To the Graduate Council:

I am submitting herewith a dissertation written by Timothy Allen Tufts entitled "Photoinitiated Cationic Polymerization." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

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PHOTOINITIATED CATIONIC POLYMERIZATION

A Dissertation

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Doctor of Philosophy

Degree

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Timothy Allen Tufts

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ABSTRACT

Several compounds were investigated for their effectiveness in the photoinitiated cationic polymerization of cyclohexene oxide. Two types of compounds were studied; those with a p-methoxyphenyl substituent, and several vinyl halides. The effects of initiator, initiator concentration, and irradiation time on isolated polymer yield and molecular weight were studied. In addition, several mechanisms leading to polymer degradation were investigated.

The p-methoxyphenyl compounds were found to be ineffective as photoinitiators, giving very low polymer yields in the dark as well as when irradiated. This was attributed to various thermally induced reactions. In contrast, the vinyl halides were effective as photoinitiators. When irradiated, monomer/initiator mixtures gave polymer yields ranging from 1% to 22%, depending on initiator and irradiation time. Side reactions involved in the case of 1-iodocyclohexene caused chain degradation and a reduction in polymer molecular weight and consequently in yield of isolated polymer.

The most effective compound investigated for use as a photoinitiator was found to be (E)-1,2-dibromo-1-(4-methoxyphenyl)-2-phenylethene. It was also found to form films when a mixture of monofunctional and difunctional epoxides was used.

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An 4-Methoxyphenyl

Ar Aryl, substituted phenyl

BCH 1-Bromocyclohexene

BEB (1-Bromoethyl)benzene

BEMB 1-(1-Bromoethyl)-4-methoxybenzene

BEYB (1-Bromoethenyl)benzene

BMMB 1-(Bromomethyl)-4-methoxybenzene

CHO Cyclohexene oxide

DBCH 2,3-Dibromocyclohexene

DEB(1,1) (1,1-Dibromoethyl)benzene

DEB(1,2) (1,2-Dibromoethyl)benzene

DEMB 1-(1,2-Dibromoethyl)-4-methoxybenzene

DEO 1,2,7,8-Diepoxyoctane

DMPE (E)-1,2-Dibromo-1-(4-methoxyphenyl)-2-phenylethene

DPPH Diphenylpicrylhydrazil

EMP 1-Ethyl-4-methoxybenzene

ICH 1-Iodocyclohexene

IR Infrared spectroscopy

MPO (4-Methoxyphenyl)oxirane

MW Molecular weight

$\bar{M}_v$ Viscosity average molecular weight

NBS N-Bromosuccinimide

NMR Proton nuclear magnetic resonance spectroscopy

NVC N-Vinylcarbazole

p Para

t Tertiary

TEA Triethylamine

THF Tetrahydrofuran

TMS Tetramethylsilane

UV Ultraviolet spectroscopy

λ Wavelength

$\emptyset$ Phenyl

$h\nu$ Light

η_{sp} Specific viscosity

η_r Relative viscosity

$[\eta]$ Intrinsic viscosity

CHAPTER I

INTRODUCTION

A. Polymerization Initiation Reactions

A fundamental aspect of polymer chemistry involves the production of macromolecules. These polymerization reactions involve the combination of many small, individual molecules into a large macromolecular structure. In general, polymerization reactions can be classified as either step growth or chain growth reactions. Step growth polymerization reactions do not involve an active center, and generally proceed with the elimination of a small molecule. In contrast, chain growth polymerization involves the chain reaction addition of monomer units to an active center. This active center may be neutral (a free radical), charged (an anion or cation), or some less well-defined center (as in complex coordination catalysis). Mechanistically, further differences exist between step growth and chain growth reactions. Each reaction in a step growth polymerization reaction is exactly the same as any other, with species of all sizes gradually growing. With the exception of the complex coordination reactions, chain growth reactions can be broken down into three steps, specifically initiation, propagation, and termination. Initiation involves the production of the active center, propagation involves growth of the polymer chain by addition of monomer units to the active center, while termination deals with the destruction of the active center.

Commonly, a compound other than the monomer is responsible for the production of the active center in the initiation step. This initiating molecule can thus determine the active center generated and the types of compounds which can be polymerized. In many systems, the initiator can also have a profound effect on how the monomer units add to the active center, as well as determining the termination steps in the reaction. Many initiating compounds are inactive until activated or decomposed by chemical or physical means. Formation of the active initiating species may be induced by spontaneous chemical reaction or by gamma rays, electron beams, microwaves, UV or visible light, or heat.[1]

1. Free Radical Polymerization Reactions

Free radical initiators have been used to polymerize a large variety of monomers containing carbon-carbon double bonds using both chemically and physically induced initiation reactions. The earliest free radical polymerization was probably done in 1838 by Regnault.[2] Since then, much work has been done to discover and characterize new free radical initiators. Free radical initiation reactions can generally be placed in one of two classifications: homolytic bond cleavage by absorption of energy leading to free radicals, and electron transfer (donor-acceptor) interactions.[1] The former is more widely used and known, and will be considered first.

A wide variety of compounds has been investigated as free radical initiators, in conjunction with a number of methods for

decomposition of these compounds. High energy particles, thermal, electromagnetic, mechanical, electrical, and sonic energy have been used to homolytically cleave covalent bonds and thus initiate free radical polymerization. The initiators used typically have a weak covalent bond and/or form a relatively stable free radical. Peroxides and hydroperoxides are widely used and can be decomposed by UV irradiation or heat.[3] At low temperatures, some tertiary amines promote the rapid decomposition of peroxides.[4] Azo,[5] N-nitroso,[6] and related compounds are thermal initiators. A limited number of these are also effective photolytic initiators. Disulfides are also initiators, but much higher temperatures are needed to induce decomposition.[7] In addition, disulfides are photolytically active, as are various organometallic compounds,[8] inorganic ions,[9] ketones, and aldehydes.[10] Certain transition metal chelates also form useful free radicals when heated. Benzoin,[11] benzoin ethers, and benzil[12] are active photoinitiators. High energy radiation and high energy particles can often be used without added initiator.[13] In these cases, free radicals are produced from the monomer molecules. Thus, a wide range of compounds and energies can be used to initiate free radical polymerization through the homolytic cleavage of a covalent bond.

Several reactions involving electron transfer are useful as free radical initiators. Many redox and electrochemical reactions can be used to produce free radicals. Direct electron transfer from an alkali metal to monomer may also initiate polymerization. Redox reactions involve a large number of inorganic and organometallic ions

in conjunction with compounds such as peroxides, hydroperoxides, disulfides, and persulfates.[14] Electrochemical reactions may be typified by the Kolbe reaction which employs alkali metal carboxylates as radical precursors.[15] The electrolysis of tetraethylammonium tetrafluoroborate generates both anions and radicals. Radical and/or radical ion complexes may also be generated when certain solvents are used in conjunction with alkali metals and certain aromatic compounds.

2. Complex Coordination Polymerizations

Coordination catalysts, often referred to as Ziegler-Natta catalysts, are of extreme industrial importance. In contrast to the other types of chain growth reactions, these reactions cannot be considered to involve three distinct steps. Indeed, the entire mechanism, and particularly the exact nature of the active center, is poorly understood.[17] Many transition metal compounds have been found to exhibit this catalytic activity, but these reactions usually involve true catalysts (usually heterogeneous) that are not initiators.

3. Anionic Polymerization Reactions

In contrast to free radical and cationic polymerization reactions which have been known for many years, anionic polymerization reactions have been known only since the early 1900's.[19] These reactions have recently been widely utilized for synthesizing block co- and ter-polymers with unique properties.[19] As is implied by the name, the active centers in these reactions are negatively charged. This negative center is often a carbanion, though not always. For example, N-based

anions are proposed for the polymerization of lactams,[20] acrylamides,[21] and isocyanates.[22] The initiators in anionic polymerizations produce anions or anion-radicals which can attack suitable monomers. In contrast to free radical generation, solvolysis and electron transfer reactions are the primary mechanisms for anion production, as will be illustrated.

The first compounds polymerized by an anionic mechanism were various conjugated dienes, including butadiene, isoprene, 1-phenylbutadiene, and 2,3-dimethylbutadiene.[23] Styrene was anionically polymerized in 1914,[24] but other mono-olefin monomers such as acrylates and acrylonitriles were not employed until much later. In addition to many olefin monomers, various heteroatom ring compounds can be polymerized anionically. These include cyclic esters,[25] cyclic amides,[26] N-carboxyanhydrides,[27] and epoxides.[28] Anions may also induce the polymerization of a variety of carbonyl compounds.[29]

Basic compounds can be used to generate initiating anions. These bases can exist in several forms in solution. As given in Winstein's solvolysis scheme,[30] these may be represented as: a) covalent compound, b) intimate ion pair, c) solvent separated ion pair, and d) solvated free ions.

$$\underset{a}{B\text{-}M} \rightleftharpoons \underset{b}{B^- M^+} \rightleftharpoons \underset{c}{B^-/S/M^+} \rightleftharpoons \underset{d}{B^-\text{-}S + M^+\text{-}S}$$

Free ion initiation involves simply addition of the anion to the monomer molecule. However, depending upon the base, the anion, the

cation, solvent polarity, monomer, and temperature, initiation may occur at stages other than the free ion pair. In these cases, a different mechanism is invoked which involves the countercation coordinating with the monomer, followed by electron rearrangement to give the monomer-anion addition product.[31] The type of monomer determines the strength of base needed to initiate polymerization. For compounds with a double bond, electron withdrawing substituents can stabilize the anion formed and thus can allow polymerization with relatively weak bases. Extremely weak bases such as water, ketones, or alcohols can polymerize vinylidene cyanide because of the two strong electron withdrawing cyano groups attached to the double bond. At the other extreme, very strong bases such as n-butyllithium are needed to polymerize butadiene.

Organo-alkali metal compounds are quite reactive and widely used as initiators.[32] Amide ions in liquid ammonia[32] have been used, as have alkali metal alkoxides, to initiate anionic polymerization of certain monomers. A variety of acetylenes and amines can produce initiating reactions, as can Grignard reagents.[34] The organic anion producing species indene, flourene, xanthene, and triphenylmethane also polymerize some monomers.[35]

The second type of anionic initiation reactions are electron transfer reactions, which were the first reactions used to polymerize compounds anionically. It has been proposed that there are three distinct types of these reactions which can initiate anionic polymerization. The first type involves electron transfer to the monomer to

form the active center. The second type involves electron transfer to an intermediate compound which forms a stable, soluble ion-radical. This complex then transfers the electron to monomer. The third type also involves electron transfer to an intermediate which then dimerizes to form a difunctional initiator. In many solvents, the monomer radical-anions formed in all of these reactions undergo rapid radical combination to form dimeric anions.

Alkali metals are active polymerization initiators, with sodium being the most widely used.[36] Soluble, stable alkali metal complexes are more efficient due to the homogeneous nature of the reaction.[37] These are generally produced by the reaction of alkali metals with polynuclear aromatics or solutions of alkali metals in liquid ammonia. Aromatic compounds used include naphthalene, biphenyl, phenanthrene, and anthracene. Some monomers can be polymerized by alkali metals in ethers,[38] but these systems are not as active as the alkali metal-aromatic complexes. An example of the third type of electron transfer reaction is the use of alkali metal ketyls as initiators.[39] Benzophenone is the predominant ketone used.

High energy radiation may also give anionic polymerization in some systems.[40] In these cases, the initiating species are generated by an external agent, in contrast to the more common case in which a spontaneous chemical reaction produces the initiating species.

4. Cationic Polymerization Reactions

The second type of ionic polymerization reaction involves polymerization via a positively charged active center. These charged

centers may be carbocations, oxonium ions, sulfonium ions, or immonium ions. Cationic polymerization has been known since 1789, when H_2SO_4 was used as an initiator,[41] and thus is the oldest known type of polymerization.

Early investigations involved compounds with a carbon-carbon double bond. Aliphatic aldehydes,[42] some ketones,[43] and ketenes are polymerizable by a cationic mechanism. Cyclic ethers,[44] cyclic acetals,[45] and cyclic formals[46] polymerize via an oxonium ion ring-opening reaction. Other cyclic monomers include cyclic sulfides,[47] disulfides,[48] imines,[49] esters,[50] and amides.[51] For each of these cyclic monomers, ring size plays a large part in determining reactivity. This is illustrated by the fact that a cyclic alkane, cyclopropane, is cationically polymerizable because it is very strained. An unusual example of cationic polymerization is the polymerization of diazoalkanes.[52] These compounds polymerize in a chain reaction mechanism with the elimination of nitrogen.

Cationic initiation can be accomplished by acids and by other cation-forming compounds. Acid catalysis is the most common and will be considered first. Both classical protonic acids and Lewis acids can be effective in polymerizing various monomers. Protonic acids including HCl, HBr, HI, HNO_3, H_3PO_4, $H_3C_2O_2H$, H_2SO_4, $HClO_4$, Cl_3CCOOH, and F_3CCOOH have been used to initiate polymerization.[53] Extremely strong acids, which can be generated in situ, include HBF_4, $HAsF_5$, $HSbF_6$, and $HOSO_2CF_3$.[54] Initiation involves dissociation of the acid, followed by addition of the proton to monomer forming a cation

which is more stable than the initiating cation. In compounds with a carbon-carbon double bond, rearrangement can occur if a more stable cation is produced upon rearrangement. This is the case for 3,3-dimethylbutene-1.[55] The degree of dissociation of the acid and subsequent addition to monomer depend a great deal on the polarity and hydrogen-bonding ability of the solvent employed.

Lewis acids made from Group III and transition metal halides can also initiate cationic polymerization. Originally, these compounds were thought to be initiators when used alone. It has now been established that nearly all of these compounds require the presence of a co-catalyst to function as initiators.[56] Water, protonic acids, and alkyl halides are effective co-catalysts. In some cases, a stable ion pair is proposed. In other cases, no stable species have been isolated or detected. In these cases a complex between monomer and Lewis acid may form and then react with the co-catalyst to form the active initiating species.[57]

Many of the metal halide types of initiators are actually catalysts since they are not consumed during the reaction. In contrast, the third type of cationic initiators are true initiators. These initiators generate cations and anions in some manner. They include primarily ionic compounds such as acyl and alkyl perchlorates,[58] triphenylmethyl and tropylium halides,[59] acyl and alkyl tetrafluoroborates,[60] and iodine.[67] Various stable oxonium and sulfonium salts, such as xanthylium tetrafluoroborate and pyrylium hexafluoroborate, can also initiate polymerization.[62] Similarly, interhalogen compounds[63] and high energy radiation[64] may be used for cationic

polymerization. UV irradiation may be used to cause formation of initiating cations from certain compounds, and these will be discussed later.

B. Curing Reactions of Films and Coatings

Films and coatings have become an important part of the polymer industry. Some of this technology has been used for centuries, such as in paints, varnishes, etc., while other synthetic polymer coatings have just come into recent importance (e.g. Teflon). Coatings are important because they allow materials to have widely differing bulk and surface properties. For example, a cheaper or stronger material could be used as the mass of a structure. A coating or film may then be applied which is not as cheap or strong, but has many desirable properties that the primary (bulk) material does not. These could include stability to heat or UV light, solvent resistance, corrosion and chemical resistance, and/or vapor barrier properties. Thus, the proper coating could make possible the use of one bulk structural material in a variety of service conditions and applications.

For some applications, the coating is applied by lamination. In many other applications, the coating is applied as a liquid and is then cured in place. The curing process, usually comprised of polymerization and crosslinking reactions, is of principal interest here. In many cases, it is desirable to apply a polymerizable liquid coating formulation without a sacrificial carrier solvent. The curing reactions of these coatings systems can be visualized as occurring in a thin bulk

reaction system. Two of the normal drawbacks to bulk polymerizations, specifically control of temperature and of viscosity during polymerization,[65] are not problems in coatings reactions. Since a small volume of monomer or prepolymer is spread over such a large area, heat dissipation is relatively efficient and temperature control is therefore not a problem. Viscosity is of principal concern during application of the mixture to the surface, but usually not during the polymerization reaction. The mixture before curing may consist of small molecule monomers or oligomeric prepolymers, which can exhibit a wide range of functionality. Similarly, the polymerization mechanism can be ionic or free radical, and the methods used to cause the reaction are widely varied. Depending upon the end use, the system may also contain additives such as antioxidants that dictate the curing method used.

Many of the coatings used today employ prepolymers that are cured by means of free radical polymerization reactions. These types of curing reactions have several drawbacks.

The most serious problem with free radical curing reactions stems from the ability of the propagating radicals to react with radical traps and transfer agents, particularly atmospheric oxygen. Controlled, reproducible results demand the exclusion of oxygen in some manner. Ordinarily, one of two methods has been used for this. The first approach is to exclude oxygen by blanketing the coating with an inert atmosphere, usually nitrogen. The second approach involves a two stage curing process. In the first stage, the outer surface is cured under

an inert atmosphere. Since this effectively eliminates the access of oxygen to the interior, the final curing stage may take place in an uncontrolled atmosphere. Both of these types of curing procedures are successfully used, but the disadvantages still exist.

The second area of concern deals with the use of radiation energy to cause initiation of polymerization. Using some type of radiation energy to cure coatings is an old idea. This type of cure enables a mixture of monomer/initiator to be stored for a long period of time, then applied and cured when needed by the proper dose of energy. Some types of energy are more desirable than others, however, as efficiency and pollution are most important in modern industry. Gamma ray, electron beam, microwave, and sonic production of radicals from initiators is undesirable for most applications because of cost and/or pollution. Thermal energy is also inefficient in many cases, often because the whole of the substrate material is heated unavoidably while the curing reaction takes place only on the surface of the structure. Possibly the most useful energy source is some type of light - often UV or visible. This can allow only the coating to absorb the energy and thus is energy efficient and relatively pollution free. The source is usually portable and highly affordable.

The fact that radical curing reactions can be induced by radiant energy absorption and that many of the initiators used are sensitive to a wide range of radiant energy brings up a third weakness. This problem is the shelf stability of initiators and initiator/monomer mixtures. Often, extended shelf storage is impossible except

under closely controlled conditions. Many of these compounds, in order to be useful over long periods, need to be stored under cold, dark conditions in an inert atmosphere.

Of lesser importance is the unreacted double bonds left in the coating after curing. No curing process will be 100% efficient, and as viscosity increases, some double bonds will be trapped unreacted. These bonds can react with oxygen and light to cause radical reactions resulting in discolorations and polymer degradation. In order to suppress this, antioxidants or UV stabilizers may be added, but these then may interfere with, and thus dictate, either the free radical curing reaction or the curing energy used. This could then have an impact on several of the other areas discussed.

A further drawback to free radical curing of coatings is their limitation to compounds containing a carbon-carbon double bond. This excludes many monomers and their resulting polymers which have useful properties for coatings. In most cases the principal obstacles to commercial use of free radical curing processes have been overcome, or the economics of the system have dictated use inspite of the drawbacks.

Curing of coatings by ionic chain growth processes has not been widely utilized, even though these reactions offer several potential advantages over radical reactions. Step growth ionic chemical reactions for curing of adhesives, epoxy resins, etc. are well-known, but most involve the mixing of two or more components and a subsequent working time. The limited time available between mixing and

formation of unworkable material severely limits the usefulness of these types of reactions for many applications. In considering chain reaction ionic polymerizations, several advantages and disadvantages will be discussed.

Since ionic reactions are not sensitive to oxygen, an inert atmosphere is not required. However, these reactions are sensitive to water, the presence of which must be avoided during curing. A wide range of monomers can be polymerized ionically, including many of the same monomeric compounds used in free radical curing. This would enable new coatings with different properties and applications to be produced.

A major disadvantage is the fact that almost all ionic initiators cause polymerization immediately upon mixing with the monomer. This fact practically eliminates these reactions from use in curing of coatings. Ionic reactions induced by high energy irradiation have been used in some cases, but cost, pollution, and health hazards limit this type of curing. Therefore, for use in the curing of coatings, a latent ionic initiator sensitive to some specific type of energy would be extremely useful. As mentioned previously, UV or visible light would be the energy of choice because it is usually efficient, relatively cheap, available, mobile, and pollution free. In searching for an ionic initiator sensitive to light, a description of the required characteristics would be helpful. Thus, the "ideal ionic photoinitiator" should:

(a) be inexpensive,

(b) be stable indefinitely to any stimulus other than that of the appropriate wavelength of light,

(c) decompose rapidly when the proper wavelength of light is applied. (Useful wavelengths range from 220 nm to approximately 800 nm, implying the compound should have a significant absorption band in this region),

(d) not produce any side products upon decomposition. (Volatile side products can cause bubbles in a coating, while trapped non-volatile products that are not bound to the polymer chain may later migrate out of the film, causing adverse effects to the environment),

(e) be efficient. (Each initiator molecule should start a polymer chain),

(f) be easily prepared, purified, handled, and stored,

(g) be soluble in a wide range of monomers, solvents, and prepolymers, and

(h) have a high initiating power. The active species produced should cause the polymerization of a wide range of compounds.

The search for ionic photoinitiators has intensified in the last few years, and several systems have been investigated.

C. Literature Review

Only one case of anionic photoinitiation has been reported. When a solution of nitroethylene in THF was irradiated, polymerization followed to give poly(nitroethylene).[66] A ground state charge-transfer complex was shown by UV spectra.

A good deal more work has been done in the area of cationic photoinitiated polymerization, however. As early as 1964, Strohmeier and Barbeau investigated the polymerization of propylene oxide by dimanganese decacarbonyl.[67] When a solution of monomer and initiator was irradiated with UV light, the theoretical amount of carbon monoxide was given off and a substance precipitated. Upon subsequent heating to 80°C or 120°C, polymerization occurred. Polymers having intrinsic viscosities from 1.18 to 2.46 dl/g were obtained. No polymerization mechanism was proposed.

Another manganese carbonyl compound, methylcyclopentadienyl manganese tricarbonyl [$MeCpMn(CO)_3$], was shown by Anderson to be a photosensitizer for conventional epoxy resins.[68] An example was given in which 2.5% of $MeCpTi(CO)_3$ in a commercial epoxy resin was photocured on a plate using a GE high pressure mercury arc lamp for 15 minutes at a distance of 30 cm. The plate was heated for two hours at 125°C. Carbon monoxide bubbles were formed, but collapsed before gellation. An anhydride was added to aid curing, but a room temperature cure was attained by using a trimercaptan curing reagent. Ten hours curing time was found to be necessary for these formulations. "Pot lives" of

several weeks were reported, and a range of irradiation sources used. Irradiation sources included sunlight, sunlamps, black lights, low pressure mercury arc lamps, and Co^{60} gamma radiation, although longer exposure times were necessary. Additives may be present in the mixture without affecting the cure. The proposed curing mechanism involves the photo-oxidation of the manganese compound to a Mn(II) salt which then catalyzes the addition of the anhydride or mercaptain curing agent to the epoxy units. This is an example of an ionic step growth cross-linking reaction. Several limitations should be noted. First, $MeCpTi(CO)_3$ is extremely toxic and must be handled with care. Secondly, post irradiation curing is necessary either at elevated temperature or over long time periods. A more important problem is the residual catalyst which remains in the cured resin. The Mn(II) salts are simply trapped in the matrix, and subject to later migration into the environment.

Much of the work on cationic photoinitiators has been done with transition metal salts which have electron accepting properties. Japanese researchers reported in 1965 the photosensitized polymerization of β-propiolactone using uranyl nitrate as photosensitizer.[69] In 1967, another group reported the photosensitized cationic polymerization of NVC and β-propiolactone (PL) using sodium tetrachloroaurate ($NaAuCl_4\ 2H_2$).[70] Yields of over 90% poly(NVC) after thirty minutes irradiation were reported using nitrobenzene as solvent. PL gave only 40% polymer after four hours. Additives were used to elucidate the polymerization mechanism. Oxygen, DPPH, and nitrobenzene, all of which

are radical trapping agents, did not inhibit the polymerizations. Ammonia is a strong inhibiting agent for this polymerization, and addition of water caused the degree of polymerization to decrease. For these reasons, a cationic mechanism was proposed. Limitations of the system include poor thermal stability of the original mixture. After two hours, 67% polymer was reported with no irradiation. Over 80% polymer was reported when an NVC-nitrobenzene solution was irradiated without initiator. Water, normally an efficient termination agent for cationic polymerization, does not lower polymer yield even when present in large concentrations. This seems to contradict the conclusion of a cationic mechanism.

Further kinetic work on the NVC-gold salt systems was carried out by the original researchers.[71] Two anhydrous tetra-n-butylammonium tetrahaloaurate compounds (halo=Cl, Br) were used as photosensitizers of NVC.[72] These initiators were found to exhibit lower activities in photo- and thermal polymerizations than $NaAuCl_4\ 2H_2O$. Various solvents were investigated also. Polymer yields typically were 50% after two hours of irradiation or 10% after two hours of thermal polymerization. The effects of additives were confusing. Under similar conditions, methanol lowered polymer yields about 50%, while oxygen lowered yields about 35%. From this data, it was concluded that methanol inhibited polymerization, but oxygen did not inhibit polymerization. DPPH actually accelerated the reaction in some cases. Several cationic mechanisms were proposed using excited donor-acceptor complexes, but none were proven conclusively.

The same researchers have reported the photo-sensitized cationic polymerization of NVC initiated by silver (I) perchlorate in benzene.[73] An 80% polymer yield was reported after 20 hours irradiation, while the thermal reaction at 30°C gave only 10% polymer after 20 hours in the dark. Small amounts of water inhibited polymerization, and oxygen reduced the polymerization rate. A cationic mechanism was later proposed, with initiation occurring by photo-excitation of the strong NVC-$AgClO_4$ complex.[74] This later work also included silver (I) tetrafluoroborate, with both silver salts used in a variety of aromatic solvents. It should be noted that NVC can form a wide variety of active species, and that it polymerizes readily both cationically and free radically, leading to many difficulties in isolating a single mechanistic path.

Another donor-acceptor system studied used tetracyanobenzene as an acceptor and α-methylstyrene as the monomeric donor.[75] When irradiated at -30°C, the donor-acceptor complex becomes excited and dissociates into ions in polar solvents. The ions then initiate cationic polymerization. A 7% conversion was reported after two hours of irradiation. The mechanism was determined by using additives. Small amounts of water or triethylamine inhibited polymerization, while oxygen retarded polymerization. This was taken as an indication of cationic polymerization.

Cyclohexene oxide has also been polymerized using pyromellitic dianhydride or tetracyanobenzene as electron acceptors to form a complex.[76] The photoinitiation was studied in methylene

chloride solution and in bulk liquid and solid states. Cationic inhibitors such as water and triethylamine completely suppressed polymer formation, leading to the conclusion that the mechanism was cationic in nature. Photoexcitation of the donor-acceptor complex followed by heterolytic dissociation into an ion pair was proposed as the initiating mechanism.

Kaeriyama and Shimura reported the photoinitiated polymerization of styrene, two vinyl ethers and epichlorohydrin, but their initiator did not polymerize vinyl acetate, methyl methacrylate, and phenyl glycidyl ether.[77] The initiator used was bis(cyclopentadienyl) titanium dichloride [$(Cp)_2TiCl_2$]. When used as an initiator for styrene, a radical mechanism was assumed because pyridine did not completely inhibit the reaction. Low polystyrene yields of less than 10% were reported. When Cp_2TiCl_2 was used in epichlorohydrin, polymer yields of 10-13% were reported after 40 hours of irradiation. Cp_2TiCl_2 is nearly insoluble in ethyl vinyl ether, but 97% polymer yields were obtained when irradiated. 2-Chloroethyl vinyl ether gave a polymer yield of 80% after three hours of irradiation. The initiation mechanism was investigated by observing the affect of additives on polymer yields. When pyridine was added (1% by volume), no polymer was formed. When the same amount of water and ethanol was added, polymer yields were 18% and 89% respectively. With no additives in the presence of air, a 7.5% yield was found. They reported an induction period of about one hour, during which the liquid became green. A mechanism was tentatively assumed that was based on the color of the liquid and the

fact that light frequently reduces metallic compounds. The green catalyst is thus considered to be titanocene monochloride. The experimental evidence given for the effect of additives seems contradictory. Pyridine, water, and ethanol should all quench cationic polymerization quite readily. In this case, however, ethanol actually increases the polymer yield. The proposed mechanism involving titanocene monochloride is suspect because the authors readily admit that this compound has been shown not to be an initiator for vinyl ethers. Aside from these considerations, other limitations exist. Trapped initiator residue would be a problem in this case as well, along with initiator toxicity. Sensitivity to air also limits the utility of this system.

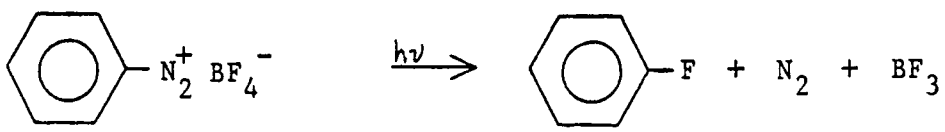
Marek and Toman photoinitiated the polymerization of isobutylene at temperatures from 0°C to -78°C.[78] Various metal halides, including VCl_4, $TiCl_4$, $TiBr_4$, TiI_4, $AlBr_3$, and $SnCl_4$ were investigated in bulk and in n-heptane solution. $TiBr_4$, TiI_4, and $SnCl_4$ did not cause polymerization in any case. Thermal polymerizations were observed for all compounds when temperatures above 10°C were used. VCl_4 caused polymerization to a very small extent (2% yield) in the dark but gave 99% yield when illuminated at -78°C. $AlBr_3$ actually gave more polymer in the dark than when photolyzed. In the dark at -78°C, $TiCl_4$ gave polymer yields ranging from 0.3% to 85.5% using the same conditions. This raises questions about the importance of catalyst preparation and system purity. Bulk polymerizations gave higher yields than solution polymerizations.

Complex formation was assumed to occur due to the changes in color when catalyst and monomer were mixed. The proposed initiating species was a radical cation, but no ESR signal could be detected during the polymerization. Oxygen did inhibit the polymerization. Polymer yields varied widely with catalyst and with differences in temperature. Later spectrophotometric investigations by the same workers showed that a complex between VCl_4 and isobutylene is probably the initiator.[79] The lack of shelf stability of these systems is a major limitation; prolonged storage would not be practical. Trapped initiator residue is also a problem. Further, the initiator may not be of general use, as complex formation is assumed to be necessary for polymerization. Short irradiation times, high yields, and high intrinsic viscosities of the resulting polymers are positive aspects of this system.

Cationic photoinitiation of epichlorohydrin was reported by Kaeriyama.[80] The initiators used were complexes of ferrocene and $TiCl_4$, $AlCl_3$, $SnCl_4$, $FeCl_3$, or $SbCl_3$. Polymers from epichlorohydrin were obtained when complexes of $SnCl_4$, $AlCl_3$, and $TiCl_4$ were used as initiators, but not with complexes of $FeCl_3$ or $SbCl_3$. The $SnCl_4$ complex gave 6% yield after seven hours irradiation, while the $AlCl_3$ complex and the $TiCl_4$ complex gave 34-37% with 2.5 to 6 hours of irradiation. An induction period of about one hour was observed, after which the polymerization continued when heated in the dark. Purely thermal polymerization at 60°C in the dark gave a small amount of polymer. Careful catalyst preparation was found to be crucial. The

above results were obtained when the complexes were prepared in air. When an inert atmosphere was employed in their preparation, the complex showed equal thermal and photoinitiated behavior. No mechanism was proposed. Problems associated with this system are similar to those encountered in previous systems, with the principal problem being the presence of trapped initiator residues in the polymer.

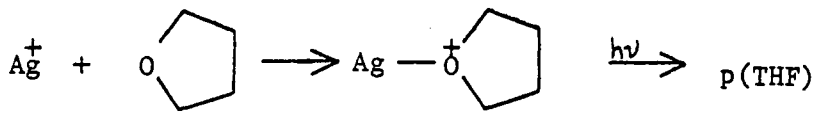
Some of the first initiators used to initiate polymerization via photolytic decomposition were "stable" diazonium salts.[81] These salts decompose as illustrated below.



The BF_3 can be utilized in polymerization of monomer by the usual Lewis acid initiation mechanism, presumably by reaction with protonic impurities. The evolution of nitrogen is a serious drawback for use in curing reactions of coatings. Even though highly non-nucleophilic anions are used, the most stable diazonium salts are still subject to thermal decomposition, giving very limited shelf life of monomer/initiator mixtures. Initiator fragments are also produced in this system and thus create a problem.

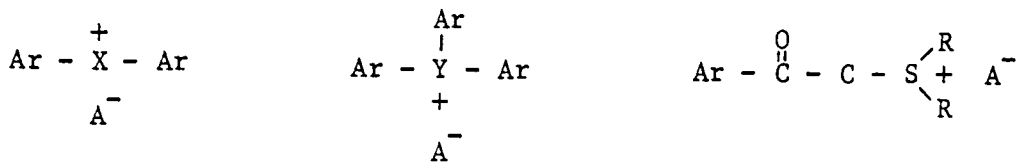
Several soluble silver salts have been shown to initiate the polymerization of THF.[82] Highly non-nucleophilic anions, BF_4^-, PF_6^-, SbF_6^-, and $CF_3SO_3^-$ were used in these polymerizations. The reaction was presumed to proceed by complex formation upon addition of initiator.

This complex, when irradiated, initiates the polymerization as shown below.



Yields of 50% were reported using these salts. In addition to the precipitation of silver metal as a fine powder, another limitation of this system is that only soluble salts can be used. This latter fact limits the use of these initiators to a few monomers which can complex with and dissolve these silver salts. A further limitation is the long irradiation time of 13.5 hours, followed by 11.5 hours in the dark.

Crivello and Lam have investigated a variety of salts of the types shown below,[83] which have been found to be efficient and powerful initiators of cationic polymerizations.



where Ar= phenyl or substituted phenyl
X = I, Br, Cl
Y = S, Se
A = BF_4, AsF_6, PF_6, SbF_6, ClO_4, CF_3SO_3, $SbCl_6$

Yields ranged from 14% to 97% depending on initiator, monomer, and irradiation time. These compounds absorb primarily below 300 nm,

although irradiation from 220 nm up to 365 nm is effective for initiation. The proposed decomposition and initiation mechanism for the halonium and triaryl sulfonium salts is shown below.

$$Ar_2X^+A^- \xrightarrow{h\nu} [Ar_2X^+A^-]$$

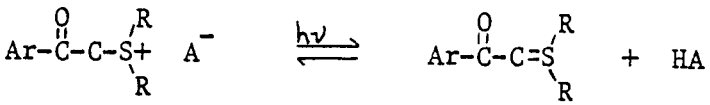
$$[Ar_2X^+A^-] \longrightarrow ArX^+ + Ar + A^-$$

$$A^- + ArX^+ + S\text{-}H \longrightarrow ArX^+H + S$$

$$A^- + ArX^+H \longrightarrow ArX + H^+A^-$$

$$H^+A^- + M \longrightarrow HM^+A^-$$

The extremely strong protonic acid HA is the active species that presumably initiates polymerization of monomer (M). The decomposition of the dialkylphenacyl sulfonium salts involves a reversible elimination of H^+.



A wide variety of monomers have been polymerized by the halonium and sulfonium salts, including styrenes, vinyl ethers, epoxides, cyclic acetals, cyclic sulfides, and lactones. Most polymerizations were carried out at 25°C in bulk. Photoinitiation of epoxides, cyclic acetals, and vinyl ethers was accomplished with dialkylphenacyl sulfonium salts, although these salts would not polymerize THF, ε-caprolactone, and α-methylstyrene. The diaryliodonium salts

are the most thermally stable. Monomer/initiator mixtures stored at 160°C for one year showed no polymer formation, indicating outstanding stability. Dye sensitization was explored in an attempt to extend the range of useful irradiation into the visible range. This attempt was largely successful, although lower yields and lower molecular weight products were found. The diarylchloronium and bromonium salts were not stable and decomposed readily in the dark. The dialkylphenacyl sulfonium salts exhibit good thermal stability. All of these salts have two limitations. First, these salts are not attractive from a synthetic point of view, as expensive reagents and low yields are involved. Secondly, various aryl initiator fragments remain trapped in the polymer.

In summary, many of the photolytic initiators which have been discussed suffer common problems. These problems are:

a) poor thermal stability,

b) production of initiator residue which is subsequently trapped in the polymer matrix,

c) specificity for certain monomer systems that can form complexes with the initiator, and

d) synthetic difficulties.

D. Statement of the Problem

In view of the potential usefulness of ionic polymerization reactions in the curing of coatings, it was decided to explore a different type of cationic photoinitiator. A photolytic initiator was

sought due to the ease of initiating polymerization with UV light and its efficiency as an energy source. As can be seen in the literature review, photoinitiated ionic polymerizations have not been widely studied. None of the previously investigated systems have involved initiation by a cation formed directly from photolytic decomposition. Thus, in each case, the initiator fragments are not attached to the polymer chain and are subject to migration out of the polymeric coating.

Therefore, the problem entailed finding a different photolabile molecule that would eliminate or minimize some of the limitations of the current cationic photoinitiators.

CHAPTER II

ANISYL-TYPE COMPOUNDS

A. Introduction

For a compound to be considered a photoinitiator, it must interact with light to produce an initiating species. Photolytic decomposition requires a bond that can be broken by energy available from the UV portion of the spectra. This corresponds to roughly 130 Kcal $mole^{-1}$ available at 220 nm. Table 1 gives a few examples of bond strengths in organic compounds,[84] illustrating that light of this wavelength has sufficient energy to induce decomposition of most single bonds. However, because this energy must first be absorbed and then be localized into a particular bond to cause rupture, many compounds are not readily decomposed by UV irradiation. Therefore, a weak bond and sufficient absorbance is desirable for facile UV induced cleavage.

Even when light is absorbed and bond cleavage does occur, this cleavage is nearly always homolytic in nature. Thus, to photolytically produce ions for use as initiators, a significant bias towards ion formation is necessary. This bias could be provided by stabilization of ions or a large difference in electronegativity between the two fragments.

A group which satisfies each of the above requirements is the p-methoxyphenyl group, also known as the anisyl group (An). The phenyl

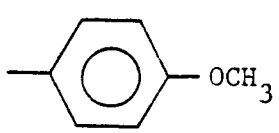
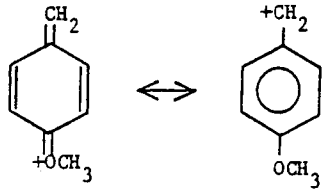
anisyl = 

TABLE 1

COMMON BOND STRENGTHS OF ORGANIC COMPOUNDS

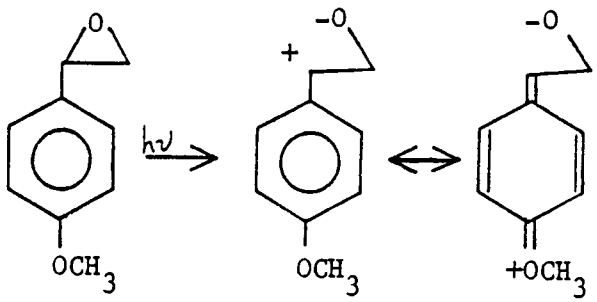
Bond	Bond Strength, kcal.
H-H	104
H_3C-H	104
Br-Br	46
H_3C-Br	70
H_3C-CH_3	88
C_6H_5-H	112

ring provides absorption in the UV region. The p-methoxy group can provide resonance stabilization to cations at the benzylic position.



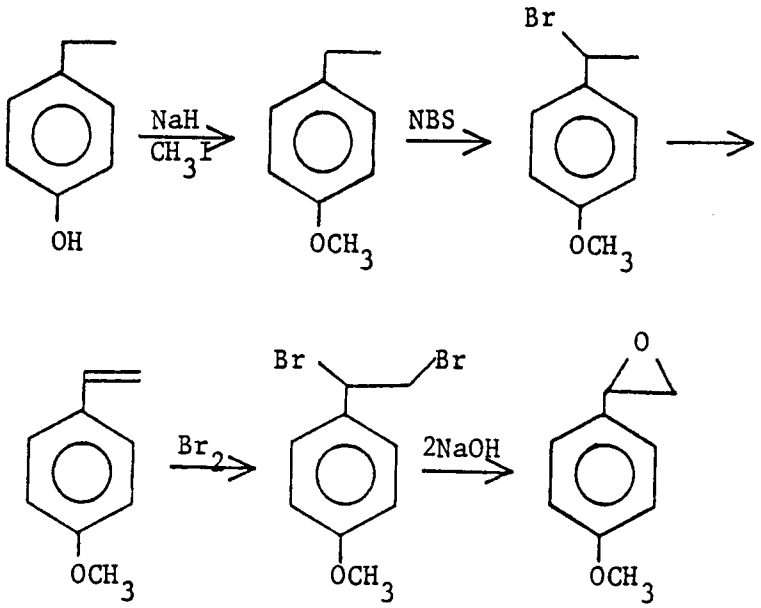
By appropriate choice of leaving group at the benzylic position, low bond strength and a large difference in electronegativity can be obtained.

(4-Methoxyphenyl)oxirane (MPO) has been shown to be photolytically active,[85] reportedly undergoing oxirane ring opening upon photolysis.

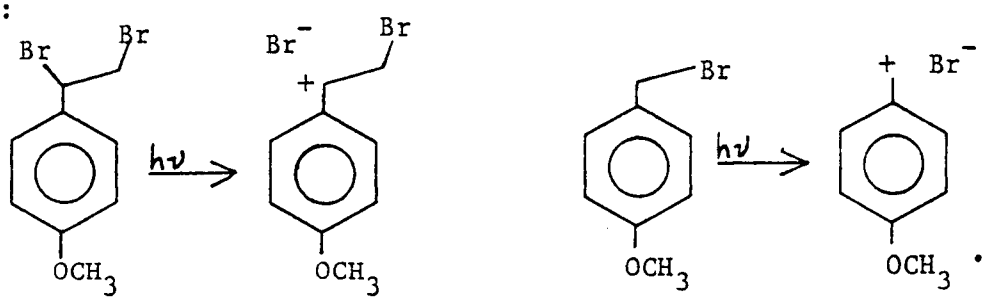


MPO

Resonance stabilization of the resulting benzylic cation is also shown. Ring opening chemical reactions of epoxides are well-known. The three membered ring is strained and relatively easy to open. Therefore, an important restraint in the synthetic route employed is that no heat treatment (distillation, etc.) can be used to purify MPO due to its sensitivity to thermal decomposition. With this in mind, the following synthetic scheme was constructed from the literature.[85,86,87] This scheme was modified when a synthetic shortcut was developed. The shorter final synthesis and its development will be discussed in the next section.



Other compounds with a substituent anisyl group were also investigated. 1-(1,2-Dibromoethyl)-4-methoxybenzene (DEMB), an intermediate in the MPO synthesis, was readily available. 1-(Bromomethyl)-4-methoxybenzene (BMMB) was synthesized from 1-methyl-4-methoxybenzene. It was proposed that the photolysis of these compounds could proceed as shown:

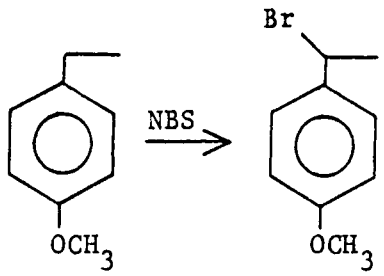


DEMB BMMB

Benzylic carbon-bromine bonds are weak and the resulting cation can be resonance stabilized. In addition, the bromide ion is not highly nucleophilic and thus might be a useful counterion.

B. Results and Discussion

Synthetic problems were encountered in the bromination of 1-ethyl-4-methoxybenzene (EMB). According to the literature,[86] a



EMB BEMB

10% molar excess of NBS was employed in the reaction mixture, giving high yields of 90-95%. Even after repeated attempts with purified reagents, these results could not be duplicated. A second product was also being synthesized in this reaction, causing decomposition of the reaction product when isolated. A deep purple color developed with concomitant formation of a solid and generation of heat when the isolated products were allowed to stand. Literature reports[87] indicated that DEMB developed a purple color upon standing. By preparing DEMB through bromination of a commercial sample of 1-(ethenyl)-4-methoxybenzene, a proton nuclear magnetic resonance (NMR) spectrum was obtained of DEMB (see Figure 1). An NMR spectrum of the reaction mixture was then analyzed (Figure 2) and found to contain both DEMB and 1-(1-bromoethyl)-4-methoxybenzene (BEMB). Further, when the reaction mixture was cooled below 0°C, white crystals precipitated which proved to be DEMB as analyzed by NMR. Experiments with 1:1 molar mixture of N-bromosuccinimide (NBS) to EMB gave 90% BEMB and no DEMB, indicating that the excess NBS was responsible for the formation of

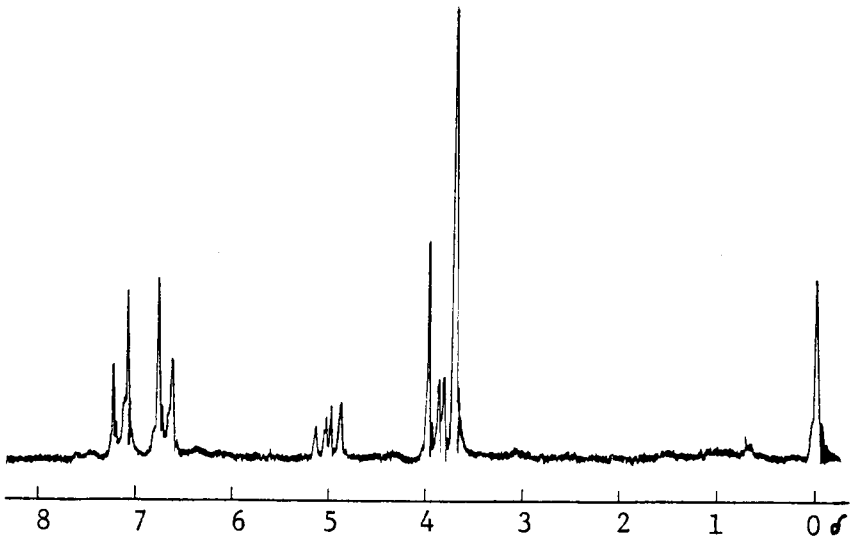


Figure 1. NMR spectrum of 1-(1,2-dibromoethyl)-4-methoxybenzene in $CDCl_3$ with TMS as internal standard.

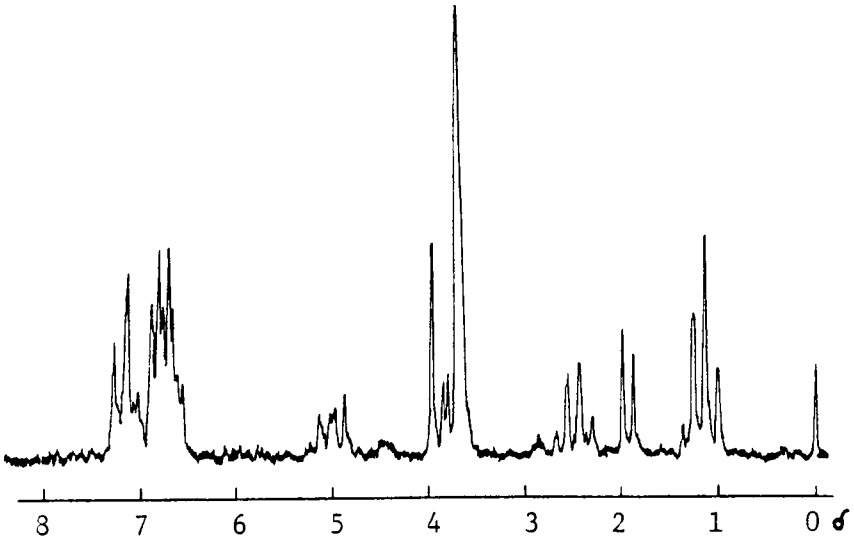
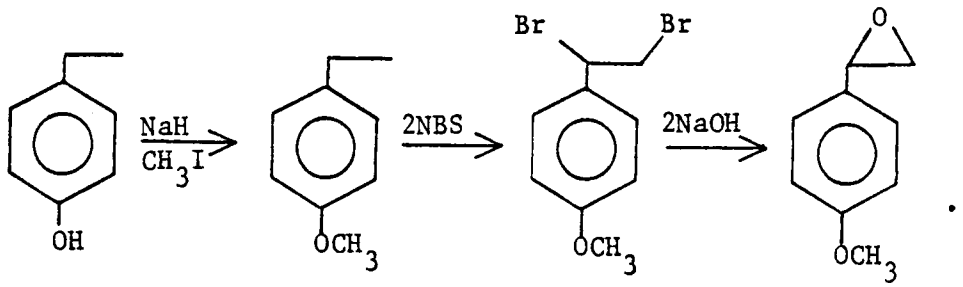


Figure 2. NMR spectrum of NBS reaction on 1-ethyl-4-methoxybenzene in CCl_4 with TMS as internal standard.

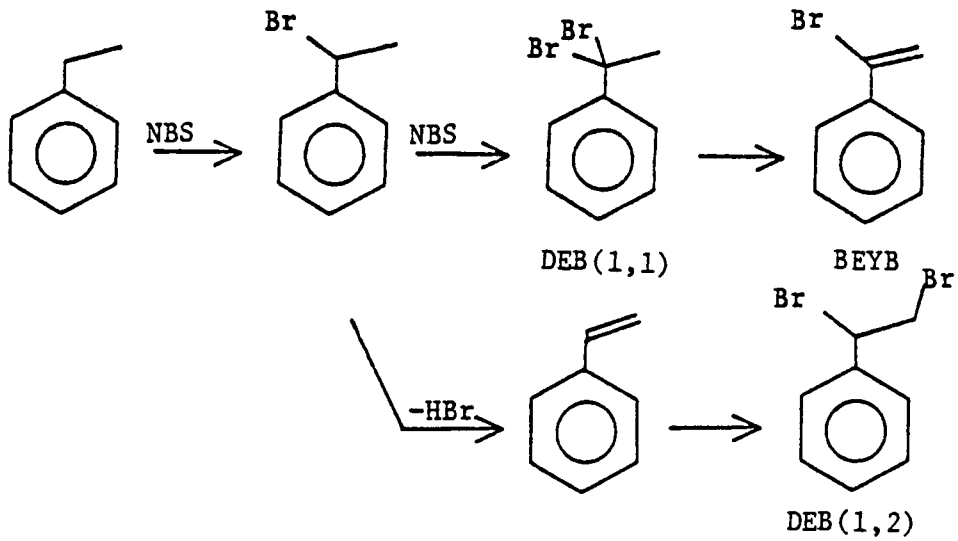
DEMB. Because DEMB was desired at a later stage of the synthesis, an attempt was made to maximize the production of this "side product." After a number of experimental variations of time, temperature, stoichiometry, and addition rate of NBS, a satisfactory procedure was developed. When two equivalents of NBS were added and the mixture refluxed overnight, a 70% yield of recrystallized DEMB was obtained. Full details of the experimental procedure are given in the Experimental section of this chapter. Thus, the overall synthetic scheme was significantly shortened to the following:



The question still remained as to the exact mechanism by which this reaction was occurring. To clarify this, two additional experiments were performed. In one, ethylbenzene was brominated with two equivalents of NBS. The other involved the bromination of (1-bromoethyl)benzene (BEB) with one equivalent of NBS. The products from each reaction were the same, indicating the initial production of BEB. Shown in Figure 3 is the NMR spectrum of the reaction mixture of

BEB

NBS and BEB. When the reaction mixture was concentrated and cooled below 0°C for 48 hours, a white crystalline solid precipitated. The NMR of this solid is shown in Figure 4. It was concluded from the NMR that this compound was (1,2-dibromoethyl)benzene[DEB(1,2)]. Three structures can be assigned from this spectrum in Figure 3, notably (1,1-dibromoethyl)benzene[DEB(1,1)], [DEB(1,2)], and (1-bromoethenyl)-benzene (BEYB). A proposed mechanistic pathway to each of these products is given below. The BEB has two reaction pathways available. In one, HBr is eliminated to give styrene. The HBr then reacts with the NBS to produce Br_2. This step is the second propagation step



in a common NBS chain reaction bromination. The Br_2 then adds to the double bond to give DEB (1,2). Alternatively, the BEB may be brominated at the benzylic position, giving DEB (1,1). This then eliminates HBr to give BEYB.

Because the p-methoxy group in 1-ethyl-4-methoxybenzene (EMB) should facilitate the elimination of HBr by stabilization of the forming

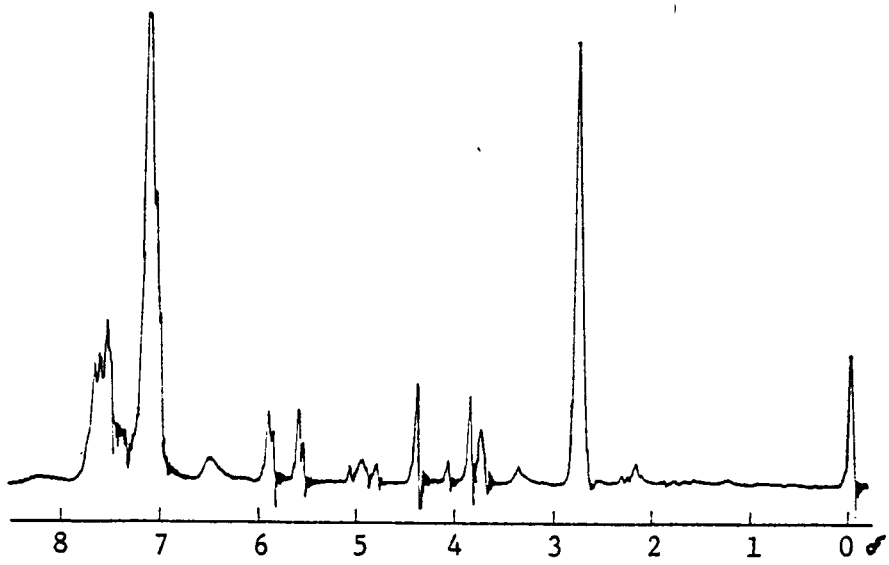


Figure 3. NMR spectrum of NBS reaction on (1-bromoethyl)benzene in CCl_4 with TMS as internal standard.

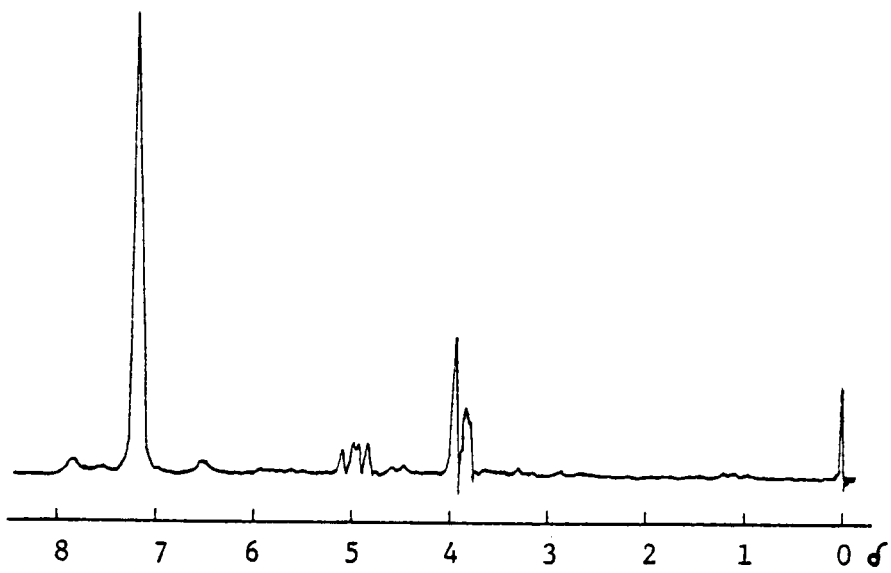
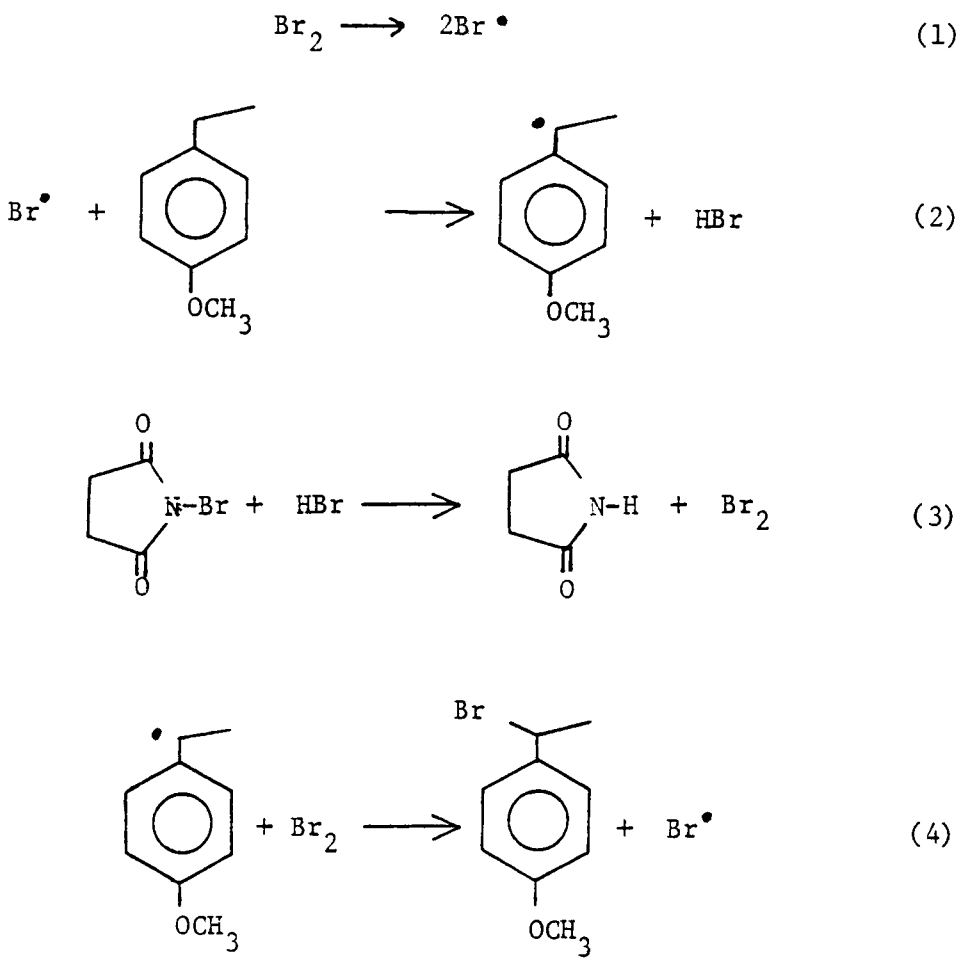
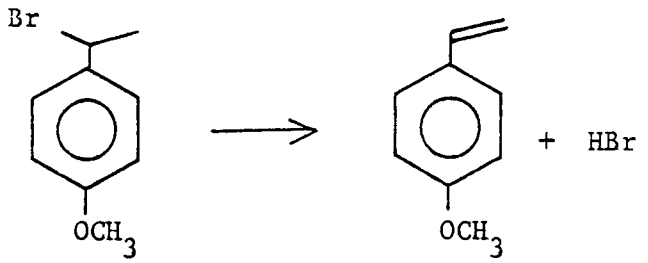


Figure 4. NMR spectrum of (1,2-dibromoethyl)benzene in $CDCl_3$ with TMS as internal standard.

cation, the elimination of HBr from EMB should be highly favored over formation of the geminal dibromo product. The initial formation of BEMB is assumed because the reaction can be carried out in two stages. Initially, one equivalent of NBS can be used, with a second equivalent added after several hours. Before the addition of the second equivalent of NBS, BEMB can be obtained if the reaction is stopped. Alternatively, two equivalents of NBS can be added at the beginning. Either method gives the same product, although the first method gives slightly better yields (typically 60% versus 70%). On this basis, the proposed mechanism for the synthesis of DEMB from EMB is given here.





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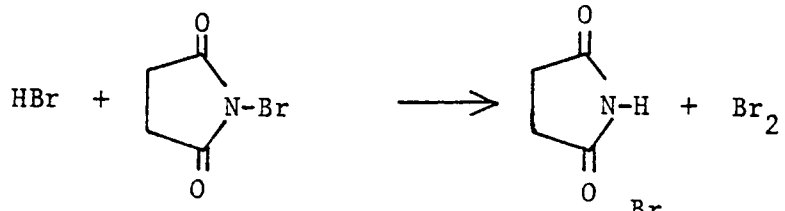

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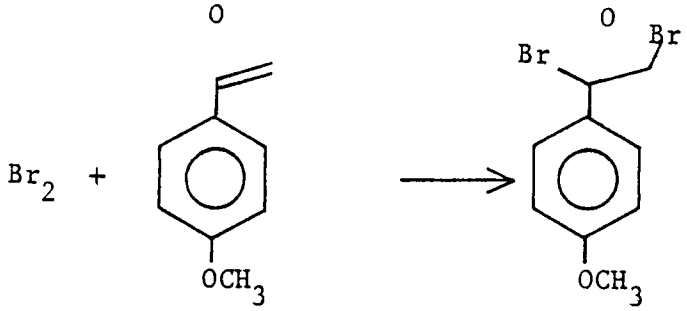
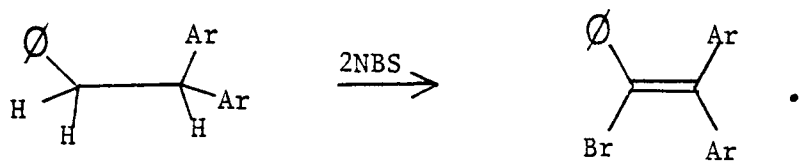


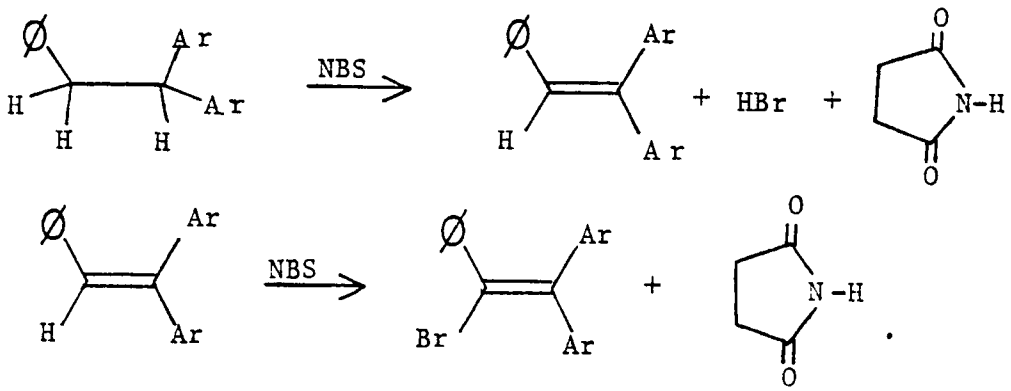
(7)

In the mechanism, the first four steps comprise the normal NBS chain reaction. The elimination of HBr, step 5, is aided by the p-methoxy substituent on the benzene ring. Step 6 is the same as step 3, and consumes the second equivalent of NBS while consuming HBr and producing Br_2. Production of a phenyl substituted diene through the use of one equivalent of NBS can be seen in Fieser and Fieser.[88] Allylic bromination followed by dehydrobromination upon further heating was proposed to explain their product.

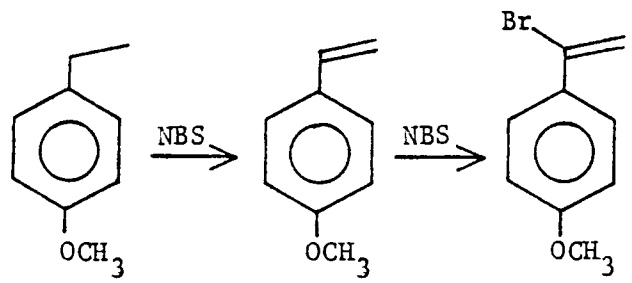
One other literature reference has been made to the simultaneous use of two equivalents of NBS. K. Sisido, K. Okano, and H. Nozaki reported the following synthesis:[89]



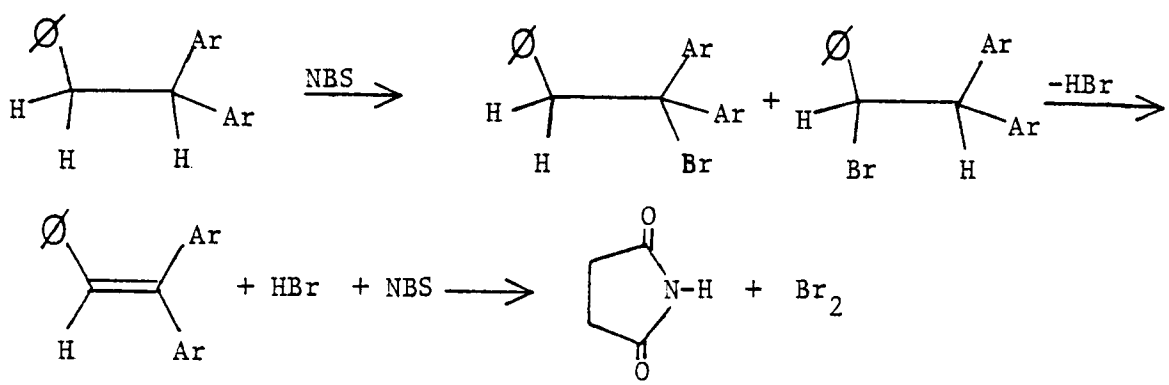
Substitution on the aryl rings is p-methoxy or p-ethoxy. The mechanism proposed is:

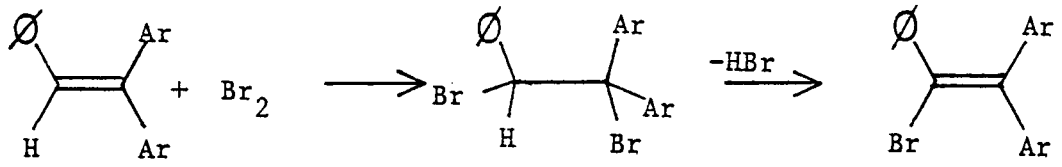


Simultaneous dehydrogenation and bromination was claimed. Our case is analogous but not identical. If EMP is used and the above mechanism is invoked, the following should occur.

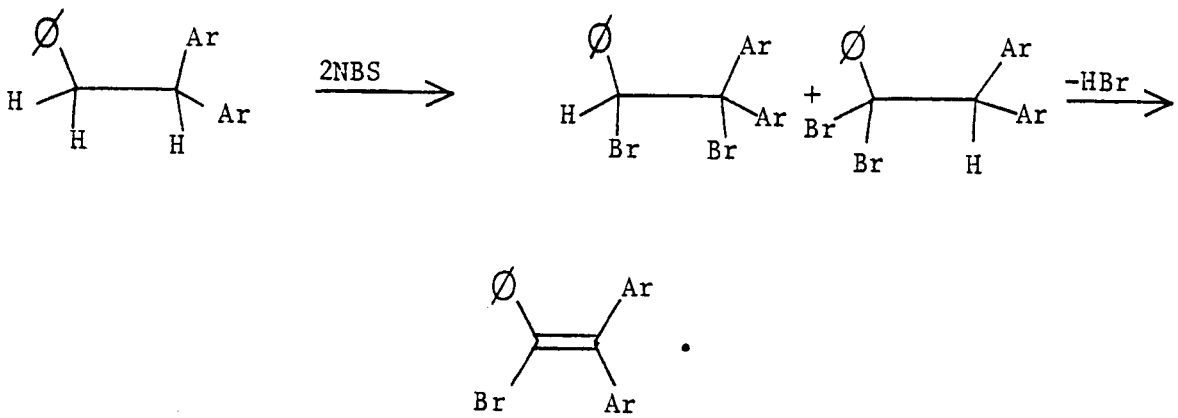


This is not the product obtained. On the other hand, the mechanism proposed by this research predicts the product that they obtained without the necessity of proposing a dehydrogenation step.





Thus, the mechanism proposed in this dissertation seems to be more general. Another less likely path may be:



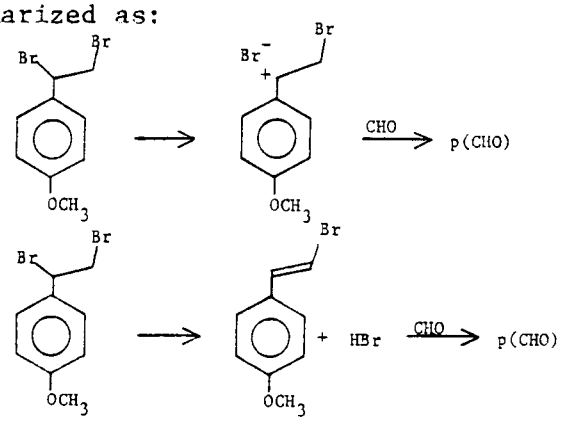
This is also consistent with our proposed mechanism.

The reaction of DEMB to give the epoxide, the final step of the synthesis, was straightforward. Purification of MPO was a problem, however. Dioxane, the solvent in the final step, was difficult to completely remove without destroying the unstable MPO. Several hours at 1 mm pressure and 25°C was sufficient to remove nearly all of the dioxane.

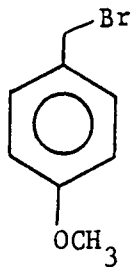
Experiments showed that MPO was not an effective photo-initiator. Extremely small amounts of polymer (less than 1%) were

formed upon irradiation of MPO-monomer mixtures, but similar amounts were also found when no irradiation was employed. The monomer used was 7-oxabicyclo(4.1.0)heptane, more commonly known as cyclohexene oxide (CHO). Polymerization was therefore attributed to the extreme instability of the MPO. Polymer was presumably formed from thermal ring opening reactions. The literature reports polymer formation when MPO is stored neat for over 48 hours.[87] This instability, coupled with the synthetic difficulties encountered, led to a decision to abandon further work on this compound as a photoinitiator.

DEMB looked attractive, however, as it could be readily prepared, purified by vacuum sublimation, and was a fairly stable solid. Polymerization experiments with this compound and CHO gave 25-30% yields of isolated polymer, but irradiation was not necessary to cause polymerization. Two processes could be responsible for initiation of polymerization; solvolysis involving the benzylic bromine, and elimination of HBr. In spite of the fact that CHO has a relatively low dipole moment, solvolysis of a secondary benzylic bromine is possible. This was shown in the subsequent studies of BMMB. HBr elimination is probably more favored, as DEMB slowly decomposes at room temperature with the release of HBr. These possible initiation reactions can be summarized as:



The possibility of solvolysis led to the investigation of BMMB. HBr elimination is not possible with this compound. However,



solvolysis in this case would produce a primary benzylic cation. This should not be as facile as production of the secondary benzylic cation as in DEMB. Polymerization with BMMB gave less than 1% polymer, with polymer being formed in the dark as well as upon irradiation. This seems to indicate solvolysis is active in initiation of polymerization in this system, although in small amounts.

None of these compounds proved useful as photoinitiators due to compound instability and/or polymerization reactions that are not caused by irradiation. Although some interesting synthetic and mechanistic chemistry was found, these compounds did not satisfy the requirements of an ionic photoinitiator.

C. Experimental

1. Materials

All materials used as received unless otherwise indicated.

Argon: Selox, passed through KOH and anhydrous $CaSO_4$ before use.

(1-Bromoethyl)benzene: Eastman, distilled immediately before use, bp 50°C at 2 mm.

N-Bromosuccinimide: Fisher, certified, recrystallized from water.

Calcium hydride: Fisher, purified, lump.

Calcium sulfate: Drierite, anhydrous.

Carbon tetrachloride: Fisher, certified, dried over 4A molecular sieves.

Cyclohexene oxide: Aldrich, dried with CaH_2 overnight, then distilled. The middle fraction, bp 40°C at 30 mm, was taken and stored over CaH_2 in the dark under argon.

Diethylether: Fisher, lab grade.

Dimethylformamide: Fisher, certified, dried with NaH, distilled immediately before use, bp 50°C at 20 mm.

1,4-Dioxane: Fisher, certified.

Ethylbenzene: Aldrich, distilled, bp 135-136°C.

1-Ethyl-4-hydroxybenzene: Eastman.

Ligroin: Eastman, practical, boiling range 63-75°C.

Magnesium sulfate: Fisher, anhydrous.

Methanol: drum grade.

Methyl iodide: Aldrich.

Sodium hydride: Alfa Products, 50% oil dispersion.

Sodium hydroxide: Fisher certified, aqueous solutions made to concentrations given.

Tetrahydrofuran: Fisher, certified, dried over $LiAlH_4$ and distilled before use (bp 65-66°C).

2. Equipment

Mercury arc lamp: Hanovia, 100 watt medium pressure mercury arc.

Nuclear magnetic resonance spectrometer: Varian, model T60.

Rotary evaporator: Buchi Rotovapor-R.

Sample tubes: 5 mm ID medium wall quartz tubes, 25-30 cm in length and sealed at one end.

Sunlamp: 275 W Sylvania.

Syringes: various sizes.

Vacuum oven: Precision Scientific Co., Thelco, Model 19.

Vacuum pump: Welch Duo Seal.

3. Experimental Procedures

a. Synthesis of 1-ethyl-4-methoxybenzene. EMB was synthesized according to the method given in the literature.[90] To 1.22 g (0.01 moles) of 1-ethyl-4-hydroxybenzene in 50 ml of tetrahydrofuran (THF) plus 5 ml dimethylformamide was added 2.13 g (0.015 mole) methyl iodide and 5 g (0.2 mole) NaH. The mixture, protected with a drying tube, was heated at reflux for 24 hours. The solvent was evaporated, and the residue distributed between 25 ml water and 100 ml ether. The ether was washed twice with H_2O, dried over $MgSO_4$, and then removed by a rotary evaporator. The liquid was washed with 1 N NaOH and then

distilled twice at 50°C and 2 mm pressure (lit.[90] bp 83-84° at 15 mm). The yield of EMB was 60%. The NMR spectrum of EMB has the following peaks: aryl, 4H, mult., 6.9 ; OCH_3, 3H, sing., 3.6 ; CH_2, 2H, quart., 2.6 ; CH_3, 3H, trip., 1.3 .

b. Synthesis of 1-(1,2-dibromoethyl)-4-methoxybenzene. A 22 g (0.12 mole) portion of NBS was placed into a three necked, 250 ml round bottom flask equipped with a mechanical stirrer and condenser. Then, 150 ml of dried CCl_4 and 13.6 g (0.10 mole) of EMB were added in succession. The suspension was stirred rapidly with simultaneous stirring and irradiation from a 275 W Sylvania sunlamp. After two hours, 18 g (0.10 mole) of NBS was added and the heat and radiation continued for two more hours. The light was then turned off with heating continuing to maintain reflux overnight. The mixture was then cooled, suction filtered, and the CCl_4 removed on a rotary evaporator. The residue was recrystallized from hot ligroin. The filtered succinimide was washed with 100 ml hot ligroin and this solution added to the recrystallizing solution. When cooled overnight, light tan needles of DEMB (mp 77-80°C, lit.[91] mp 80-81°C) precipitated, giving 65-70% yield. The NMR spectrum gives the following peaks: aryl, 4H, mult., 6.9 ; CH, 1H, quart., 5.5 ; CH_2, 2H, mult., 3.8-4.0 ; OCH_3, 3H, sing., 3.6 .

c. Synthesis of 4-methoxyphenyloxirane.[86] An 8.8 g (0.03 mole) portion of DEMB was dissolved in 50 ml of 1,4-dioxane. Then, 50 ml of 1.4 N NaOH was added in one portion with stirring at room

temperature. The mixture became turbid immediately. After 15 minutes mixing, the mixture was diluted to 500 ml with H_2O and extracted with ether. The ether solution was dried over $CaSO_4$ and the ether removed by rotary evaporator, giving a pale yellow oil. A vacuum of 1.0 mm mercury was applied at 25°C for several hours to remove residual dioxane. The product was stored at 0°C under dry argon. Yield of MPO was 70%. No bp was recorded as decomposition occurred upon heating. The NMR spectrum of MPO showed the following peaks: aryl, 4H, mult., 6.9 ; OCH_3, 3H, sing., 3.6 ; CH, 1H, mult., 2.9 ; CH_2, 2H, mult., 2.6 .

d. Reaction of ethylbenzene with NBS. Ethylbenzene, 10.6 g (0.10 mole), was added to 150 ml CCl_4 and 37 g (0.21 mole) NBS. The suspension was mechanically stirred with heating and irradiation for four hours, followed by heating with no irradiation for 15 hours. Reaction products were identified by NMR in solution. When the solution was cooled, white crystals precipitated. NMR showed these to be DEB (1,2). No isolated yields were obtained. The following NMR peaks were assigned for DEB (1,2): aryl, 5H, mult., 7.1 ; CH, 1H, quart., 5.0 ; CH_2, 2H, doub., 3.8 . For DEB (1,1) the NMR peaks are: aryl, 5H, mult., 7.1 ; CH_3, 3H, sing., 2.8 . For BEYB, the NMR peaks are identified as the following: aryl, 5H, mult., 7.1 ; CH_2, 2H, 2 doub., 5.9 and 5.6 .

e. Reaction of (1-bromoethyl)benzene with NBS. BEB, 18.5 g (0.10 mole) was added to 150 ml CCl_4 and 20 g (0.11 mole) NBS. Reaction conditions were identical to the NBS reaction described in

part d, as were products [DEB (1,2), DEB (1,1) and BEYB], analysis, and NMR assignments. No isolated yields were obtained.

f. Synthesis of 1-(bromomethyl)-4-methoxybenzene. A 12.1 g (0.10 mole) portion of 1-methyl-4-methoxybenzene was added to a stirred suspension of 20 g (0.11 mole) NBS in 150 ml CCl_4. The mixture was irradiated for two hours with simultaneous heating to maintain reflux. Upon cooling, the mixture was suction filtered, and the CCl_4 removed by rotary evaporator. The BMMB was then distilled (bp 80°C at 2 mm, lit.[92] bp 128-129°C at 16 mm) giving 19.0 g (90% yield) of clear liquid. NMR peak assignments were as follows: aryl, 4H, mult., 6.9 ; CH_2, 2H, sing., 4.3 ; OCH_3, 3H, sing., 3.5 .

g. Polymerization and isolation. CHO was dried over CaH_2 and distilled at 30 mm Hg and 40°C. The CHO was then placed into a dark bottle and sufficient initiator added to give the most concentrated initiator/monomer mixture desired. The bottle was closed with a septum and dry argon injected.

Thirty cm quartz sample tubes were prepared from quartz tubing (7 mm OD by 5 mm ID) by sealing one end. The tubes were placed in a KOH/methanol bath for 15 hours, washed with H_2O a minimum of ten times and left in a HCl/ethanol bath for 15 hours. The tubes were washed repeatedly with H_2O again and dried in an oven at 100°C for 24 hours. When ready for use, the tubes were removed and immediately closed with a septum secured by wire. A vacuum of 1 mm Hg was then applied using a vacuum hose equipped with a needle. While evacuating

the tube, a bunsen burner was used to heat the tube for twenty minutes. The tube was then allowed to cool and dry argon was injected. While the argon was flowing, the monomer/initiator mixture was injected with a syringe. Dilutions to lower initiator concentrations were done in the sample tubes by adding CHO to the appropriate amount of monomer/ initiator mixture. Most samples were five ml in volume.

The samples were irradiated with a 100 watt medium pressure mercury arc lamp. The lamp was cooled with a quartz immersion cooling well and the lamp and samples immersed in a water bath at 20-25°C. Distance between the sample and the lamp was 5-7 cm.

After the samples were irradiated, they were then poured into 120 ml of rapidly stirred methanol, the polymer allowed to settle, and liquid decanted off. The polymer was dried under vacuum at 40°C for 10 hours and then weighed to determine yield. Yield was calculated as a weight percentage of isolated polymer compared to initial monomer.

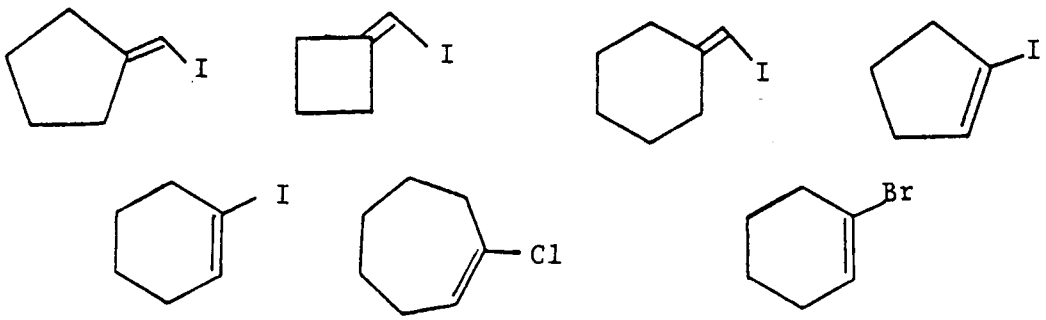
CHAPTER III

VINYL HALIDES

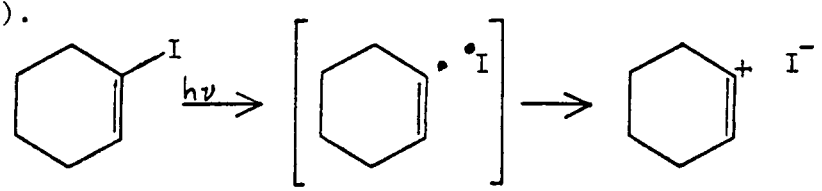
A. Introduction

Stable carbocations have been used as polymerization initiators for some time, as has been discussed in Chapter I. These carbocations have a positive charge located on a carbon atom that has three substituents, and are also known as trisubstituted carbenium ions. These ions have been known and studied for many years and play an important role in modern mechanistic organic chemistry. In contrast, the disubstituted carbenium ion, or vinyl cation, has only been studied for the last fifteen years. The lack of reactivity of vinyl halides in solvolysis reactions was largely responsible for the traditional view that vinyl cations did not exist. In recent years, however, many vinyl cations have been found as intermediates,[93-96] and many of the rearrangements observed in trisubstituted carbenium ions have also been found to occur in vinyl cations. The production of vinyl cations is greatly enhanced by electron donating substituents such as aryl and vinyl groups, as well as by non-classical stabilization from cyclopropyl groups. Vinyl cation production via solvolysis is also assisted greatly by the use of good leaving groups such as triflate and nonaflate. Using both of these techniques, a large variety of disubstituted carbenium ions has been studied.

Production of vinyl cations by the use of UV irradiation was first reported by McNeely and Kropp.[97] They irradiated a variety of vinyl halides and analyzed the photolysis products to determine the



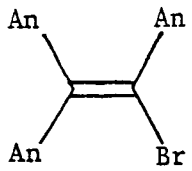
mechanistic pathway(s) of their decompositions. They found vinyl cations produced from each vinyl halide shown above. The proposed mechanism given for cation production is illustrated for 1-iodocyclohexene (ICH).



ICH

Initial homolytic cleavage of the carbon-halogen bond gives free radical products, followed by an electron transfer to give an ion pair. The amount of free radical and ionic products vary according to the vinyl halide used and solvent employed. Products from both ionic and radical pathways were found for these compounds, along with products resulting from rearranged ions in some cases.

Another vinyl halide has also been found to be photolytically active.[98] This tri-anisyl vinyl bromide was irradiated and the resulting vinyl cation was trapped with azide ion and then analyzed. Other than



the cited studies, very little work has been done in the area of vinyl halide photolysis, as reflected in a recent book on the subject of vinyl cations.[99]

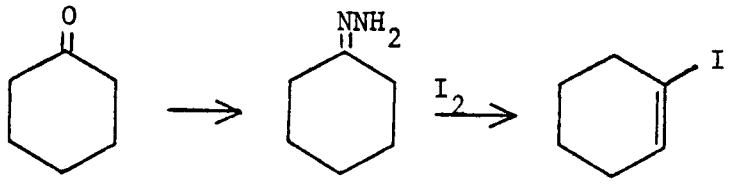
Several considerations make vinyl halides attractive as ionic photoinitiators for polymerization. First, vinyl halides are generally unreactive in many chemical reactions, indicating desirable stability. Thus, monomer/initiator mixtures should have a long shelf life. Another positive aspect is the instability of the resulting vinyl cation, indicating the possibility of polymerization of a wide range of monomers and a rapid initiation step. Lastly, a range of compounds can be synthesized to provide a variety of choices in absorbance ranges, cation stabilities, and useful counterions.

B. Results and Discussion

1. 1-Iodocyclohexene as Photoinitiator

The vinyl iodide ICH seemed a likely candidate for initial experiments to determine the feasibility of using vinyl halides as photoinitiators. Of the cyclic vinyl halides investigated by McNeely and Kroop, this compound gave more ionic products upon irradiation than any of the other compounds.[97] From a synthetic viewpoint, ICH was also

attractive, as several routes were available, one of which involved only two steps. The synthetic path thus chosen is shown below.[100]



This route offers simplicity and utilizes common starting materials and reagents. Overall yields are about 40-50%.

The choice of monomer was also affected by several factors. First, an ionically polymerizable monomer was needed. If possible, the monomer should be polymerizable by only a cationic mechanism. This would aid in elimination of alternative initiation mechanisms. Reasonable molecular weights should be attainable via this mechanism to aid isolation procedures. This implies good reactivity and lack of rapid termination steps.

The monomer should give a fairly well-characterized polymer and be fairly readily available. One of the most important requirements is transparency in the UV region necessary for initiation. Depending on the compound used as initiator, UV transparency above 230 nm would be most desirable. A monomer fitting all the above requirements was 7-oxabicyclo(4.1.0)heptane, commonly known as cyclohexene oxide (CHO). The absorbance UV spectrum is given in Figure 5, showing CHO is suitably transparent above 235 nm. CHO readily polymerizes via a cationic mechanism,[101] but produces only oligomers via anionic polymerization,[102] and does not polymerize by a

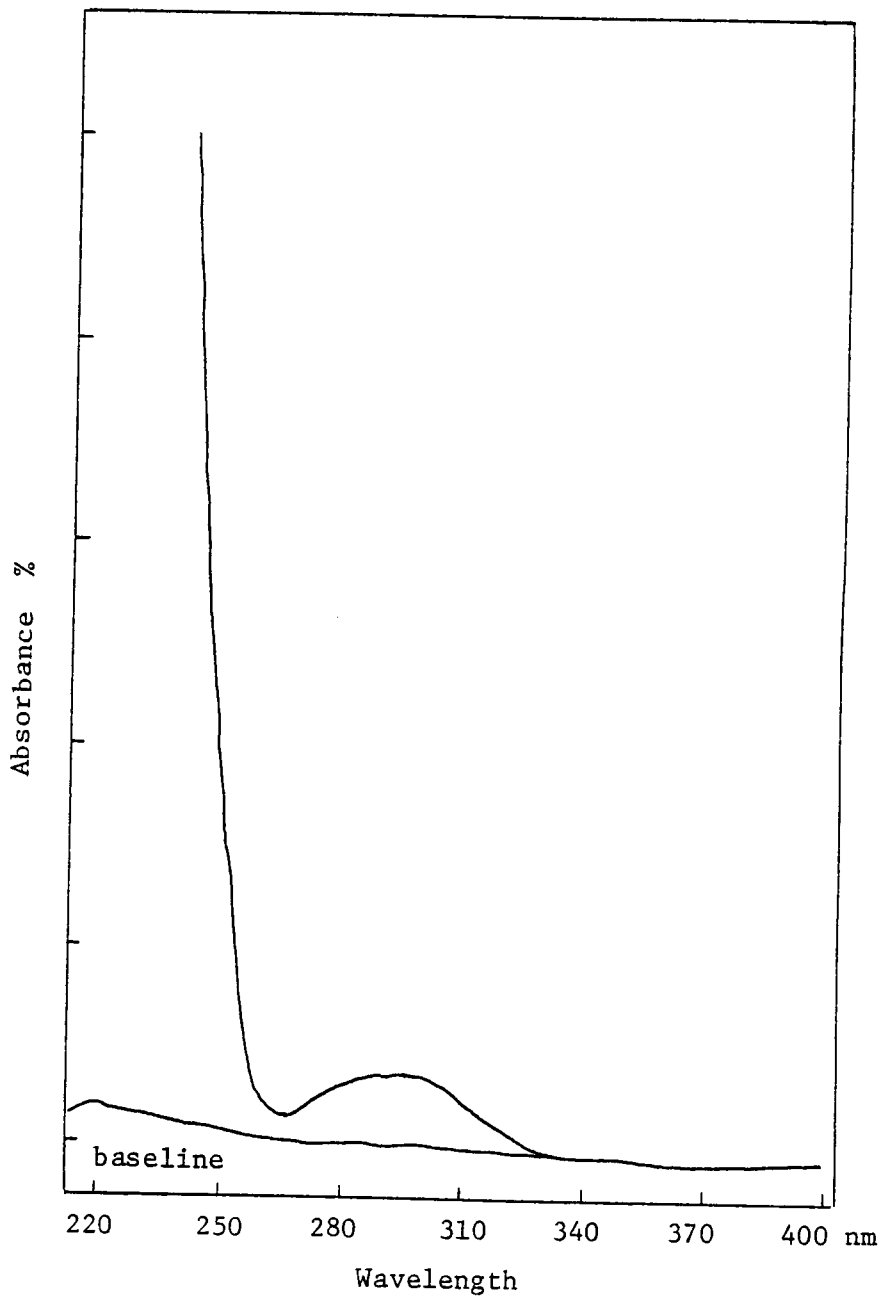


Figure 5. UV spectrum of cyclohexene oxide (50% in ether).

free radical mechanism. It is also fairly readily available. Thus, CHO was the monomer of choice for our investigations.

Using the same polymerization technique as previously described, ICH was used to polymerize CHO in bulk. Polymer was formed, as shown by formation of a white precipitate when a sample was dropped into methanol. The IR and NMR spectra of poly(CHO) are shown in Figures 6 and 7, confirming the expected polymer structure. The experimental results of photoinitiated polymerizations of CHO initiated by ICH are given in Table 2 and Figures 8 and 9. As can be seen, no polymer is produced when irradiation is absent. After nine months in the dark at 25°C, ICH/CHO mixtures showed no polymer formation. Even when heated to 100°C for three hours, no polymer was formed, indicating good shelf stability. However, yields of polymer are quite low even when irradiated. This was attributed to two factors. The UV absorbance of ICH is not great, as shown in Figure 10. Thus, many photons of light are not absorbed and thus are not effective in initiating polymerization. Secondly, the vinyl cation is quite unstable and thus difficult to form. This instability is increased because the preferred vinyl cation geometry is linear. A linear structure is prohibited in this case because of the cyclic nature of the cation. This relative instability contributes to low quantum yields. Of the photons that are absorbed, only a few are effective in causing bond cleavage. Even when bond cleavage takes place, side reactions and recombination in the solvent cage can occur. A further problem which may also be present

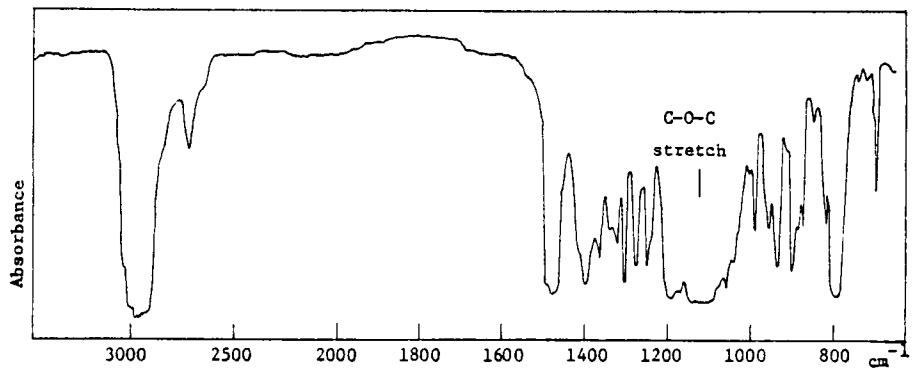


Figure 6. IR spectrum of poly(cyclohexene oxide).

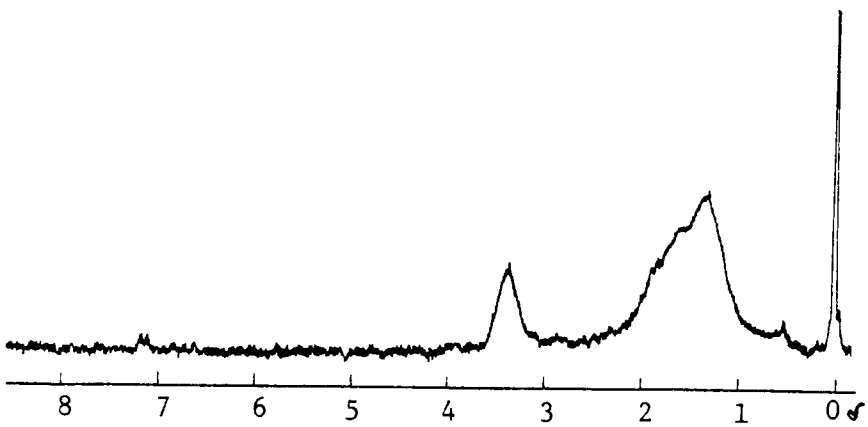


Figure 7. NMR spectrum of poly(cyclohexene oxide) in $CDCl_3$ with TMS as internal standard.

TABLE 2

EXPERIMENTAL DATA FOR ICH PHOTOINITATION OF CHO

ICH conc.,%	Irradiation time, hr.	Polymer Yield,%
0	24	0
3.0	0	0
1.5	25	2.0
1.5	25	2.1
3.0	25	2.2
3.0	25	2.5
6.5	25	1.4
6.5	25	1.6
9.5	25	1.1
16.0	25	0.9
3.0	4	1.0
3.0	6	2.0
3.0	9	2.2
3.0	12	3.0
3.0	15	3.1
3.0	19	2.9
3.0	23	2.8
3.0	26	2.6
3.0	32	2.3

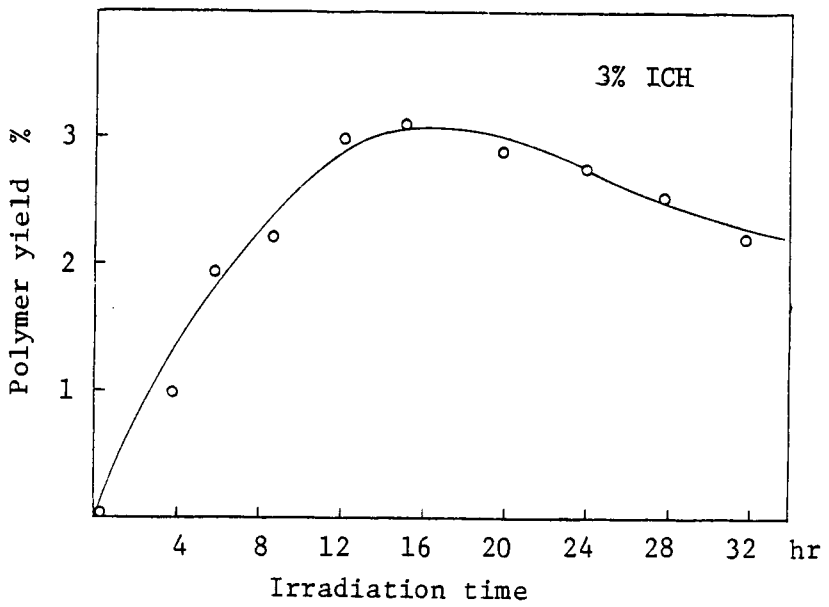


Figure 8. Polymer yield as a function of irradiation time for ICH initiation of CHO.

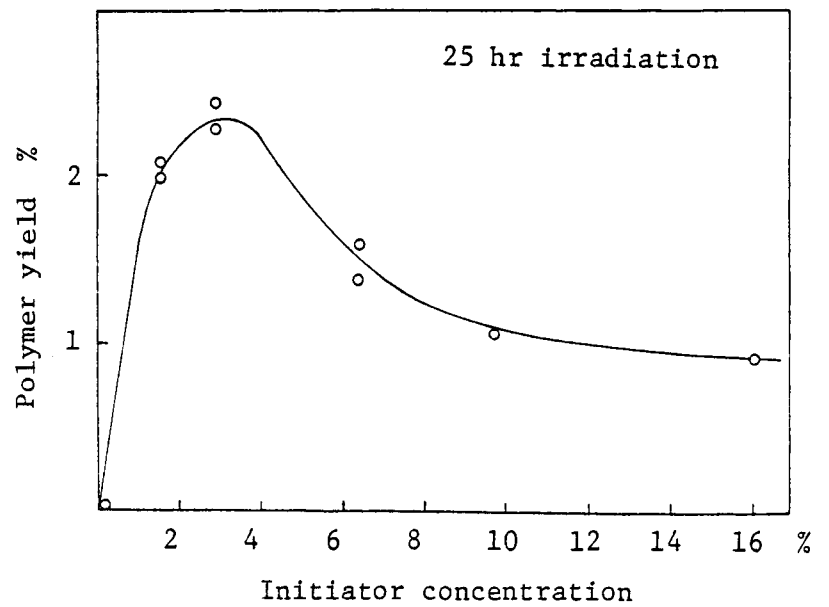


Figure 9. Polymer yield as a function of initiator concentration for ICH initiation of CHO.

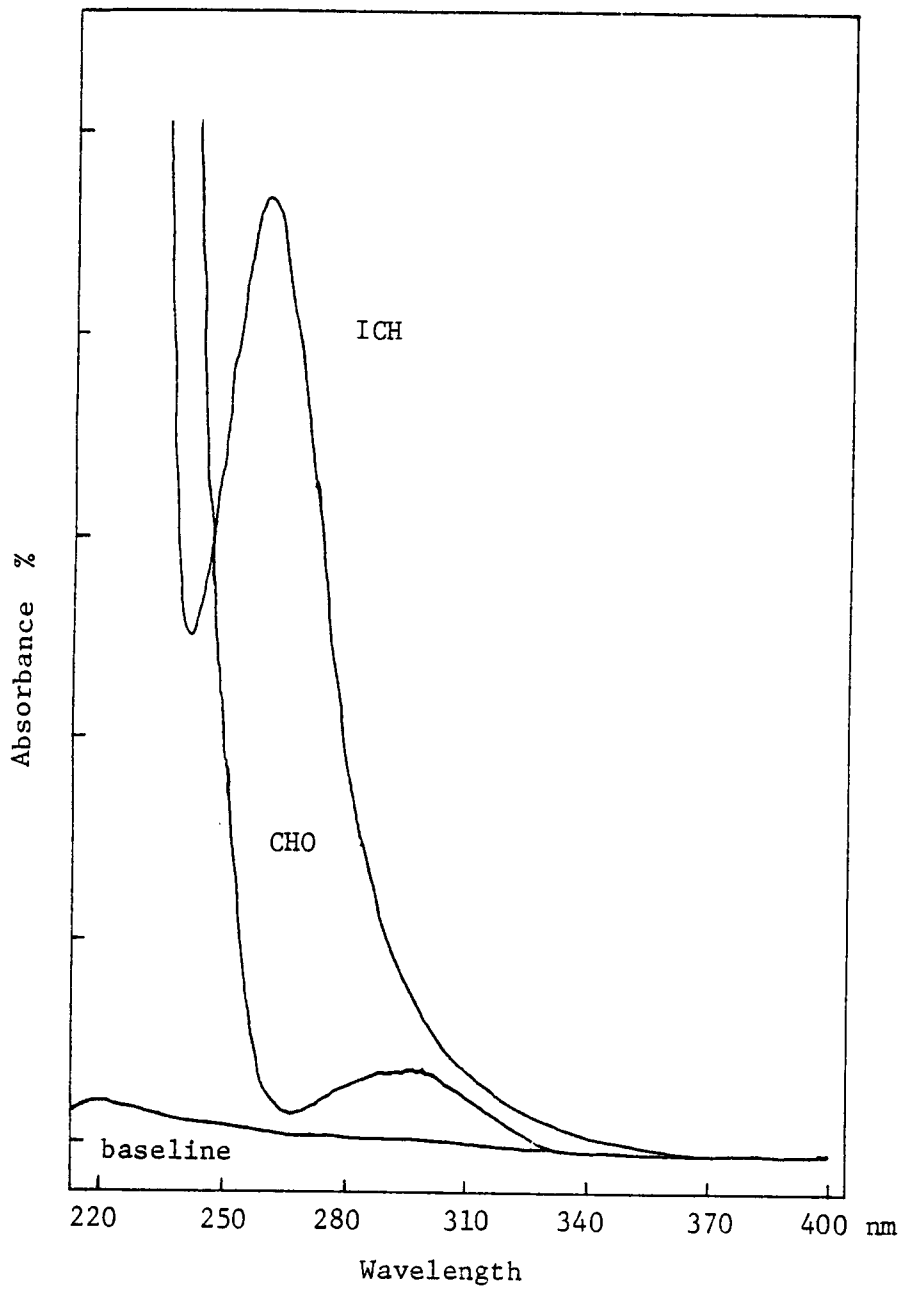
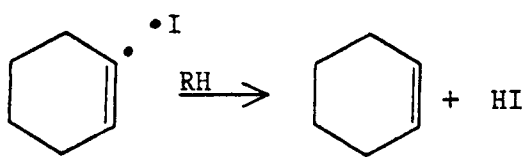


Figure 10. UV spectrum of ICH (0.82 g/l) and CHO (50%) in ether.

is that of the exclusion of oligomeric products from the isolated polymer. These oligomers may be fractionated out in the isolation step due to their solubility in methanol. Therefore, these would not be accounted for in the isolated polymer yields. A GPC analysis of the sample would show this, but this analytical tool was not available during the research.

After 24 hr irradiation, only 0.56% of the initiator molecules initiated polymerization, as calculated from molecular weights and initiator concentrations. The molecular weights of polymer samples at ICH concentrations of 1.5 wt % and 10 wt % are 31,000 and 22,000 g/mole, respectively. These were determined by dilute solution viscosity as described later, using $[n]=3.5 \times 10^{-5} \bar{M}_v^{0.83}$. From flow times, intrinsic viscosities were found. These values were calculated from extrapolation of $\ln \eta_v$ and η_{sp}/C versus concentration.

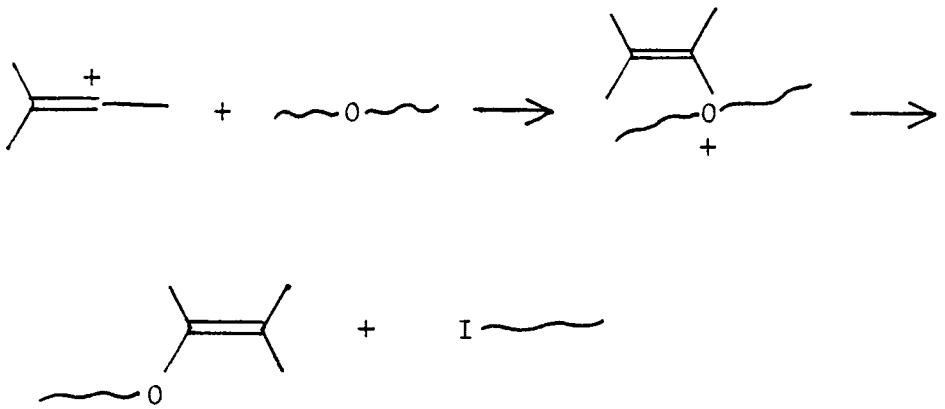
Lower molecular weight oligomers may be produced by degradation of previously formed polymer chains. Using ICH and long irradiation times, three mechanisms may be responsible for oligomer production: HI cleavage of the ether bonds, photolytic degradation, and vinyl cation attack on the polyether chain. HI can be produced in a free radical side reaction as shown below. This protonic acid is



known to cleave low molecular weight ethers, and thus could also cause breakage of the polyether main chain. Polyethers are also subject to

photolytic degradation. In the case of p(CHO), the extent of this degradation was determined experimentally. A solution of 10% p (CHO) in CHO was irradiated for 48 hours. Isolated polymer yields were about 90% of original polymer as compared to isolation of 95% for a non-irradiated solution of 10% p(CHO) in CHO. This indicates a 5% loss of polymer due to degradation and subsequent fractionation. Molecular weights were 15,500 g/mole (±1500) before irradiation, and 15,000 g/mole (±1500) after irradiation. This indicates little or no contribution to polymer degradation.

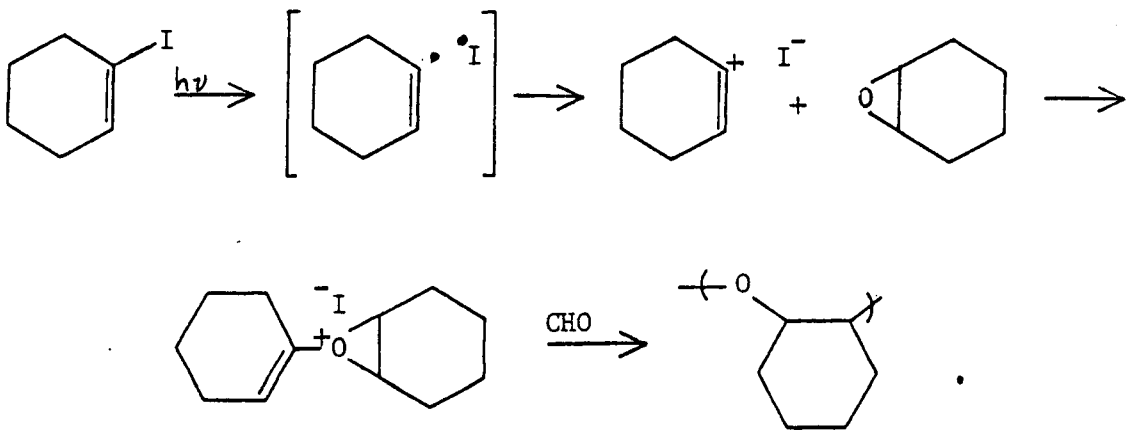
The third degradation mechanism involves attack on the polyether chain by the vinyl cation. After initial formation of polymer, photolysis of initiator molecules may cause degradation as shown.



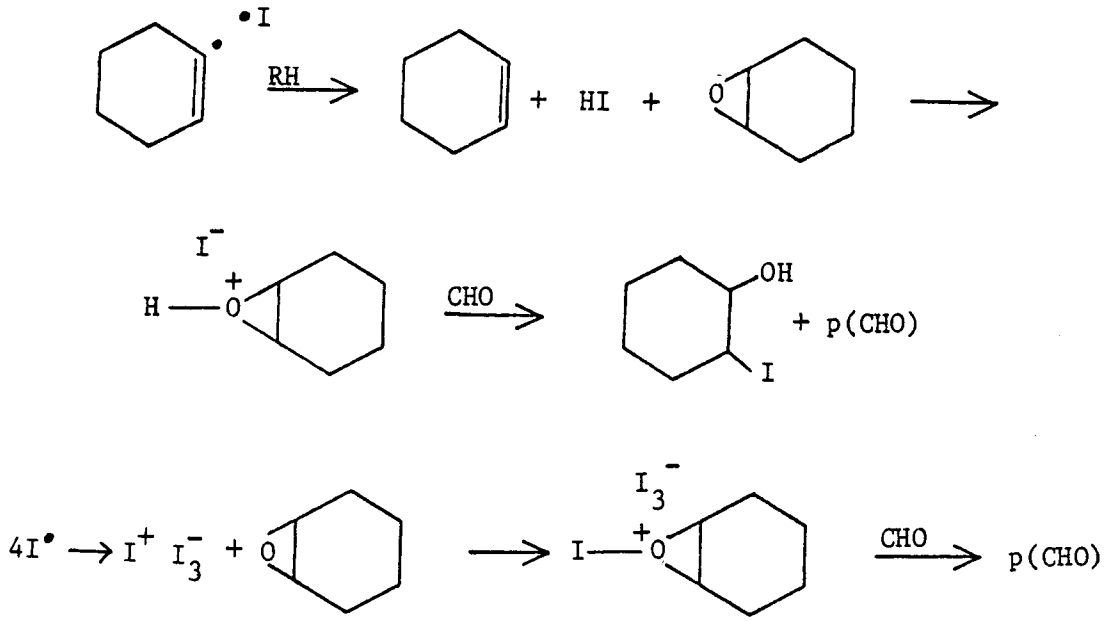
These effects might be isolated and observed if a solution of known molecular weight polymer and initiator was photolyzed and then isolated and analyzed. The task of finding an ideal solvent proved overwhelming, so a marginal substitute was employed. Cyclohexane was chosen as solvent because of its transparency to UV light and ability to dissolve p(CHO). However, it is a poor choice because of its nonpolar nature and

inability to solvate ions effectively. A 5% solution of CHO in 40 ml cyclohexane with 1% ICH was photolyzed for 20 hours at 25°C. The isolated polymer was determined by dilute solution viscosity to have an $\bar{M}_v$ of 12,500 g/mole, as compared to $\bar{M}_v$=15,000 before irradiation. This is presumed to be primarily due to a combination of degradation via HI and vinyl cation attack on the polyether chain. As will be shown later, vinyl cation attack has been eliminated as a degradative mechanism. This leaves HI as the primary contributor to chain degradation. These degradation mechanisms, coupled with the possible fractionation in the isolation procedure, could produce the maximum observed in Figures 8 and 9 (p 57).

The proposed mechanism for polymerization is given as follows:



Side reactions involving the free radical intermediates might also cause the formation of polymer. These reactions are shown below. As shown in the first reaction, if abstractable hydrogens are present, the initial free radical products may react to form HI. As these were



bulk reactions, the most available source of hydrogen is CHO. To ascertain the extent of polymer formation due to hydrogen abstraction by I•, the effectiveness of HI as a polymerization initiator was investigated. Gaseous HI was produced by the method described in Vogel.[105] Dry HI causes a brown color to form in CHO, along with extremely small amounts of polymer (less than 1%). The brown color could be due to formation of halohydrin by ring opening addition of HI.

The second side reaction involves polymerization by iodine. Molecular iodine initiates polymerization of CHO, shown by addition of I_2 to CHO and precipitation of the polymer in methanol. This possible side reaction would be more important at high initiator concentrations. Polymer yields from I_2 were 30-50% and the product was slightly yellow.

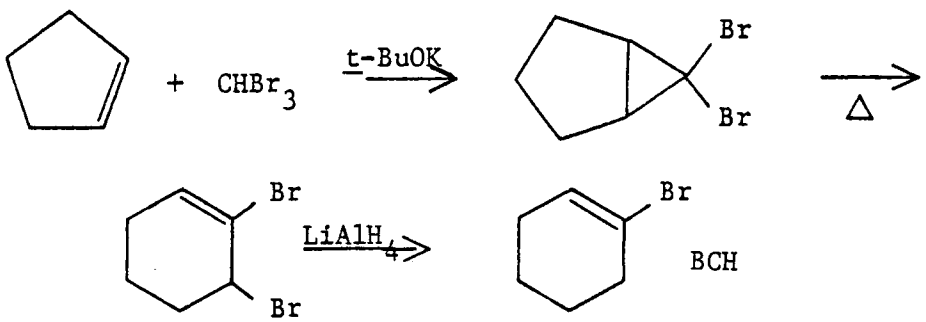
The exact contribution of each of these reactions to polymer yield cannot be determined. However, additives were used to aid in the determination of the polymerization mechanism. Water (0.1 ml) and

triethylamine (TEA)(0.1 ml) were added to separate solutions of 2% ICH in CHO and irradiated for 24 hr. Upon addition to excess methanol, no precipitate or cloudiness was observed. Because H_2O and TEA are efficient inhibitors of cationic reactions, while anionic polymerization should not be inhibited by TEA, the polymerization mechanism was shown to be cationic. The high molecular weights found are also evidence against an anionic mechanism. When a radical inhibitor, 4-t-butylpyrocatechol (3%), was used as an additive and the sample irradiated for 24 hr, a 1% yield of polymer was isolated. This compares to a 3% yield under the same conditions without an additive. The fact that polymer was formed indicates that polymer was initiated by the vinyl cation. The reduction in yield suggests three possibilities. First, some of the initial products of the homolytic cleavage are being consumed by the radical inhibitor before undergoing the electron transfer step. Secondly, some of the polymer in the uninhibited case may indeed be coming from the side reactions shown above. When the free radical trap is present, these reactions are much less important, thus lowering polymer yield. The third possibility involves the termination of cationic chain growth polymerization by 4-t-butylpyrocatechol. Alcohols can terminate cationic polymerization and this inhibitor has a phenol group. The efficiency of 4-t-butylpyrocatechol as a cationic inhibitor is not great, but may contribute to a reduction in polymer yield. Attempts were made to use ICH as a photoinitiator for 1,2,7,8-diepoxyoctane (DEO). Because this monomer is difunctional, crosslinked and insoluble polymers could be expected. When pure DEO

samples with ICH were irradiated for 22 hours, no polymer could be isolated. A 50:50 volume ratio (60:40 molar ratio) of CHO:DEO with ICH irradiated for 22 hr gave cloudiness when poured into methanol after irradiation. No significant amount of crosslinked material was formed, however.

2. 1-Bromocyclohexene as Photoinitiator

A second cyclic vinyl halide, 1-bromocyclohexene (BCH), was also synthesized and used as a photoinitiator. Even though McNeely and Kropp's work showed that this compound gave a lower yield of ionic products and a higher percentage of free radical products,[97] BCH was readily synthesized and had interesting possibilities as a photoinitiator. The synthesis of BCH is shown below.[104] The overall yield of BCH was 40%.



When BCH was used to polymerize CHO, polymer was obtained when the mixture was irradiated, but no polymer was produced in the absence of irradiation. The polymer has the same structure as the polymer produced from ICH initiation. Experimental results of BCH initiation are shown in Figures 11 and 12 and Table 3. Monomer/initiator mixtures were stable for up to nine months at 25°C in the dark.

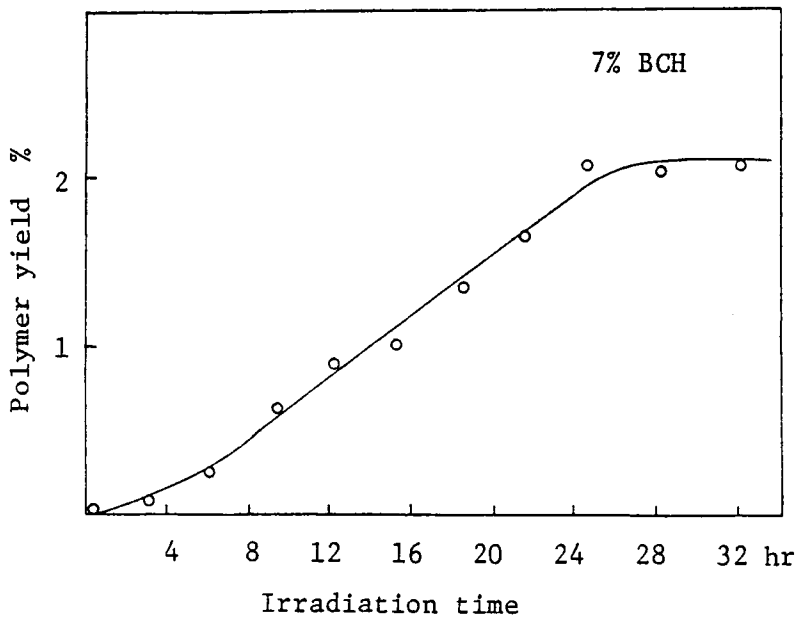


Figure 11. Polymer yield as a function of irradiation time for BCH initiation of CHO.

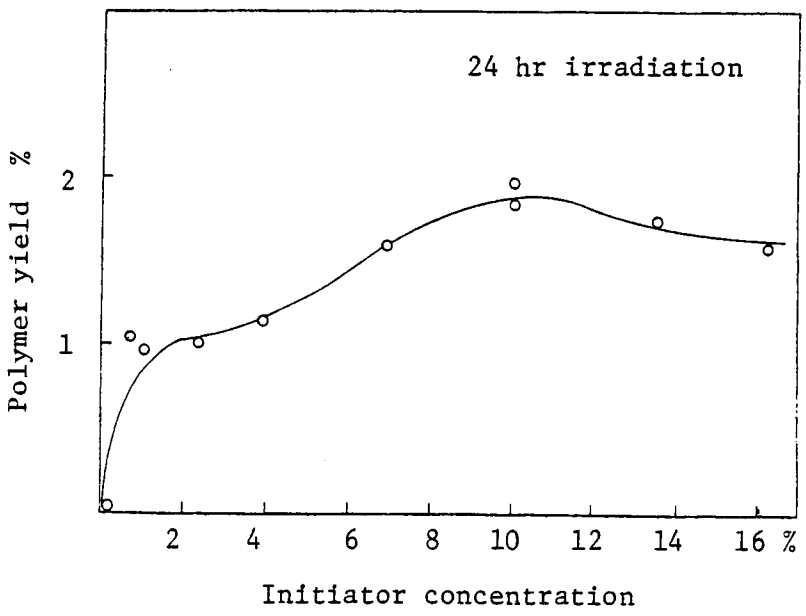


Figure 12. Polymer yield as a function of initiator concentration for BCH initiation of CHO.

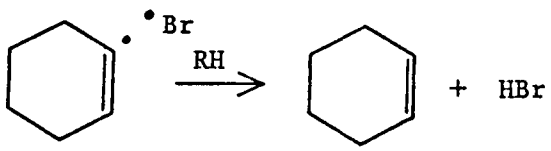
TABLE 3

EXPERIMENTAL DATA FOR BCH PHOTOINITIATION OF CHO

BCH Conc.,%	Irradiation time, hr.	Polymer Yield,%
0	24	0
4.0	0	0
0.8	24	1.1
1.0	24	0.9
2.5	24	1.0
4.0	24	1.2
7.0	24	1.6
10.0	24	1.8
10.0	24	2.0
13.5	24	1.7
16.0	24	1.6
7.0	3	0.1
7.0	6	0.3
7.0	9	0.6
7.0	12	0.9
7.0	15	1.0
7.0	19	1.4
7.0	22	1.6
7.0	24	2.1
7.0	28	2.0
7.0	32	2.0

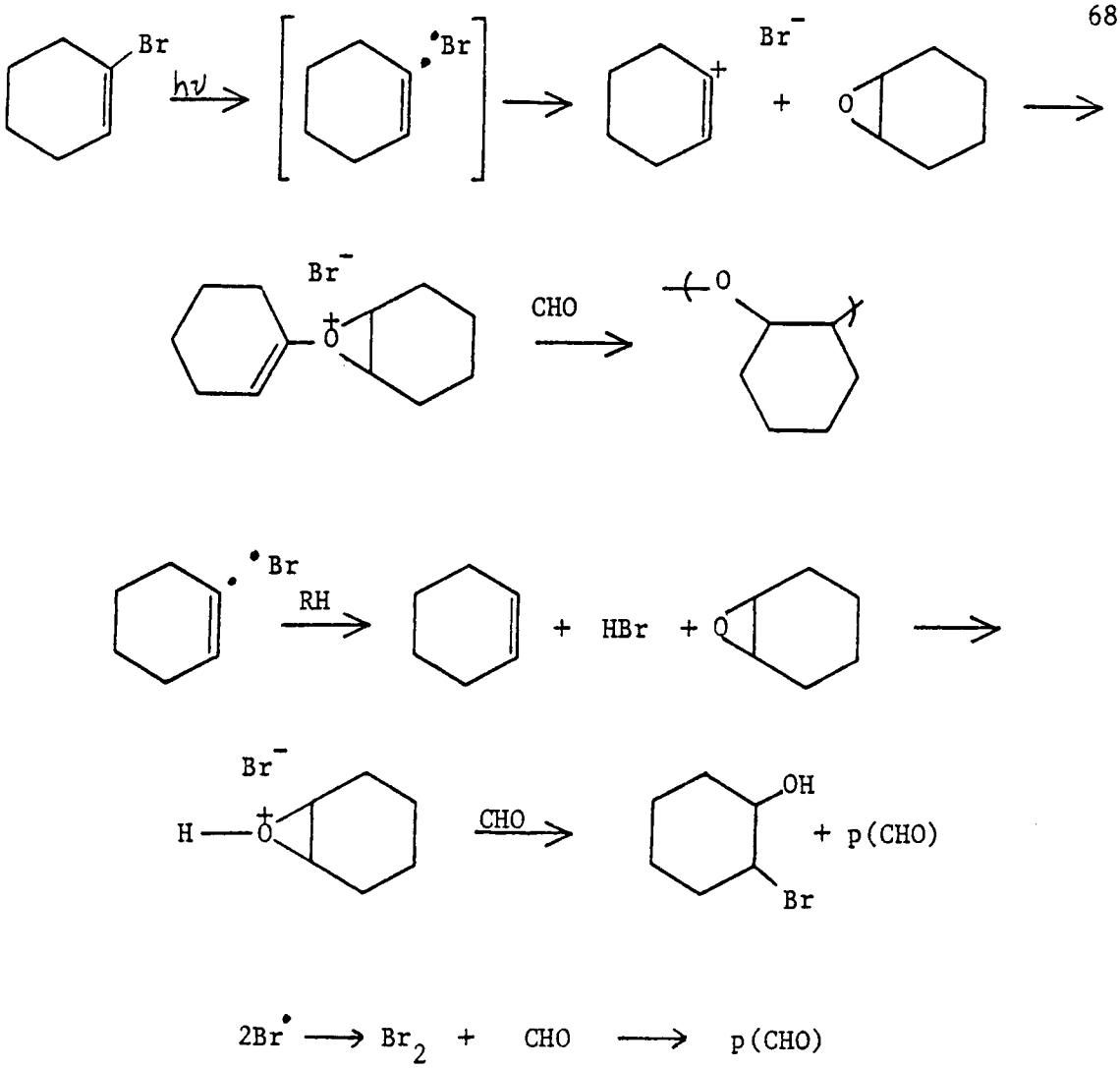
Polymer yields were low, as they were in the ICH case, and this can be attributed to the same factors discussed in the ICH section. The molecular weight of these polymers at 5% initiator and 24 hr irradiation was 15,000 g/mole.

A much less distinct maximum is shown in Figure 11 for BCH when compared to the ICH initiation, Figure 8, p 57. Analogous to ICH, BCH could produce HBr by free radical side reactions. HBr is known to be much less active than HI in cleavage of ethers. Therefore, less



chain degradation should occur and polymer yields should not decrease as greatly. When a 5% p(CHO), 1% BCH solution in cyclohexane was photolyzed for 20 hr, no change in the molecular weight was observed. Thus, little or no degradation can be attributed to HBr, irradiation, and vinyl cation attack.

The initiation mechanism for BCH is strictly analogous to the one for ICH. The side reactions are also analogous, but more important, because the free radical products are more prevalent in the BCH case. These side reactions may contribute to polymer formation as shown here. Gaseous HBr, when produced independently and bubbled into CHO, forms polymer readily. Br_2 also gives polymer yields of greater than 50%, but the initiation mechanism has not been elucidated in the literature.



$$2Br^{\bullet} \longrightarrow Br_2 + CHO \longrightarrow p(CHO)$$

Thus, because the free radical products constitute a major portion of the photolysis products, these latter reactions may constitute the primary polymerization mechanisms.

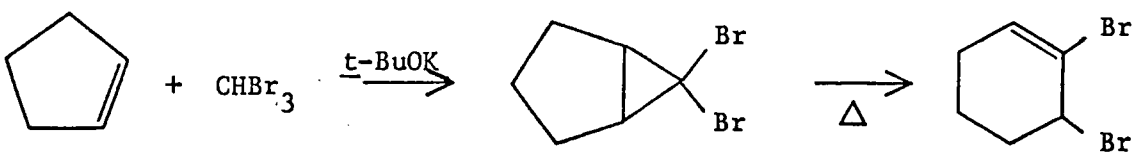
Slightly different results were obtained when inhibitors were used with BCH initiated polymerization when compared to polymerization initiated by ICH. The affect of H_2O and TEA were identical, with no polymer being formed in either case. However, when

4-t-butylpyrocatechol was used, no polymer was isolated in the BCH reaction, although cloudiness was observed when the reaction mixture was dropped into methanol. This seems to imply that the majority of the polymer yield comes from initiation by the free radically derived side products, or that 4-t-butylpyrocatechol does inhibit cationic polymerization to some extent.

Attempts were made to utilize BCH as a crosslinking agent for DEO and mixtures of DEO and CHO. When DEO/BCH mixtures were irradiated for 22 hr, no polymer was formed. In a mixture of 50:50 DEO:CHO, a slight haziness developed upon addition to methanol, but no isolable product was formed.

3. 2,3-Dibromocyclohexene as Photoinitiator

A third cyclic vinyl halide was investigated because of its ready availability. In the synthesis of BCH, the isolated intermediate 2,3-dibromocyclohexene (DBCH) is produced upon distillation of the bicyclic dibromo product of the initial carbene insertion reaction.



DBCH

The experimental results of DBCH photoinitiation of CHO are shown in Figures 13 and 14, as well as Table 4. The polymer yields are similar to those exhibited by the other cyclic vinyl halides. No photolysis studies of DBCH were found in the literature. A brief photolysis study was attempted which yielded more questions and no

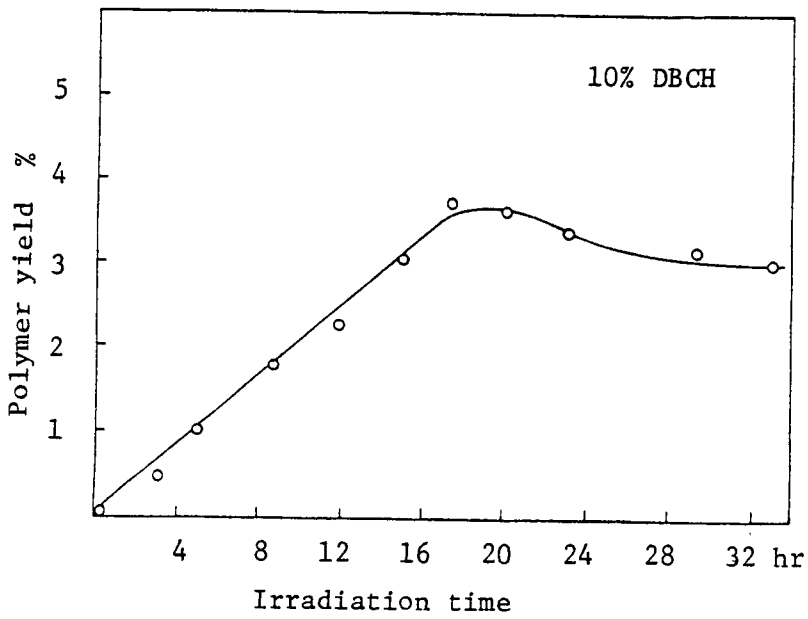


Figure 13. Polymer yield as a function of irradiation time for DBCH initiation of CHO.

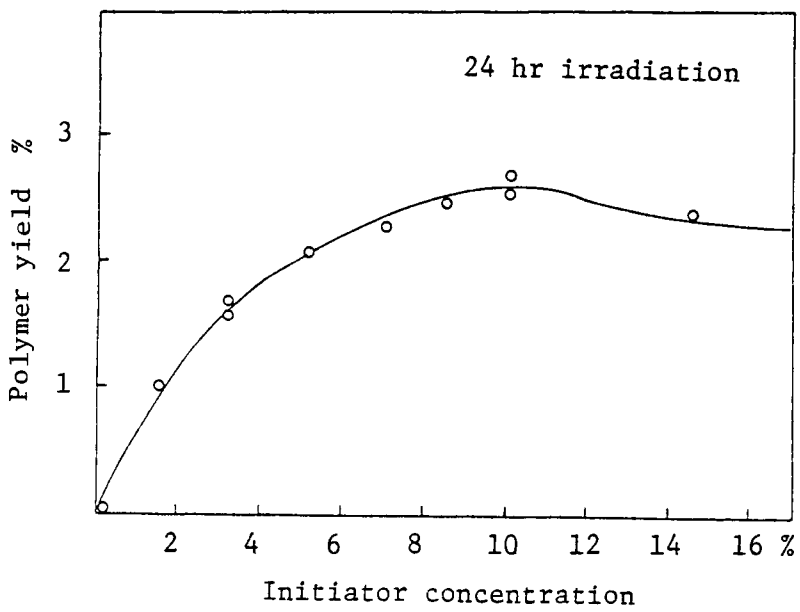


Figure 14. Polymer yield as a function of initiator concentration for DBCH initiation of CHO.

TABLE 4

EXPERIMENTAL DATA FOR DBCH PHOTOINITIATION OF CHO

DBCH Conc.,%	Irradiation time, hr.	Polymer Yield,%
0	24	0
5.0	0	0
1.5	24	1.0
3.2	24	1.6
3.2	24	1.7
5.2	24	2.0
7.0	24	2.3
9.0	24	2.5
10.1	24	2.6
10.1	24	2.8
14.8	24	2.4
10.0	3	0.5
10.0	5	1.0
10.0	9	1.8
10.0	12	2.2
10.0	15	3.0
10.0	18	3.7
10.0	20	3.6
10.0	23	3.2
10.0	29	3.1
10.0	33	3.0

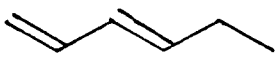
answers. Because this was not the primary purpose of this research, no further investigations were carried out. The photolytic decomposition is complicated by the allylic bromine. Free radical reactions could be involved with cleavage of this C-Br bond. HBr was generated during photolysis as evidenced by white acidic vapors which could be trapped in methanol, but not in methylene chloride. Because the mechanism is complicated and as yet unproven, none will be proposed. Use of DBCH in DEO or a DEO/CHO mixture gave no crosslinking or evidence of polymer formation.

Inhibitors used in the DBCH initiated polymerizations gave the same results as the inhibition of BCH. Water and TEA completely eliminated polymer formation, while 4-t-butylpyrocatechol inhibited polymerization to the extent that no polymer was isolated, although slight cloudiness was observed upon addition to methanol. This would again indicate either initiation by some product which is radically derived, or cationic inhibition by 4-t-butylpyrocatechol. Irradiation of 5% p(CHO) and 1% DBCH in cyclohexane gave no change in molecular weight. Polymer degradation in this case is thus negligible.

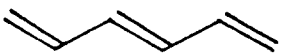
As can be seen from the experimental data for the cyclic vinyl halides, long irradiation times were required for even very low polymer yields. It would be desirable to both increase polymer yields and shorten irradiation times. The UV spectra of the previous compounds show that the UV absorbances of these compounds are below 260 nm and relatively weak. This is to be expected from an isolated double bond.

If the absorbance could be increased, the possibility for a cleavage reaction would be increased. One of the simplest methods to increase absorbance, while shifting the absorbance to higher wavelengths, is to increase the length of conjugation of a doubly bonded system. This is illustrated in the following compounds:[105]

λ_{max} = 190 nm



λ_{max} = 217 nm



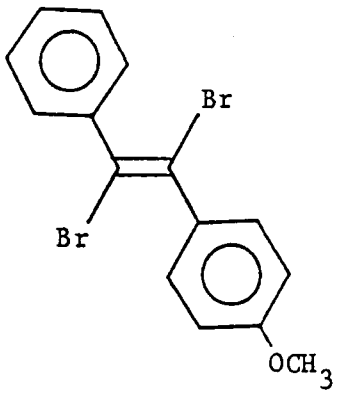
λ_{max} = 244 nm

A second problem associated with these compounds is the strength of the carbon-halogen bond, coupled with the instability of the resulting vinyl cation. As discussed in the Introduction to this chapter, vinyl cations can be stabilized by attaching electron donating groups to the double bond. The resulting stabilization of the carbocation allows easier solvolysis with poorer leaving groups. In photolysis reactions, this should mean more facile production of the vinyl cation with less energetic wavelengths of light. This comparison is quite rough and is useful for only the most qualitative predictions of relative initiator activity.

A possible solution to low yields and long irradiation times thus seems to be an increase in absorbance and stabilization of the resulting cation. This improvement was sought by attaching a phenyl and a substituted phenyl group to a vinyl halide. In addition, use of an acyclic vinyl halide would relieve the strain inherent in the nonlinear vinyl cations produced from cyclic halides. The synthesis of

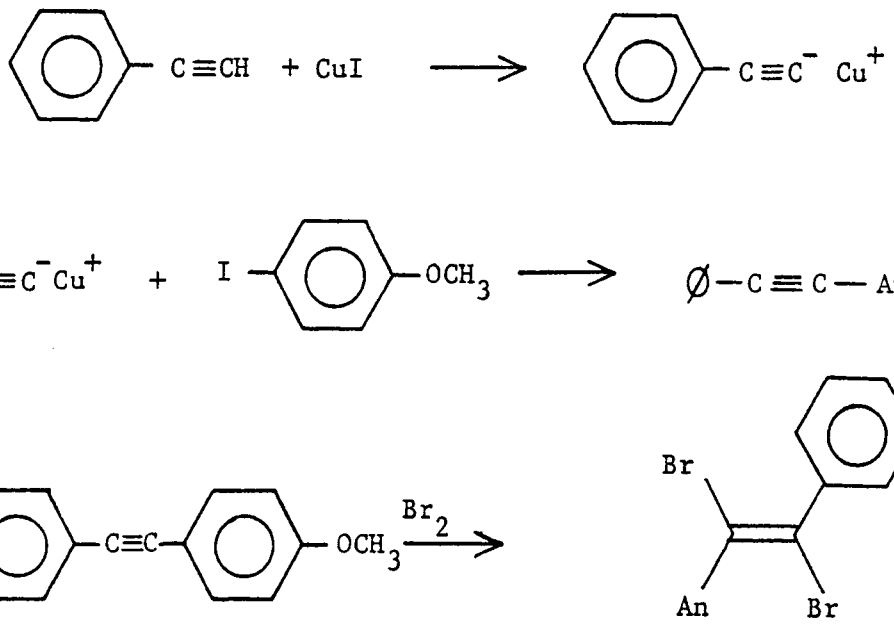
this compound must also be fairly simple, short, and use readily available materials and reagents.

A compound which meets these requirements is (E)-1,2-dibromo-1-(4-methoxyphenyl)-2-phenylethene(DMPE). This compound has extensive conjugation, as well as electron donating groups, and two



DMPE

vinyl bromines. The UV absorbance is at much higher wavelengths, as can be seen in its UV spectrum in Figure 15. The synthesis of DMPE requires three steps, all in high yields.[106]



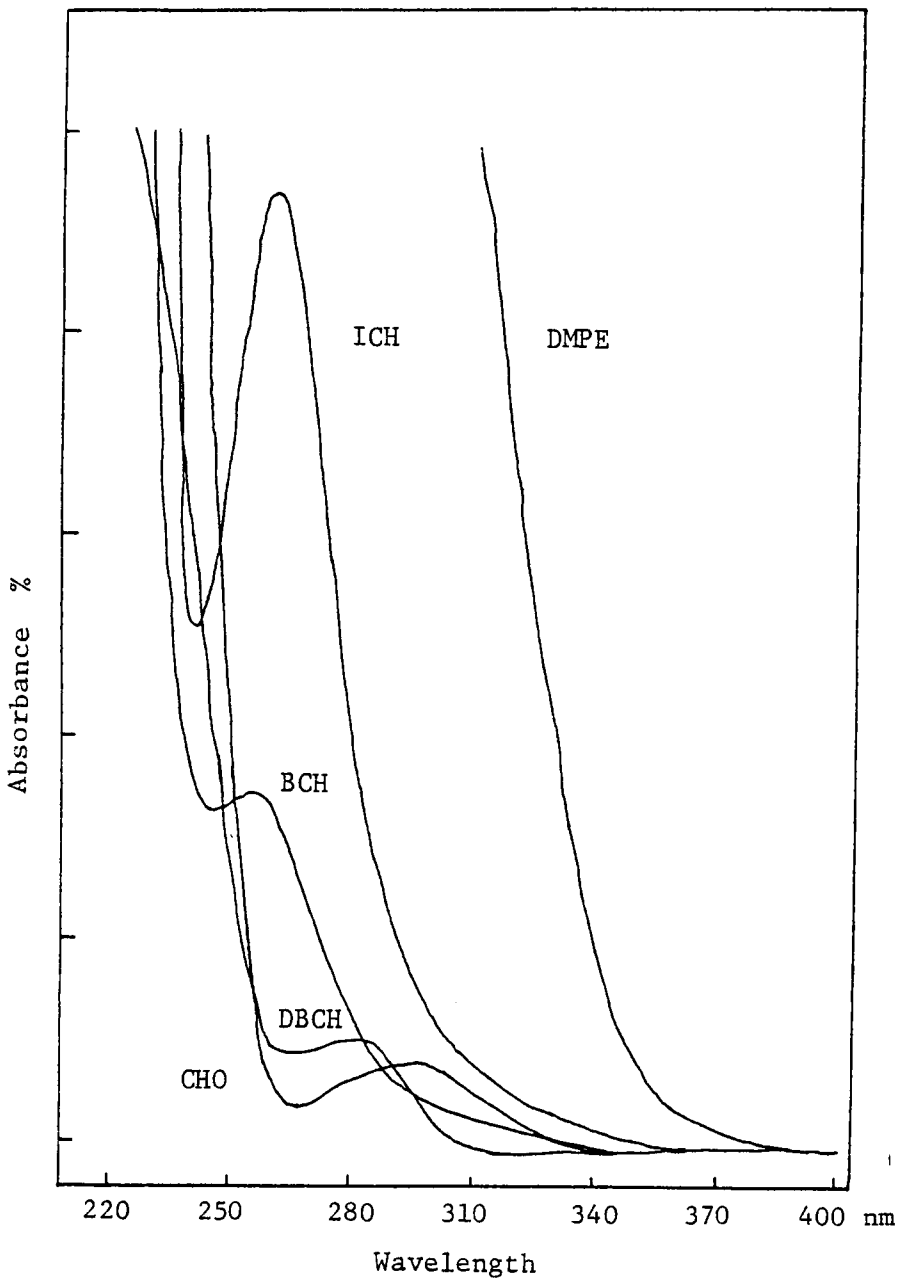
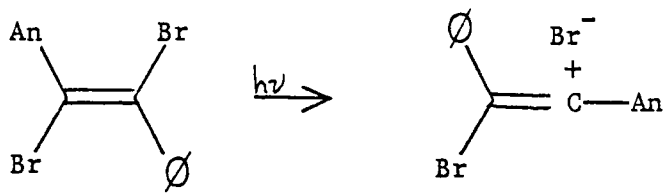


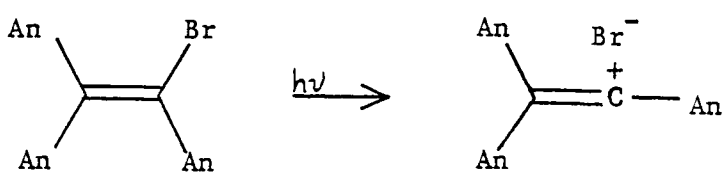
Figure 15. UV spectra of DMPE (0.75 g/l), CHO (50%), ICH (0.87 g/l), BCH (0.89 g/l), and DBCH (0.80 g/l) in ether.

The final product is a white crystalline solid which is stable at ambient conditions in an open vial. Overall yields of 70% were obtained.

DMPE has only a limited solubility in CHO of about 6% at 25°C. When compared to the cyclic vinyl halides, DMPE gives much higher polymer yields at much shorter irradiation times, as seen in Figures 16 and 17 and Table 5. Monomer/DMPE mixtures are stable for months at room temperature, with no polymer formed in the absence of irradiation. Molecular weights of p(CHO) prepared with DMPE are 29,000 g/mole at 1.0 wt % DMPE, and 25,000 g/mole at 6% DMPE. The photolytically induced decomposition mechanism is not known, but undoubtedly vinyl cations are produced. It is not known whether an initial



homolytic cleavage occurs, followed by an electron transfer reaction, or whether a single step mechanism is operating. The effects of additives, discussed later, seem to indicate the same two step decomposition which has been shown for the cyclic vinyl halides. A compound similar to DMPE has been reported to undergo ion production,[98] as discussed in the Introduction to this chapter.



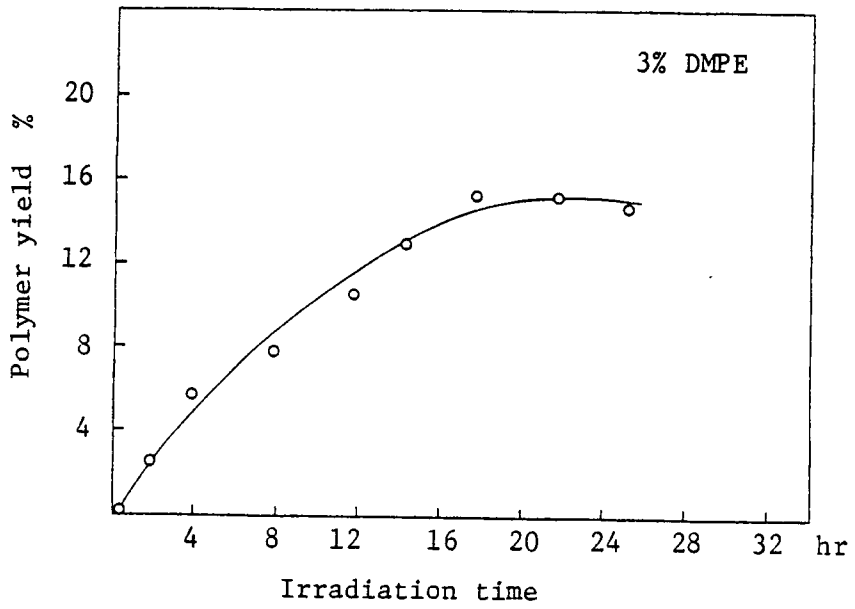


Figure 16. Polymer yield as a function of irradiation time for DMPE initiation of CHO.

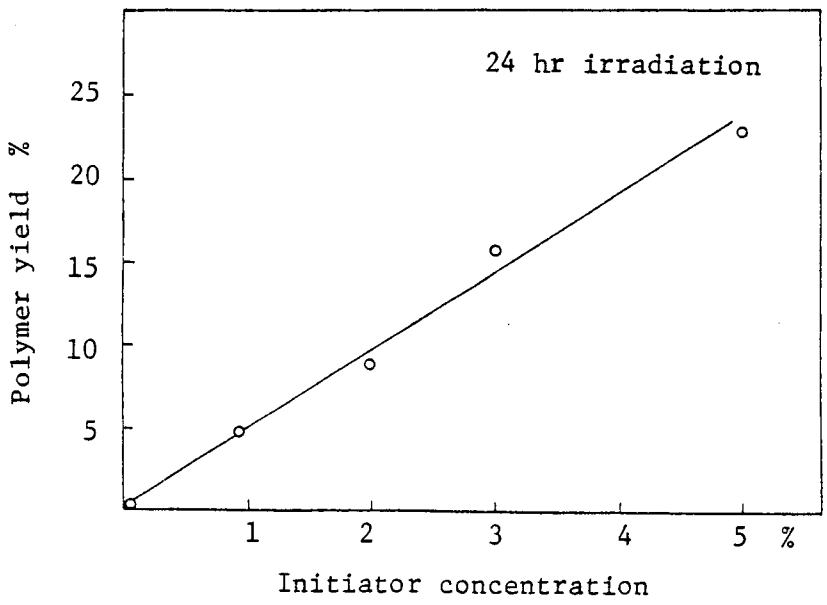


Figure 17. Polymer yield as a function of initiator concentration for DMPE initiation of CHO.

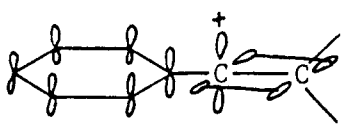
TABLE 5

EXPERIMENTAL DATA FOR DMPE PHOTOINITIATION OF CHO

DMPE Conc.,%	Irradiation time, hr.	Polymer Yield,%
0	24	0
3.0	0	0
1.0	24	5.0
2.0	24	8.5
3.0	24	15.5
5.0	24	23.0
3.0	2	2.6
3.0	4	5.7
3.0	8	7.7
3.0	12	10.9
3.0	14	13.0
3.0	18	15.1
3.0	22	15.0
3.0	25	14.5

Photolysis of trans aryl vinyl halides has been shown to lead to elimination in some cases.[99] In this case, Br_2 may be eliminated from DMPE, giving rise to the possibility of initiation of CHO by Br_2, which has been shown to be a good initiator. This contribution to polymer yield is very small, as spectroscopic evidence indicates. Poly(CHO) initiated by DMPE was purified and analyzed by NMR and UV. The NMR spectrum showed aryl peaks at high amplitude, while the UV spectrum indicated high absorbance above 350 nm. These results are only qualitative, but indicate the presence of initiator fragments bound to the polymer chain.

Several factors could be limiting polymer production. Because of the high absorbance of DMPE, its concentration in the sample, and the path length through the sample tube, light below 350 nm is totally abosrbed in the first few mm of the mixture, creating inhomogeneous irradiation. As the viscosity of the mixture increases, initiator mobility into a region of effective irradiation is decreased, causing less initiation to occur. A second factor which could affect initiation is the increased steric hindrance imposed by the large aryl groups attached to the cationic center. Because the preferred geometry of the vinyl cation is linear as shown, steric hindrance should not be a much greater factor than in a trisubstituted carbenium ion. Although the exact extent of this effect is unknown, it must act to slow the rate of cation addition to monomer.



Although no polymerization reactions were carried out in solution, solution reactions may be able to eliminate the viscosity problem by reducing the concentration of initiator and lowering the viscosity of the sample. Selection of a suitable solvent is difficult, however. It must satisfy the following requirements:

a) be transparent to UV irradiation above 300 nm,

b) be inert, i.e. not subject to attack by vinyl cations or free radicals,

c) be polar, and

d) dissolve monomer, polymer, and initiator.

A solvent satisfying these requirements has not been found.

Several additional experiments were carried out with DMPE, as it seemed a much more efficient initiator than the cyclic vinyl halides. Irradiation of CHO/DMPE mixtures with a sunlamp filtered by pyrex also produced polymers, although in much lower yields than in the unfiltered case. Under these conditions, irradiation for 2 hr produced a 4% polymer yield. To determine the possible usefulness of DMPE in formation of crosslinked films, experiments with a difunctional monomer were carried out.

When a DEO/CHO mixture of 50 vol% in quartz sample tubes was irradiated with the mercury arc lamp for 15 hr, polymer was formed as shown by precipitation in methanol of 1% polymer. This was soluble, and therefore not crosslinked. On the tube surface closest to the lamp, a film was formed which was insoluble in toluene, acetone,

methanol, and benzene. This indicates a crosslinked structure. From this evidence, DMPE may have usefulness as a curing initiator for ionically polymerizable precursors used in film forming reactions. Inhomogeneous irradiation may be a problem here also, causing formation of a very limited amount of film. In a coating system, however, the system would be very thin, giving a fairly uniform irradiation intensity.

By using various inhibitors, it was established that the mechanism of polymerization was cationic. Water and TEA completely suppressed polymer formation, while 4-t-butylpyrocatechol addition reduced polymer yield from 15% when no additive was present, to 9% with additive. This seems to suggest the possibility of capture of the free radicals produced in an initial step, or the effectiveness of free radically derived side products in initiation of polymerization. As previously discussed, this may also be attributed to inhibition of cationic polymerization by 4-t-butylpyrocatechol. Degradation experiments similar to those carried out for each of the other initiators showed no decrease in $\bar{M}_v$ and hence no substantial polymer degradation. This seems to eliminate the possibility of chain degradation due to vinyl cation attack on the polyether chain. DMPE should produce cations quite readily, but no degradation occurred. As concluded previously, the ICH degradation studies thus seem to pinpoint HI as the primary cause of polymer degradation in that system.

In summary, it was found that vinyl halides offer some promise as photoinitiators for ionic polymerization reactions. They

are stable in CHO when not subject to irradiation, giving no polymer for up to nine months. Upon irradiation, polymer is produced in all cases investigated, although in varying yields. In general, irradiation times are long and polymer yields are low. These problems are the basis for more work in this area. Potential utility for use in ionic curing of coatings was demonstrated for DMPE, but not for any of the cyclic vinyl halides.

C. Experimental

1. Materials

Unless stated otherwise, all materials were used as received or as given in Chapter II.

Bromine: Mallinckrodt, analytical grade.

Bromoform: Aldrich, 96%.

4-*t*-Butylpyrocatechol: Eastman, practical.

Chloroform: Fisher, certified.

Copper (I) iodide: Aldrich, 98%.

Cyclohexane: Fisher, certified, dried over 4A sieves.

Cyclohexanone: Aldrich.

Cyclopentene: Aldrich.

1,2,7,8-Diepoxyoctane: Pfaltz and Bauer, distilled before use, bp 96-98°C at 3 mm, stored over CaH_2.

Ethanol: drum grade.

Hydrazine: Eastman, 64% aqueous solution.

Hydriodic acid: Fisher, certified, 56% aqueous solution.

Hydrochloric acid: Fisher, 3N.

Iodine: Fisher, certified.

1-Iodo-4-methoxybenzene: Aldrich, 98%.

Lithium aluminum hydride: Alfa Products.

Molecular sieves: Fisher, 3A and 4A.

Nitrogen: Selox, prepurified, passed through KOH and $CaSO_4$ before use.

Pentane: Eastman.

Phenylacetylene: Aldrich, 98%.

Potassium bicarbonate: Fisher, certified, 5% aqueous solution.

Potassium-t-butoxide: Aldrich.

Potassium carbonate: Fisher, certified, 5% aqueous solution.

Potassium thiosulfate: Fisher, certified, 5% aqueous solution.

Pyridine: Fisher, certified, dried with KOH, distilled before use, bp 115°C.

Red phosphorus: Fisher, amorphous.

Sodium bromide: Fisher, certified.

Sodium chloride: Fisher, certified, saturated aqueous solution.

Sulfuric acid: reagent, concentrated.

Tetralin: Eastman.

Toluene: Fisher, certified.

Triethylamine: Fisher, certified.

2. Equipment

Unless listed here, the equipment used in these experiments is the same as that listed in Chapter II.

Infrared spectrometer: Perkin Elmer 257 grating spectrometer.

Melting point: Melt-Temp, all mp uncorrected.

Sample tubes, large: overall length 30 cm, 20 cm of which constructed from medium wall (25 mm ID) quartz tubing sealed at one end; the open end was sealed to a smaller quartz tube 10 cm in length, 5 mm ID.

Ubbelohde viscometer: Cannon #0, modified to contain 120 ml fluid and to increase flow times.

Ultraviolet spectrometer: Varian, Cary 17.

Water bath for viscometer: insulated, automatic thermostat control of temperature to ± 0.02°C.

3. Experimental Procedure

a. HBr production and initiation. HBr gas was produced by dropping concentrated H_2SO_4 onto NaBr under a flow of N_2. The gas was bubbled through dry tetralin to convert any Br_2 into HBr, and then introduced into CHO. The polymer produced was isolated as described before.

b. HI production and reactions. A three necked flask was equipped with an argon inlet and outlet, and a dropping funnel. As argon was used to flush the system, amorphous red phosphorus was placed into the flask. The dropping funnel contained 50 ml of I_2 in 57% aqueous HI (2:1 ratio by weight I_2:HI solution). The solution was dropped slowly onto the phosphorus at room temperature. The gaseous HI produced is then passed through a trap cooled with CCl_4/ dry ice and then bubbled into CHO. A brown color developed immediately. When poured into methanol, a small amount of polymer was isolated as previously described.

c. Initiation by iodine. Dry I_2 (0.05 g) was added to 5 ml CHO under dry argon. After 24 hours, the polymer was isolated as before. The polymer was a light yellow.

d. Initiation by bromine. Br_2 (0.03 ml) was added to 5 ml CHO, causing a brown color to form. After several minutes, the color disappeared. After ten hours, a white polymer was obtained by the usual methods.

e. Synthesis of 1-iodocyclohexene. A 10 g (0.1 mole) portion of cyclohexanone was added dropwise to hydrazine hydrate, 20 g (0.50 mole), with vigorous stirring. The resulting yellow mixture was heated on a steam bath for one hour. The cooled solution (milky white) was extracted with chloroform (2 x 40 ml), the extract was washed with H_2O and dried over $CaSO_4$. The solvent was then removed on a rotary evaporator.

A saturated solution of I_2 in ether was added at room temperature to a solution of the hydrazone, 10 g (0.09 mole), in a mixture of ether (30 ml) and TEA (70 ml) until the reaction was complete as judged by the cessation of N_2 evolution and the persistence of iodine color. The reaction was instantaneous. The mixture was diluted with ether (100 ml) and washed with 5% $Na_2S_2O_3$, 3 N HCl, 5% Na_2CO_3, saturated NaCl solution, and then dried over $CaSO_4$. The ether was removed on the rotary evaporator and the product distilled over a 15 cm Vigreux column under vacuum. The fraction of ICH collected (10.4 g, 50% yield) had a boiling point of 44°C at 1.0 mm Hg (lit.[100] bp 40°C at 0.4 mm) and was stored over CaH_2 in a vial closed with a septum at 4°C. The IR spectrum gave the C=C stretch at 1640 cm^{-1}. The NMR peaks were assigned as follows: vinyl, 1H, mult., 6.2 ; CH_2, 2H, mult., 2.5 ; CH_2, 2H, mult., 2.1 ; CH_2, 4H, mult., 1.7 .

f. Synthesis of 2,3-dibromocyclohexene.[104] A 35.3 g (0.15 mole) portion of bromoform was added dropwise to an ice-salt cooled, vigorously stirred slurry of cyclopentene, 10 g (0.15 mole), 16.8 g (0.15 mole) of potassium t-butoxide, and dry pentane (65 ml). The temperature was allowed to rise to 25°C over a two hour period after addition was complete. The muddy brown mixture was poured onto crushed ice. The aqueous layer was extracted with three 200 ml portions of pentane. The pentane extract was washed with H_2O (3 x 200 ml), dried over $MgSO_4$, and concentrated on the rotary evaporator. The remaining liquid was vacuum distilled through a 15 cm Vigreux column. The clear

liquid product (13.2 g, 40% yield) had a boiling point of 85°C at 4 mm Hg (lit.[104] bp 105-106°C at 9.5 mm). The DBCH was stored in a septum closed vial over 3A molecular sieves at 4°C. The IR showed a C=C stretch at 1650 cm^{-1}. The NMR spectrum showed the following peaks: vinyl, 1H, mult., 6.0 ; CH_2, 2H, mult., 2.4 ; CH_2, 2H, mult., 2.1 ; CH_2, 4H, mult., 1.7 .

g. Synthesis of 1-bromocyclohexene.[104] THF was dried with $LiAlH_4$ and stored over sodium. To a refluxing solution of $LiAlH_4$ (5.0 g, 0.13 mole) in THF was added dropwise a solution of 28.4 g (0.12 mole) of DBCH in 25 ml THF. After 64 hours refluxing, the excess $LiAlH_4$ was destroyed, and the mixture diluted, with 400 ml H_2O. The aqueous layer was extracted three times with pentane (200 ml) and the pentane washed with H_2O (3 x 200 ml) and saturated NaCl (100 ml) and dried over $MgSO_4$. Two distillations gave 10 g (53% yield) of BCH with a boiling point of 45°C at 7 mm Hg (lit.[104] bp 63°C at 20 mm). This was stored at 4°C over CaH_2 in a vial closed with a septum. The IR spectrum gave a C=C stretch at 1680 cm^{-1}. The NMR spectrum contained the following peaks: vinyl, 1H, mult., 6.1 ; CH, 1H, mult., 4.7 ; CH_2, 6H, mult., 2.1 .

h. Synthesis of (E)-1,2-dibromo-1-(4-methoxyphenyl)-2-phenylethene. Cuprous phenylacetylide was prepared by adding an aqueous ammoniacal solution of 20 g (0.10 mole) cuprous iodide to a solution of 10.7 g (0.105 mole) phenylacetylene in 500 ml ethanol. After standing for 15 minutes, the bright yellow precipitate was

filtered off and washed five times with H_2O, then stirred in H_2O overnight. The solid was filtered again, and then washed with ethanol five times and ether five times. The solid was dried in a rotary evaporator for three hours.

A three necked round bottom flask was equipped with a stirring magnet, an argon inlet and a reflux condenser fitted with a bubbler. Pyridine (100 ml) and 7.1 g (0.03 mole) 4-iodo-1-methoxybenzene were added and the flask purged with argon while stirring. Cuprous phenylacetylide, 5.0 g (0.3 mole), was added and a yellow solution formed upon heating. The flask was heated in an oil bath at 120°C for 10 hr. The solution was then cooled and diluted with 300 ml of H_2O. The mixture was extracted three times with ether and the extracts washed three times each with dilute HCl, 5% $NaHCO_3$, and H_2O, and dried over $MgSO_4$. Ether was removed at reduced pressure, and the concentrated solution was cooled overnight, producing tan crystals. Decolorization with Norit and recrystallization from methanol gave 5.0 g of white crystals (80% yield). Melting point of this compound was found to be 59°C (lit.[106] mp 58-60°C). The NMR spectrum peak assignments were as follows: aryl, 9H, mult., 6.7-7.6 ; OCH_3, 3H, sing., 3.7 .

A 1 g (0.005 mole) portion of the above disubstituted acetylene was dissolved in 50 ml of CCl_4 and cooled to ice-water temperature. Bromine, 0.8 g (0.005 mole), was added to 50 ml CCl_4 and this solution was added dropwise to the cooled, stirred acetylene solution. After cooling, the CCl_4 was completely removed by rotary

evaporator and the white solid recrystallized from methanol. Upon cooling, white needle crystals were produced and dried in the vacuum oven before use. Yield of DMPE was 16.5 g, or 90%. Mp was 165-168°C (lit.[107] 166-167°C). C=C stretch in the IR was at 1610 cm^{-1}. NMR peak assignments are as follows: aryl, 9H, mult., 6.7-7.6 ; OCH_3, 3H, sing., 3.8 . Molecular weight as determined by mass spectroscopy was 368 g/mole.

i. Polymerization and isolation. Initiators were stored and dried as stated. 1,2,7,8 Diepoxyoctane was dried over CaH_2, distilled (bp 96-98°C at 3 mm), and stored over CaH_2 at 4°C. DEO/initiator mixtures and DEO/CHO/initiator mixtures were prepared as described for previous polymerizations. Concentration of initiator was 3% in all cases. Isolation was the same as described previously. Purification of CHO and procedures for polymerization and isolation have been described previously.

j. Molecular weight characterization. Molecular weights were determined by dilute solution viscosity using a modified Ubbelohde viscometer in a thermostatted water bath. Mark-Houwink parameters are given for p(CHO) in toluene at 35°C.[108] This reference polymer was prepared by cationic initiation. For these conditions, the values for K and a are $K=3.5 \times 10^{-5}$, and a=0.83. Flow times were measured until a constant value (±0.1 sec) was found. Four concentrations were used, generally ranging from 0.25 g/dl to 1.0 g/dl. The data were then

treated in the usual manner to obtain ηsp/C and ηinh. These values were then plotted versus concentration and extrapolated to zero concentration to obtain [η].

k. Polymerization additives. Experiments to determine the effect of additives were carried out as follows. When H_2O and TEA were used, samples were prepared as before, then 0.1 ml of additive was injected and the samples irradiated for 20 hr. When 4-t-butylpyrocatechol was used, a 3% solution in CHO was prepared, the appropriate amount of initiator was added (2%) and the polymerizations carried out as before. Isolation followed the usual methods.

l. Degradation experiments. A large sample tube was prepared as described previously. A solution of 40 ml cyclohexane, 2 g p(CHO), and 0.5 g initiator was loaded into the tube and photolyzed as before. After isolation and drying, polymer molecular weights were determined by dilute solution viscosity.

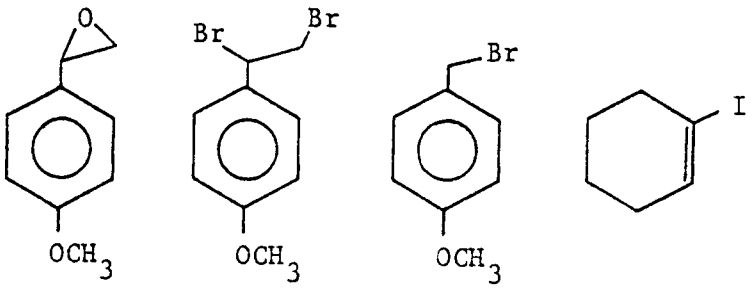
m. Qualitative end-group analysis. A 1 g sample of p(CHO) that had been polymerized by DMPE was dissolved in 100 ml toluene, and then precipitated into 1000 ml of rapidly stirred methanol. The polymer was then isolated and dried as before. NMR and UV spectra were then obtained.

CHAPTER IV

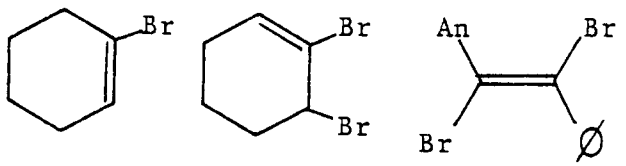
CONCLUSIONS

A. Summary of Work

Each of the compounds shown below was investigated for photoinitiation of CHO. As has been seen in Chapter II, MPO, DEMB, and



MPO DEMB BMMB ICH



BCH DBCH DMPE

BMMB were not effective as photoinitiators. MPO and BMMB gave less than 1% polymer yield in the dark as well as when irradiated. MPO initiation was attributed to thermal instability leading to ring opening reactions. In the case of BMMB, solvolysis was invoked to explain initiation of polymerization. DEMB gave 25-30% polymer yield with and without irradiation. Solvolysis or elimination of HBr could explain initiation caused by DEMB. Because these compounds are unstable in CHO in the dark, they are not useful as photoinitiators.

ICH, BCH, DBCH, and DMPE were found to be cationic photoinitiators for CHO polymerization. Figures 18 and 19 give a direct

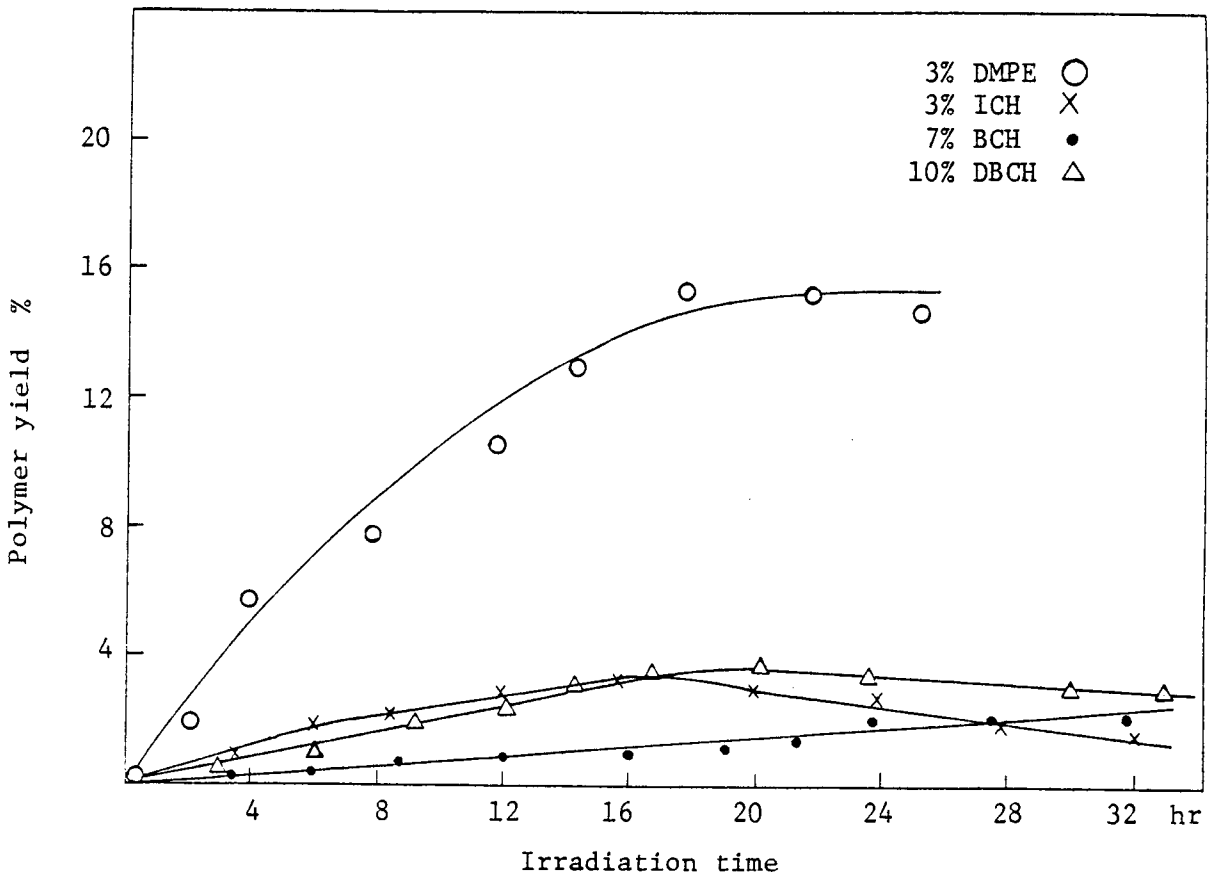


Figure 18. Polymer yield as a function of irradiation time for DMPE, ICH, BCH, and DBCH.

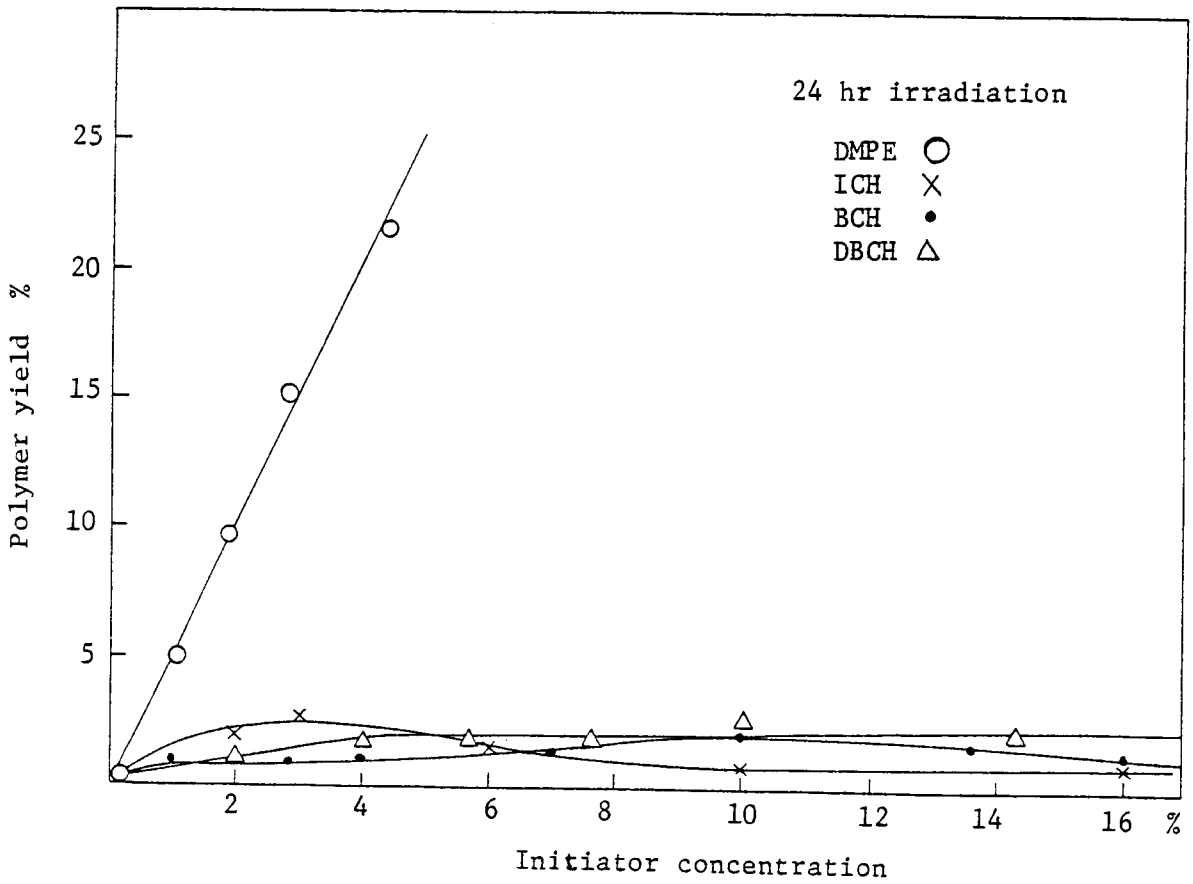


Figure 19. Polymer yield as a function of initiator concentration for DMPE, ICH, BCH, and DBCH.

comparison of the experimental results for all the vinyl halides studied. Higher polymer yields at shorter irradiation times and higher overall polymer yields indicate that DMPE is a much more efficient photoinitiator than BCH, ICH, and DBCH. DMPE has two advantages when compared to the cyclic vinyl halides. As seen in Figure 15 (p 75), DMPE has a higher absorbance at longer wavelengths. A second advantage is that the vinyl cation produced upon photolysis of DMPE is much more stable than those produced from the photolysis of ICH, BCH, and DBCH. This increased stability can be attributed to the preferred linear cation geometry in DMPE which is prohibited in the cyclic cases. The p-methoxyphenyl group also stabilizes the cation. These two factors enable the cation to be produced more easily from DMPE and thus give more efficient polymer initiation.

Each of these compounds is readily synthesized from available reagents in good yields. ICH, BCH, and DBCH are liquids which must be dried over CaH_2, protected from oxygen, and stored at lowered temperature. DMPE, on the other hand, is a white crystalline solid, stable to room atmosphere, temperature, and illumination. Vacuum drying at 40°C for several hours is sufficient to remove any inhibiting impurities. DMPE also initiates polymerization when irradiation is supplied by a commercial sunlamp filtered through pyrex. This is not the case for the other initiators, which require wavelengths shorter than 250 nm for initiation.

Shelf stability of monomer/initiator mixtures is similar for all of the vinyl halides. No polymer is formed even after nine months in

any case when irradiation is absent. These initiators also exhibit desirable thermal stability.

Of these vinyl halides, only one gave film formation when used with a difunctional epoxide. This behavior of DMPE is an advantage over the other halides. Because the end use applications generally would involve formation of a crosslinked coating, DMPE seems to be more desirable than the other compounds. All of these comparisons definitely indicate that DMPE is the most attractive photoinitiator investigated.

Inhibitor studies indicated the polymerization mechanism is cationic. Water and triethylamine completely suppressed polymer formation in all cases. Inhibition of polymer formation by 4-t-butylpyrocatechol was found for DBCH and BCH, while reducing the polymer yield in the case of ICH and DMPE. The inhibition of polymerization by DBCH and BCH was attributed to the trapping of free radical side reactions which normally contribute to the formation of species capable of initiating CHO polymerization. In the ICH and DMPE examples, interaction of the radical trap with initially formed radicals prior to the electron transfer step was proposed for the reduction in polymer yields. The possibility of 4-t-butylpyrocatechol inhibiting cationic polymerization was also discussed.

Degradation studies of polymer and initiator in solution showed the absence of significant chain degradation due to radiation induced reactions and chemical attack on the polyether by vinyl cations or HBr. On the other hand, a 20% decrease in molecular weight was observed when HI was photolytically generated from ICH.

Thus, vinyl halides have been shown to be cationic photoinitiators for CHO polymerization. Some problems exist with the systems studied, but a wide range of different compounds is now available for investigation of initiating activity. In addition to the photoinitiation process discussed in this work, a new area of cationic initiation has been opened. Previously, trisubstituted carbocations have been used as initiating species. It has now been shown that disubstituted carbocations are also effective initiating species. Some organic carbocations are too stable to initiate polymerization. Because vinyl cations are intrinsically less stable, a wide range of substitution patterns is available which should still give cations capable of initiation. Indeed, it may not be possible to generate a vinyl cation which is too stable to initiate polymerization. This is an area for future work.

B. Comparisons to Previous Initiators

Comparison of the photoinitiators studied in this research to previous initiators indicates some advantages and disadvantages. Only DMPE will be considered in Table 6, a comparison of cationic photoinitiators.

DMPE has significant advantages in several areas when compared to all previous systems except those initiators investigated by Crivello and Lam. DMPE is easy to synthesize and store, stable at ambient conditions, and stable in monomer/initiator mixtures indefinitely. All of the initiating systems which rely on

TABLE 6

COMPARISON OF CATIONIC PHOTOINITIATORS

Initiator	Ease of Synthesis	Ease of Handling/Storage	Stability	Generality	Irradiation Times	By-products of Initiation
DMPE	Good	Excellent	Excellent	?	Hours	Bound to Polymer
Halonium Salts	Poor	Excellent	Excellent-poor	Good	Minutes	Aryl
Sulfonium Salts	Poor	Excellent	Excellent	Good	Minutes	Ylids
$Mn_2(CO)_{10}$	Poor	Poor	Good	Poor	Hours	Co, Mn Salts
$MeCpMn(CO)_2$	Poor	Poor	Fair	Poor	Minutes	Mn Salts, CO
Gold Salts	Poor	Fair	Poor	Poor	Minutes	Au Salts (?)
Silver Salts	Fair	Fair	Fair	Poor	Hours	Ag Salts (?)
$(Cp)_2TiCl_2$	Poor	Poor	Fair	Poor	Hours	Organo-metallic Salts (?)
VCl_4, $TiCl_4$	Fair	Poor	Poor	Poor	Hours	Metal Salts
Tetracyano-benzene	Fair	Good	Poor	Poor	Hours	Aryl
Pyromellitic Dianhydride	Fair	Fair	Poor	Poor	Minutes-Hours	Aryl

donor-acceptor interactions are not general in scope. DMPE, however, should be able to polymerize a wide variety of monomers, although little information has been obtained. Another advantage is the bonding of initiator fragments from DMPE to the polymer chain. This eliminates diffusion of these fragments out of the polymer matrix. However, these bound fragments may absorb UV light and initiate polymer degradation reactions. This problem could be turned into an advantage by designing the initiator to function as a UV shield used to stabilize the polymer to irradiation.

When compared to the salts studied by Crivello and Lam, DMPE has two advantages and two disadvantages. One advantage of DMPE lies in its ease of synthesis using common reagents. The salt initiators are generally more difficult to prepare, give low yields, and utilize expensive reagents. DMPE has a significant advantage in that it leaves no unbound initiator fragments in the polymer matrix. The salt initiators leave unbound aryl compounds as by-products of photolytic decomposition. On the other hand, the salts are extremely efficient, rapid initiators, requiring extremely short irradiation periods. This is not true for DMPE, which requires hours of irradiation under the conditions studied here. The other advantage of the salts lies in their ability to initiate a wide variety of monomers. This has not been substantiated for DMPE.

C. Suggestions for Future Work

The primary aim of this research has been to find a different type of cationic photoinitiator. This has been successfully accomplished, although much work remains to be done. Therefore, some suggestions for future work will be discussed.

Provided that absorbances are nearly equal, and if solvolysis rates of vinyl compounds can be used as a rough guide to the rate of photolytic production of a vinyl cation, then the literature on vinyl solvolysis reactions can be very helpful in predicting which compounds should be investigated in an effort to lower irradiation times while increasing polymer yields. Effects which increase solvolysis rates include;

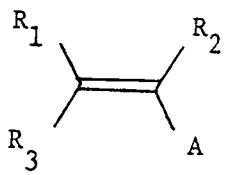
a) electron donating groups attached to the double bond,

b) resonance stabilization of the vinyl cation,

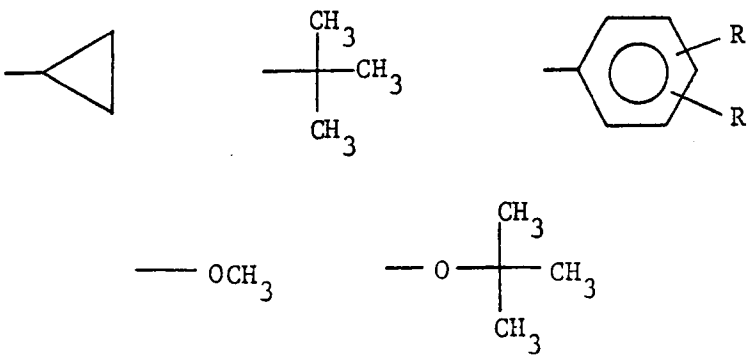
c) better leaving groups, and

d) steric crowding of the cis isomers when bulky groups are present.

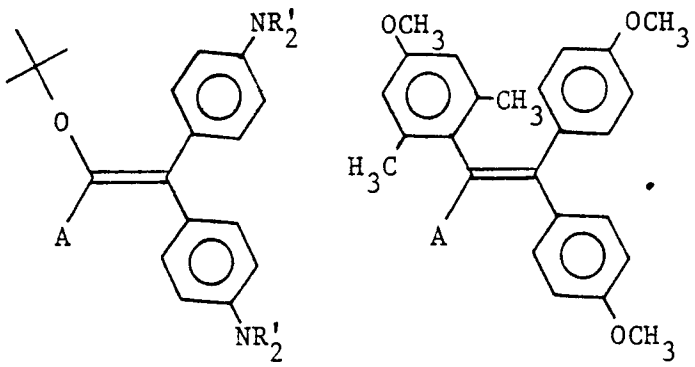
Following this reasoning, proposed compounds could include:



where A is the leaving group and A = OTf, OTs, ONf, Br, and I. R_1, R_2, and R_3, are combinations of the groups shown below.

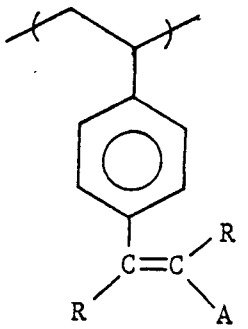


For example, two interesting compounds with good absorbances and high (predicted) solvolysis rates would be:

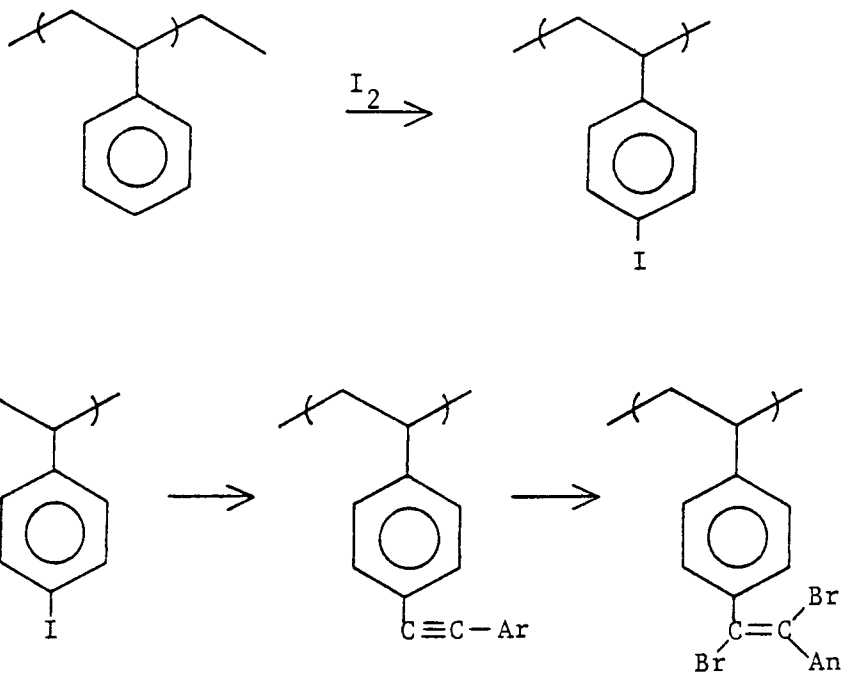


A variety of monomers should be studied, as well as solution polymerization using vinyl initiators. Utilization of these types of initiators in curing reactions of coatings should also be pursued. Extension of effective wavelengths to the visible region may be accomplished by addition of sensitizers, dyes, or inclusion of dye residues into the initiator molecules. Investigation of the use of the initiator fragments as UV shields should also be undertaken. Finally, polymer modification reactions may also be possible using an extension of the ideas presented here. A polymer of the type shown below would

have unusual properties. Photolysis of this polymer in the presence of a cationically polymerizable monomer should produce the first known photoinitiated cationic graft copolymerization. Both solution and surface grafting could be attempted.



Polystyrene could be modified to produce this photoactive polymer. According to the literature,[109,110] this reaction can be done from 10 to 100% exclusively at the para position. The iodinated polymer would then be reacted with an aryl acetylene salt. Bromination of this polymer could lead to the polymer-bound analog of the initiator DMPE.



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