photoinitiators for cationic polymerizations were not developed until the late 1970s, more than thirty years after free-radical initiators had been reported. Crivello and Lam[32] reported two classes of thermally stable photoinitiators for cationic polymerizations: diaryliodonium and triarylsulfonium salts in 1976 and 1979, respectively. Upon photolysis, these compounds undergo irreversible photo-fragmentation in which the carbon-iodine or carbon-sulfur bond is cleaved to produce an aryliodonium or an arylsulfonium cation-radical capable of initiating cationic polymerization.[18,19] While the diaryliodonium and triarylsulfonium salts actively initiate cationic polymerization in the presence of UV light, they are remarkably latent in the absence of light. In fact, fully formulated solutions of these salts in epoxide monomers have shelf lives of several years.[18]

II.6. Advantages of Cationic Photopolymerizations

UV cured coatings are widely used in the industry, with applications ranging from furniture, compact discs and car headlamp reflectors to printed circuit boards. All these coatings are cured by UV light with wavelengths between 200-400 nm. Most industrial

UV lamps emit in this region, so it is important to have photoinitiators that absorb light in this region. Some of the advantages of using radiation curing are:

1. Lower energy consumption compared to thermal curing.
2. Compact operating environment.
3. Very fast cure times, very amenable to mass production of articles.
4. Instant start and shut down of process.
5. Low overall equipment and maintenance costs.
6. Freedom from volatile solvents.
7. Heat sensitive substrates are coated without degradation.

II.7. Photopolymerizations of Epoxides and Vinyl Ethers

Laboratory studies of the cationic photopolymerizations of epoxides and vinyl ethers have provided information about the salient features of the reactions. The observed polymerization rate depends on several variables, including the type and concentration of the initiator, the intensity and wavelength of the UV light source, temperature, and the structure of the monomer. When diaryliodonium and triarylsulfonium salts are used as the photoinitiators, the optimum initiator concentrations are typically 2-3 wt%.[21,32]

The first patents[22]and journal articles[23] on cationic photopolymerizations appeared in the mid-sixties. In the early to mid seventies, patents were granted to American Can, covering the use of diazonium salts as photoinitiators for the polymerization of epoxies.[24] In brief, the reaction mechanism can be described as:

$$\mathrm{Ar{-}N\overset{+}{=}N.BF_4^-} \longrightarrow \mathrm{ArF} + \mathrm{N_2} + \mathrm{BF_3}$$

The Lewis acid (BF_3) then reacts with the oxirane rings to form the polymer. Although this chemical mechanism had certain advantages, the commercialization of the technology met with some difficulties. The aryldiazonium salts tend to react with the epoxy resins in the dark and the storage stability of the formulated system was questionable due to its susceptibility to moisture and temperature. As the reaction mechanism shows above, nitrogen gas is released during the dissociation of the initiator, which leads to practical difficulties for obtaining bubble-free cured films. Thus, the technique was restricted to films of thickness less than 10 microns. Towards the end of the decade, several triarylsulfonium and diaryliodonium salts were developed by General Electric and 3M. These salts undergo photolysis under the influence of UV light to generate cationic active centers. Various commercially available triarylsulfonium salt photoinitiators have been studied comparatively and the results have been tabulated in literature available from the manufacturers.

A major reason for the delay in the implementation of photoinitiation technology in the industry was the patent right disputes between General Electric and 3M. It was only in 1984 that a court ruling clarified the situation and decided that General Electric's base patents prevailed over the others. A lot of academic and industrial work[25] has been conducted using cycloaliphatic epoxides with most of the applications being in the coatings area. So far, no attempt to polymerize thick parts from epoxies using photopolymerization has been reported. Coatings made with just the resins have been found to be quite hard and brittle, rendering them unsuitable for most end uses. Apart form increasing the flexibility of the coatings, use of flexibilizers improves the chemical resistance, weatherability, and the cure response of the coating.

II.8. Cationic Photoinitiators

During the past couple of decades, there has been a lot of academic and industrial research on photoinitiated polymerizations as people have begun to foresee the numerous possible applications of the technique. Although photopolymerization by way of free radicals has been used since the 1950s, the field of photoinduced cationic polymerizations is relatively nascent. This disparity could be attributed to the fact that while there were many methods of producing free radicals using radiation, the number of methods of generating stable cationic active centers were much less. Also, cationic polymerizations are known to proceed very rapidly and hence are very difficult to study and model. The methods currently used to generate cationic species are by irradiating charge transfer complexes,[26] aryl onium salts,[27] inorganic salts/complexes,[27] organometallic compounds,[28] and alkyl iodides.[29,30] Of these, only the first two are mostly used. The remaining categories are limited by either their relative insolubility, specificity with respect to the monomeric species, or by their modest initiating capabilities.

Photoreactive onium salts of the Group V, VI, and VII elements of the periodic table are the most effective cationic initiators. Primary efforts have been to use diazonium salts, and their mechanistic and kinetic behavior has been well characterized and utilized.[22,24,31] Lately, halogen and sulfur based onium salts have displaced the azonium salts[27] and have been utilized in our research. Cationic chain polymerizations induced by onium salts (excited directly or photosensitized) are actually "dark" i.e. proceed unaffected by light like the conventional polymerizations caused by initiators such as Lewis or Bronsted acids.

Bronsted acids are much stronger than Lewis acids and polymerize oxirane containing molecules at much higher cure speeds. The proposed photolysis also generates free radicals, which suggests a possibility of amalgamating cationic photopolymerization with radical polymerization.

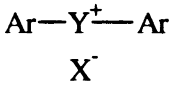
The photo-generated Bronsted acids are long-living. This means that the active centers generated during the illumination remain active even after the radiation is stopped and will continue to induce propagation. This "dark cure" phenomenon has been evidenced by previous researchers in the case of both epoxies and vinyl ethers by observing the decrease in the intensity of the absorbance bands representative for the oxirane structure. Solvent resistance of the cured films has been seen to vary with time, providing more evidence. Furthermore, the dark cure is heat-catalyzed and therefore heat producing lamps may be beneficial to use. Preheating of the wet coating or the substrate will also help the curing. This dark cure phenomenon also facilitates the cure of remote areas of coated objects which are shielded from the ultraviolet light. The advancing polymerization propagation front, combined with the high diffusion characteristics of the Bronsted acid are responsible for this. One significant advantage of using epoxies for coatings applications instead of urethanes is that they exhibit excellent adhesion to a variety of substrates, including metal. The contributing factor for this excellent adhesion is the high wetting characteristics exhibited by epoxies on metals and most plastics. Another important characteristic is that the cationic polymerization of the epoxies is associated with extremely low volume shrinkage, 1 to 2 percent, as compared to the 15-20 percent volume shrinkage for the acrylate systems that undergo free radical polymerizations.

The primary requirement of photoinitiators is that they must possess "chromophores" which absorb the incident light and undergo photochemical changes so as to generate species capable of initiating cationic polymerization. It should have a long shelf life when not exposed to light and be completely dormant when mixed with the polymerizable monomeric species. On irradiation, it should rapidly produce active centers with high quantum efficiency and not produce byproducts which could retard the initiation or polymerization. Also, it should have an absorbance spectra well resolved from other components in the system (monomer, solvents) and also, the absorbance peaks should coincide well will emission peaks in the irradiating source. The absorbance of the products and byproducts formed should be away from the absorbance of the initiator. To enhance the solubility of photoinitiators in the monomers, certain moieties are added onto the initiator molecules. Care has to be exercised such that these don't retard the efficiency of the initiator. For commercial applicability of the initiating system, toxicity, stability of active centers, color, and cost should be taken into consideration.

Diaryliodonium and triarylsulfonium salts undergo photoinduced fragmentations to generate aryl radicals and either aryliodinium or diarylsulfinium cation radicals. These onium salts can be photosensitized to respond to the longer wavelength UV and visible light. This photosensitization can be caused by compounds like anthracene and perylene by an electron transfer reaction. While the structure of the cations in the onium salts dictates the photochemistry and the rate at which the initiator fragments are produced, the nature of the anion determines the probability of the active cations to undergo termination. Photoinitiated cationic chain polymerizations employing these onium salts are used in a number of commercial processes to produce coatings, adhesives, inks, and novel photoresists for semiconductor applications.

II.9. General Characteristics of Onium Salts

Diaryliodonium, bromonium and chloronium salts belong to the category of halogenic onium salts, with a structure like



$$\underset{X^-}{Ar{-}Y^+{-}Ar}$$

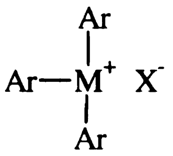
where Y = I, Br, Cl and X is a nucleophilic species such as BF_4^-, SbF_6^-. Typically, the centrally placed halogen atom possesses a '+3' oxidation state. The synthetic methods for preparation of bromonium and chloronium salts is difficult and the resulting salts are also very unstable.[32] In contrast, the diaryliodonium salts have long shelf lives and are therefore preferred for use as photoinitiators. The diaryliodonium salts are generally colorless to pale yellow crystalline compounds and are soluble in most solvents. Depending on the nature of the nucleophilic species, they are available as ionic salts or as covalent ones. The mechanism for generation of cationic active centers by shining UV light on diaryl onium salts is given below.

$$Ar_2I^+X^- \xrightarrow{h\nu} [Ar_2I^+X^-]^*$$

$$[Ar_2I^+X^-]^* \rightarrow ArI^{\bullet +}X^- + Ar^\bullet$$

In the above scheme, light is absorbed by the molecule leading to an electronically excited state. This photoexcited species then undergoes rapid decay by cleavage of the carbon-iodine bond, thus producing an aryliodonium cation radical and an aryl radical. Triarylsulfonium salts also undergo a similar reaction mechanism. The excited singlet state of the molecule is responsible for reaction in both cases.

The general chemical structure of the triaryl onium salts can be represented by:



$$Ar_3M^+ X^-$$

where M = O, S, Se, Te (Group VI of the Periodic Table) and X- is again a nucleophilic species. Of these, only the triarylsulfonium and triarylselenonium salts have been investigated for use as photoinitiators. The triarylsulfonium salts are preferred because of their ease of synthesis and their thermal stability. Most of the salts are colorless crystals and are soluble in organic solvents. Ledwith has showed that the salts are ionic and more highly dissociated than their diaryliodonium salt counterparts.[33] The mechanism of photogeneration of cationic active centers is shown below.

$$Ar_3S^+X^- \xrightarrow{hv} [Ar_3S^+X^-]^*$$

$$[Ar_3S^+X^-]^* \rightarrow Ar_2S^{\bullet+}X^- + Ar^\bullet$$

II.10. Photosensitization

Most triarylsulfonium and diaryliodonium salts absorb strongly at wavelengths between 200 and 300 nm. Chemical substitution of the aryl rings does not substantially change the region of absorbance. The lack of absorbance peaks in the region between 300 and 400 nm causes a major concern because most medium and high pressure industrial lamps emit in this spectral region and, for optimum light utilization, they should absorb here. Moreover, the products and byproducts of initiation also absorb in the same region, thus leading to lower efficiency because of the competitive absorption. Also, monomers with aromatic moieties absorb around 250 nm, leading to suboptimal operation.

This problem can be offset in two ways. One way is to synthesize photoinitiators which incorporate "chromophores" that permit absorbance at higher wavelengths. Alternately, the photolysis of onium salts can be photosensitized, facilitating the use of near UV and visible light for initiation of cationic chain polymerizations. In the past, many aromatic hydrocarbons, aromatic ketones and dyes have been used as photosensitizers. Three mechanisms have been proposed by different researchers to explain the phenomenon of photosensitization.

1. Energy transfer photosensitization
2. Electron transfer photosensitization
3. Photosensitization by free radical induced decomposition

It has been shown by many researchers that the photosensitization of onium salts takes place by the electron transfer mechanism. Analysis of the products of photosensitization has shown them to be identical to those produced when this mechanism is assumed. Additional evidence is presented by experimental observations by Gatechair[34] based on thermodynamic arguments. Essentially, the electron transfer mechanism holds ground because it satisfies both primary requirements - first, the excitation energy of the photosensitizer (E*) is greater than the net energy required to oxidize the photosensitizer (E^{ox}_{sens})and the energy (E^{red}_{onium}) to reduce the onium salt. Secondly, the magnitude of the free energy (ΔG) of photosensitization is negative, i.e. the process is exothermic.

$$\Delta G = (E^{ox}_{sens} - E^{red}_{onium}) - E^{*}$$

The general mechanism for photosensitization of onium salts is given below.

$$P \xrightarrow{hv} P*$$

$$P*+Ar_2I^+X^- \rightarrow [P*\ldots Ar_2I^+X^-] \rightarrow P^+ \cdot X^- + Ar_2I \cdot$$

$$Ar_2I\cdot \rightarrow ArI + Ar\cdot$$

$$nM \xrightarrow{P^+ \cdot X^-} -(M)_n -$$

In the mechanism shown above for diaryliodonium salts, the sensitizer absorbs the incident radiation and attains an excited state. The excited state responsible for reaction with the onium salt could be the singlet or triplet excited state of the sensitizer molecule. For anthracene, it has been shown by Nelson et al[35] to be the triplet state. Upon interaction between the sensitizer and the onium salt, an exciplex is formed which undergoes a photoredox reaction. The sensitizer undergoes oxidation to form a cation radical while the onium salt reduces to a diaryliodide radical. It should be noted that unlike direct excitation of the onium salts, the initiating species is produced from the sensitizing species.

Diaryliodonium salts have lower oxidation potentials compared to the triarylsulfonium salts, and hence are easier to photosensitize. Thus, while the former can be photosensitized by a variety of compounds, the latter is restricted to compounds with low oxidation potentials and high triplet energies. Condensed ring aromatics such as anthracene and perylene are well suited for the purpose.

II.11. Polymerization Characteristics of Onium Salts

Since the cation part of the initiator molecule is responsible for the initiation and propagation, the initiating characteristics of the salt is greatly dependent on the "chromophores" residing in that part of the molecule. The absorbance spectra of the photosensitizer determines amount of light absorbed and effectively used. Both the direct and photosensitized photolysis of onium salts generate similar initiating species, namely, aryliodinium and diarylsulfinium cation radicals.

Since the nature of the anion plays no direct role in the photochemistry of the onium salts, the quantum yields of salts with different anions but same cations is essentially the same. Nevertheless, the anions do play a part in determining the reactivity of the cations towards the monomer as well as influence the propagation and termination rates.

Photoinitiators bearing strongly nucleophilic anions such as the halogens are very weak photoinitiators. The onium salts bearing very weakly nucleophilic anions such as BF_4^-, PF_6^-, AsF_6^-, SbF_6^- exhibit excellent reactivity when irradiated. Because of the lack of reactivity of these anions, they remain in ionized form and the cationic active centers continue with the propagation. In the case of epoxide containing monomers, the reactivity of the diaryliodonium and triarylsulfonium salts has been found to increase in the following order, depending on the type of anion: $BF_4^- < PF_6^- < AsF_6^- < SbF_6^-$.

Although the reasons for this trend are not fully explained, the nucleophilicity of the anion definitely will play a part. As the nucleophilicity of the anion decreases in the order $BF_4^- > PF_6^- > AsF_6^- > SbF_6^-$, the separation between the ions increases, thus increasing the reactivity. At the same time, the susceptibility of the anion toward fluorine abstraction decreases, thus decreasing the tendency of termination.

It has been shown that heterocyclic polymerizations proceeding by a cationic mechanism will continue for very long times in the absence of terminating impurities. Such living polymerizations have been reported in the case of THF using diaryliodonium and triarylsulfonium salts.

Photoinitiated cationic chain polymerizations can be carried out in the presence of oxygen since it neither quenches the excited states of the initiator, nor does it interact with the propagating species. In cases where free radical induced decomposition of the initiator takes place, oxygen may intercept the free radicals. Bases of all types inhibit chain polymerization and should be removed. Water and other hydroxyl containing compounds can act as inhibitors or chain transfer agents depending on the amount present.

II.12. Epoxidized Soybean Oil: An Agri-based Source of Polymerizable Epoxides.

II.12.1. Motivation to Use Agricultural Feedstocks as Starting Materials

The use of renewable agricultural feedstocks for the production of chemicals and materials has been identified as a national priority. The interest in renewable feedstocks is motivated by several factors including environmental concerns, economic development of rural areas, and diversification of the resource base from the traditional petroleum feedstocks. In this research, we have attempted to meet these criteria by developing a novel and feasible process for producing polymeric materials from renewable agricultural feedstocks. Specifically, we have investigated cationic polymerizations of epoxidized natural oils, and evaluated their potential for use as substitutes to synthetic polymeric materials for bulk (non-coating) applications. While the use of monomers derived from natural feedstocks clearly meets the objectives of a renewable feedstock, the cationic photopolymerization scheme also offers significant practical processing advantages. Since this process is directly based on an agricultural commodity, traditional materials and methods for growing, harvesting and collecting the raw material can be used. In addition, cationic polymerizations are amenable to continuous processing schemes, since they exhibit rapid reaction rates and low energy requirements. These processing advantages are important since many proposed schemes based upon renewable feedstocks are limited or disqualified because they are not easily adapted to large-scale production. Since the targeted applications are bulk (thick) polymers, this method could make a tremendous impact on the substitution of synthetic polymers by agri-based polymers.

II.12.2. Traditional Methods of Producing Polymeric Films and Coatings from Natural Oils.

Natural oils and their derivatives have long been used as precursors to polymeric components in films, paints and varnishes. These current techniques for using agri-based oils in films and coatings fall into two major classes. One of the oldest methods for making films from oils is based on naturally-occurring oxidative crosslinking reactions in unsaturated "drying oils." These reactions formed the basis for many of the early lacquers and varnishes. The second class of reactions involve step reactions of oils that either naturally contain a reactive moiety or are modified with a reactive functionality. For example, maleated, epoxidized, or esterified oils may be polymerized with comonomers by a step reaction to produce a polymer product. Both of these current polymerization methods for natural oils have significant problems and limitations, and are not well suited for the mass production of polymers, especially for parts of appreciable thickness. Most of these limitations ultimately arise from the inherently slow polymerization rates associated with the current curing techniques.

II.12.3. Reactions in Natural Drying Oils.

Drying oils are liquid vegetable or fish oils which react with oxygen to form solid films. Such oils were widely used in the 19th and early 20th century as binders for paints, and are still used as raw materials for alkyd resins, epoxy esters and uralkyds. During drying, a series of complex free-radical reactions take place and ultimately lead to the formation of a crosslinked polymer. For example, the crosslinking of linseed oil, a major drying oil, is thought to consist of the following steps[36,37]: 1) an induction period during which naturally present antioxidants (tocopherols) are consumed; 2) a period of oxygen uptake and formation of hydroperoxides; and 3) a sequence of catalytic reactions where the hydroperoxides are consumed and the cross-linked film is formed. These reactions are catalyzed by heavy-metal "driers" such as cobalt, lead or zirconium salts of octanoic acid or naphthenic acid. The rate of polymerization depends on the degree of conjugation of the oil, with oils containing conjugated double bonds drying more rapidly than non-conjugated oils. In addition, free radical polymerization of conjugated oils can lead to chain-growth polymerization rather than just cross-linking, and therefore the resulting films typically exhibit better water and alkali resistance compared to films formed from non-conjugated oils.

Although drying oils have traditionally filled a niche in the coatings industry, they have lost much of their market share due to a variety of problems and limitations. First of all, the requirement of oxygen in the reaction scheme leads to relatively long cure times, and inherently limits the thickness of the cured polymer. In addition to prolonged cure times (on the order of 50 hours) several other problems associated with drying oils arise from the complex sequence of reactions which take place in the curing film. For example, rearrangement and cleavage of the hydroperoxides leads to low molecular weight volatile by-products, as well as discoloration and embrittlement of the film. Moreover, the use of the metal catalyst (the drier) not only enhances the rate of the "drying" reactions, but also catalyzes a number of post-drying reactions which lead to embrittlement and discoloration of the film. Finally, the presence of the toxic metal catalysts has raised many environmental concerns and has resulted in severe restrictions and limitations on their use.

II.12.4. Reactions of Functionalized Oils.

Alkyd Resins. The most prevalent class of functionalized oils are the alkyd resins, which are unsaturated polyesters containing carbon double bonds at the chain ends. Alkyd resins are commonly produced by the condensation reaction of oil-derived acids with polyols (forming ester linkages). Two classes of alkyd resins have been identified. The first class, oxidizing alkyd resins, cures by the same mechanism as described above for natural drying oils and are hence sometimes referred to as synthetic drying oils. For example, soybean oil is commonly combined with glycerol to form a synthetic drying oil which cures by this mechanism. In contrast, non-oxidizing alkyd resins are used as polymeric plasticizers or as hydroxy-functional resins which may be cross-linked by reaction with melamine-formaldehyde, urea-formaldehyde or isocyanate cross-linkers. This second class of alkyds cures by specific condensation reactions between groups on the alkyd and the crosslinker. The commercial use of oxidizing alkyd resins is far greater than that of non-oxidizing alkyd resins. For example, while about 120 million pounds of soybean oil were used in the manufacture of oxidizing alkyd resins, only 6-8 million pounds of oil were used in the manufacture of non-oxidizing alkyd resins.[38] However, the use of soybean oil in the manufacture of both types of resins has steadily declined since 1949.

Free-radical polymerizations of unsaturated oils. Both conjugated and non-conjugated unsaturated oils may be copolymerized with vinyl monomers such as styrene, vinyltoluene, cyclopentadiene and acrylic esters. These polymerizations proceed by the standard free radical mechanism, however they typically exhibit a high degree of chain transfer. Due to this chain transfer, the molecular weight of the product is limited, and the method typically yields a variety of low molecular weight homopolymers, short-chain graft copolymers, and dimerized drying oil molecules. Therefore, the method has very limited applicability for the production of high polymers. The only such reaction that is commercially viable is the reaction of cyclopentadiene with linseed oil to form a faster reacting drying oil. However, the dark color and odor of the oil limit its applications.

Epoxidized oils. Unsaturated oils may be epoxidized by reaction with peroxyacids to convert the carbon double bonds to oxirane functionalities. Once epoxidized, these oils may be polymerized by reaction with amine-containing monomers by the standard epoxy-amine reactions. Epoxidized oils have found modest application in specialty coating systems, however the cure rate is typically rather slow. One factor which prevents the extensive application of these oils is the relatively low reactivity of internal epoxide groups. This is a drawback for polymerization of epoxidized oils since these oils primarily contain internal oxirane groups. At ambient temperature, cure times on the order of a week are common for reactions of these oils with aliphatic amines. Other limitations of these systems arise from the inevitable trade-off between pot-life and cure rate. Ketones such as methyl ethyl ketone (MEK) have been used to extend the pot-life of the resins through an amine-blocking mechanism. Upon exposure to ambient moisture, the ketone is released, allowing cure to take place. While this ingenious scheme extends the pot-life of the resins, the use of MEK, a highly volatile organic compound, is undesirable due to its negative environmental impact.

Due to the problems described above, current utilization of natural oils in bulk polymers is largely limited to secondary roles such as plasticizers, reactive diluents and comonomers. Epoxidized soybean oil and to a lesser extent epoxidized linseed oil are used as plasticizers for PVC, and impart excellent heat and light stability.[39] Epoxidized and other functionalized oils from soybean, vernonia and castor seed have been used to form two-phase interpenetrating networks, via step reactions with amines, terephthalates and other epoxy monomers.[40,41,42] Recently Crivello and Narayan[43] demonstrated that epoxidized oils can be used to form films by cationic photo-polymerization. This technique has been used to make thin-films which possess good adhesion and mechanical properties, at relatively high reaction rates.

II.13. Need for New Polymerization Methods Based Upon Natural Oils.

Although there is a compelling motivation to develop polymers based upon natural oils, all of the techniques reported to date exhibit significant drawbacks and limitations. The above discussion illustrates many of the concerns associated with the slow cure and the environmental impact of additives in the current systems. These issues have limited the use of natural oils, even for polymer film and coating applications. Moreover, the slow rates exhibited by these methods precludes the possibility of their use for producing thick parts or bulk polymers. Clearly new, commercially viable polymerization methods must be developed if natural oils are to be extensively utilized as a feedstock for the production of polymeric materials. Cationic polymerizations may be used to rapidly polymerize epoxidized oils in either thin films or thick parts without the use of environmentally detrimental additives. This technique has significant practical advantages (high cure rates with an essentially unlimited pot-life) and is amenable to mass production by continuous process schemes.

II.14. Cationic Polymerizations of Epoxidized Oils.

Cationic polymerizations are chain reactions in which a propagating cationic center successively reacts with many monomer units to form long polymer chains. Classes of monomers which will undergo cationic polymerizations include α-olefins, 1,3-dienes, vinyl ethers, and epoxides. Cationic initiators are typically protonic or Lewis acids, and the resulting reactive cations are sufficiently stable to have a reasonable lifetime for chain growth by propagation. The polymer chain growth may be terminated by chain transfer of the reactive center, or occasionally by counterion combination. Compounds such as water, alcohols, and esters are particularly effective chain transfer agents. Although chain transfer results in a decrease in the average primary polymer chain length, it typically will not affect the polymerization rate because the resulting cation will continue to propagate.[1]

Cationic polymerizations have considerable potential for the development of a novel polymerization scheme for epoxidized oils which avoids the limitations of the current methods. They require a fraction of the energy of their thermal counterparts, and may be carried out with no diluting solvent, resulting in low emissions of volatile organic components. The cationic initiation reaction is very rapid, and the propagation reaction continues long after the irradiation has ceased, resulting in almost complete conversion of the monomer to polymer. Finally, unlike their free-radical counterparts, cationic polymerizations are not inhibited by oxygen, and therefore do not require an inert atmosphere to achieve rapid polymerization rates. Epoxides and vinyl ethers are important classes of monomers which undergo cationic polymerizations to yield polymers exhibiting excellent mechanical properties, adhesion, abrasion resistance, and chemical resistance. Despite the advantages of cationic photopolymerizations discussed above, the technique has received only limited attention (considerably less than the analogous free-radical reactions). This fact may be attributed to the lack of stable and suitable cationic photoinitiators until recent years.[44] In fact, applicable photoinitiators for cationic polymerizations were not developed until the late 1970s, more than thirty years after free-radical initiators had been reported.

Epoxidized soybean oil (ESO), which is produced by the reaction of soybean oil with hydrogen peroxide, accounts for more than half the epoxidized oil market. Soybean oil consists of triglycerideesters of long chain (16-18 carbon) unsaturated fatty acids (Figure II.1). The average molecular weight of the ESO molecule is 976 grams. Upon titration, it was found that the epoxy moieties per molecule of ESO averaged around 6. At room temperature, the epoxidized oil is lighter than water (specific gravity = 0.93) and moderately viscous (340 cP).

Olefinic double bonds in the oil are reacted with peroxy compounds to form epoxide moieties. Epoxidized soybean oil is widely used as a plasticizer for PVC, and has an annual production of 70×10^6 kg with a selling price of \$1.40/kg (\$ 0.65/lb). Although the technology to convert the agricultural feedstock (soybean oil) to the monomer exists, very little work has been done to convert the monomer to bulk polymer. This is due in part to the low rates of polymerization using conventional techniques (curing the epoxide by reaction with a diamine). Recently developed cationic photoinitiators have been used to polymerize thin films of epoxidized oils at relatively high reaction rates, and the resulting films were found to possess good adhesion and mechanical properties.[43] However, no attempt was made to polymerize bulk specimens from epoxidized oils.

The conventional curing of oxirane containing molecules such as cycloaliphatic epoxides with organic acid anhydrides, organic acids, Lewis acids, and blocked Lewis acids is widely practiced in the industry and the reaction mechanisms are well documented and described in the literature.[1,2,45] One way to describe cationic UV initiated polymerization is to say that it is the polymerization of the oxirane molecules by use of a "blocked" Lewis or Bronsted acid, which unblocks upon exposure to UV light and liberates an acid. This liberated acid in turn polymerizes the oxirane molecules through a mechanism similar to conventional curing of epoxies.

Diaryliodonium salts can be easily employed to photoinitiate cationic ring opening polymerization of epoxidized soybean oil using anthracene as a photosensitizer. Due to the multifunctional nature of the ESO molecule, a crosslinked polymer can be obtained very rapidly. A schematic of the crosslinking polymerization of ESO is shown in Figure II.2.

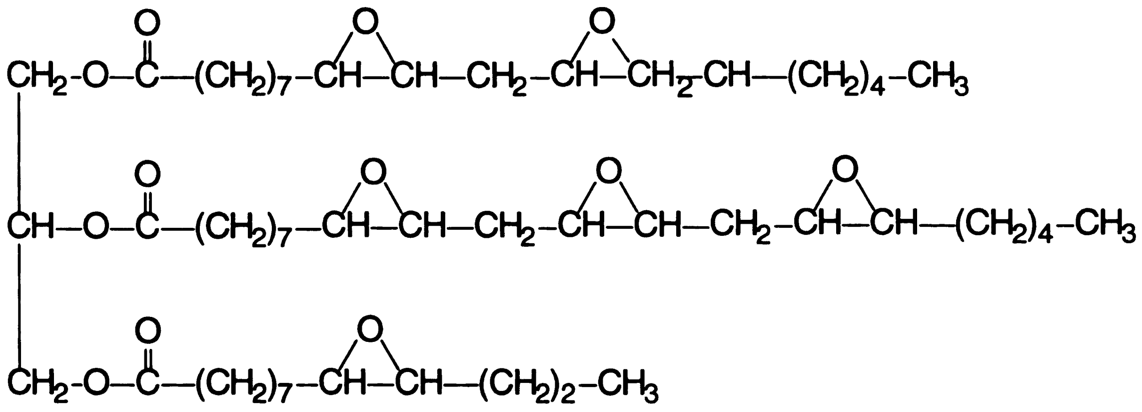


Figure II.1. Average chemical structure of the epoxidized soybean oil molecule.

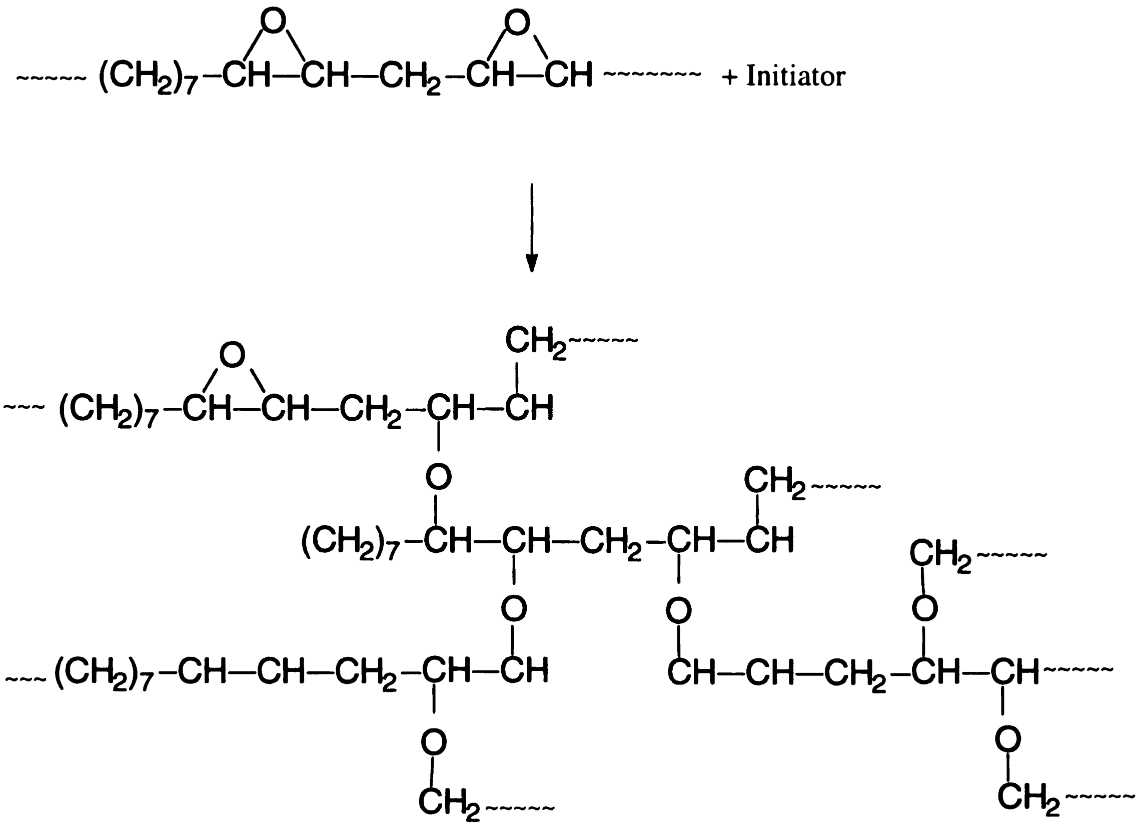


Figure II.2 Schematic of the crosslinking polymerization of epoxidized soybean oil.

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CHAPTER III.

OBJECTIVES OF RESEARCH

Based upon the motivation and background provided, it is clear that cationic chain polymerizations of vinyl ethers and epoxides initiated by UV light have considerable potential for the development of high speed, low cost, pollution free coatings, inks and thick polymer parts. It is also generally acknowledged that polymers produced from renewable agricultural resources offer several attractive advantages over traditional synthetic materials.

The overall goal of this project was to demonstrate that epoxidized oils can be rapidly and efficiently polymerized to produce usable polymers. Using cationic polymerizations, we identified suitable processing parameters necessary to establish this process as a viable technique for producing polymers from renewable feedstocks. A variety of processing conditions were investigated, including initiator and photosensitizer formulations, different light intensities, and temperatures. To characterize the reaction, the epoxide conversion was monitored as a function of time using differential scanning calorimetry.

Diaryliodonium hexafluoroantimonate salts, photosensitized by anthracene, were used to perform photoinitiated cationic ring opening polymerizations of epoxidized soybean oil. During the course of this research, we found that the photosensitization reaction between anthracene and diaryliodonium salts needs further investigation. Although this reaction has been extensively studied by various researchers in the past, the effect of viscosity on the reaction kinetics has not been investigated. Steady state fluorescence spectroscopy experiments were employed to study the effects of diffusion on the reaction. Mathematical modeling of the photosensitization mechanism using a well known theory for diffusion controlled reactions was used to corroborate the experimental findings.

Specific objectives of this project were:

i. to establish reaction conditions for the production of bulk polymers from epoxidized natural triglyceride oils;

ii. to obtain detailed profiles of oxirane conversions during the photopolymerization of epoxidized soybean oil at different light intensities and reaction temperatures;

iii. to experimentally characterize the effect of viscosity on the rate of photosensitization of diaryliodonium salts using anthracene.

iv. to provide a correlative model for the effect of viscosity on the rate of photosensitization of diaryliodonium salts using anthracene.

CHAPTER IV.

KINETIC STUDIES OF PHOTOPOLYMERIZATION OF EPOXIDIZED NATURAL TRIGLYCERIDES

Abstract

Differential Scanning Photocalorimetry (DSP) was used to investigate a series of photoinitiated cationic polymerizations at different temperatures, using epoxidized soybean oil as the monomer. The apparent propagation rate constant exhibited an initial sharp increase, decreased gradually after reaching a plateau, then decreased rapidly upon reaching a limiting conversion. The limiting conversion obtained was found to be higher for the polymerizations which proceeded at lower temperatures, although the initial rate of polymerization was found to increase with increasing temperatures. These trends were attributed to diffusional mobility effects in the rapidly polymerizing systems.

IV.1. Introduction

Natural oils such as soybean, linseed, and corn could be used as monomers for chain polymerization if the unsaturation in these triglyceride esters was utilized. Epoxidation of these oils is an excellent means of introducing oxirane moieties into the chemical structure of the oils to make them conducive to cationic polymerization. Epoxidized Soybean Oil (ESO) has been used for several years as a plasticizer for PVC,[1] and the polymers formed from ESO have been shown to be biodegradable.[2] Its source is in an agricultural crop, and hence it is a renewable source. Lately, ESO and other epoxidized oils have also been employed as reactive diluents for thermal curing with other epoxy monomers,[3] as epoxy components in the production of interpenetrating polymer networks,[4] and as toughening materials for commercial epoxy resins.[5]

Whereas almost all monomers containing unsaturation are amenable to radical polymerization, ionic polymerizations are found to be highly selective.[6] This selectivity is attributed to the unstable nature of the propagating species, hence limiting the commercial utilization of ionic polymerizations. It also has been extremely difficult to obtain reproducible kinetic data in the past for ionic polymerizations due to their very rapid reaction rates, and their sensitivity to the nature of impurities and solvents. Low temperatures are required in both anionic and cationic polymerizations to suppress termination and chain transfer reactions whereas free radical polymerizations proceed comfortably at relatively higher temperatures. Also, the activation energies for ionic polymerizations are significantly lower than their radical counterparts and are sometimes found to be negative. In the past, some solvents have been employed to stabilize the propagating species and increase their effective lifetime. In ionic polymerizations, the propagating species can be a positively charged cation or a negatively charged anion. While cationic polymerization requires electron-releasing substituents such as alkoxy, phenyl, oxirane, or vinyl in the monomer, anionic polymerization requires monomers with electron-withdrawing groups like nitrile, carboxyl, phenyl or vinyl.

In this chapter kinetic studies of cationic photopolymerizations of epoxidized soybean oil are described. Differential Scanning Photocalorimetry (DSP) was used to investigate a series of polymerizations performed at a variety of temperatures. The kinetics of cationic photopolymerizations are extremely complex and system dependent largely because the reactivity of the propagating cation depends upon the proximity of the counterion.[7] Therefore, depending on the nature of the polymerization medium, the propagating species may exist in any state between the extremes of closely associated ion pairs, and free ions. The ion pairs in cationic polymerization tend to be loose ion pairs even in moderately polar solvents because of the relatively high mobility of the cations compared to that of the negatively charged counterions which are typically large in size. The situation is further complicated by the fact that in bulk (solvent-free) polymerizations, the medium changes from a relatively low viscosity liquid at the start of the reaction, to an elastic solid at the end of the reaction, with a possible change in the dielectric constant. Therefore the proximity of the counter ion (and therefore the reactivity of the cation) may change during the course of the reaction.

The most fundamental description of the kinetics of cationic polymerizations would be based upon the identification of the nature of the propagating species and the proximity of the counterion. However, such a determination is practically impossible for bulk polymerizations in which the nature of the propagating ion may change during the course of the reaction. Therefore, a useful approach which provides the important information about the effect of reaction conditions on the kinetics is to evaluate the effective propagation rate constant defined as the proportionality constant between the rate of polymerization and the product of the epoxide concentration and the active center concentration. This effective propagation rate constant contains contributions from all the types of active centers ranging from ion pairs to separated ions.

In general, termination of active centers in polymerizing systems occurs by combination, disproportionation or by chain transfer to similar or different species. Termination in cationic polymerizations is limited to chain transfer to solvent, monomer, or another polymeric chain because, in contrast to free radical polymerizations, the combination of active centers does not lead to termination in ionic polymerization. Due to this fact, the initiation and termination velocities are rendered unequal and the steady state approximations generally held true for polymerization mechanisms cannot be employed for the cationic polymerization scheme. In bulk polymerizations without the use of a solvent, the termination can occur only by chain transfer to a monomer or a polymeric chain. Although the chain transfer to a monomer causes a decrease in the average molecular weight, the degree of polymerization or conversion remains unaffected. Termination by chain transfer in bulk polymerizations with negligible amounts of impurities can be considered to be a facile (surface) reaction only. Hence, the polymerizing system can be considered to be a non-terminating or "quasi-living" system.

Differential Scanning Photocalorimetry (DSP) has been used to characterize the kinetics of photopolymerizations- free radical[8,9,10,11,12] as well as cationic reactions.[13] This simple analytical method utilizes the enthalpy of polymerization to characterize the extent of reaction with time. DSP is especially suited to the study of reactions which are highly exothermic since it measures the extent of reaction by monitoring the heat released from the polymerizing sample. The rate of heat released from the polymerizing sample can be profiled with time to provide the instantaneous rate of propagation reaction which can then be used to calculate the kinetic parameters.[14] Although this technique has been employed to study photopolymerizations that proceed by the free radical mechanism, it has received little attention in studying cationic photopolymerizations. This is because, typically, cationic photopolymerizations proceed very rapidly and also have large exotherms. The typical response time of a DSC[15,16] is on the order of 2-3 seconds which makes it crucial for the calorimeter to remove the heat at a sufficiently rapid rate so as to maintain the temperature constant in the sample cell. By using samples of smaller size and also using initiating radiation of low intensity during photoinduced polymerizations, these problems can be circumvented.

The Differential Scanning Photocalorimetric technique is very well suited to our application because the enthalpy release is about 20 kilocalories per mole of oxirane ring reacted. By manipulating the level of radiation and the size of the sample, the reaction can be made to proceed at rates such that the response of the DSC is rapid enough that the profile obtained is free of instrumental artifacts due to thermal instability.

In the studies presented here, photocalorimetry was used to study the photosensitized cationic polymerization of the oxirane moieties in epoxidized soybean oil (ESO) to form a crosslinked thermoset polymer network. Although the viscosity of epoxidized triglyceride oils is considerable (200-300 cP at room temperature), it is completely non-toxic and also exhibits a very low vapor pressure. An added advantage is that, since it is based on a natural agricultural feedstock, it is a renewable resource. The films formed by homopolymerization of ESO have been shown to exhibit excellent adhesion, abrasion and optical properties.[2] Although chain polymerization of ESO has been utilized and studied,[2] a detailed analysis of the photopolymerization mechanism and kinetics has not yet been reported. A study of the rapid cationic photopolymerization of ESO is important because of the increasing number of applications for rapid, solvent free curing of polymer films as well as thick geometries. The rapid rate of polymerization renders the process amenable to mass production.

This contribution includes the proposition of a simple correlative reaction mechanism for the ring-opening photopolymerization of the oxirane rings much similar to that employed for the cationic chain polymerization of monomeric species containing carbon double bonds.[13] Experimental DSP results for different values of isothermal system temperature and intensity of initiating light are presented and analyzed. The reaction was initiated by a diaryliodonium salt which was photosensitized by anthracene. The sensitizer was used to shift the initiating spectral window from the deep UV (where the onium salts absorb light) to the near UV part of the spectrum (300-400 nm). Isothermal DSP runs were performed to determine the kinetic constants at different temperatures. The activation energy of propagation is obtained by plotting the propagation rate constants against the absolute temperature of the experiment. For these calculations, previously obtained values of initiation rate constants and activation energy for initiation were utilized.[13] The resulting profiles obtained for the propagation rate constants and the overall conversion of the epoxy moieties provided an insight into the nature of the cationic photopolymerization and how it could be used to obtain desirable properties for the polymer product.

IV.2. Experimental

IV.2.1. Materials

In the photocalorimetric studies described, epoxidized soybean oil, obtained as a gift from FMC Corporation was employed as monomer. The monomer was dried over molecular sieves to remove any traces of water. A commercially available photoinitiator (UV9310C, GE Silicones) was utilized. Its formulation was: 5-10 wt % linear alkylate dodecylbenzene, ~50 wt % 2-ethyl-1,3-hexanediol, and ~50 wt % bis (4-dodecylphenyl) iodonium hexafluoroantimonate. The diol in the initiating mixture acts as a solvent and helps to prevent cyclization during polymerization. The dodecyl chains were added on to the initiator to impart solubility in the monomer. Initiator concentrations specified henceforth correspond to the total UV9310C concentration. The photosensitizer, anthracene, was purchased from Aldrich Chemical Company and was used as received.

IV.2.2. Absorbance and Calorimetric Experiments

Absorbance measurements were conducted using a Hewlett-Packard UV-Visible Spectrophotometer model 8452A. The DSP experiments were conducted using a Perkin-Elmer Differential Scanning Calorimeter, model DSC-7. The experimental setup is shown in Figure IV.1. The light source used in the study was a 200 watt Hg(Xe) arc lamp from Oriel Corporation (model number 6291). Magnetic stirbars were used to dissolve the initiator (~1% by weight) and the anthracene sensitizer (~0.01% by weight) in ESO to prepare the photopolymerizable samples. Sample sizes were about 10-15 milligrams. The samples were placed in uncovered aluminum DSC pans obtained from Perkin-Elmer and cured at different reaction conditions in the DSC. Glass slides from VWR Scientific were placed above the sample and reference cells of the DSC to filter out the deep UV light from the lamp (<300 nm) so that the sensitization phenomenon could be studied, isolated from the direct initiation of the diaryliodonium salts. This was done to simulate conditions in industrial environments where the low and medium pressure mercury lamps used do not emit considerably in the deep UV region. Apart from absorbing most of the light which could directly activate the initiator, the glass slides help in preventing the loss of thermal energy to surrounding air, thus keeping the system isothermal. Therefore, the conversion we observe is the result of photosensitized initiation caused by anthracene only. The contribution of thermal initiation is minimal because of the low range of temperatures used for studying these reactions. The reactions were maintained isothermal by a water cooling mechanism. Light intensity measurements were performed using a High Energy UV Integrating Radiometer (Uvicure Plus, EIT, Inc.) The emission spectra of the lamp source was obtained using an SD1000 Dual Channel Fiber Optic Spectrophotometer from Ocean Optics, Inc. The spectra were calibrated using the radiometer reading in the range of 320-390 nanometers (UV-A region) by integrating the area under the curve and setting it equal to the radiation dose from the lamp in this spectral region. More than 60% of the irradiance in this range is provided by the mercury line of the lamp at about 363.8 nm. This is very close to one of the anthracene absorbance peaks and hence the sensitizer is very effective in causing the reaction. The unique chemical structure of anthracene with three fused aromatic rings helps it to sensitize the diaryliodonium salt by electron transfer.[19] The triplet state of anthracene rather than the singlet state is responsible for this excited state photochemical reaction.[13]

IV.3. Results and Discussion

IV.3.1. Proposed Mechanism

Eq. IV.1 through Eq. IV.4 describe the proposed mechanism for ring-opening photopolymerization of epoxidized soybean oil. In these photopolymerizations, the cationic active centers are generated through a photosensitization reaction in which an electron is transferred from an excited anthracene in its triplet state to the initiator.[19] Although the reaction mechanism is a composite of several photochemical reactions, it can still be represented by a simple second order reaction scheme as in Eq. IV.1. We assume that there is only one active center produced by the photochemical dissociation of each anthracene molecule. Also, we assume that all active centers generated are fully and equally capable of propagating.

$$A + I + h\nu \xrightarrow{k_i} I^+ \qquad \text{Eq. IV.1}$$

$$I^+ + M \xrightarrow{k_p} M^+ \qquad \text{Eq. IV.2}$$

$$M_n^+ + M \xrightarrow{k_p} M_{(n+1)}^+ \qquad \text{Eq. IV.3}$$

$$M_p^+ \xrightarrow{k_t} M_p + I \qquad \text{Eq. IV.4}$$

The rate of active center generation is directly proportional to the intensity of light at the sensitizing wavelength. The concentrations used in the system being investigated are such that the molar concentration of the diaryliodonium salt (6.08 mM) is about 10 times that of the sensitizer (0.505 mM). Hence, the initiation mechanism can be assumed to be first order with respect to anthracene and zeroth order with respect to the initiator.

$$\text{Rate of active center generation} = k_i[A][I] = k_i^*[A] \qquad \text{Eq. IV.5}$$

where k_i is directly proportional to the intensity of incident UV light. k_i^* is the pseudo first order initiation rate constant and includes the effects due to the diaryliodonium initiator concentration and the incident light intensity. An unsteady state balance on the active propagating species gives

$$\frac{d[M^+]}{dt} = k_i^*[A] - k_t[M^+] \qquad \text{Eq. IV.6}$$

After a little modification and integration, we get an equation for the temporal profile of the cationic active centers.

$$d[M^+] = k_i^*[A]dt - k_t[M^+]dt \qquad \text{Eq. IV.7}$$

$$[M^+] = [A_o]\frac{k_i^*}{k_t - k_i^*}\left(e^{-k_i^* t} - e^{-k_t t}\right) \qquad \text{Eq. IV.8}$$

Figure IV.2 shows a typical exotherm obtained from the calorimeter. As can be seen, the exotherm does not return to the same value that it started with. This implies the difference in the specific heats of the initial monomer sample and the final polymer product. For calculation of the reaction parameters from the experimental data, different types of base lines can be utilized. A sigmoidal base line is the most effective but it is cumbersome to devise because of its non-objective nature. A straight base line with a constant slope is one of the simplest and most practical. After drawing the straight base line and subtracting it from the exotherm curve, we get the corrected DSC data shown in Figure IV.3.

Utilizing the direct proportionality between the heat released by the sample and the reaction rate of propagation, we can calculate the kinetic parameters for polymerization. The rate of propagation is readily obtainable from the calorimetric measurements by utilizing the expression below:

$$R_p = \frac{d[M]}{dt} = \frac{\text{Height of exotherm (W / g) x density (g / l)}}{\Delta H_p \text{ (J)}} \qquad \text{Eq. IV.9}$$

Using Eq. IV.8, the propagation rate can be obtained as

$$R_p = k_p[M][M^+] = [Ao]\frac{k_p k_i^*}{k_t - k_i^*}(e^{-k_i^*} t - e^{-k_t} t)[M] \qquad \text{Eq. IV.10}$$

$$[M] = [M_o] - \left[\frac{\text{Exotherm area x } \rho}{\Delta H_p}\right] \qquad \text{Eq. IV.11}$$

Using the instantaneous values for $[M^+]$ and [M] obtained from Eq. IV.8 and Eq. IV.11 respectively, the instantaneous value of the propagation rate constant k_p can be calculated. The total activation energy of the polymerization is equal to the algebraic sum of the activation energies of the individual steps. The negative sign for the termination term is because it causes the destruction of the carbocation.

$$E_R = E_P + E_I - E_T \qquad \text{Eq. IV.12}$$

IV.3.2. Absorbance Results

Figure IV.4 shows the effect of epoxidation on the spectral absorbance of the soybean oil. The soybean oil has a sharp absorbance peak at 205 nm and diminishing absorbance up to 250 nm. The epoxidized soybean oil has two absorbance peaks at 205 nm and 240 nm with considerable absorption until 260 nm. Figure IV.5 contains the absorbance spectra of the photoinitiator and the photosensitizer as a function of the wavelength of light. The two important absorbance peaks of the diaryliodonium photoinitiator are located at 205 and 240 nm. As can be seen from these two figures, the absorbance window of the ESO monomer considerably overlaps that of the initiator. Hence, the use of a sensitizer like anthracene is necessitated if higher reaction rates are desired. Apart from the high absorbance in the deep ultraviolet region, the anthracene molecule exhibits four sharp absorbance bands between 300 and 400 nm. These four closely spaced peaks in the absorbance of anthracene are well away from the absorbance bands of the monomer and the initiator and can be used to excite the molecule without competitive absorption from the other components of the reactive formulation. Also, as the anthracene dissociates, the products of the dissociation do not absorb in the same region. Hence, these peaks decrease in size rapidly, creating a self-eliminating window and making it possible for the light to penetrate further into the sample. This phenomenon is very conducive for production of thicker polymers and our attempt to utilize it is published elsewhere.[17]

IV.3.3. Calculation of Termination Rate Constants

Dark cure DSP experiments were performed to determine the termination rate constant k_t for the cationic polymerization of ESO. The polymerizing samples were exposed to the initiating light for a short period of time and then the light source was removed. The remaining cure was monitored without any exposure to UV light. The time of exposure was limited to 3 minutes such that the epoxy conversion in the sample did not exceed 5% of the total epoxy concentration. This was done to ensure that the DSC decay profile obtained was due to the reduction in polymerization rate caused by unavailability of the cationic active centers and not a result of monomer depletion.

Upon comparison of the decay profiles obtained with polymerizable samples and just the ESO monomer, little difference was observed. This led us to believe that the cationic active centers did not undergo termination at an observable rate. Cationic active centers have been previously known to exhibit relatively long lifetimes and small termination rate constants compared to their free radical counterparts. The termination rate constants for the polymerization of divinyl ethers[13] has been shown to be an order of magnitude less than the rate constant for photoinitiation. We conclude that the contribution of the termination reaction is negligible and for all practical calculations, k_t can be equated to zero.

IV.3.4. Calculation of Initiation Kinetic Constants

The initiation rate constants for different photocalorimetric experiments were determined by solving the photophysical rate expressions developed by Nelson et al.[19] The incident light intensity on the sample was calculated by correcting the emission scan (Figure IV.6) from the lamp source for the distance from the lamp source and the absorbance of the cover glass slides. The intensity of light varies inversely as the square of the distance from the lamp source. The transmittance through the glass slide can be calculated from the absorbance data collected for it using the following equation where A is the absorbance at a specified wavelength and T is the percent transmittance through the sample.

$$A = \log\left(\frac{100}{T}\right) \qquad \text{Eq. IV.13}$$

Nelson et al[19] have calculated the activation energy for the photosensitization reaction between diaryliodonium salts and anthracene from fluorescence measurements of the photosensitization reaction to be $E_I = 28.5 \pm 1.6$ kJ mol^{-1}. Using this value, the effect of reaction temperature on the kinetics of the photosensitization reaction can be estimated. The value of k_i^* thus obtained can be used to calculate the instantaneous reactive center concentration, $[M^+]$, during the photopolymerization experiments.

The emission spectrum of the Hg(Xe) lamp is obtained using a fiber optic spectrophotometer and is shown in Figure IV.6. The radiation dose between 320 and 390 nm was measured using a Uvicure radiometer and was used to calibrate this emission spectrum. The data from this spectrum when combined with the extinction coefficient of anthracene at different wavelengths provide us with the kinetic constants for the photosensitization reaction. k_i^* obtained as a function of temperature at different light intensities has been plotted in Figure IV.7.

IV.3.5. Effect of Light Intensity

To study the effect of light intensity on the propagation reaction profile, DSP experiments were carried out at different incident light intensities, keeping the temperature constant. To vary the incident light intensity on the sample and reference cells, the distance between the light source and the cells was changed by elevating or lowering the lamp or by changing the condensor and rear reflector position in the lamp assembly. At very high intensities, the reaction does not remain isothermal and goes out of control. At very low intensities, the reaction proceeds very slowly, such that the polymerization is not complete in a reasonable amount of time.

Figure IV.8 profiles the heat released with time for different incident light intensities. The ordinate is a direct measure of the velocity of the propagation reaction (see Eq. IV.9). Each of the curves shown in Figure IV.8 is an average of several profiles obtained at each light intensity and therefore could be wider and shorter than the original experimental data. However, they represent the general shape and provide an accurate representation of the average time of maximum heat flux and the exotherm area. As expected, an increase in the initiating light intensity resulted in an increased reaction rate, thus reaching its maximum more rapidly. As calculated above, the complete conversion of the epoxy groups will release a total heat of 582.13 joules per gram of ESO polymerized. Therefore, the quotient of the heat released and the above value provides us with the percent conversion of the epoxides. For example, at an intensity of 0.518 mW/cm^2 at 365 nm, the heat flux reached the maximum at 17.97 ± 0.43 minutes and had an average exotherm area of 292.81J/g. The photopolymerization at an intensity of 1.555 mW/cm^2 had the maximum heat flux at 4.33 ±0.32 minutes and an average exotherm area of 315.68 J/g of sample. The polymerization at an intermediate intensity of 1.037 mW/cm^2 peaked at 11.65 ± 0.51 minutes. Although the rate of propagation increases rapidly for experiments at higher incident radiation, the final conversion of epoxide groups does not increase much. This may be because of the "non-terminating" nature of the cationic active centers. Although the initiation proceeds at higher rates in the beginning, the total number of active centers that can be generated in the course of the polymerization is approximately the same for both cases. The slightly higher conversion obtained in the case of higher light intensity is due to the fact that the more rapid generation of active centers led to the active centers reaching the epoxide groups earlier and hence leading to more conversion.

IV.3.6. Effect of Temperature

The photopolymerizations of ESO, initiated by UV9310C and photosensitized by anthracene, were carried out at a series of temperatures from 50°C to 110°C in order to characterize the activation energy over a large temperature range. Preliminary studies revealed that no appreciable thermal initiation of the samples occurs at these timescales for temperatures below 200°C. The polymerization rate profiles obtained from the DSP experiments conducted at different temperatures keeping the incident light intensity constant have been plotted in Figure IV.9. As can be expected, the initial reaction rate increases with increasing temperature as illustrated by the fact that the exotherms reach a maximum value earlier and also the peak value of heat flux is higher. Surprisingly, on integration and comparison of the areas under the exotherm at different temperatures, we found that the reactions at lower temperatures reach a higher final conversion, though they start very slowly.

The conversion of the epoxy moieties in the monomer was calculated using the theoretical value of the enthalpy of oxirane ring opening. This value is 94.5 kJ/mol of oxirane group. This translates to about 582.13 joules/gram of ESO since the average ESO molecule has six oxirane rings with a molecular weight of 974 grams. The conversion at any point of time can be calculated by division of the area under the DSP exotherm by this number.

$$\text{Conversion of epoxide moities} = \left(\frac{\text{Exotherm area}\left({}^{J}\!/_{g} \right) \rho \left({}^{g}\!/_{l} \right)}{\Delta H_p \, [M_o]} \right) \qquad \text{Eq. IV.14}$$

As can be seen from Figure IV.10, the final limiting conversion obtained is higher for lower experimental temperatures. This phenomenon of limiting conversions is not due to thermodynamic equilibrium effects because the high ring strain of the epoxides causes the polymerizations to proceed irreversibly.[18]

The effect can be explained in terms of viscosity and gelation effects. Our explanation of this phenomenon is that the decrease in rate is due to the lack of mobility of the cationic active centers at higher conversions of the epoxide group. At polymerizations proceeding at lower temperatures, the viscosity of the system is high and the reaction progresses at a moderate pace such that the local viscosity rises slowly until solidification (vitrification) of the system at which point the polymerization rates are drastically reduced. At higher temperatures, the reaction starts to occur very rapidly because of the low initial viscosity of the monomer. The rapid polymerization causes an enormous increase in the local viscosity of the system, severely restricting the movement of the cationic sites. The oxonium ions are hence "trapped", causing a phenomenon of limiting conversion at higher temperatures.

For each exotherm obtained for the photopolymerization reaction, a profile of the quantity $k_p[M^+]$ may be obtained using the empirical profiles of R_p and [M]. Based upon the DSP exotherm, this product may be determined using the following equation.

$$k_p[M^+] = \frac{R_p}{[M]} \qquad \text{Eq. IV.15}$$

Profiles of $k_p[M^+]$ obtained in this manner are shown in Figure IV.11. As shown in this figure, the value of $k_p[M^+]$ increases rapidly initially. The maximum value attained by $k_p[M^+]$ is directly proportional to the reaction temperature. After it reaches a maximum value, it decreases slowly with time because it reaches a limiting conversion. The shape of the profiles indicates that the apparent propagation rate constant k_p changes as the reaction proceeds. If k_p had remained constant throughout the reaction, the value of $k_p[M^+]$ would have been dictated solely by the steady increase in the active center concentration. That is, the value of $k_p[M^+]$ would have increased monotonically till it led to the complete consumption of the photosensitizer.

Further information about the behavior of k_p may be obtained by coupling the information on $k_p[M^+]$ with that of k_i^*. We can utilize the photosensitization kinetic parameters for anthracene proposed by Nelson et al[19] for the cationic photopolymerization of epoxidized oils. Using the initiation expression obtained, assuming that the polymerization reaction is non-terminating, and using the values calculated for R_p and $[M^+]$, we can calculate the intrinsic propagation rate constant profile. Figure IV.12 shows k_p as a function of the oxirane ring conversion in the photopolymerizable sample. The curves exhibit a similar characteristic shape as the curves for $k_p[M^+]$ of Figure IV.11 although the plateau value of the rate coefficient is higher, owing to the small numerical value of the active center concentration. The similarity in the shapes indicates that the effects observed in $k_p[M^+]$ are relatively more dependent upon k_p, rather than $[M^+]$.

The initial large rapid increase in the propagation rate coefficient can be explained in terms of diffusional mobility effects. Initially, the propagation reaction caused by the cationic active centers is slow because of the close proximity of the negatively charged counterions. As polymerization proceeds, it leads to rapid increase in the local viscosity of the reaction system. On account of their larger size compared to the cationic active centers, the negatively charged counterions are unable to diffuse rapidly and thus are unable to keep up with the considerable mobility of the cations attained through propagation by reaction with the monomeric molecules. This 'reaction diffusion' mobility has been mentioned in the literature,[11,13,20] and can be a very probable contributing factor in crosslinking polymerizations. The large hexafluoroantimonate counterions are thus separated from the carbocations because of their limited diffusivity. Since separated ions are much more reactive compared to ion pairs,[6,7] this leads to a large increase in the propagation rate coefficient.

The steady and comparatively slower decrease in the rate coefficient after it reaches the maximum (Figures IV.11 and IV.12) can be explained in terms of trapping of active centers in the crosslinked polymer formed. This is the reason that a limiting conversion is observed for the cationic photopolymerizations for epoxides and vinyl ethers.[13] As previously mentioned, this analysis is based upon the assumption that one carbocationic active center is produced for each anthracene molecule consumed, and that all reactive centers thus generated are equally and fully capable of propagating the polymerization reaction.[21]

For calculation of activation energy of the propagation reaction, we need the kinetic constant unhindered by the diffusion parameters. An average initial reaction rate was determined for each temperature by measuring the time required to reach 20 % conversion of the monomer. A low value of the conversion was chosen because the constants will represent the kinetic parameters in case of excess monomer. At higher conversions, the reaction kinetics might be dictated by the availability of the monomer in the vicinity of the initiator. Using the relationships presented in Eq. IV.9 through Eq. IV.13, the apparent propagation rate coefficient was calculated at different temperatures. An Arrhenius fit of the intrinsic propagation rate coefficients at the specified conversion provides us with the activation energy for the propagation step (E_p = 4.3 kJ/mol).

As the complexity of the chemical structure of an organic compound increases, its viscosity becomes a more acute function of the temperature. The effect of temperature on viscosity of liquids can be estimated by the Guzman-Andrade equation.[22]

$$\mu = Ae^{B/T} \qquad \text{Eq. IV.16}$$

As Figure IV.13 shows, the viscosity of the epoxidized soybean oil is higher than that of soybean oil and is a stronger function of temperature. It follows an exponential curve and in the range of temperatures used for calorimetric experiments, it decreases from 160 cP to below 30 cP. Figure IV.14 shows the close agreement of the ESO viscosity to that predicted by the Andrade equation. As the temperature is increased, the intrinsic viscosity of the system decreases. We know that the diffusivity is an inverse function of the viscosity and hence the propagation proceeds relatively rapidly at higher temperatures. Because of this accelerated reaction, higher local conversions are reached, hence causing local increases in viscosity. These increases cause microscopic gelation and entrapment of the cationic active centers. On the other hand, polymerizations conducted at lower temperatures proceed at a much slower pace, causing the viscosity to increase more uniformly across the whole system. The gelation can hence be called more "macroscopic" in nature. For this reason, we see the increase in the propagation rate coefficient continue for longer times at lower temperatures. If our supposition of gelation effects is true, we should be able to see a definite cross-over for the intrinsic propagation constants for the various temperatures at a definite percentage conversion. From Figure IV.12, this appears to be around 23% conversion of the epoxide moieties. The theory of a diffusion controlled reaction is also corroborated in the low value calculated for the activation energy.

IV.4. Conclusions

In this contribution, Differential Scanning Photocalorimetry (DSP) has been used to study the photopolymerization kinetics of epoxidized soybean oil (ESO). The DSP technique offers a direct method for evaluating the heat generated during a polymerization reaction. The reaction exotherms were used to characterize the polymerization kinetics and evaluate the kinetic constants. The DSP experiments were challenging to design because of the rapid polymerization rates coupled with the highly exothermic nature of the reaction. Using small sample sizes and low light intensities, we could increase the reaction time so that the kinetic parameters could be easily characterized.

Isothermal DSP experiments were conducted for a series of unsteady state ESO polymerizations at different temperatures and incident light intensities. The initiation system used was a diaryliodonium hexafluoroantimonate salt photoinitiator photosensitized by anthracene. This system has been studied by several investigators and the photosensitization mechanism and kinetics are well characterized. Using the sensitization rate constants from these, the kinetic constants for the propagation of the ring-opening polymerization of ESO were obtained. As expected, an increase in the initiating light intensity resulted in an increase in the reaction rates. However, the final conversion obtained remained almost constant. The effect of temperature on the polymerization was much more complicated. An increase in the isothermal reaction temperature led to an increase in the rate of propagation but a decrease in the final conversion obtained. This can be explained as an effect of the lack of mobility of the cationic active centers at higher conversions of the epoxide group. With polymerizations proceeding at lower temperatures, the initial viscosity of the system is high and the reaction progresses at a moderate pace such that the local viscosity rises slowly until solidification (gelation) of the system. At this point, the polymerization rates are drastically reduced. At higher temperatures, the reaction starts to occur very rapidly because of the low initial viscosity of the monomer. The rapid polymerization causes an enormous increase in the local viscosity of the system, severely restricting the movement of the cationic sites. The oxonium ions are hence "trapped" thus causing a lower limiting conversion.

To determine the termination rate constant k_t, dark cure experiments were conducted using the DSC. The decay profile of the exotherm from the point at which the initiating light source was removed, seemed to be very similar for a polymerizing and a non-polymerizing sample. This led us to believe that the cationic active centers possess very long lifetimes and relatively small termination rate constants compared to their free radical counterparts. This can be attributed to the fact that the cationic active centers do not terminate by combination with other cations. Moreover, the polymerizing system is free of moisture and solvent thus leading to a decrease in chain transfer.

From the DSP reaction profiles, an apparent propagation rate constant k_p was calculated. As the reaction temperature was increased, a higher value of k_p was observed. The apparent propagation rate constant for an isothermal photopolymerization reaction underwent a rapid initial increase, leveled to a plateau and then underwent a gradual decrease. This implied that the propagation rate constant changed drastically as the reaction proceeded. The initial large increase can be explained to be due to changes in the reactivity of the cationic species due to the proximity of the counterion. During the polymerization, the large hexafluoroantimonate counterion of the initiator experiences a rapid decrease in mobility as the viscosity increases. Meanwhile, the active carbocation retains its diffusional mobility by reacting with neighboring oxirane rings, thus leading to separation of the two species. This increases the reactivity of the cationic active center. The final decrease in k_p is due to trapping of the active centers in the rapidly formed crosslinked polymer network. Therefore, a limiting conversion is observed in spite of the presence of "live" cationic species.

The profiles obtained for the propagation rate constant have provided valuable insight into the nature of crosslinking photopolymerizations. Understanding these kinetic aspects is important because of the rapidly increasing number of applications for rapid, solvent free curing polymerizations. Conventional methods of polymerization have been discounted for production of polymeric materials from agricultural feedstocks. This research on cationic photopolymerization of epoxidized oils has provided proof that useful polymers can be obtained from renewable natural resources by a process amenable to rapid, mass production.

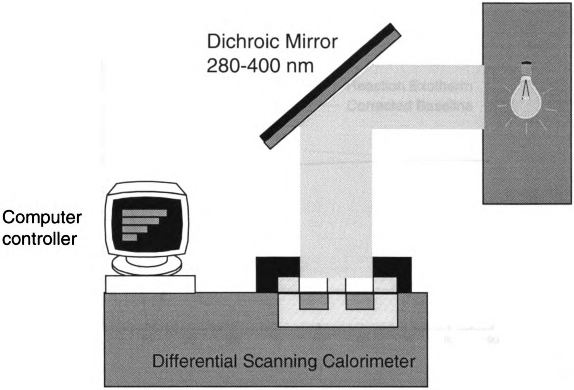

Figure IV.1 Experimental setup for Differential Scanning Photocalorimetry Studies.

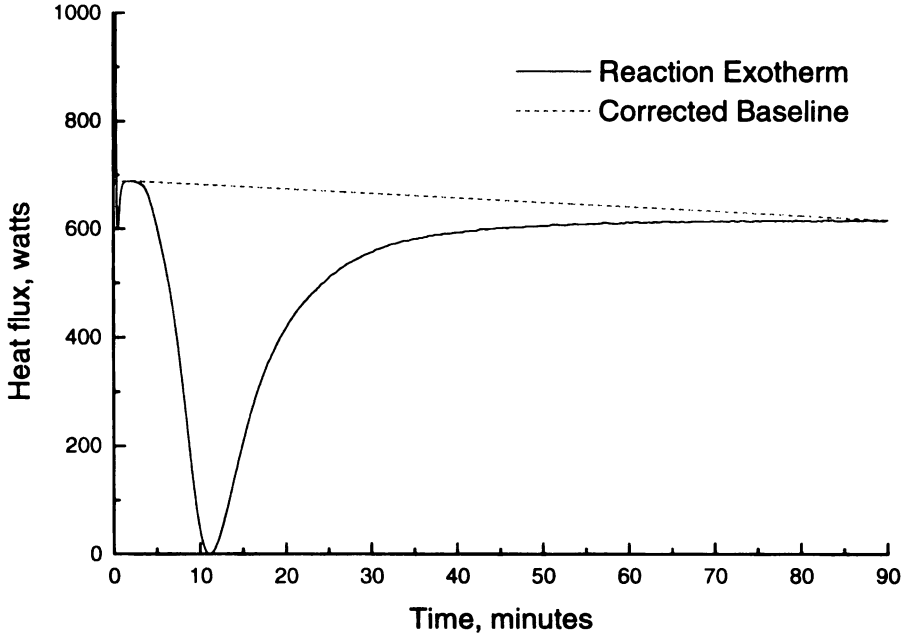

Figure IV.2. Typical Exotherm Obtained During Polymerization of Epoxidized Soybean Oil (ESO).

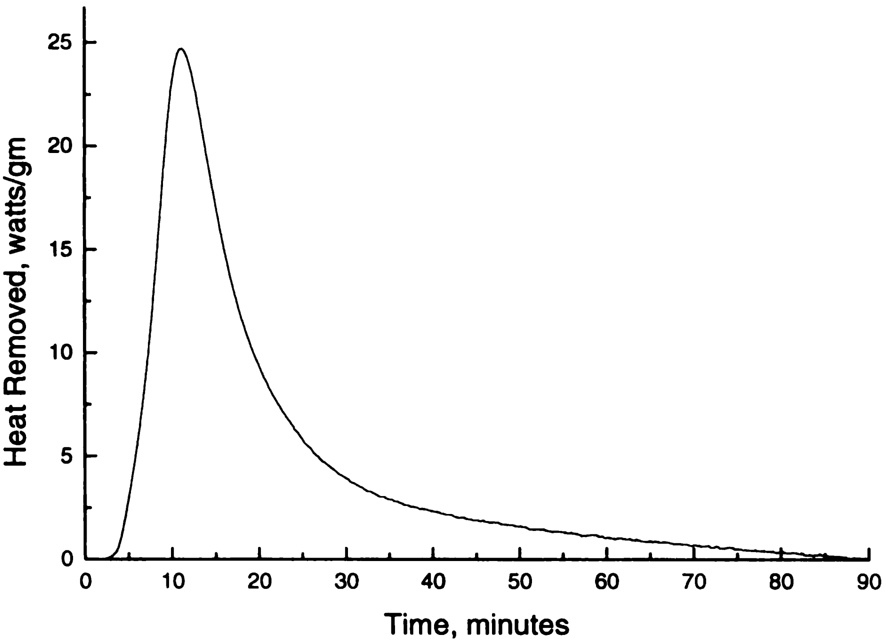

Figure IV.3. Corrected exotherm obtained from the DSC after subtracting the baseline.

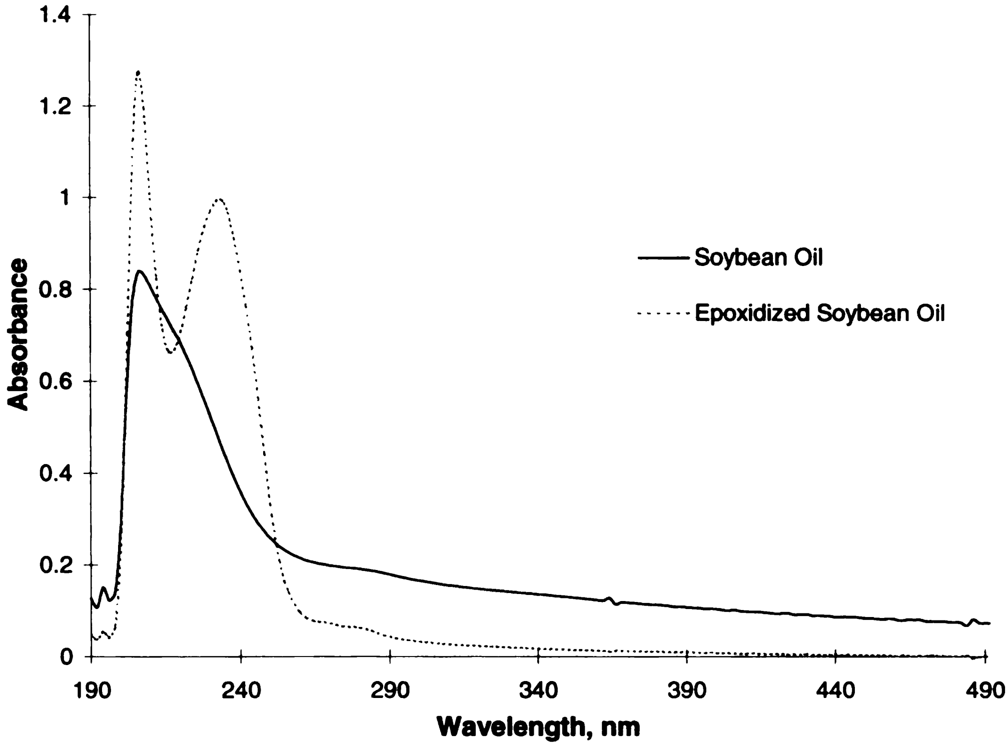

Figure IV.4. Effect of epoxidation on the UV and visible absorbance of soybean oil.

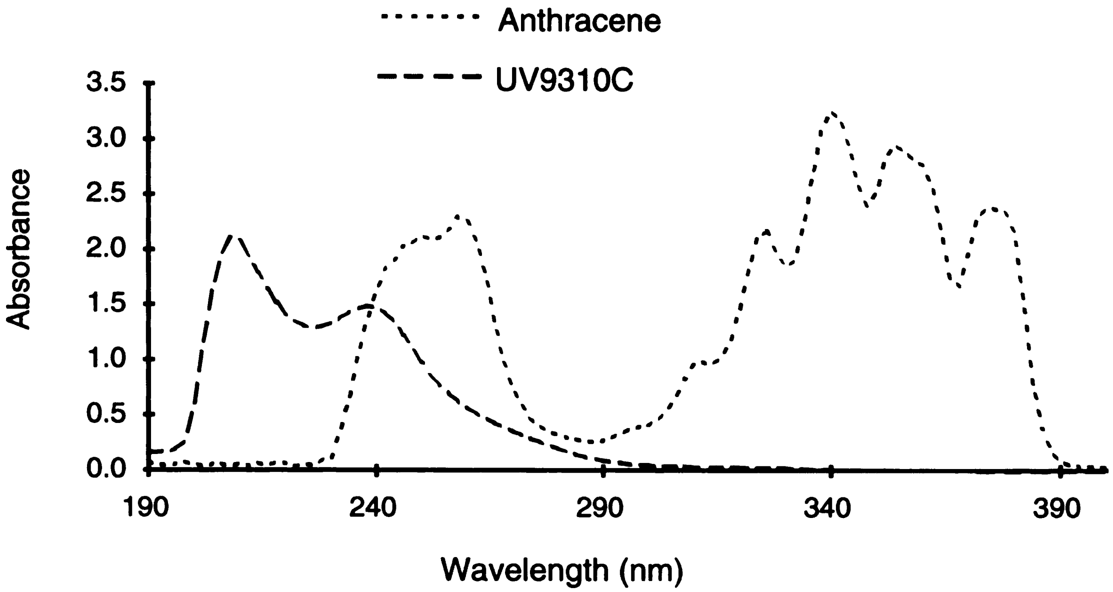

Figure IV.5. Spectral absorbance of diaryliodonium initiator and anthracene photo-sensitizer as a function of wavelength.

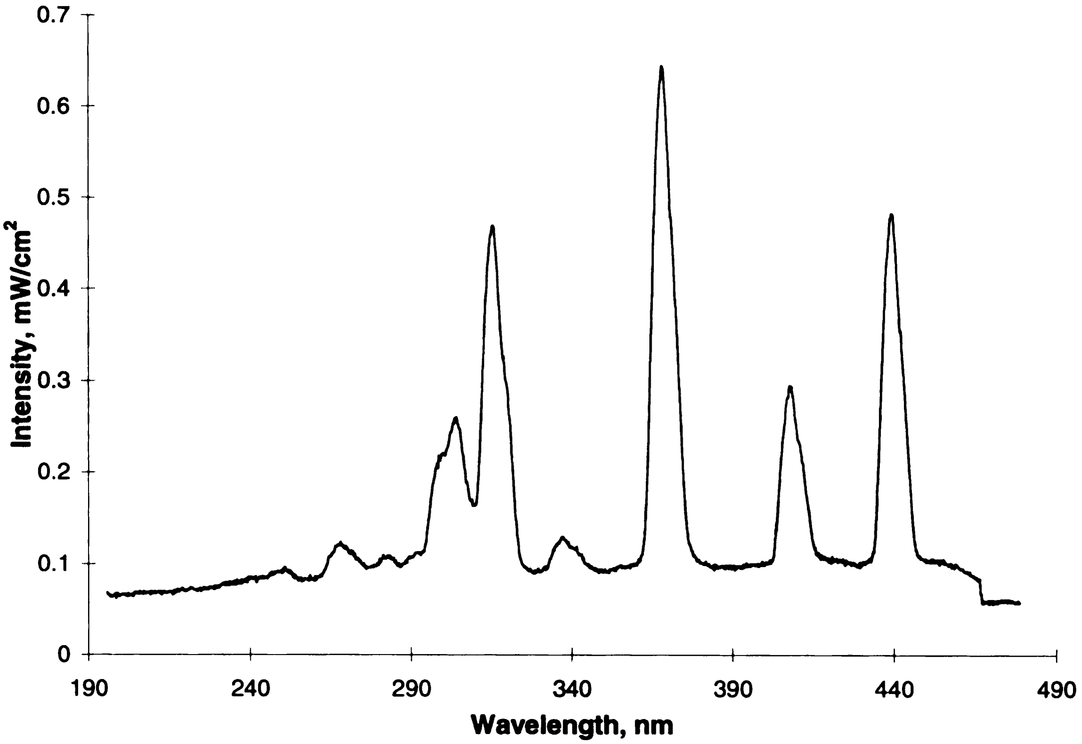

Figure IV.6. Emission scan from the Hg(Xe) lamp source used for DSP experiments.

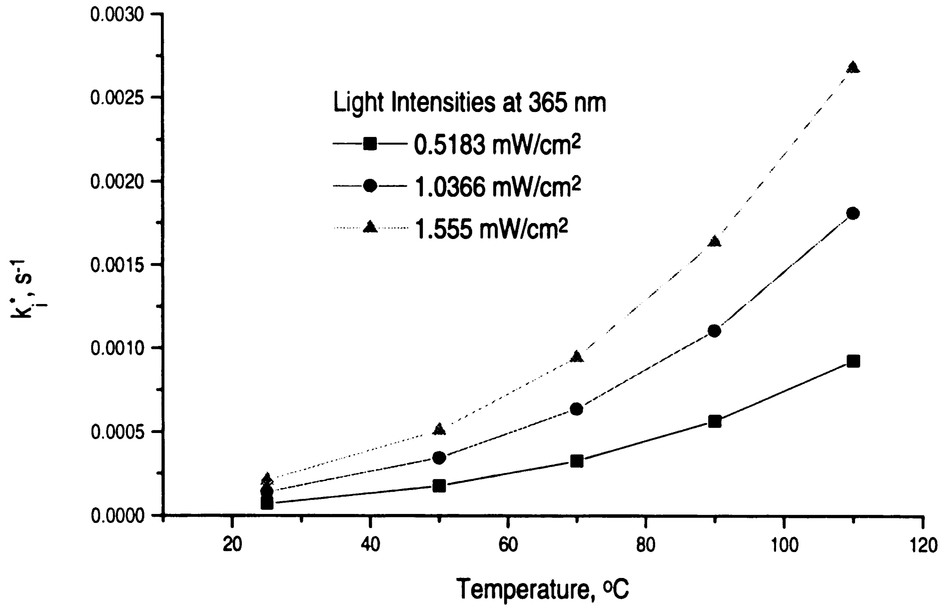

Figure IV.7. Initiation rate constant as a function of temperature at different UV light intensities.

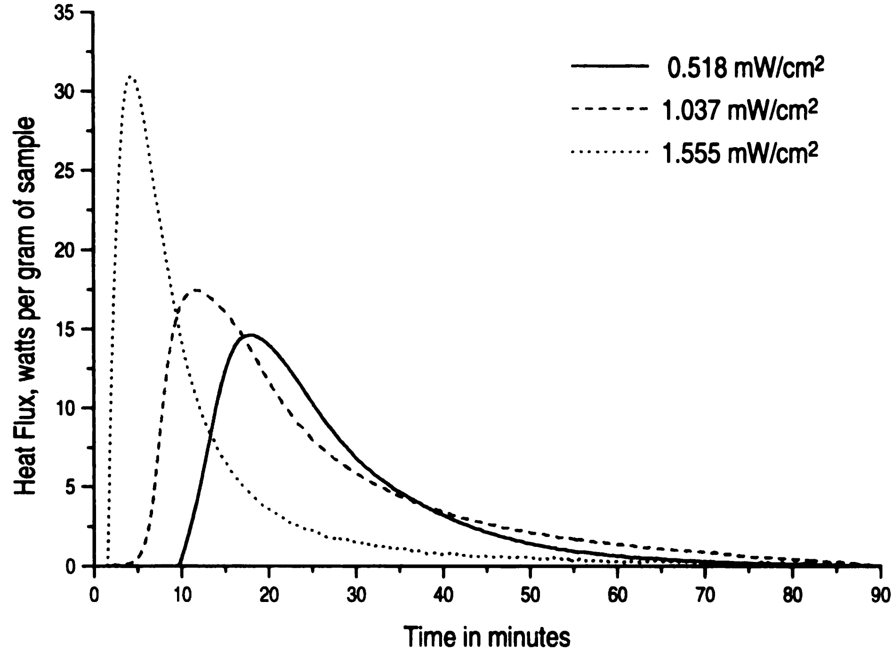

Figure IV.8. DSP exotherms for the cationic photopolymerization of ESO at different incident light intensities.

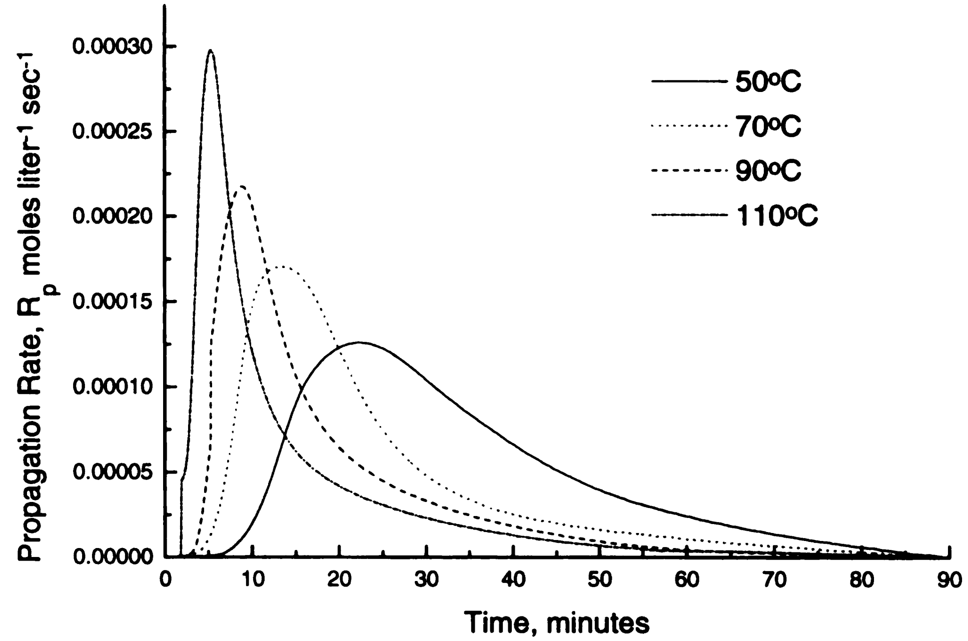

Figure IV.9 Overall rate of propagation versus time for ESO polymerization with 1% diaryliodonium hexafluoroantimonate photosensitized by 0.01% anthracene.

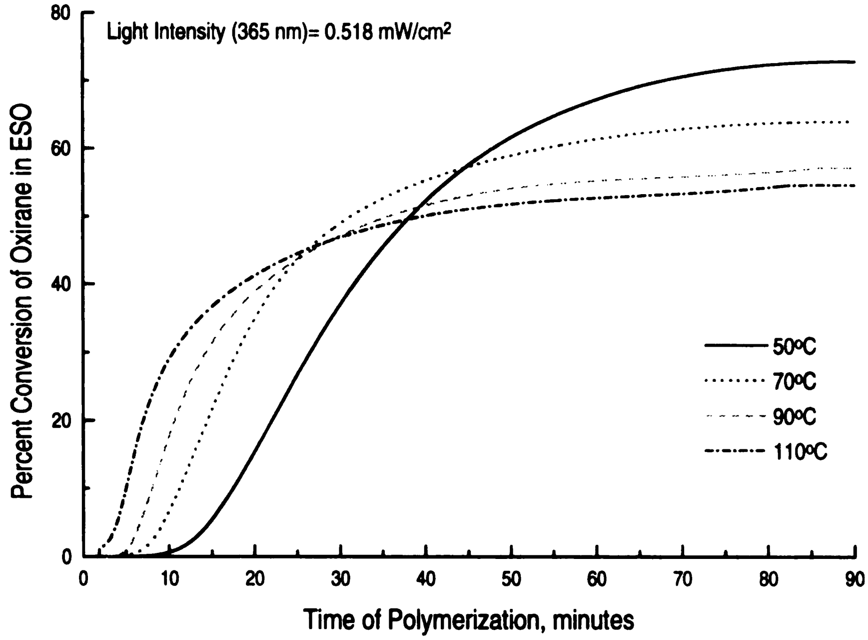

Figure IV.10. Conversion profile of epoxy moieties in ESO during photopolymerization at various temperatures.

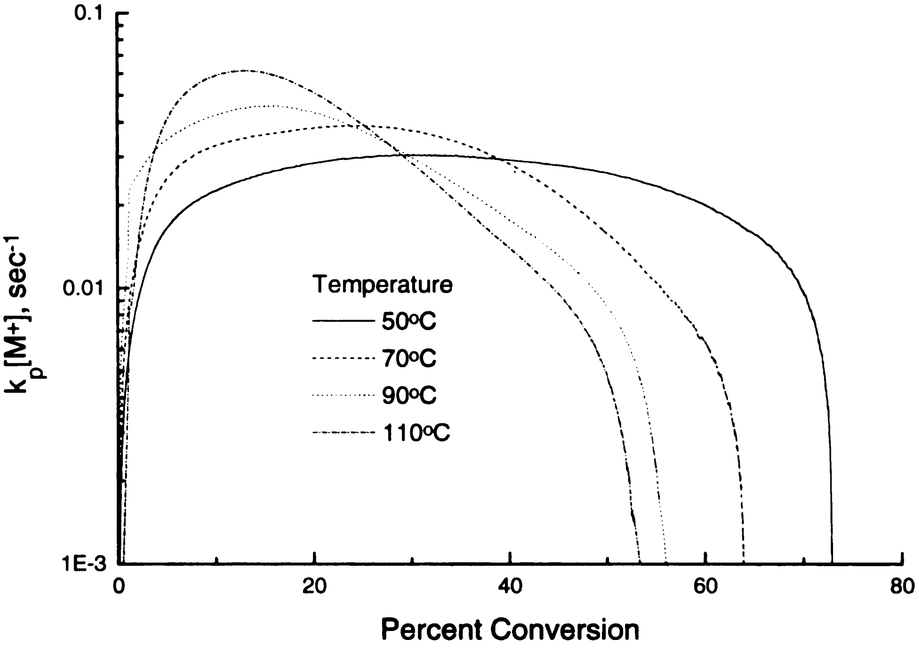

Figure IV.11. $k_p[M^+]$ as a function of conversion for ESO photopolymerization at various temperatures.

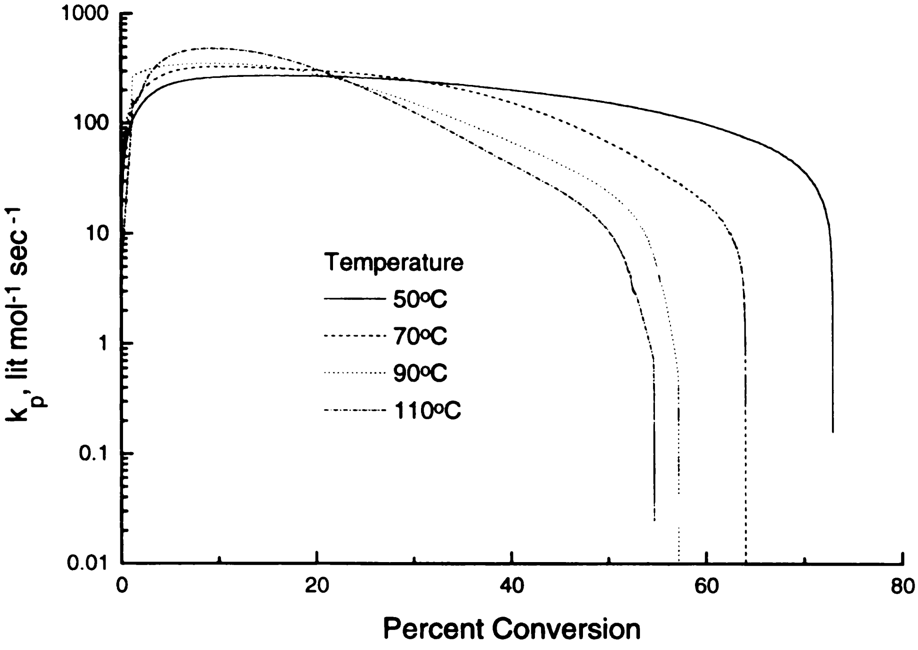

Figure IV.12. Apparant propagation rate constant k_p as a function of conversion for ESO photopolymerization at various temperatures.

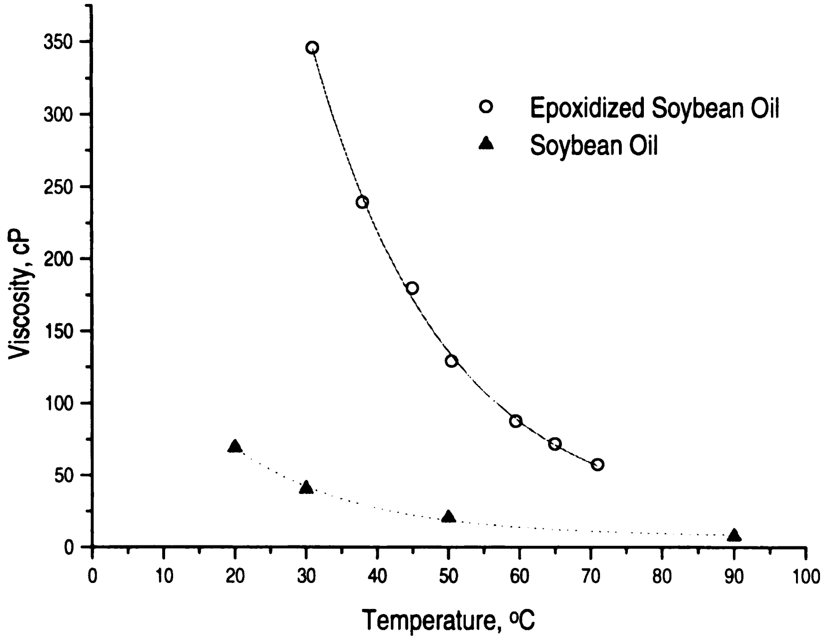

Figure IV.13. Viscosity of epoxidized soybean oil as a function of temperature.

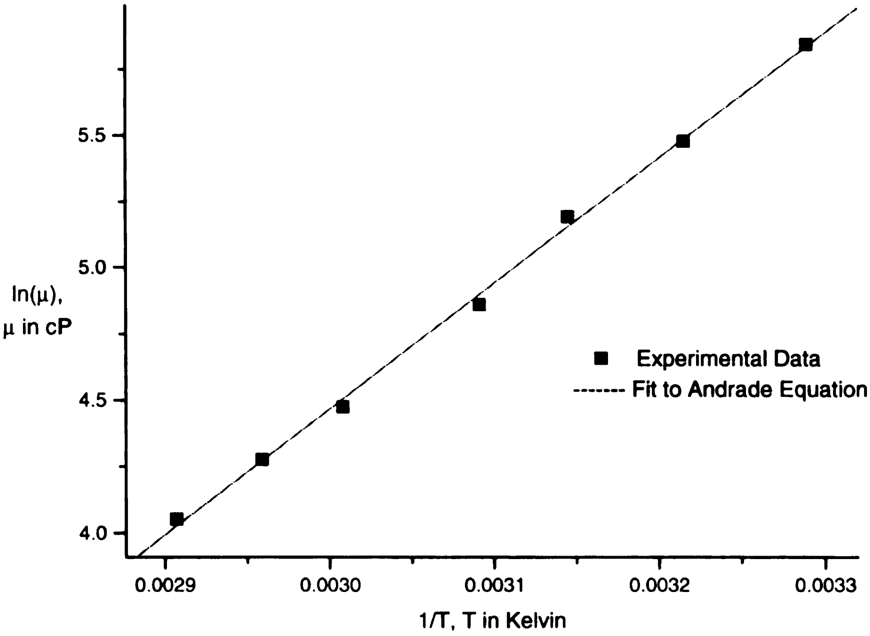

Figure IV.14. Viscosity of epoxidized soybean oil as a function of inverse absolute temperature.

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CHAPTER V.

THE EFFECT OF VISCOSITY ON THE RATE OF PHOTOSENSITIZATION OF DIARYLIODONIUM SALTS BY ANTHRACENE

Abstract

An attempt has been made to characterize the effect of viscosity on the reaction rate of photosensitization of diaryliodonium salts by anthracene. A well-established theory for diffusion controlled reactions has been used to qualitatively explain the effect, and a comparison of the predicted behavior with experimental data has been presented. Upon addition of an adjustable parameter, the model has been shown to reasonably accurately describe the photosensitization rate at any viscosity. In conjunction with the knowledge of the activation energy of the reaction, the model can be used to predict the photosensitization rate at any given combination of temperature and viscosity.

V.1. Introduction

The utilization of light to induce polymerization reactions results in more than a few advantages. In addition to attaining rapid reaction rates, it also helps in exercising superior spatial and temporal control over the reaction. Photopolymerizations require an order of magnitude less energy than conventional thermal means of polymerization.[1]

Since the process precludes the need for solvents, it leads to a decrease in the emission of volatile organic chemicals, thus rendering the process environmentally benign.

Cationic photopolymerizations of epoxides and vinyl ethers offer tremendous potential in high-speed, solvent-free curing of films and coatings. The polymers formed exhibit excellent clarity, adhesion, abrasion and chemical resistance.[2-4] In addition, UV-initiated cationic polymerizations offer several processing advantages. These reactions are not inhibited by oxygen and can be carried out without an inert atmosphere. In addition, cationic species do not terminate by combination with each other, as do free radicals. The cations generated are able to diffuse much faster than the large, negatively charged counterions. Because of these reasons, cationic polymerizations proceed long after the irradiation has ceased and may penetrate areas where the light does not reach.[5,6] Finally, several vinyl ether monomers are available, which exhibit low vapor pressures, low viscosities and low toxicity, but polymerize rapidly to form films exhibiting excellent properties.[7-14] The excellent polymer properties and processibility have resulted in a surge in research devoted to characterizing the mechanism and kinetics of these reactions, as well as the physical properties of the polymeric films obtained. Because of the advantages listed above, photoinduced polymerizations are being increasingly utilized in making a large variety of products such as coatings for various substrates, inks, photoresists used in semiconductor applications and also recently, fiber-reinforced composites.[15,16]

Interest in UV-initiated cationic photopolymerizations was fueled by the development of two classes of thermally stable photoinitiators. Diaryliodonium and triarylsulfonium salts have been used in the last decade to rapidly photoinitiate polymerizations in solvent free systems like epoxides and vinyl ethers.[3,17] While these salts are most efficiently initiated by deep-UV (225-275 nm), their applicability is severely challenged by the fact that most monomers also absorb in the same region of the ultraviolet spectrum and may compete for the incident radiation. The absorbance range of these initiators may be expanded by combined use with photosensitizers or co-initiators such as anthracene and perylene which shift the effective spectral window to well above 300 nm, the region where most industrial medium and high pressure mercury lamps have strong emission bands. The absorbance of a typical diaryliodonium photoinitiator and anthracene as a function of wavelength is shown in Figure V.1. Also, if the products of photosensitization do not absorb in the same region as the photosensitizer, this fact can be used to produce thick polymer products.[18] Understanding the mechanism of photosensitization is critical to the optimal use of photopolymerization techniques to produce adhesive coatings as well as thick polymer composite parts.

Photosensitization reactions are very rapid, with the life times of the excited singlet and triplet states of anthracene being on the order of nanoseconds and microseconds, respectively.[17] As a result, reactions involving these species, like several other chemical reactions, are limited by the rate of diffusion of reactants and/or products. The time taken for any species to diffuse is directly proportional to the square of the distance to be traveled. On a molecular scale, these distances are normally on the order of a few nanometers and as a result, only very rapid reactions tend to be affected by diffusion. It is our hypothesis that the photosensitization reactions are diffusion limited and factors such as viscosity play an important role in determining the rate of reaction.

Smoluchowski theory[19] explains the behavior of rapid chemical reactions which are hindered by diffusion. This theory assumes that equally sized, spherical, reacting molecules diffuse by a simple random walk. When combined with Stokes law and the Einstein diffusion equation, it results in the Smoluchowski-Stokes-Einstein (SSE) equation which states that the rate constant of a diffusion controlled reaction is inversely proportional to the solution viscosity.

In this contribution, we have studied the effects of viscosity on the rate of the photosensitization reaction. Using steady state fluorescence spectroscopy, we have monitored the rate of reaction between anthracene (photosensitizer) and diaryliodonium hexafluoroantimonate salt (photoinitiator), in propanol/glycerol solutions of different viscosities. The results have been analyzed by numerical solutions of the photophysical kinetic equations in conjunction with the mathematical relationships provided by the Smoluchowski theory. The applicability of a modified Smoluchowski theory by the addition of an adjustable parameter has also been investigated.

V.2. Experimental

V.2.1. Materials.

The 1-propanol, glycerol, and anthracene were obtained from Aldrich Chemical Company and were used as received. The initiator (UV9310C; GE Silicones) had a composition of 5-10 wt % linear alkylate dodecylbenzene, ~50 wt % 2-ethyl-1,3-hexanediol, and ~50 wt % bis (4-dodecylphenyl) iodonium hexafluoroantimonate. The chemical structure of the photoinitiator and photosensitizer are presented in Figure V.2.

In this initiator, various dodecyl isomers have been attached to the phenyl rings of the diphenyliodonium salt to impart solubility in the monomer and do not have any effect on the reactivity of the initiator.[1] The hexanediol has been added to hinder the formation of cyclic polymers.

V.2.2. Fluorescence Measurements.

The fluorescence experiments to measure the effect of system viscosity on the sensitization rate were performed in the LASER Laboratory at Michigan State University. A schematic diagram of the experimental setup is shown in Figure V.3. The excitation source used was a Coherent Innova 200 Argon ion laser operating at 363.8 nm. The same light source serves to excite the anthracene to cause the photosensitization as well as help us to study the fluorescence caused by its excitation to the singlet state. To ensure the simultaneous start of illumination and fluorescence data acquisition, a Newport 845HP01 digital shutter system was opened with an electronic pulse from the detector controller. Unfocused laser radiation of 15 milliwatts in a beam of about 3 mm diameter was directed upon the quartz capillary tube (1 mm i.d., 2 mm o.d., 25 mm long) placed perpendicular to the beam direction. A Scientech 362 power/energy meter was used to measure the illumination. The fluorescence was collected at a right angle from the incident beam and right angle from the longitudinal axis of the capillary tube. A Spex 1877 Triplemate spectrometer was used to analyze the fluorescence signal. The spectrometer had two stages - a subtractive dispersion filter stage and a spectrograph stage. A diffraction grating of 150 gratings per inch was employed. A gated EG&G Princeton Applied Research Model 1530 C/CUV CCD, cooled with liquid nitrogen to -

120°C to minimize dark charge levels, was used to detect the signal, and was interfaced with an EG & G Princeton Applied Research Model 1463 OMA 4000 detector controller. The OMA 4000 software was used to analyze the fluorescence data.

All steady state fluorescence experiments were conducted with the sample placed in a thermo-statted cell with temperature maintained at 30°C. The concentrations of anthracene and initiator used were 0.000505 and 0.00608 moles per liter respectively. The relative quantities of solvents (n-propanol and glycerol) were adjusted to achieve solutions of different viscosities, while maintaining the same molar concentration of the reactive solutes.

V.3. Results and Discussion

V.3.1. Steady State Fluorescence Measurements

Figure V.4 is a time overlay chart and shows the decay in the fluorescence spectrum of anthracene in a representative sample. Since the photosensitization reaction results in the consumption of anthracene, monitoring the fluorescence decay of anthracene provides a convenient method for measuring the rate of reaction. The initial increase in the fluorescence can be attributed to an instrument artifact and is not a consequence of the reaction mechanism. The intensifier in the detector operates in a fashion similar to a photomultiplier tube. When a photon strikes the intensifier surface, a number of photons are generated. This process requires incident light to initiate and takes a finite length of time to reach its full value of enhancement after multiple reflections of the photons. This artifact does not affect our technique of data analysis and the important kinetic information can still be deduced.

During the reaction, as the anthracene reacts to form free radicals and radical cations,[20] a majority of it degrades to dihydroanthracene. This product does not possess appreciable absorbance in the region between 300 and 400 nm. As time proceeds, the slight shift in the fluorescence peak is due to partial degradation of the anthracene to 9,10 divinyl anthracene and 9,10 diphenyl anthracene. By monitoring the steady state anthracene fluorescence peak at 425 nm with reaction time, we can obtain a measure of the concentration changes of anthracene in the sample. After fitting the fluorescence profile to a mathematical model, normalizing the fluorescence intensity with respect to the initial molar concentration of anthracene in the sample allows us to obtain the anthracene concentration as a function of time (Figure V.5). Although the photosensitization reaction is a second order reaction, the concentration profile of anthracene closely follows an exponential decay which is typical of a first order reaction. This is due to the fact that the initiator concentration exceeds that of the photosensitizer by more than a factor of ten, resulting in a pseudo-first order reaction. This steady state fluorescence experiment can be repeated for photosensitizer and initiator solutions of various viscosities and the concentration profile obtained can be used to arrive at a decay rate coefficient for anthracene at different viscosities.

The effect of viscosity on the rate of reaction is shown in Figure V.6, where it can be seen that the rate coefficient decreases as the viscosity of the system is increased. As we move from a solution of the reactants in pure propanol to a solution in pure glycerol, the viscosity of the system rises by three orders of magnitude. Steady state fluorescence experiments of these solutions show that the reaction rate coefficient decreases as we increase the viscosity. This is commonly observed in diffusion-controlled reactions, and therefore we propose to use Smoluchowski theory for diffusion-limited reactions to understand and explain this behavior.

V.3.2. Analysis of the Photosensitization Mechanism

The photosensitization reaction is the sum of many individual reactions between various reaction species. The kinetics of the various photophysical reactions occurring during the process of photosensitization in an inert solvent have been described by Nelson et al.,[20] who have modeled the photoinitiation process as a set of nine reactions. These reactions, which are shown below, represent the electronic state transitions of anthracene (A) as well as reaction of excited state anthracene (S-singlet, T-triplet) with the initiator (I). The symbols Rs and Rt denote the reactive centers formed by reaction with the onium salt by the singlet and the triplet state anthracene respectively.

$$A + h\nu \xleftrightarrow{k_{abs}} S \qquad \text{Eq. V.1}$$

$$S \xrightarrow{k_{fluor}} A + h\nu \qquad \text{Eq. V.2}$$

$$S \xrightarrow{k_{isc}} T \qquad \text{Eq. V.3}$$

$$S \xrightarrow{k_{nonfluor}} A \qquad \text{Eq. V.4}$$

$$T \xrightarrow{k_{nonphos}} A \qquad \text{Eq. V.5}$$

$$S + A \xrightarrow{k_{\dim er}} 2A \qquad \text{Eq. V.6}$$

$$T \xrightarrow{k_{phos}} A + h\nu \qquad \text{Eq. V.7}$$

$$S + I \xrightarrow{k_{senfluor}} Rs \qquad \text{Eq. V.8}$$

$$T + I \xrightarrow{ksenphos} Rt \qquad \text{Eq. V.9}$$

This set of photochemical reactions can be well understood with the help of a energy level diagram for anthracene (Figure V.7). As shown in the figure, the ground state anthracene absorbs the incident light energy to reach the excited singlet state. The anthracene in the singlet state may take one of four reaction paths. It can revert back to the ground state with or without the simultaneous release of light energy in the form of fluorescence. It can transfer an electron to a neighboring onium salt molecule to generate a cationic active center. Alternately, it can undergo an intersystem crossing to form the triplet excited state. The anthracene in the triplet state can go back to the ground state with or without simultaneous release of phosphorescence. The triplet state is also capable of donating an electron to an initiator molecule to form a reactive cationic species. The reaction in which an excited singlet state anthracene interacts with a ground state anthracene (Eq. V.6) has not been shown in the energy level diagram. This reaction has very little bearing on the overall kinetics and can be neglected for all practical calculations.

V.3.3. Simulation of the Photosensitization Mechanism

To simulate and model the photosensitization of diaryliodonium hexafluoroantimonate by anthracene, the kinetic parameters for the equations presented above were either obtained from the literature or independently established. Based upon the known values of the laser power and the beam cross sectional area, the photon flux onto the sample was calculated. Using the value of the photon flux and the extinction coefficient of anthracene at 365 nm, the value of k_{abs} was calculated to be 5.979 s^{-1} for our experiments. Using fluorescence lifetime experiments, the sum of the rate constants k_{fluor} and $k_{nonfluor}$ was determined by Nelson et al[17,20] to be equal to 1.38 x 10^8 s^{-1}. Similar experiments with phosphorescence lifetime experiments have shown the sum of k_{phos} and $k_{nonphos}$ to be 1.0 x 10^5 s^{-1}. By conducting fluorescence and phosphorescnce lifetime experiments in the presence of initiator, the values of $k_{senfluor}$ and $k_{senphos}$ have been obtained to be 8.20 x 10^7 lit mol^{-1} s^{-1} and 2.50 x 10^6 lit mol^{-1} s^{-1} respectively. The kinetic constant for intersystem crossing between the singlet and triplet states of anthracene in solution has been reported to be between 7.38 x 10^7 to 1.12 x 10^8.[21,22] An average of the reported values (0.929 x 10^8 s^{-1}) was utilized in our calculations. The reaction between the singlet and the ground state anthracene has a kinetic constant of 4.0 x 10^9 lit mol^{-1} s^{-1}. These kinetic parameters were used in conjunction with the mass balance and the resulting set of differential equations were solved simultaneously using the Rosenbrock Method for stiff systems.[23]

Figure V.8 contains the simulation results in the form of concentration profiles for the various chemical species in the reaction system. The anthracene concentration decreases exponentially with time, while the active centers generated from both the singlet and the triplet states of anthracene increase monotonically. The singlet and triplet state concentrations remain very low compared to those of the active centers generated from them. This can be attributed to their very short lifetimes. At the start of illumination, their concentrations increase with time, reach a maximum and then begin decreasing. The triplet state concentration is always 2-3 orders of magnitude greater than the singlet state. This fact, coupled with the fact that the lifetime of the triplet is higher than the singlet, proves that under the reaction conditions, the triplet is responsible for more than 90% of the photosensitization reaction.[17]

$$\frac{d[A]}{dt} = k_{abs}([^1A]-[A]) + (k_{fluor} + k_{nonrad})[^1A] + (k_{phos} + k_{nonrad})[^3A] \tag{Eq. V.10}$$

$$\frac{d[^1A]}{dt} = k_{abs}([A]-[^1A]) - (k_{fluor} + k_{nonrad})[^1A] - k_{isc}[^1A] - k_{senfluor}[^1A][I] \tag{Eq. V.11}$$

$$\frac{d[^3A]}{dt} = k_{isc}[^1A] - (k_{phos} + k_{nonrad})[^3A] - k_{senphos}[^3A][I] \tag{Eq. V.12}$$

$$\frac{d[I]}{dt} = -k_{senfluor}[^1A][I] - k_{senphos}[^3A][I] \tag{Eq. V.13}$$

$$\frac{d[Rs]}{dt} = k_{senfluor}[^1A][I] \tag{Eq. V.14}$$

$$\frac{d[Rt]}{dt} = k_{senphos}[^3A][I] \tag{Eq. V.15}$$

The values of the rate constants suggest that the photosensitization reactions are extremely rapid, and may be diffusion controlled. In a polymerizing system, as the reaction proceeds, the viscosity of the reaction system increases rapidly, thus drastically affecting the photosensitization reaction velocities. Although the increase in viscosity has no effect on the single order reactions in the scheme presented above, the bimolecular reaction rates will be adversely affected. The second order reactions of interest to us are those that lead to generation of active centers from the singlet and triplet states, i.e. Eq. V.8 and Eq. V.9. Equation V.6 is also a bimolecular reaction leading to reaction between the singlet and the ground state anthracene. To simulate the changes in the reaction coefficients, we need to use a theory which describes diffusion-limited reactions.

V.3.4. Diffusion Limited Reactions - The Smoluchowski Theory

A chemical reaction between two reactive solutes in an inert solvent can be pictured to proceed in two stages - the approach of the reactants from a large separation distance to a distance at which the chemical forces become dominant and the subsequent reaction while in this close configuration. This can be schematically described as:

$$A + B \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [AB] \xrightarrow{k_a} \text{Products}$$

Depending on the nature of interaction between A and B, the species [AB] can be described by different terms. If [AB] is at the saddle point of the potential energy surface between A and B, it can be described as an activated complex. When A and B are in contact, but little or no interaction takes place between them, then [AB] can be termed as a collision pair. Usually, the type of interaction is hard to decipher, but will most probably be between these two extremes. The separation distance between the chemical species may extend from essential contact to where they are separated by about one radius of the solvent molecule. The rate of reaction can be calculated as follows:

$$Rate = k_a[AB] = \frac{k_a k_d}{k_{-d}}[A][B] \qquad \text{Eq. 16}$$

Assuming a steady state reaction and that the complex [AB] is in very small concentration, the overall rate coefficient is $k_d k_a/(k_{-d}+k_a)$. When the reaction of the encounter pair to form products becomes rapid compared to the diffusive forward and backward processes, the rate of formation of products becomes more dependent on the rate at which the reactants can diffuse together to form the encounter pair.

Smoluchowski[19] suggested that the reactants A and B have to diffuse together until they are close enough to interact chemically. For statistical and mathematical simplicity, this theory assumes that A is the limiting reactant and B diffuses towards A to try and deplete it by reaction. Because A and B disappear upon reaction, there is a concentration gradient of B around A. From this concentration gradient of B about A, the flux and hence the current of B towards A can be calculated. The rate of reaction is simply the current of B diffusing towards A multiplied by the molar concentration of A.

A simple transport equation

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho = D\left[\frac{\partial^2 \rho}{\partial r^2} + \frac{2}{r}\frac{\partial \rho}{\partial r}\right] \qquad \text{Eq. V.17}$$

can be written for the diffusion of B, assuming a spherically symmetric distribution of B about A. The density distribution of species B around A can be given by:

$$\rho(r,t) = \frac{[B](r)}{[B]_0} \qquad \text{Eq. V.18}$$

The initial density distribution at time t=0, i.e. the initial condition can be written as:

$$\begin{aligned} \rho(r,0) &= 0 \qquad (r \le R) \qquad \text{Eq. V.19} \\ &= 1 \qquad (r > R) \end{aligned}$$

The boundary conditions during reaction suggested by Smoluchowski and co-workers are:

$$\rho(r \to \infty, t) = 1 \qquad t \ge 0 \qquad \text{Eq. V.20}$$

$$\rho(R,t) = 0 \qquad t \ge 0 \qquad \text{Eq. V.21}$$

To solve Eq. V.17 subject to the density distribution given by Eq. 18, the boundary conditions given by Eq. 20 and Eq. 21 and the random initial distribution represented by Eq. 19 is straightforward. Using Laplace transforms and few mathematical maneuvers, we can arrive at the expression for the rate coefficient:

$$k(t) = 4\pi R^2 D \left.\frac{\partial \rho}{\partial r}\right|_R = 4\pi RD\left[1 + \frac{R}{(\pi Dt)^{0.5}}\right] \qquad \text{Eq. V.22}$$

Typical values of R and D are 0.5 nm and 10^{-9} m^2s^{-1}, respectively. For these values and at times of the order of seconds, the first term in Eq. V.22 becomes relatively more important.

$$k(\infty) = 4\pi RD \qquad \text{Eq. V.23}$$

The Einstein equation for diffusion in non-reactive solvents is:

$$D = \frac{k_B T}{\zeta} \qquad \text{Eq. V.24}$$

where ζ is the friction coefficient, k_B is the Boltzmann constant and T is the absolute temperature. Stokes law shows that

$$\zeta = 6\pi\eta a \qquad \text{Eq. V.25}$$

where a is the radius of the diffusing particle and η is the viscosity of the solution. This equation may be off by as much as 50% since Stokes law is not exactly valid on a molecular scale, but the general trend should remain valid.

From the above equations, we see that the reaction rate coefficient is inversely proportional to the viscosity of the reaction system. Hence, according to Smoluchowski-Stokes-Einstein[19] theory, the reaction rate constants should correlate with the reciprocal viscosity. However, in the reaction mechanism described above, only bimolecular reactions will be diffusion controlled, and therefore affected by viscosity. We have therefore adjusted the kinetic constants k_{dimer}, $k_{senfluor}$ and $k_{senphos}$ to account for the increased viscosity.

$$k_{senfluor}\Big|_{\eta_2} = k_{senfluor}\Big|_{\eta_1} \frac{\eta_1}{\eta_2} \qquad \text{Eq. V.26}$$

$$k_{senphos}\Big|_{\eta_2} = k_{senphos}\Big|_{\eta_1} \frac{\eta_1}{\eta_2} \qquad \text{Eq. V.27}$$

The differential equations were then solved using these viscosity-adjusted constants. The results of the simulations are plotted in the form of anthracene decay profiles in Figure V.9. At low viscosities, the decay rate constant is very high and leads to rapid exponential decrease of anthracene concentration. At higher viscosities, the decay rate is much slower. The rate constants obtained from the slopes of these profiles are compared with experimental data in Figure V.10. It can be seen that while the simulations describe the trend seen in the experimental data, they are not quantitatively accurate. The differences are attributable to several reasons. First of all, the Smoluchowski analysis assumes that the reacting molecules are spherical and of approximately equal size. In reality, the anthracne molecule with its fused aromatic rings has a hard, planar structure whereas the initiator molecule having a linear chain of 20 carbon atoms and two phenyl rings has a long molecular structure.

By modifying the simplistic inverse behavior suggested by the Smoluchowski theory and inserting an adjustable parameter as the exponent for the viscosity term, we can better describe the trend seen in the experiment. Figure V.11 compares the experimental results with the simulation trend having the bimolecular rate constants varying as $\eta^{-0.55}$. This implies an almost inverse square root dependence of the kinetic constant on the viscosity.

V.4. Conclusions

The viscosity of the solvent has a significant effect on the overall rate of the reaction. As the viscosity of the solvent increases, the overall rate of the photosensitization reaction decreases, suggesting that these reactions are diffusion controlled. The decrease in the rate of reaction is qualitatively explained using the Smoluchowski-Stokes-Einstein equation and numerical solutions of the photophysical equations. Based on the studies presented here, we would expect a profound effect on the rate of initiation in a polymerizable mixture. As the reaction proceeds, the viscosity of the mixture increases due to polymerization, and this increase in viscosity will reduce the rate of initiation. It is therefore expected that the rate of initiation will become extremely low after a certain degree of polymerization, and that any further reaction will be almost exclusively from propagation of active centers.

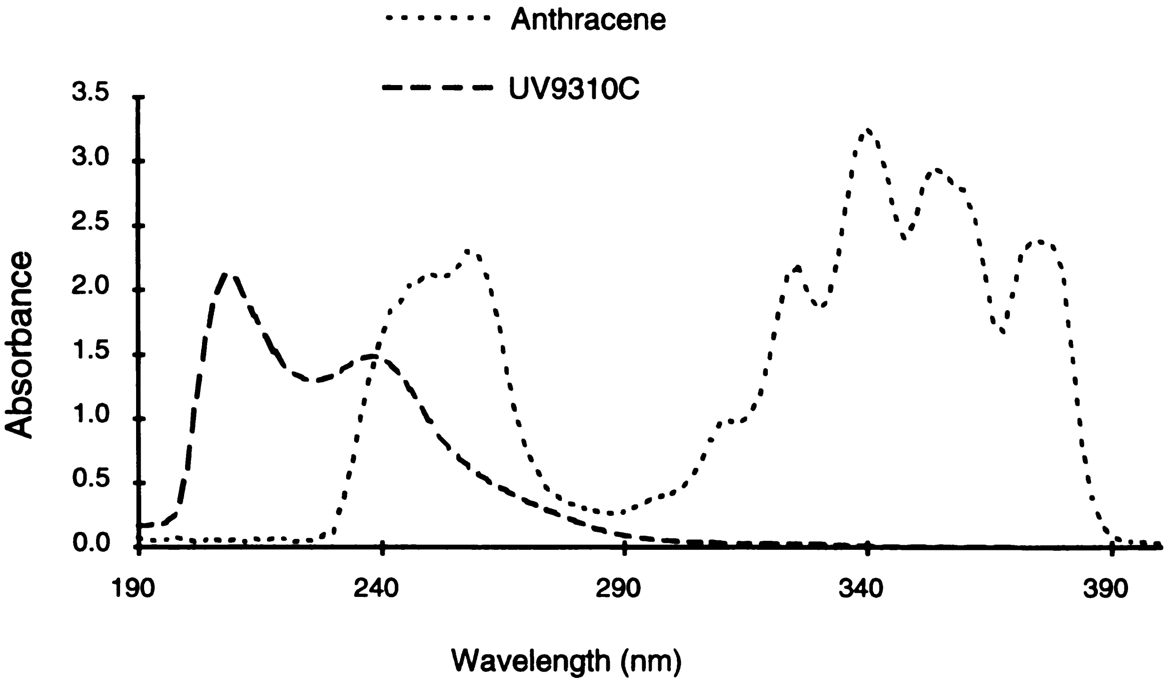

Figure V.1. Absorbance of the photoinitiator (UV9310C, GE Silicones) and the photosensitizer (anthracene) as a function of wavelength.

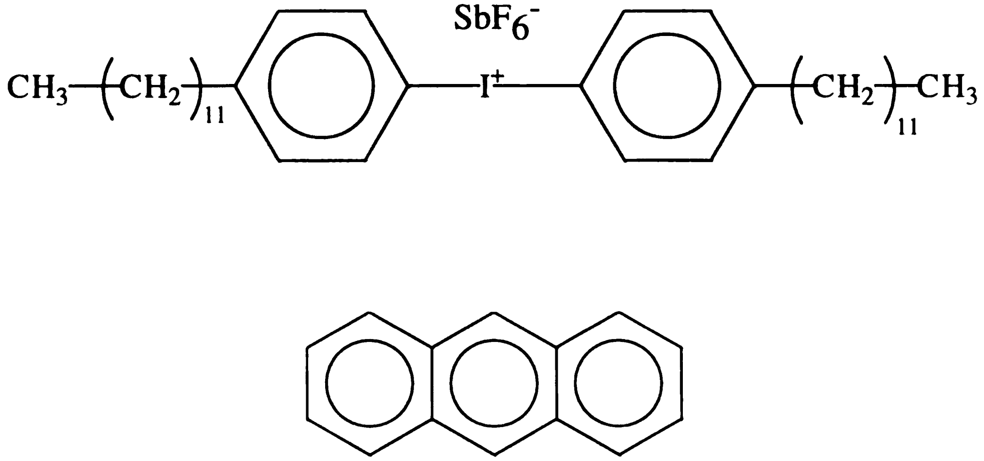

Figure V.2. Chemical Structure of the photoinitiator, bis (4-dodecylphenyl) iodonium hexafluoroantimonate and the photosensitizer, anthracene.

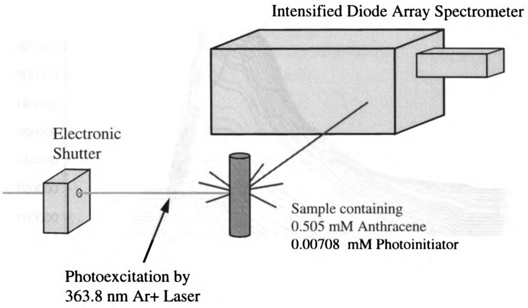

Figure V.3. Experimental setup for measuring the steady state fluorescence of anthracene during the photosensitization of a diaryliodonium hexafluoroantimonate salt.

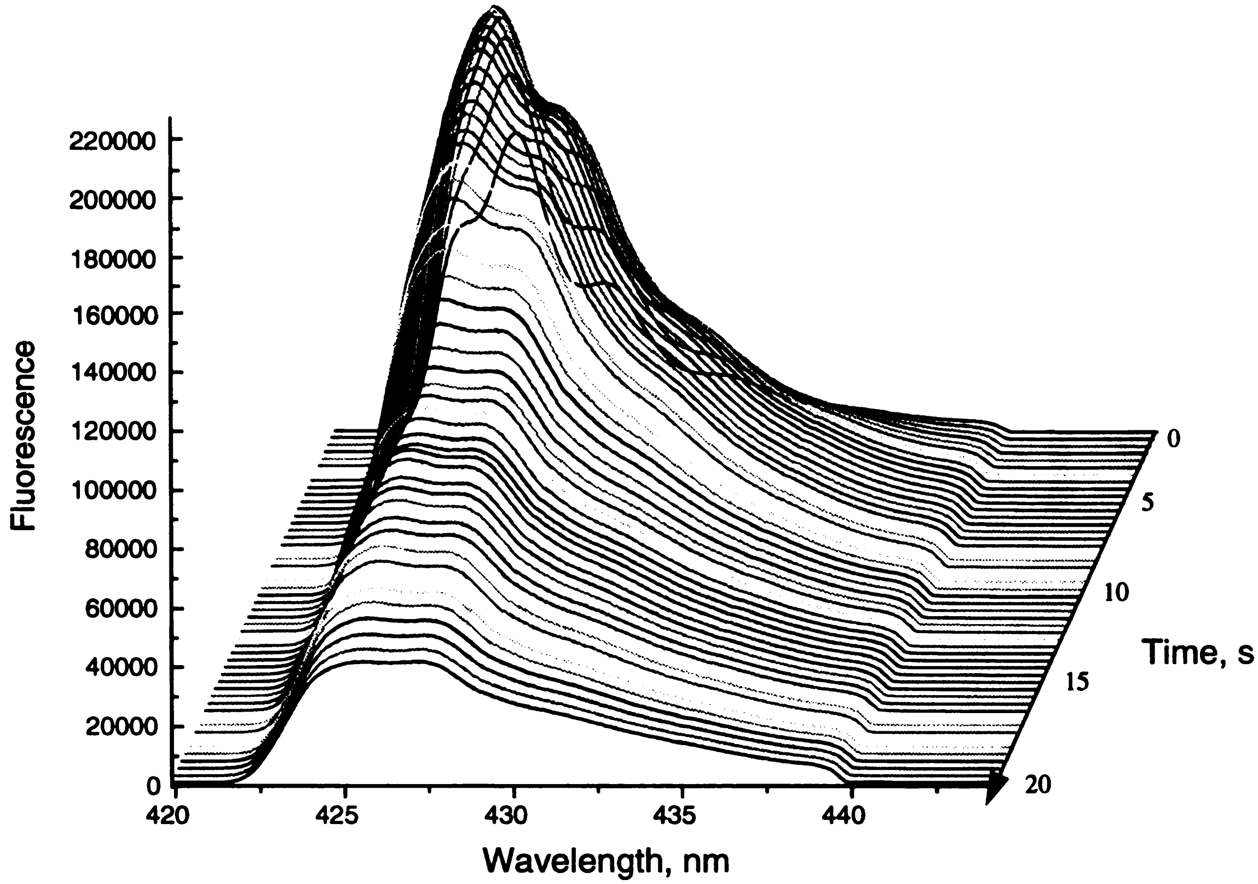

Figure V.4. Typical fluorescence profile of anthracene during the photosensitization of diaryliodonium salts by exciting at 363.8 nm.

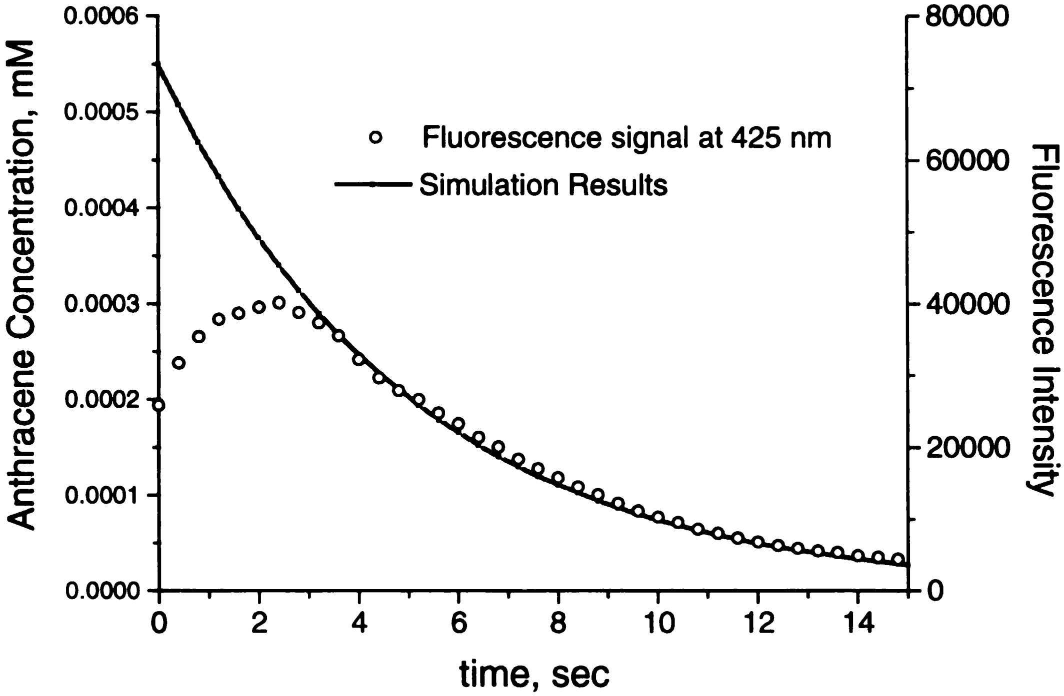

Figure V.5. Comparison of computer simulation and experimental photosensitizer fluorescence intensity for reaction of anthracene and diaryliodonium hexafluoroantimonate.

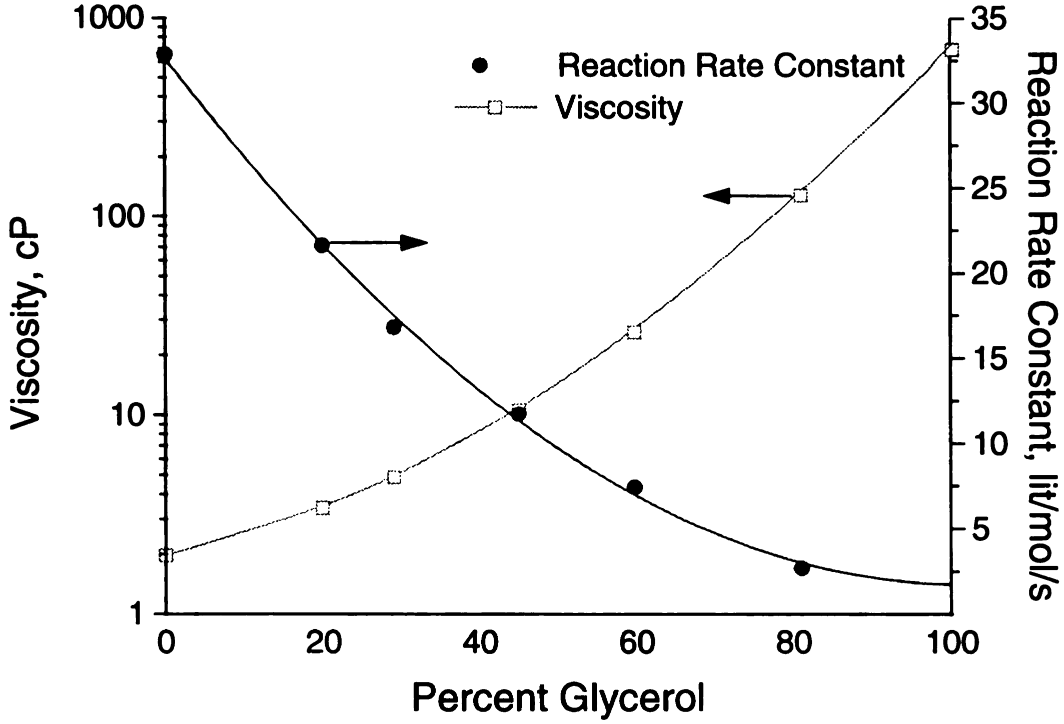

Figure V.6. The effect of glycerol content on solution viscosity and reaction rate constant.

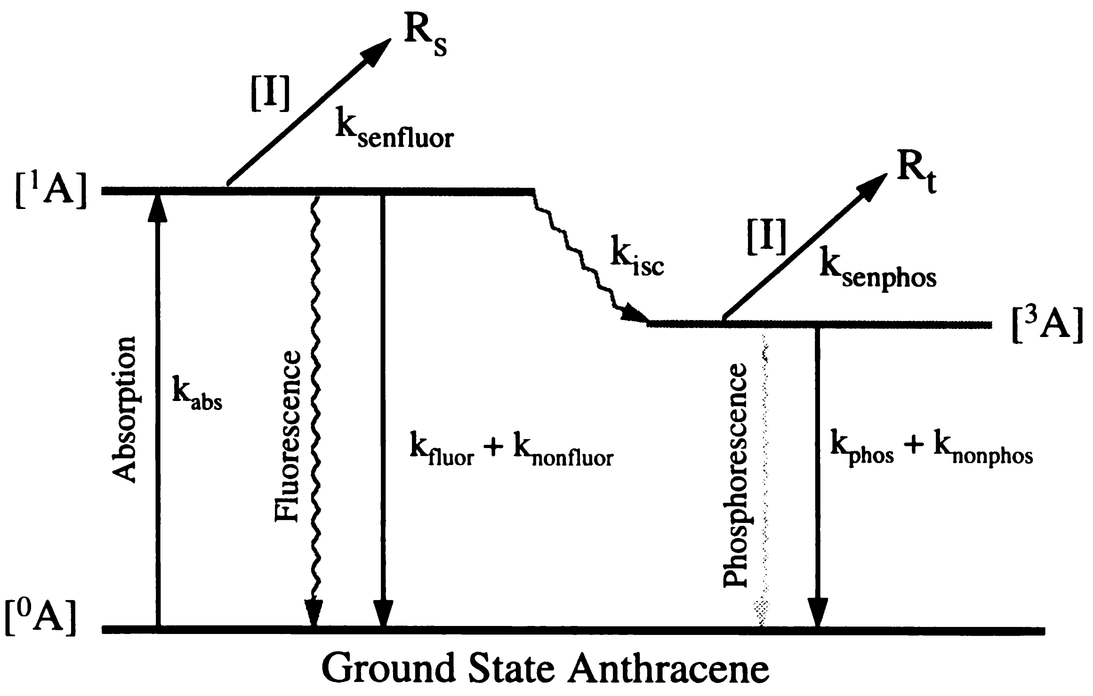

Figure V.7. Electronic energy level diagram for anthracene fluorescence and phosphorescence.

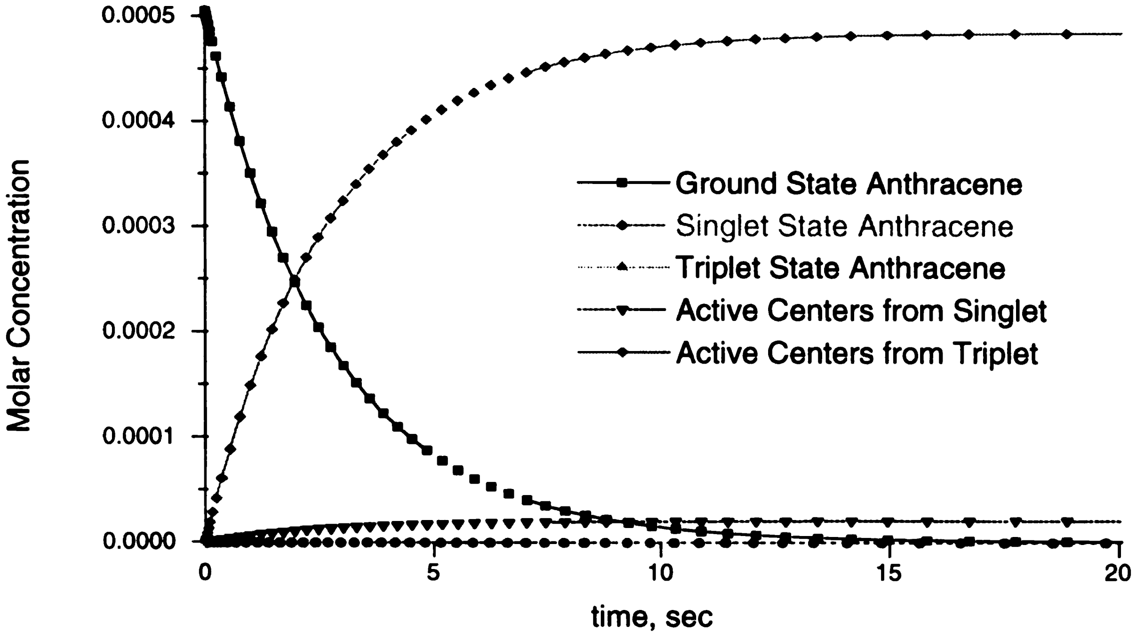

Figure V.8. Simulation results for the concentration profiles for various chemical species in the photosensitization reaction. The initial anthracene concentration was 0.505 mM and the initiator concentration was 6.08 mM.

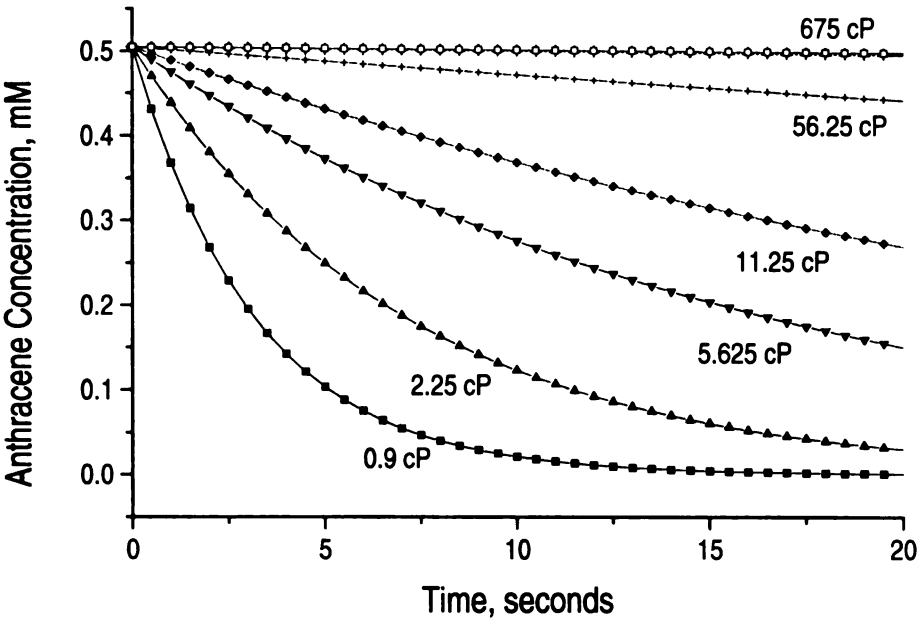

Figure V.9. Simulated decay profiles of anthracene during photosensitization at different viscosities.

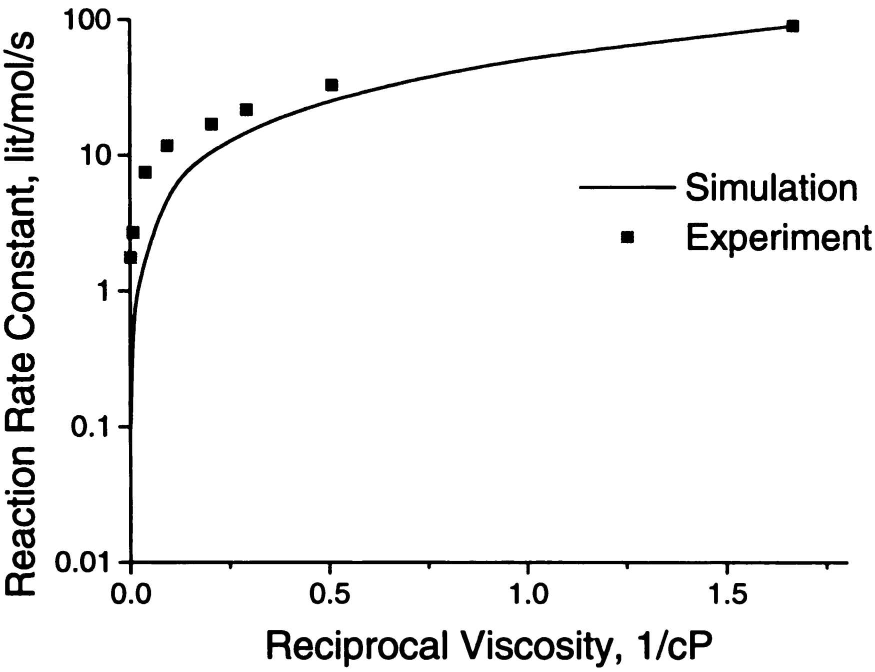

Figure V.10. Comparison of experimental data with numerical solutions of the photophysical equations using SSE modified kinetic constants.

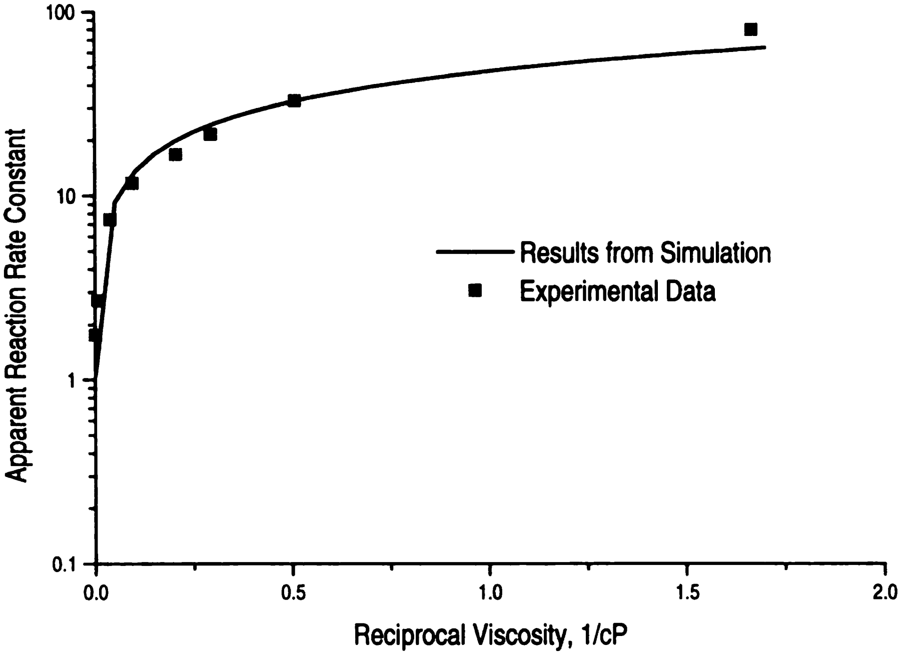

Figure V.11. Comparison between experimental data on reaction rate coefficient and simulation with adjusted constants.

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CHAPTER VII.

CONCLUSIONS AND RECOMMENDATIONS

The work reported in this thesis has contributed to the understanding of the kinetics and mechanisms of cationic photopolymerizations of epoxides and vinyl ethers. It will lead to a better understanding of the photosensitization mechanism and hopefully to an increased use of renewable agricultural resources like natural oils in the production of polymers. The fundamental experimental and theoretical investigations presented in this thesis complement the more macroscopic studies currently available in the literature. Furthermore, novel techniques for cure monitoring such as differential scanning photocalorimetry and steady state fluorescence monitoring have been highlighted and their utility for studying reactions of widely varying kinetic characteristics has been demonstrated. In this chapter, some general conclusions and suggestions for future work will be presented.

VII.1. Summary of Results

This research has provided considerable insight into the mechanism and kinetics of cationic ring-opening photopolymerization of epoxidized natural oils. Several distinct aspects of the photopolymerizations were investigated. A series of isothermal differential scanning photocalorimetric studies were performed at various light intensities and temperatures to characterize the polymerization reaction kinetics. A series of studies using steady state fluorescence monitoring were conducted to gain better insight into the diffusion controlled behavior of the photosensitization reaction between anthracene and diaryliodonium salts. The photophysical equations describing the photosensitization reaction were solved in conjunction with relationships provided by a theory for rapid, diffusion-limited, chemical reactions and the simulation results was compared with experimental results.

VII.1.1. Differential Scanning Photocalorimetry Studies

Differential Scanning Photocalorimetry (DSP) was employed to investigate a series of photoinitiated cationic polymerizations at different temperatures using epoxidized soybean oil as the monomer. The apparent propagation rate was found to increase sharply in the beginning, but after reaching a peak, it decreased gradually. Also, the overall conversion obtained was found to be higher for the polymerizations which proceeded at lower temperatures, although the initial rate of polymerization was higher for reactions at increased temperatures. We have tried to explain both of these phenomena using arguments pointing to diffusion effects in a rapidly polymerizing system.

During the polymerization, the large hexafluoroantimonate counterion of the initiator experiences a rapid decrease in mobility as the viscosity increases. Meanwhile, the active carbocation retains its diffusional mobility by reacting with neighboring oxirane rings, thus leading to separation of the two species. This increases the reactivity of the cationic active center. The final decrease in k_p is due to trapping of the active centers in the rapidly formed crosslinked polymer network. Therefore, a limiting conversion is observed despite the presence of "live" cationic species.

VI.1.2. Steady State Fluorescence Studies

The photosensitization mechanism was investigated using in-situ, steady state fluorescence spectroscopy. The direct dependence of the anthracene fluorescence intensity at 425 nm on the concentration of anthracene in the sample was utilized to monitor the reaction kinetics. The experimental fluorescence profiles show that the anthracene concentration follows an exponential decay, suggesting kinetics similar to a first order reaction. This can be attributed to the fact that the concentration of diaryliodonium hexafluoroantimonate initiator in the sample was an order of magnitude higher than that of anthracene. As the viscosity of the sample was increased, the rate of photosensitization appeared to decrease, suggesting a diffusion limited reaction mechanism. Photophysical equations were formulated for the different steps in the reaction scheme and a well known theory for diffusion controlled reactions was employed to model the behavior. Using an adjustable parameter, an empirical relationship was arrived at between the viscosity of the reaction system and the photosensitization kinetic constant.

VI.2. Recommendations for Future Work

Cationically polymerizable systems have received limited attention in the past as viable techniques to produce solvent-free coatings, films and composites. The research described in the previous chapters has proven the usefulness and applicability of this technique to various applications. Also, the experimental techniques described in this thesis can be employed to study other systems with alternate initiators, photosensitizers, and monomers. Since we have already proved that polymers with excellent physical properties can be produced from renewable agricultural resources, further research in this area is warranted to further enhance the curing properties as well as the final mechanical and thermal properties of these polymers.

As described in detail below, future research conducted in the following areas will aid in our understanding of cationic photopolymerizations:

i) Investigation of alternate photosensitizers such as thioxanthones.
ii) Fluorescence and phosphorescence lifetime experiments on anthracene at different viscosities.
iii) Epoxidation and subsequent photopolymerization of other natural oils.
iv) Hydrolysis of epoxidized oils or epoxidation of hydrolyzed oils before polymerization.
v) Mechanical and thermal characterization of polymers obtained from photopolymerizations of epoxidized oils.
vi) Accelerated weathering tests on polymers to test feasibility for different applications.

vii) Succeptibility to photooxidation of polymers produced by UV light.

VI.2.1. Alternate Non toxic Photosensitizers

Conventionally, the photosensitizers used in conjunction with diaryliodonium salts are anthracene, perylene and pyrene. Benzophenone has also been employed as a photosensitizer. Although the conjugated nature provided by the fused aryl rings in these compounds makes them very photoreactive and suitable for use as free-radical initiators and cationic photosensitizers, these compounds are classified as toxic. The concentrations of these sensitizers in coating formulations is on the order of hundredths of a percent, but they may still be restricted from use in consumer products.

Thioxanthones are non-toxic radical photoinitiators being increasingly used in the polymer coating industry for pigmented systems (See Figure 6-1 for chemical structures). Isopropyl thioxanthone (ITX) has been used as a free radical initiator for photopolymerizations in clear as well as pigmented coatings. The ability of the thioxanthone structure to generate radical moieties as a result of photochemical reactions, can be exploited to photosensitize diaryliodonium salts for conducting cationic polymerizations. These compounds exhibit maximum absorbance in the range from 380 to 420 nm ($e=10^4$ litres/mol cm) and give reduced yellowing in the polymer product compared to other initiators. These initiators have thus ingratiated themselves with manufacturers of printing inks and white pigmented lacquers.

Thioxanthones however have significant disadvantages. Since an amine co-initiator is needed, the thioxanthones can only be used in acrylate based systems, and not in systems containing unsaturated polyesters and styrene.[12] Further, the amines cause yellowing of the coating which increases with exposure to light. Flash photolysis of a wide variety of differently substituted thioxanthone derivatives revealed that the α-aminoalkyl radicals act as the initiating species for these systems.[3] Since the parent thioxanthone is poorly soluble in most formulations, substituted derivatives are used. Alkyl- and chloro-substituted derivatives are the most prominent and commercially available. Isopropylthioxanthone (ITX) has an absorbance maxima at 383 nm and is widely used in pigmented systems. The initiating performance of thioxanthone derivatives has been continually improved. 1-Chloro-4-propoxythioxanthone (CPTX) which has been recently introduced in the commercial market has been shown to be twice as reactive for certain printing ink applications.[4] The nature and position of substituents on the thioxanthone nucleus is closely related to the absorbance characteristics of these compounds.[5] Electron donating substituents in the 2 or 7 position as well as electron withdrawing substituents in the 3 or 6 position cause shifts in absorbance bands toward longer wavelengths. A methyl group in the 1 position deactivates the molecule probably via intramolecular hydrogen abstraction while a chlorine group in the same position leads to a pronounced activating effect. Methyl groups in the 3 and 4 position also activate the molecule. Ether groups in the 2 and even more in the 4 position result in more reactive photoinitiators than those with alkyl groups at these positions. CPTX is the most promising derivative so far, because of its high reactivity as well as its ease of synthetic preparation. It has a strong absorbance peak at 387 nm besides the short wavelength maximum at 254 nm. An additional peak is observed at 314 nm because of the 4-position substitution. This absorbance peak is ideally placed to accept photons from the 313 nm radiation band from medium pressure mercury lamps and probably is a significant contributor to the high photo-reactivity exhibited by this molecule.

Upon illumination with ultraviolet light, all thioxanthones exhibit fluorescence in the 450-500 nm region and this property can be exploited to study polymerizations caused by these compounds.

VI.2.2. Fluorescence and Phosphorescence lifetime experiments.

To further enhance our understanding of the effect of viscosity on the photosensitizaton reaction mechanism and kinetics, we need to conduct in situ, time resolved fluorescence and phosphorescence lifetime studies on anthracene at different vsicosities. This will provide us with information on the effect of viscosity on the lifetimes of the singlet and triplet excited state anthracene, respectively. The relative contribution of these two species toward photosensitization is a function of their lifetimes. Hence, it is quite possible that the change in viscosity of the formulation may affect the sensitization kinetics.

VI.2.3. Epoxidation and subsequent photopolymerization of other natural oils.

Other natural triglyceride oils have chemical structures very similar to that of soybean oil. For example, the composition and different properties of corn oil are compared with soybean oil in Table 6-1. The iodine value of an oil is an accurate measurement of reactive unsaturation present in the oils. This unsaturation can be exploited to introduce epoxide moieties and study polymerization. The similar iodine values of soybean and corn oil and their similar chemical composition suggest that corn oil could also be epoxidized and subsequently photopolymerized like soybean oil. Corn oil is also available at a price close to that of soybean oil ($0.26/lb).

VI.2.4. Hydrolysis of epoxidized oils or epoxidation of hydrolyzed oils before polymerization.

The average representation of a soybean oil molecule is a triglyceride ester with three branches of 16-18 carbons each. If the triglyceride molecule is hydrolyzed, we obtain the consituent saturated and unsaturated acids as shown in Table 6-1. The mixture of acids could be epoxidized using hydrogen peroxide and acetic acid to provide a polymerizable mixture. Photopolymerization of this mixture of oils has definite advantages over photopolymerization of epoxidized soybean oil. First, the effective size of the polymerizable monomer is reduced while maintaining the multifunctional nature of the molecule. The polymers thus obtained will definitely have better physical properties. To make the process even more efficient, the unsaturated components of the oil mixture can be separated from the saturated components using standard techniques described in the literature. An alternate route is to epoxidize the natural oils first before hydrolyzing them.

VI.2.5. Mechanical and thermal characterization of polymers obtained from photopolymerizations of epoxidized oils.

The thermal and mechanical properties of the crosslinked polymers formed by cationic polymerizations of epoxidized oils can be characterized using standard techniques such as differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and thermal mechanical analysis (TMA). These experiments will allow the glass transition temperature (if any), the degradation temperature, and the expansion coefficient to be established. The flow properties of the polymers can be investigated using a Dynamic Mechanical Analyzer. Using standard procedures, this technique can be used to measure the loss and storage moduli of the resulting polymers for a spectrum of frequencies, using standard time-temperature superposition principles. Similar measurements can be performed on systems which contain short chain epoxide moieties, and the system will be adjusted to obtain superior mechanical properties.

Preliminary studies have shown that the polymers formed from epoxidized soybean oil had a coefficient of thermal expansion of about 210 μm/m °C. These polymers were quite stable at elevated temperatures and showed negligible weight loss at temperatures below 200°C. In fact, at 300°C, the weight loss (as measured by TGA) was less than 2%. Above 350°C the ESO polymers rapidly degrade and lose most of their weight. Differential scanning calorimetry of a cured ESO polymer did not show a definite glass transition. These polymers appeared to be rubbery but, upon stressing, failed in brittle mode.

As expected, preliminary studies have shown that the addition of an epoxy resin as a comonomer resulted in an increased modulus and a considerably tougher material. Commercial resins such as DER 331 (Dow Chemicals) can be employed to obtain enhanced mechanical and thermal properties.

Our preliminary swelling studies indicate that ESO polymers swell only very slightly in water, swell to about 20% in acetone and partially degrade in benzene. Again, the solvent resistance may be enhanced by copolymerization with the aforementioned epoxy resins. Extensive swelling studies could be performed using other solvents. Any change in the properties of the polymer upon exposure to the solvents should be thoroughly characterized.

VI.2.6. Accelerated weathering tests on polymers

The weatherability and chemical resistance of the polymers also need to be characterized. ASTM weatherability studies can be performed using Weatherometer Q Panel Testers. This state-of-the-art instrument allows samples to be maintained at controlled environmental conditions (temperature, UV exposure, humidity, etc.). These accelerated aging tests can be performed to identify superior formulations for potential use in automotive and exterior coating applications.

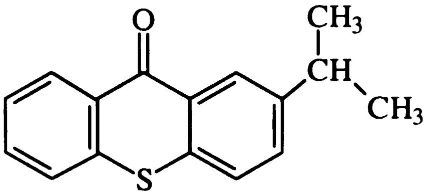
VI.2.7. Photooxidation of polymers produced by UV light.

The photoaging of polymers is mainly caused by solar radiation reaching the earth surface (mostly with wavelengths greater than 300 nm) via complex oxidative processes.[6] This photo-oxidative process is often accompanied by thermal oxidation depending on the environmental and weather conditions. Photo- and photo-thermal oxidative degradation cause chemical changes in the polymer structure with the build-up moieties such as carbonyls, acids, esters and alcohols, apart from causing chain scissions and crosslinking. In addition to severe drops in the mechanical and thermal properties of the polymers, the polar functional groups generated also lead to decrease in performance by causing a drop in water repellence, transparency, and dielectric properties.

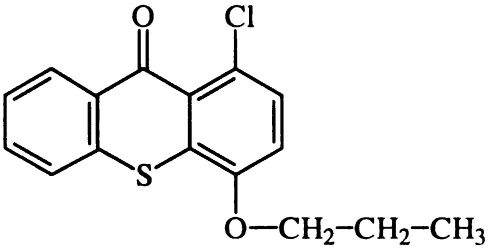
Photo-oxidation is a radical chain process which can be initiated in various ways. First, the photoactive functional groups present in the polymer structure, the residual initiator, or the impurities may absorb light and give rise to free radical active centers. The propagation of the oxidation commonly takes place by hydroperoxidative cycles involving peroxiradicals as intermediates.[6] Since our polymerizations are conducted with carbocationic active centers and not free radicals, the photodegradation should not be a very critical issue. Nevertheless, the investigation of this could lead us to design better formulations for various applications.

Table VI.1. Comparison of Soybean and Corn Oil

Acids	Chemical Formula	% in Soybean Oil	% in Corn Oil
Saturated Acids			
Palmitic	$C_{15}H_{31}COOH$	6.5	6.0
Arachidic	$C_{19}H_{39}COOH$	0.7	1.0
Stearic	$C_{17}H_{35}COOH$	4.5	2.0
Unsaturated Acids			
Oleic	$C_{17}H_{33}COOH$	33.5	37.0
Linoleic	$C_{17}H_{31}COOH$	52.5	54.0
Linolenic	$C_{17}H_{29}COOH$	2.3	0.0
Relative Unsaturation		145.4	145.0
Iodine value		122 - 134	111 - 128



Isopropyl thioxanthone (ITX)



1-Chloro-4-propoxythioxanthone (CPTX)

Figure VI.1. Chemical structures of thioxanthones employable as photosensitizers in conjunction with diaryliodonium initiators.

VI.3. List of References

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